## INVESTIGATION OF STRUCTURALLY DIVERSIFIED HOMO AND HETEROMETALLIC COMPLEXES Ph.D. Thesis

By VEENU MISHRA



## DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2016

# INVESTIGATION OF STRUCTURALLY DIVERSIFIED HOMO AND HETEROMETALLIC COMPLEXES

## A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by VEENU MISHRA



## DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2016



## INDIAN INSTITUTE OF TECHNOLOGY INDORE

## **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **INVESTIGATION OF STRUCTURALLY DIVERSIFIED HOMO AND HETEROMETALLIC COMPLEXES** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **DISCIPLINE OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE**, is an authentic record of my own work carried out during the time period from JULY 2011 to JULY 2016 under the supervision of Dr. Shaikh M. Mobin, Assistant Professor, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

# Signature of the student with date VEENU MISHRA

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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# DEDICATED TO MÝ RESPECTED PARENTS AND MÝ BELOVED HUSBAND

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#### ABSTRACT

Investigations embodied in thesis entitled "INVESTIGATION OF STRUCTURALLY DIVERSIFIED HOMO AND HETEROMETALLIC COMPLEXES" were initiated in July 2011 in the Department of Chemistry, Indian Institute of Technology Indore, Simrol Indore 452020.

The objectives of this thesis were to develop N-containing pyridine ligand based homometallic and heterometallic metal complexes and their high dimensional networks *via* coordinate bond and non-covalent secondary interactions. These complexes have been mainly synthesized either by *insitu* metal ligand reaction or by alteration of reaction medium by using Cd and Hg as well as noble metal (Au) at ambient conditions.

This thesis has been divided into six chapters. The **chapter 1** is introductory chapter which includes the brief introduction of pyridine based ligands and their metal complexes then it moves towards the hydrothermal or solvothermal one pot *in-situ* metal ligand reactions technique as well as effect of reaction medium on structural variation of metal complexes. Further discussion has been extended with the isolation and structural characterization of metastable intermediate. This chapter also includes the the role of noble metal such as Au in the formation of supramolecular network *via* its own relativistic effect as Au···Au or Au···H–C interactions and their luminescent properties.

**Chapter 2** deals with synthesis and characterization of Hg(II) based C–C coupled 1D polymeric chain at ambient conditions with 1:1 ratio *via in-situ* metal/ligand reaction. However, a new class of  $\mu$ -oxo and  $\mu$ -chloro bridged other polymeric chain has been obtained by altering the metal : ligand ratio to 1 : 2). Furthermore, three other 1D polymeric chains of Hg(II) and Cd(II) have been developed under the same reaction conditions.

In **Chapter 3**, a double open cubane tetramer of Cd(II) has been synthesized by the reaction of CdCl<sub>2</sub> with hep-H [hep-H = 2-(2-

hydroxyethyl)pyridine] in MeOH at room temperature. This discrete tetramer on reaction with methanolic HCl,  $HNO_3$ , and  $H_2SO_4$  transformed into a two one-dimensional (1D) polymeric chain and one three-dimensional network with topology seh-4,6-C2/c net, respectively. Similar to tetramer, two other Cd based polymeric chains have been developed upon treatment of methanolic HCl, on 1D polymeric chains synthesized in chapter 1.

**Chapter 4** deals with the isolation as well as structural characterization of a kinetically controlled metastable heterometallic 1D polymeric intermediate along with the thermodynamically driven Cu(II)–Hg(II) 1D polymeric chain and a monomeric Cu(II) complex obtained during recrystallization in methanol.

**Chapter 5** includes the synthesis characterization and structural aspect of dimeric and trimeric complexes of Hg(II) and Cd(II) with the amide ligand,  $H_2L$  ( $H_2L = N,N'$ -bis[2-(2-pyridyl)methyl]pyridine-2,6dicarboxamide). Molecular structures of both complexes were confirmed by single crystal X-ray studies. The varying coordination modes of  $H_2L$  gave rise to different electrochemical behavior of dimer and trimer, which were also rationalized by theoretical calculations.

**Chapter 6** presents, synthesis and characterization of new anthracene derived dinuclear Au(I)-diacetylide complex in which two Au(I) units are attached at 9,10- positions of ethynyl anthracene moiety. This complex exhibited rare non-covalent intermolecular Au···H–C interactions, leading to the formation of a supramolecular 2D-network. Further, to understand the effect of Au(I) units at different position, two other complexes were synthesized, where Au(I) units were attached to 2,6- and 1,8- positions of anthracene, respectively. The absorption and emission spectra of all the complexes have been studied and surprisingly complex having Au(I) at 9, 10 position was found to be highly fluorescent with high quantum yield compared to 2,6 and 1,8 positions this may be due to more perturbation of Au(I) on  $\pi$  system. Complexes have been characterized by elemental

analysis, NMR and Mass spectroscopy and authenticated by their singlecrystal X-ray structures.

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#### Conferences

- "Frontier Lecture Series in chemistry" organized by Discipline of Chemistry, IIT Indore, Indore, January 30-31, 2014 (Poster presentation).
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- "Frontiers in Inorganic Chemistry and Organometallics" organized by Discipline of Chemistry, IIT Indore, Indore, April 14-15, 2016 (Oral presentation).
- "Chemical Research Society of India 2016" February 5-7, 2016 organized by Punjab University Chandigarh. (Poster presentation).

## LIST OF ABBREVIATIONS

CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane
THF	Tetrahydrofuran
CHCl <sub>3</sub>	Chloroform
Cu(OAc) <sub>2</sub>	Copper (II) acetate
AuClPPh <sub>3</sub>	Chloro(triphenylphosphine)gold(I)
MeOH	Methanol
Et <sub>3</sub> N	Triethylamine
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	Bis(triphenylphosphine)palladium(II)dichloride
ACN	Acetonitrile
PPh <sub>3</sub>	Triphenylphosphine
CDCl <sub>3</sub>	Deuterated chloroform
DMSO-d <sub>6</sub>	Deuterated dimethyl sulfoxide
MeOH d <sub>4</sub>	Deuterated methanol
ESI-MS	Electrospray ionization mass spectrometry
AcOH	Acetic acid
DMF	Dimethylformamide
EtOAc	Ethylacetate
PhCO <sub>2</sub> H	Benzoic acid
hmp-H	(2-(2-hydroxymethyl pyridine
hep-H	(2-(2-hydroxyethyl pyridine
hpp-H	(2-(2-hydroxypropyl pyridine
RT	Room temperature
PXRD	Powder X-ray diffraction

ICPAES	Inductive coupled plasma atomic emission spectroscopy
HgCl <sub>2</sub> ,	Mercuric chloride
CdCl <sub>2</sub>	Cadmium chloride
HgBr <sub>2</sub>	Mercuric bromide
CPs	Coordination polymers
HCl	Hydrochloric acid
HNO <sub>3</sub>	Nitric acid
$H_2SO_4$	Sulfuric acid
TGA	Thermo gravimetric analysis
IR	Infrared spectroscopy
KBr	Potassium bromide
Hg(OAc) <sub>2</sub>	Mercury acetate
Вру	Bipyridine
2–ABA	2-aminobenzoic acid
3–ABA	3-aminobenzoic acid
4–ABA	4-aminobenzoic acid
2–HBA	2-hydroxy benzoic acid
4–HBA	2-hydroxy benzoic acid
TLC	Thin layer chromatography
DIPSA	3,5-diisopropylsalicylic acid
THF	Tetrahydrofuran
DFT	Density functional theory
NLO	Nonlinear optical property
НОМО	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital

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## **CHAPTER 1**

#### Introduction

#### **1.1. General introduction**

Coordination chemistry of group 12 metals such as Zn(II), Cd(II), and Hg(II) and their pyridine based derivatives has gained much attention due to their potential applications in various fields such as catalysis, <sup>[1]</sup> ion exchange, <sup>[2]</sup>absorption, <sup>[3]</sup> separation, <sup>[4]</sup> electrical conductivity, <sup>[5]</sup> sensing <sup>[6]</sup> luminescent properties<sup>[7]</sup> and magnetism. <sup>[8]</sup>

Pyridine and its derivatives are commercially important in various fields such as medicinal drug, agricultural products, fungicides and plant growth regulators. Pyridine is well known heterocyclic aromatic compound in coordination chemistry as a single ligand or incorporated in polydentate ligands, such as in the bipyridyl, terpyridyl etc. The great versatility of the pyridine allows the synthesis of several ligands with different functionalization. The pyridine-based chelating ligands form numerous coordination complexes provide varying coordination geometry and nuclearity. These ligands are able to afford several types of stable metal derivatives, providing excellent control of the spectroscopic and electronic properties of the discrete and polymeric framework.<sup>[9]</sup>

Variation of the substituents such as  $-NH_2$ , -COOH -OH and  $-CONH_2$  groups on the pyridine ring, especially at the 2- and 2,6positions assist coordination with metal ions because N atom of pyridine ring is close to these positions which are favorable for the coordination. Among several derivatives of pyridine, like pyridine alcohol, pyridine mono and di-carboxylic acids and their amide derivatives are multidentate ligands from crystal engineering point of view. These ligands have the structural malleability for both the metal-ligand coordination as well as the H-bonding interactions. The complexes of these ligands self-assemble into 1D, 2D or 3D frameworks using H-bonding and other noncovalent interactions.<sup>[10]</sup>

#### 1.2. Pyridine substituted ligands at 2 and 2,6 positions

#### **1.2.1. Pyridine alcohols**

Pyridine alcohols having oxygen and nitrogen donor atoms are found to be valuable from the coordination point of view. Their coordination mode can be altered sometimes, depending on the experimental conditions but generally they are bound to the metal center by both N and O atom forming a chelate ring. Some of the utilized pyridine alcohols in several reports are hep–H = 2-(2-hydroxyethyl)pyridine, hmp–H = 2-(2-hydroxypropyl)pyridine.

In pyridine alcohols, the alcohol group attached to the 2-position of the pyridine nitrogen has been exploited in synthesizing variety of metal complexes with other co-ligands. These ligands can in principle bind to the metal ions as monodentate or bidentate chelating ligands both at the mononuclear and polynuclear levels and can also function as a bridging ligand in polynuclear complexes. Pyridine alcohol can bind with the metals in following binding modes (**Figure 1.1**).



Figure 1.1. Several binding modes of pyridine alcohols.

#### 1.2.2. Pyridine carboxylic acids

The pyridine carboxylic acids and their amide are of enormous importance in the field of coordination chemistry. The pyridine nitrogen as well as the amide/acidic oxygen take part in coordination simultaneously to form a bridge between metal centers and propagate the expansion in various directions (**Figure 1.2**). There is a number of pyridine carboxylic

acids reported with different metals such as pyridine 2-carboxylic acid, pyridine 4-carboxylic acid and pyridine 2,6 dicarboxylic acid. Among them, the pyridine 2,6 dicarboxylic acid has much importance in the field of coordination as well as the synthesis of ligand precursors.



Figure 1.2. Possible binding mode of carboxylates.

#### 1.2.3. Pyridine 2,6 dicarboxylic acid

The pyridine-2,6-dicarboxylic acid, typically called as dipicolinic acid is also an important ligand from crystal engineering point of view. It has a rigid 120° angle between the central pyridine ring and two carboxylate groups, henceforth could potentially provide various coordination motifs to form both discrete and consecutive metal complexes under appropriate synthetic conditions.<sup>[11]</sup> Metal complexes of these ligands, therefore, have been exploited as interesting model systems. Apart from usual O–N–O tridentate coordination mode, it can also act as a bridge between metal centers to form networks (**Figure 1.3**).



Figure 1.3. Binding modes of pyridine 2,6-dicarboxylic acids.

#### 1.2.4. Pyridine dicarboxamide

Pyridine-2-carboxamide and pyridine-2,6-dicarboxamide-based chelating ligands form a variety of coordination complexes with metal ions, providing different coordination geometry and nuclearity. Pyridine-amide based ligands not only offer structural flexibility and their ability to adjust to the geometrical requirements essential for the construction of a supramolecular architecture but also offer coordinating functional groups (i.e. pyridine). The structural flexibility originates from the facile rotation of functional groups attached to an amide group, –CONH–. Interestingly, such a structural flexibility allows the possibility of several geometrical isomers of an amide-based ligand and thus provides another architectural parameter. The ability of pyridine carboxamide to form not only monomer and helical dinuclear complexes, but also more elaborate double helical trinuclear, tetranuclear macrocyclic and heterometallic complexes studied in details (**Scheme 1.1**).<sup>[12]</sup>





Scheme 1.1. Complexes of pyridine 2,6 dicarboxamide.

Kinoshita *et al.* <sup>[13]</sup> have reported a dibromo mononuclear complex of Cu(II) binding with ligand [ $\{N,N^2$ -bis[(S)-1-2-(pyridyl) ethyl]pyridine-2,6-dicarboxamide] (**L3**) which undergoes reversible conversion to a dinuclear, chiral helicate. The helicate formation, which is controlled by the removal or addition of HBr, involves a self-recognition feature such that only the (*M*)-*S*,*S* and (*P*)-*R*,*R* helicates are formed from a racemic mixture of the carboxamide ligand and CuBr<sub>2</sub> (**Scheme 1.2**).



Scheme 1.2. Reversible helical dimer of pyridine 2,6 dicarboxamide.

Apart from pyridine core, bipyridyl ligands have been studied for many years due to their utility in the formation of supramolecular structures. 2,2'-bipyridine (bpy) and its derivatives form a large number of mononuclear mono, bis and tris complexes while 4,4'-bipyridine are promising supramolecular reagents for the construction of coordinated or hydrogen-bonded inorganic–organic hybrid material.<sup>[14]</sup>

#### **1.3.** *In-situ* metal ligand reactions C-C coupling

Hydrothermal or solvothermal *in-situ* metal ligand reactions have recently been aroused in very active research of the crystal engineering of coordination polymers as well as in synthetic organic chemistry. Chemists are now at the earlier stage of investigations on solvothermal metal/ligand reactions; hence some of these reactions were accidentally discovered rather than designed. However, as outlined in this account, several important types of solvothermal, one-pot *in-situ* metal/ligand reactions which are very attractive in view of synthetic organic chemistry have been established to generate products usually inaccessible or not easily obtainable by conventional methods.<sup>[15]</sup> These unusual reactions include dehydrogenative carbon-carbon coupling, hydroxylation of aromatic rings, cycloaddition of organic nitriles.<sup>[16]</sup> Among them, carbon-carbon C-C bond formation is a crucial reaction in modern organic synthesis and the essence of organic synthesis that provides a basis for generating more complicated organic compounds from simpler ones.<sup>[17]</sup>More importantly, the current progress strongly indicates that it is possible to rationalize some complicated solvothermal *in-situ* metal/ligand reactions, as well as to exploit these reactions in the synthesis of new and useful organic compounds and the assembly of coordination molecular architectures with desired properties. Here we have discussed well documented examples of solvothermally developed C-C bond.

Lin and coworker reported the first example of unprecedented C–C coupling.<sup>[18]</sup> They describe the unexpected oxidative coupling of methanol to oxalate (**L4**) by the reaction of  $Zn(NO_3)_2.6H_2O$  and pyridine in methanol at 140°C for five days yielded 2D (methylpyridinium)<sub>2</sub>[Zn<sub>2</sub>(ox)<sub>3</sub>]. They further tried this reaction with zinc

perchlorate in place of zinc nitrate but failed. This indicated the nitrate groups were suggested to be the oxidant for the oxidative coupling of methanol to oxalic acid (**Scheme 1.3**).



Scheme 1.3. C–C coupling in Zn(II) complex.

Tong *et al.*<sup>[19]</sup> carried out hydrothermal treatments of  $Cu(OH)_2$  with bpp, 1,4-cyclohexanedicarboxylic acid, and water in a dilute HCl medium at 175-190°C. Here, they observed a dehydrogenative coupling and hydroxylation of bpp into a dihydroxylcyclohexane ligand *a,a*-1,4-dihydroxy-*e,e,e*,*e*-1,2,4,5-tetra(4-pyridyl)cyclohexane (chtpy) in its Cu(I) coordination polymers, which could be isolated by demetallization with Na<sub>2</sub>(H<sub>2</sub>edta) (**Scheme 1.4**).





Scheme 1.4. Hydrothermally synthesized Cu based 2D and 3D-network.

Kurmoo *et al.*<sup>[20]</sup> have demonstrated the *in-situ* generation of 1,2-bis(8-hydroxyquinolin-2-yl)ethane-1,2-diol from 2-(hydroxymethyl)- quinolin-8-ol (**L6**) by the rare C–C coupling reaction resulted in the formation of the unique cluster, where the organic ligand wrapped a vertex-shared dicubane cobalt(II) unit in a trefoil fashion. The complicated synthesis provides an unexpected structure of heptanuclear Co(II) (**Scheme 1.5**).



**Scheme 1.5.** Heptanuclear Co(II)complex synthesized *via* C–C coupling *in-situ* metal ligand reaction.

*In-situ* carbon carbon bond formation in the crystal engineering of complexes was first recognized by Champness *et al.*<sup>[21]</sup> They obtained crystals of the three-dimensional (3D) coordination polymer

 ${Ag[tpct]BF_4}n$  (1) (tpct = 1,2,3,4-tetrakis(4- pyridyl)cyclobutane) from the reaction of AgBF<sub>4</sub> and 1,2- *trans*-(4-pyridyl)ethene (bpe) in MeCN/CH<sub>2</sub>Cl<sub>2</sub> solution in the presence of light. The *in-situ* cyclization of bpe to yield the ligand tpct is responsible for the formation of the 3D framework of **D** (Scheme 1.6).



Scheme 1.6. Ag(I) based complex developed through *in-situ* metal ligand reaction.

Another excellent example of Cd(II) based C–C coupling was discovered by Feng *et al.*<sup>[22]</sup> They had started with the mixture of  $Cd_{10}S_4(SPh)_{12}$ , 4,4trimethylenedipyridine, Na<sub>2</sub>SO<sub>4</sub> and water at 190°C for three days which yielded the crystals of  $[Cd_8(SC_6H_5)_{12}(tpbz)_2SO_4](HSO_4)_2(H_2O)$ . The dehydrogenative coupling between two 4,4 trimethylenedipyridine units was established as three dimensional framework of **C**. High temperature and pressure may be responsible for this *in-situ* metal ligand synthesis reaction (**Scheme 1.7**).




**Scheme 1.7.** Cd(II) based C–C bonded complexes synthesis *via in-situ* metal ligand reaction.

Li and coworker<sup>[23]</sup> have reported an unusual example of solvothermally synthesized *in-situ* metal ligand reaction based on Ni(II) complex. The experiment was performed by heating the mixture of **L9** and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O in MeOH/MeCN at 70 °C under solvothermal conditions. As the temperature of the mixture was increased to 90 °C, namely, treatment of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O with 2 equiv of **L9** in MeOH another compound was produced. The most remarkable feature of this reaction is the *in-situ* formation of the **L10** ligand, which was assumed to be generated *via* C–C coupling reaction and oxidation of methylene to form a carbonyl. The ligand **L10** was isolated and characterized by the NMR spectroscopy. A prominent feature regarding the synthesis of this complex, MeOH is the simultaneous formation of C–C and C–N bonds in a one-pot reaction (**Scheme 1.8**).



Scheme 1.8. Solvothermally synthesized Ni(II) based C–C bonded complex.

Rademeyer *et al.*<sup>[24]</sup> synthesized solid-state novel structures by the reaction of cadmium and mercury dihalide with benzopyridine- and benzopyrazine-type N-donor ligands. These structures can be classified as one-dimensional halide-bridged polymers of composition  $[M(\mu-X)_2L)]_{\infty}$ , and one-dimensional dimers that are linked by long, semi-coordinate M– X····M–X interactions to form pseudo-halide-bridged polymers. Here the metal ion displays a coordination number of five with two different geometries. They also studied the structural features in detail and explained the effect of an increase in the width of the N-donor ligand on the halide-bridged chain (**Scheme 1.9**).



Scheme 1.9. Synthesis of psuedohalides bridge based Cd(II) and Hg(II) complexes.

# 1.4. Effect of acidic and basic medium on metal complexes

The formation of well-ordered architecture is highly influenced by various factors, such as the molar ratio of reactant reagents, a solvent used, medium of the reactions, and the selection of a secondary ligand. In these factors, the medium of the reaction plays a crucial role in extending and reconstructing the structure. There are the number of reports which show, how the medium affects the structural diversity of the metal complexes.

Zhao *et al.*<sup>[25]</sup> have developed a method where they employed concentrated acid yielded metal organic framework. Here one porous coordination networks MOF-1 was synthesized by solvothermal reaction of Zn(II) nitrate with anthrancene-9,10-dicarboxylic acid through tuning the molar ratio of metal salt and ligand in presence of concentrated acid

HBF<sub>4.</sub> After the introduction of 4,4'-bpy into reaction system, MOF-2 and MOF-3 were obtained in acidic medium (**Scheme 1.10**).



Scheme 1.10. Zn(II) MOFs developed in acidic medium.

Du *et al.*<sup>[26]</sup> have constructed a series of Cd(II), Co(II), Ni(II), and Pb(II) mixed-ligand coordination complexes based on 5-sulfoisophthalic acid (**L15**) and the bent dipyridyl ligand 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (3-bpo) or its 4-pyridy-IN-donor analogue (4-bpo) have been synthesized. The significant effect of acidic medium on the assembly of the Cd(II) complexes has been demonstrated, which leads to the formation of distinct crystalline products, whereas the other metals such as Co(II), Ni(II), and Pb(II) systems are independent to acidic condition of the synthetic reaction. Complexes display various coordination motifs with different existing forms, conformations, and coordination modes of the organic ligands. Further, extended supramolecular networks are constructed *via* secondary interactions such as hydrogen-bonding and aromatic stacking.

Solid-state properties of thermal stability and fluorescence for these crystalline materials are also presented (**Scheme 1.11**).





Scheme 1.11. Structural diversity of Co, Ni, and Pb complexes in acidic medium.

The pH value of the reaction system plays a crucial role in the ligand deprotonation and the assembly of the metal–organic polymers. Two Cd(II) and two Zn(II) compounds containing dicarboxyl-functionalized arylhydrazone of barbituric acid (**L16**) have been produced by the Pombeiro and coworker<sup>[27]</sup> by varying pH under hydrothermal conditions. Compound **1** and **3** were obtained at acidic pH whereas **2** and **4** had been synthesized in basic conditions forming one dimensional double chain-like structures. The metal ions are coordinated *via* ligand carboxylate groups and the amide functional group (**Scheme 1.12**).



Scheme 1.12. Effect of acidic and basic medium on Zn and Cd complexes.

Zhu *et al.*<sup>[28]</sup> have systematically investigated the relationship between the structures and various external stimuli. In this work, they exploited 4-pyrimidyl-benzoic acid (**L17**) and  $Co(NO_3)_2.6H_2O$  as a starting material. By altering the medium or pH of the reaction system, two new Co(II) coordination polymers, were obtained. One is 2D layer framework, formed

at pH 8 using (0.5M) NaOH solution while other is 0D independent structure obtained at pH 4 by (0.5M) HNO<sub>3</sub> hydrothermally (Scheme 1.13).



**Scheme 1.13.** Hydrothermally synthesized Co(II) complexes in presence of acid and base.

The effect of reaction medium on structural diversity of Cd(II) based complexes was explored by Cai et al.<sup>[29]</sup> Here they have synthesized Cd(II) complexes by the reaction of  $N_2O_2$  donor tetradentate asymmetrical Schiff base ligand 2-{[2-(dimethylamino) ethylimino]methyl}-6methoxyphenol (L18), and  $CdCl_2$  under different reaction conditions at room temperature. The diverse structures show the marked sensitivity of the structural chemistry of the tetradentate asymmetrical Schiff base ligand L18. Trinuclear complex has been formed in basic medium at pH 10 exhibiting a rare zero-dimensional structure of Cd(II). At pH = 8-9, a dinuclear Cd(II) complex is formed. The reaction at pH=5-7 leads to two one-dimensional structures and further decrease of the pH to 3-5 results in a zero-dimensional structure. The results further show that conversions of complex (a-e) can also be achieved by adjusting the pH value of the reaction solution,  $a \rightarrow b pH 8 b \rightarrow c pH 3$  and  $d \rightarrow e pH 5$ .Comparing these experimental results, it is evident that the pH plays a crucial role in the formation of the resulting structures, which simultaneously provides very

effective strategies for constructing the Cd(II) compounds with  $N_2O_2$  donor tetradentate asymmetrical Schiff base ligand (Scheme 1.14).



Scheme 1.14. Structural variation of Cd complexes at different pH.

## **1.5. Isolation of metastable intermediate**

In order to determine the mechanistic pathway, reaction intermediates play a major role in the field of organic as well as inorganic chemistry. Structural characterization of an intermediate is difficult but it has been done by the NMR and Mass spectrometry. Moreover, the isolation and crystallographic characterization of a metastable intermediate is still an arduous challenge. Only few reports are available which deal with the isolation and crystallographic characterization of metastable intermediate.

Carmona *et al.*<sup>[30]</sup> discovered an example based on organometallic intermediate. They investigated that the Diels–Alder (DA) reaction of acyclic enals with cyclopentadiene was efficiently catalyzed by aquacomplex  $(S_{Ir},R_C)$ –[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(Prophos)(H<sub>2</sub>O)][SbF<sub>6</sub>]<sub>2</sub>. It is supposed that the pathway for the DA reaction between enals and dienes catalyzed by one-point-binding half-sandwich transition metal complexes involves the diene attack to the coordinated enal followed by displacement of the

coordinated adduct by the enal. Therefore, to get a proper mechanism of the catalytic reaction, the isolation and completely characterization of involved metal-enal intermediate complex  $(S_{Ir},R_C)$ -[( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(Prophos)(ethylacrolien)][SbF<sub>6</sub>]<sub>2</sub> **D** has been attempted (**Figure 1.4**).



Figure 1.4. Organometallic intermediate synthesized during the catalysis.

Barbour *et al*<sup>[31]</sup> have worked on a known pillar layered metal–organic framework of Co(II) which undergoes a change in degree of interpenetration from a highly porous doubly-interpenetrated framework (**2a**) to a less porous triply-interpenetrated framework (**3a**). The transformation involves an intermediate empty doubly interpenetrated phase (**2a'**) which has been isolated for the first time for this kind of phenomenon by altering the conditions of activation of the as-synthesized material (**Scheme 1.15**).



Scheme 1.15. Isolation of intermediate in solid state structural transformation.

Conejero and coworker.<sup>[32]</sup> have investigated that upon addition of  $Br_2$  or  $I_2$  to unsaturated 14-electron cationic Pt(II) alkyl complexes yields carbon–halogen coupling Pt(II) products. At low temperature experiment, they isolated a mononuclear, paramagnetic Pt(III)-alkyl stable intermediate species which exhibits an unprecedented see-saw geometry. This complex can be further oxidized to a Pt(IV)-alkyl dibromo derivative that was found to be unstable towards reductive carbon–halogen coupling (Scheme 1.16).



Scheme 1.16. Organometallic Pt(II) metastable intermediate.

#### **1.6. Supramolecular interactions**

The intermolecular non-covalent interactions in the metal complexes have been recognized to be an efficient tool to design the highly ordered supramolecular network with selective physicochemical properties.<sup>[33]</sup> The awareness of intermolecular non-covalent interactions in the crystal has brought the subject into the mainstream of supramolecular chemistry.<sup>[34]</sup> To achieve this goal, one requires not only the right choice of molecular building blocks but also a better understanding of the degree of control on the interactions between molecules in the crystal lattice.<sup>[35],[36]</sup> Since most intermolecular forces are weak and often non-directional therefore, strong directional non-covalent interactions such as hydrogen bonding, metal metal and metal hydrogen interactions are involved in constructing supramolecular arrays. These interactions were used to study the molecular recognition as well as photo-physical properties. M.M interactions in some of heavier metals such as, Cu, Pt and Au which were responsible for the rich photo physical properties in solid state. In case of Au, well established aurophilic interactions *i.e.*, Au···Au have been recognized which were used in the formation of a well-designed highly ordered framework. Besides aurophilic interactions, some rare interactions *i.e.*, Au····H-C interactions were involved in the formation of dinuclear

and 1D polymeric chain. Supramolecular network was still unexplored *via* Au····H–C interactions.

Aforementioned discussion has been aimed to underscore the significance of hydrothermally developed *in-situ* metal ligand reaction and their role in the formation of 0D to high dimensional network by employing Cd, Cu, Co and Ag metals. Some of the noble metals such as Au have profound applications in the construction of supramolecular arrays *via* their Au…Au and Au…H–C non-covalent secondary interactions.

#### **1.6.1.** Supramolecular interactions in gold

Chemical inertness of metallic gold makes it a unique element and a measure of wealth. The development of gold based carbon-rich materials containing alkynyl systems have been an active area of research in last decades. <sup>[37]</sup> This can be attributed to their distinctive photophysical and aurophilic properties as well as their ability to build supramolecular architectures based on the linear coordination environment. <sup>[38]</sup> The carbon rich alkynyl bridge has the capability to connect the two metal centres, which provides a pathway to communicate/couple electronically through its p-conjugated units. It is visualized that the possible communication between gold centers might allow to be exploited as molecular wires and non-linear optical devices. Recently, alkynylgold(I) complexes have also been explored for their luminescence properties. Also, variations in the nature of metal centers and alkynyl ligands would provide an efficient means of tuning the photophysical and photochemical properties of the system.

Yip *et al.*<sup>[39]</sup> have demonstrated the effect of auration on tetracene and tetracenylacetylide on the photophysical properties of the organic chromophore particularly, metalation leads to a significant red shift of the absorption band and the corresponding fluorescence. An interesting supramolecular honeycomb network of tetracenyldiacetylide Au(I) was formed which was mainly supported by aurophilic interactions (**Scheme 1.17**).



Scheme 1.17. Formation of supramolecular 2D-network through Au…Au interactions.

The important Au···H–C interactions in gold complexes for the first time was reported by Baukava *et al.*<sup>[40]</sup> They investigated successfully a complicated system of intramolecular Au····H–C contacts in two organogold derivatives of diphenymethane and diphenylethane. These interactions involve the H atom of bridging alkyl group (–CH<sub>2</sub>, and–CH<sub>2</sub>–CH<sub>2</sub>–) of aforementioned organogold complexes and further rationalized by the IR and low temperature NMR spectroscopy (**Scheme 1.18**).



Scheme 1.18. Intramolecular Au…H–C interactions.

Haukka *et al.*<sup>[41]</sup> have reported the role of noncovalent gold–hydrogen and aurophilic interactions in the formation of extended molecular systems of gold. Here the Au(I) complexes are coordinated in a distinctive linear geometry, leaving open access to noncovalent contacts to interact with the metal atom. These weak Au····H–C contacts are the strongest intermolecular interactions and render substantial contribution in the assembly of the supramolecular structures of complexes. Though the Au····H–C contacts are weak and often shadowed by stronger interactions, they should not be ignored when considering the supramolecular ensembles of gold complexes. These contacts can provide additional stabilization of the structures and also influence the supramolecular arrays (**Figure 1.5**).





Figure 1.5. Au…H–C interactions forming 1D polymeric chain.

#### **1.7. Scope of present work**

The aforesaid brief discussion highlights selective modern aspects of metal complexes of pyridine based ligands then it moves towards the hydrothermal or solvothermal one pot *in-situ* metal ligand reactions technique as well as effect of reaction medium on structural variation of metal complexes. Further discussion has been extended with the isolation and structural characterization of metastable intermediate. The present

thesis work originates from the perspectives of developing selective newer homometallic complexes of Cd, Hg, Au and heterometallic complexes of Hg, Cu by incorporating the pyridine based ligands like 2-(2hydroxyethyl)pyridine (hep–H), 2-(2- hydroxymethyl)pyridine (hmp–H), 2-(2- hydroxypropyl)pyridine (hpp–H), as well as polyaromatic hydrocarbons such as anthracene. The outlines of present work are as follows–

1. Synthesis characterization and well-ordered high dimensional structural architect of Cd and Hg metal complexes using pyridine based ligands, have been described thoroughly. All the reactions were carried out through one pot *in-situ* metal ligand reaction at room temperature.

2. Synthesis and crystallographic characterization of heterometallic Cu(II)-Hg(II) polymeric metastable intermediate as well as heterometallic 1D polymeric chain at ambient conditions.

3. Photophysical and solid state structural properties of organometallic metal diacetylides based on Au(I) through unique noncovalent Au····H–C interactions have been studied.

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# **CHAPTER 2**

# Formation of a 1D-Polymeric Chain of Hg Building Blocks Through C–C Coupling Under Ambient Conditions

## **2.1. Introduction**

*In-situ* metal/ligand reactions have evoked copious research interest for past few decades and act as a bridge between coordination chemistry and organic chemistry. It facilitates the generation of new organic reactions, elucidation of reaction mechanisms, and generation of novel molecular frameworks which are otherwise difficult or even impossible to obtain through designed synthetic routes.<sup>[1,2]</sup> Recently reported *in-situ* metal ligand reactions involve dehydrogenation, carbon-carbon coupling, hydroxylation of aromatic rings, cycloaddition of organic nitriles with azide and ammonia and transformation of inorganic and organic sulfur, leading to synthesis of novel ligands.<sup>[3,4]</sup>

*In-situ* reactions have been largely performed only under hydrothermal or solvothermal conditions till date. There have been few reports documented on *in-situ* synthesis of discrete novel ligand through C–C coupling and their isolation. However, the isolation of an *in-situ* C–C couple ligand formed in polymeric material has been a challenging task and not known.<sup>[5]</sup> C–C coupling reactions are among the essential processes in organic synthesis as they provide a foundation for generating more complicated organic compounds from simpler ones.<sup>[6]</sup> The formation of C–C bond leads to the construction of biaryl scaffolds including the dimerization of phenols.<sup>[4]</sup> Metal ion assist activation of ligand precursors thus play a crucial role in *in-situ* metal/ligand reactions. Transition metals such as ruthenium, rhodium, palladium exhibit redox behavior in the presence of organic species.<sup>[6,5]</sup> Tao *et al.*<sup>[7]</sup> have reported a new heptanuclear copper(II) complex, where ligand has been synthesized *insitu* through C–C coupling process in the presence of Cu(II) (Scheme A).



Scheme A. In-situ synthesis of ligand through C-C coupling process.

Interestingly, a unique phenomenon was obtained by Su and coworkers where *in-situ* metal/ligand reaction, leads to the formation of double C–C coupling on CHCl<sub>3</sub>. This reaction involves cleavage of three C–Cl bonds of CHCl<sub>3</sub> and the formation of two new C–C bonds at the same carbon center during the synthesis of Mn<sup>2+</sup> 1D-polymeric chain under solvothermal conditions. (**Scheme B**).<sup>[8]</sup>



Scheme B. Formation of C–C coupled product *via* the solvothermal method.

In this chapter, we have reported the formation of an unprecedented C-C coupled 1D polymeric chain in 1 of Hg, where two terminal Cl atoms attached to the neighboring Hg centers were in the cis orientation, and (ii) a  $\mu$ -oxo/ $\mu$ -chloro bridged 1D polymeric chain in 2. 1 and 2 were obtained by the reaction of  $HgCl_2$  with the ligand hmp-H (2-(2-hydroxymethyl pyridine)) in 1 : 1 and 1 : 2 molar ratios, respectively, in MeOH at ambient conditions. The unusual results have been obtained as in case of 1 and 2 by using Hg(II) at ambient conditions. Further, we explored our work with Cd(II) as well as the series of pyridine alcohol. The reactions of  $HgCl_2$  and  $CdCl_2$  with hpp-H [hpp-H = 2-(2hydroxypropyl)pyridine] in 1 : 1 or 1 : 2 molar ratio, produced 1D polymeric chain  $[(Cl)Hg(\mu-Cl)_2(hpp-H)]_n$  (3), where hpp-H coordinated to the Hg(II) ions in a monodentate fashion via pyridine nitrogen donor while the *ortho*-positioned  $-(CH_2)_3OH$  group of hpp-H remained pendant. Similarly, the reactions of  $CdCl_2$  with hmp-H [hmp-H = 2-(2-hydroxy methyl)pyridine] and hpp-H [hpp-H = 2-(2-hydroxypropyl)pyridine] in MeOH at ambient condition yielded 1D polymeric chains  $[Cd(\mu_2 Cl_2(hmp-H)]_n$  (4) and  $[Cd(\mu_2-Cl)_2(hpp-H)]_n$  (5), respectively, where hmp-H and hpp-H coordinated to the Cd(II) ions in a bidentate fashion with the pyridine nitrogen donor and hydroxyl oxygen donor. 1-5 have been characterized by elemental analysis and authenticated by their single crystal X-ray studies.

#### 2.2. Results and discussion

**2.2.1.** Synthesis and characterization. The two 1D-polymeric chain 1 and 2 have been synthesized by the reaction of  $HgCl_2$  with the ligand hmp–H (2-(2-hydroxymethyl pyridine)) in 1 : 1 and 1 : 2 molar ratios, respectively, in methanol at RT (Scheme 2.1). Subsequent slow evaporation of the solvent at room temperature yielded single crystals suitable for X-ray diffraction which established the 1D-polymeric chains of 1–2. Single crystal X-ray studies of 1 and 2 revealed an unprecedented

C–C coupled 1D polymeric chain of Hg(II) and a new class of 1D polymeric chain of Hg(II) containing uncommon  $\mu$ –oxo/ $\mu$ –chloro bridged building block. **1** and **2** have been further characterized by elemental analysis however; (ICP-AES) spectroscopy were performed to rationalize expected metal content.



Scheme 2.1. Synthetic route for 1 and 2.

**2.2.2. Structural aspects of 1. 1** crystallized in the monoclinic *C*2/c space group with a crystallographically imposed inversion center and one lattice water molecule. The 1D-polymeric framework of **1** consisted of symmetrically bridged dimeric building units of  $\{[Cl(hmp^-)Hg-(\mu-Cl)_2Hg(hmp^-)Cl]\}$ , where the building units were connected through the newly formed C–C bonds between the adjacent two terminal hmp<sup>-</sup> ligands (**Figure 2.1, Table A1**). Each Hg(II) atom in the polymeric chain **1** was bonded to the N(1) and O(1) donors of the hmp<sup>-</sup> ligand with Hg(1)–N(1)

and Hg(1)–O(1) distances of 2.206(8) Å and 2.740(2) Å, respectively. The bond distances of bridging Cl(2)/Cl(2A) atoms and the terminal Cl(1) atom in the same dimeric unit were 2.682(3) Å/ 2.763(3) Å and 2.351(3) Å, respectively, leading to a distorted square pyramidal geometry. The central Hg<sub>2</sub>Cl<sub>2</sub> unit formed a puckered ring with a deviation of 22.06(4)° from the mean plane. It should be noted that **1** represented the first example where the terminal Cl atoms in the building dimeric unit {ClHg( $\mu$ -Cl)<sub>2</sub>HgCl} along the polymeric chain were in the *cis* configuration. Both the chelated hmp<sup>-</sup>ligands were in *cis* orientation.



**Figure 2.1.** (a) A perspective view of the 1D-polymeric chain of **1**. (b) The newly formed C–C bonds are shown in pink. (c) Formation of intermediate dimer in **1** (Water molecule was removed for clarity).

However, the adjacent dimeric units in the polymeric chain of **1** were arranged in an anti-fashion and interconnected *via* the C–C coupling process (**Figure 2.1b**, **c and Table A2**).

**2.2.3. Structural aspects of 2.** The 1D-polymeric chain **2** crystallized in triclinic  $P_{\overline{1}}$  space group with a crystallographically imposed inversion center (**Figure 2.2, Table A1**). The asymmetric unit of **2** consisted of a doubly chloride bridged building dimeric unit {Cl(hmp<sup>-</sup>)Hg(µ–Cl)}<sub>2</sub>

which was further linked to the adjacent dimeric unit along the polymer chain *via* the oxygen donors of the chelated hmp<sup>-</sup> ligands (**Figure 2.2**).



Figure 2.2. A perspective view of the 1D-polymeric chain of 2.

This, in effect, yielded the first example of an alternate  $(\mu-Cl)_2$  and  $(\mu-O)_2$  bridged polymeric mercury framework. Each Hg(II) ion was in a distorted octahedral geometry, bonded to two bridging Cl atoms, (Hg(1)–Cl(2) 2.801(13) Å, Hg(1)–Cl(2A) 2.760(12) Å, two bridging O atoms from hmp<sup>-</sup> Hg(1)–O(1) 2.618(4)Å, Hg(1)–O(1A) 2.846(10)Å in the equatorial plane, while the axial position was occupied by the N atom of hmp<sup>-</sup> Hg(1)–N(1) 2.180(4) Å and the terminal Cl atom Hg(1)–Cl(1) 2.350(12) Å (**Table A2**). The Hg(1)–O(1) was in the range of secondary interactions which was close to the reported Hg–O distances.<sup>[9]</sup> The bond distances revealed that the Hg<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>O<sub>2</sub> rings in **2** were symmetric and unsymmetric, respectively. Further, in the dimeric [Cl(hmp<sup>-</sup>)Hg( $\mu$ –Cl)]<sub>2</sub> unit the terminal Cl atoms and hmp<sup>-</sup> ligands were arranged in a trans fashion, and the two hmp<sup>-</sup> ligands were having the chair configuration (**Figure 2.3**).



Figure 2.3. Chair configuration of 2.



Figure 2.4. A perspective view of the hydrogen bonded 2D-network in 1.

**2.2.4.** Packing diagram of 1. The packing diagram of 1 revealed the existence of intra- and inter-molecular hydrogen bonding interactions (Figure 2.4, Table A3). The intramolecular C–H···Cl hydrogen bonding involved the hydrogen atom H(1) of the coordinated pyridine ring of hmp<sup>-</sup> and the bridging Cl(2) atom along the polymeric chain. The intermolecular interactions comprise O–H···Cl, O–H···O and C–H···O hydrogen bonding. The water molecules were trapped between two adjacent H-bonded layers which are separated by 8.023 Å.

**2.2.5.** Packing diagram of 2. The packing diagram of 2 showed intra and intermolecular (C–H···Cl) hydrogen bonding interactions (Figure 2.5 Table A3). The intramolecular interaction involved the H(1) atom of hmp<sup>-</sup> and the bridging Cl(2) atom of the same 1D layer. The intermolecular interactions involve H(2) and H(3) atoms of the coordinated pyridine of hmp<sup>-</sup> and terminal Cl(1) and bridging Cl(2) atoms of two adjacent layers, yielding the 2D-network.



Figure 2.5. A perspective view of the hydrogen bonded 3D-network in 2.

Moreover, this 2D-network was further linked by a methylene H(6A) atom and a terminal Cl(1) atom of another layer forming a hydrogen bonded 3D-network (**Table A3**). In **1** both hmp<sup>-</sup> ligands and Cl atoms were arranged in a *cis* fashion in contrast to **2**.

Unlike 2, in 1 the Hg<sub>2</sub>Cl<sub>2</sub> ring was nonplanar. In 2 the O atom of the coordinated hmp<sup>-</sup> ligand was further extended *via* elongated primary interactions Hg(1A)–O(1A) 2.846(10)Å resulting in a planar Hg<sub>2</sub>O<sub>2</sub> ring. As we have used the same ligand *i.e.*, hmp–H in case of 1 and 2 both were creating a five-membered ring around the metal center with a same metal bite angle of 67.9° The Hg–Hg separations in 1 were observed as 3.96Å and in 2 it was calculated as 4.32Å.

**2.2.6.** Inductively coupled plasma atomic emission spectroscopy experiment (ICP-AES) of 1. To confirm that whether this C–C coupling was happening due to mercury or any impurity present in the complex, we have performed inductively coupled plasma atomic emission spectroscopy experiment (ICP-AES) which showed that the presence of only Hg(II) with the expected composition (50%). The absence of any other

impurities, therefore, suggested that Hg(II) was acting as a catalyst for the C–C coupling.

In order to explore pyridine alcohol ligand with Hg(II), where we obtained some unprecedented results of **1** at ambient condition, the compounds **3**, **4** and **5** have been designed and synthesized. Here we initiated again with HgCl<sub>2</sub> as well as with CdCl<sub>2</sub> with hmp–H [(hmp-H = 2-(2-hydroxymethyl) pyridine) and hpp–H [(hpp–H = 2-(2-hydroxypropyl)pyridine)], in methanol at same reaction conditions as in **1** and **2**. Unlike **1** and **2**, we obtained **3** where hpp–H was coordinated to Hg(II) *via* N-atom only in monodentate manner and **4–5** where hmp–H and hpp-H were coordinated to Cd(II) ion in a N, O bidentate fashion forming *zig-zag* 1D polymeric chain (**Scheme 2.2**).



Scheme 2.2. Synthetic outline for 3, 4 and 5.

**2.2.7. Structural aspects of 3. 3** crystallized in the triclinic  $P_{\overline{1}}$  space group with a crystallographically imposed inversion center (**Figure 2.6**, **Table A4**). Crystal structure of **3** consisted of dimeric unit where both the Hg(II)
ions bonded to the N atom of a hpp-H ligand as well as Cl<sup>-</sup> ion. The two dimeric units were connected via bridging halides to give a zig-zag polymeric chain in which the Hg(II) ion exhibited distorted tetrahedral coordination geometry (3Cl<sup>-</sup>, 1N-atom). The hpp–H ligand in **3** was linked to the Hg(II) ions only through the neutral pyridine nitrogen donor leaving the suitably ortho-positioned (CH<sub>2</sub>)<sub>3</sub>-OH a potential pendant donor [Hg···O(hpp-H)] non-bonding distances was 5.79Å in 3, similar to that reported in the discrete monomeric *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)(hep-H)] and the dimeric  $[Ag_2(sac)_2(hep-H)_2]$  (sac = saccharinate) complexes.<sup>[10]</sup> These contrast with other discrete molecular frameworks, as well as polymeric complexes, in which the hpp ligand was specifically bonded as a monoanionic bidentate N, O donor. The two coordinated hpp-H ligands attached to the two adjacent Hg(II) ions in 3 existed in trans configuration, and the same pattern continues along the polymeric chain. The Hg-N (hpp-H) distances in **3** were found to be 2.23(4)-2.24(8) Å along the polymeric chain. The Hg–Cl distances in 3 vary significantly viz, Hg(1)– Cl(1), 2.510(3) Å, Hg(1)–Cl(2) 2.354(4) Å and Hg(1)–Cl(3) 2.772(4) Å (Table A2), and while moving from one Hg(II) center to another Hg(II) center along the polymeric chain in the same Hg-Cl distances again varied slightly, Hg(2)–Cl(1) 2.815(4) Å, Hg(2)–Cl(3) 2.513(3) and Hg(2)–Cl(4) 2.338(4) Å (Table A2).



Figure 2.6. Molecular structure of 3.

2.2.8. Structural aspects of 4 and 5. 4 and 5 were crystallized in orthorhombic *Pbcn* and monoclinic  $P2_1/c$  space group, respectively, with crystallographically imposed inversion center (Figures 2.7-2.8 Table A4). Each Cd(II) atom exhibited hexacoordinated environment with distorted octahedral geometry. The four coordination sites were occupied by bridging Cl atoms {Cd(1)-Cl(1) 2.5484(6) Å, Cd(1)-Cl(1') 2.6656(6) Å, Cd(1)–Cl(2) 2.5352(7) Å, Cd(1)–Cl(2) 2.7129(7) Å Cd(1)–Cl(1) 2.6748(9) Å, Cd(1)-Cl(1) 2.6015(9) Å, Cd(1)-Cl(2) 2.5767(9) Å, Cd(1)-Cl(2) 2.6444(9) Å}, while the remaining two were occupied by N, O donor atoms of pyridine alcohol Cd(1)-N(1) 2.294(2) Å, Cd(1)-O(1)2.411(2) Å Cd(1)-N(1) 2.331(3) Å, Cd(1)-O(1) 2.432(3) Å (Table A5). Cl(1) and Cl(2) form a doubly bridging unit between two successive Cd(1)ions, producing zig-zag 1D polymeric chains. In the polymeric chain of the complexes, the hmp-H and hpp-H ligands were present in trans fashion. In 4, the hmp-H bound the Cd(II) center via N and O atoms in a bidentate manner, creating a five-membered ring around the metal center with a metal bite angle of  $70.22^{\circ}$ .



Figure 2.7. Molecular structure of the 1D polymeric chain of 4.



Figure 2.8. Molecular structure of 1D polymeric chain of 5.

However, hpp–H was attached to the Cd(II) center through N and O atoms, resulting in a rare seven-membered ring around the Cd(II) center with a metal bite angle of 89.30°. The observed bite angles in **4**, and **5** suggested that a successive increase in the number of methylene groups from hmp–H to hpp–H led to a stepwise increase in the bite angle by approximately 10°. The Cd–Cd separations in **4**, and **5** were observed to be in the range 3.761(5)-3.992(4) Å.

**2.2.9.** Packing diagram of 3. The packing diagrams of 3 revealed the presence of following intramolecular and complicated intermolecular hydrogen bonding interactions (Figures 2.9, Table A6). The intramolecular C–H···Cl hydrogen bonding involved the interaction between one of the hydrogen atoms of the pendant b-CH<sub>2</sub> group H(7B) and H(9) atoms of hpp–H ligands and terminal and bridged Cl atoms Cl(3) and Cl(4).



Figure 2.9. Intramolecular H-bonded 1D-polymeric chain of 3.

The coordination polymeric layer of 3 was connected with the neighboring layer via intermolecular C-H···Cl hydrogen bonding between the hydrogen atoms of the pyridine ring of hpp-H ligands in one layer to the terminal Cl(1) and Cl(4) atoms of upper and lower layers, respectively, along the c-axis. 3 showed C-H···Cl hydrogen bonding interaction between hydrogen atom of the pyridine ring of hpp-H in one layer and the bridging Cl(3) atom in the adjacent layer (Figure 2.10).

**(a)** 



Figure 2.10. (a) Molecular structure of 3 with intermolecular H-bonding forming 2D network. (b) 3D-network of 3 formed *via* intermolecular H- bonding along the *c* axis.

2.2.10. Packing diagram of 4 and 5. The polymeric chains in 4 and 5 showed the presence of intermolecular H-bonding involving pyridine H and bridging Cl atoms; however, intramolecular H-bonding also found in **5** involving H atom of alcoholic (OH) of pyridine ring and bridging Cl atom. Each 1D polymeric chain was extended to H-bonding 2D network through the pyridine H atom of one layer and bridging Cl atom of adjacent layer, further, in complex **5**  $\pi \cdots \pi$  interactions (3.345 Å) between pyridine rings of two layers generated 2D polymeric network (**Table A6, Figures 2.11, 2.12**).



**Figure 2.11.** (a) Intermolecular H-bonding interactions between two adjacent 1D polymeric chain in 4 involves the H(3) of pyridine ring of hmp–H and terminal Cl (1) of another chain C(3) –H(3)····t–Cl(1) 2.941(1) Å, yielding 2D network along tilted c axis. (b) H-bonded 3D-network of 4 along the c axis.



**Figure 2.12.** (a) Intramolecular H-bonded 1D polymeric chain of **5** involved interactions were H(1) of pyridine ring of hep–H and Cl(1) of neighbouring Cd(II) ion C(1)–H(1)  $\cdots \mu$ –Cl(1) 2.873(1) Å, C(6)–H(6A)  $\cdots$ Cl(1) 2.861(1) Å, O(1)–H(101)  $\cdots$ Cl(1) 2.433(53) Å. (b) Intermolecular H-bonding and  $\pi \cdots \pi$  interactions 3.345 Å between pyridine rings of two layers forming 2D polymeric network of **6** tilted along the *b* axis (A represents centroid of the pyridine ring).

### **2.3.** Conclusions

Present chapter demonstrated an unprecedented novel 1D polymeric chain of **1** *via* a C–C coupling process at room temperature in metal: ligand ratio 1 : 1. By varying the metal : ligand ratio, to 1 : 2 another new 1Dpolymeric chain **2** has been developed *via* the formation of unusual Hg<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>O<sub>2</sub> rings along the polymeric chain. On the other hand three other 1D polymeric chains **3–5** have been synthesized under the same reaction conditions. In case of **3**, the ligand was coordinated through N-atom or monodentate manner while in **4–5** they were attached as bidentate manner through N and O atoms.

#### **2.4. Experimental Section**

**2.4.1. Materials and physical measurements.** The commercially available starting materials, HgCl<sub>2</sub>, CdCl<sub>2</sub>, 2-methylhydroxy pyridine (hmp–H) and 2-propylhydroxy pyridine methanol were used without further purification. Elemental analyses were carried out with Thermoscientific elemental analyzer. Inductively Coupled Plasma: Atomic Emission Spectrometer (ICP-AES) were recorded on CCD equipped ARCOS System.

**2.4.2. Synthesis of (1).** A solution of hmp–H (109 mg, 1 mmol) in MeOH (4 ml) was added to  $\setminus$  HgCl<sub>2</sub> (271 mg, 1 mmol) in MeOH (40 ml) solution and kept for stirring for overnight at room temperature. The solution was then passed through the filter paper to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. Transparent colorless crystals of insoluble **1** were obtained within 15 days by slow evaporation of the solvent. Yield 59%, **Anal. Calcd** for C<sub>12</sub>H<sub>14</sub>Cl<sub>4</sub>Hg<sub>2</sub>N<sub>2</sub>O<sub>4</sub>, (Mw =793.23): C, 18.17; H, 1.78; N, 3.53. Found: C, 18.31; H, 1.75; N, 3.32. ICPAES: Hg, 50.63% (Calcd: Hg, 50.57).

**2.4.3.** Synthesis of (2). A solution of hmp–H (218 mg, 2 mmol) solution in MeOH (4 ml) was added to a HgCl<sub>2</sub> (271 mg, 1 mmol) solution in MeOH (40 ml) and kept for stirring for overnight at room temperature. The solution was then passed through the filter paper to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. Transparent colorless crystals of insoluble **2** were obtained within 7 days by slow evaporation of the solvent. Yield 63%, **Anal. Calcd** for C<sub>12</sub>H<sub>12</sub>Cl<sub>4</sub>Hg<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, (Mw =759.22): C, 18.98; H, 1.59; N, 3.69. Found: C, 18.87; H, 1.47; N, 3.58. ICP-AES: Hg, 52.43% (Calcd: Hg, 52.84%).

**2.4.4. Synthesis of (3).** A solution of hpp–H (137 mg, 1 mmol) solution in MeOH (4 ml) was added to  $HgCl_2$  (271 mg, 1 mmol) solution in MeOH (40 ml) and kept for stirring overnight at room temperature. The solution was then passed through the filter paper to remove any unreacted

materials. The filtrate was allowed to stand at room temperature for crystallization. Transparent colorless crystals of **3** were obtained within 7 days by slow evaporation of the solvent. **Anal. Calcd** for,  $C_8H_{11}Cl_2HgNO$  (Mw = 408.67): C 23.51, H 2.71, N 3.42 Found: C 24.14, H 2.89, N 4.02. **IR** (KBr, cm<sup>-1</sup>): v(C=N) 1608 cm<sup>-1</sup> v(Cd=O) 778 cm<sup>-1</sup> v(Cd=N) 668 cm<sup>-1</sup>

**2.4.5.** Synthesis of (4). A solution of hmp–H (109 mg, 1 mmol) solution in methanol (5 mL) was added to a CdCl<sub>2</sub> (201 mg, 1 mmol) solution in methanol (40 mL), and kept for stirring for 10h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of **4** were obtained after 10 days. **Anal. Calcd** for,  $C_{12}H_{14}Cd_2Cl_4N_2O_2$  (Mw = 584.85): C 24.27, H 2.46, N 4.79. Found: C 23.92, H 2.34, N 4.65. **IR** (KBr, cm<sup>-1</sup>): vC=N 1604 cm<sup>-1</sup> v(Cd–O) 762 cm<sup>-1</sup> v(Cd–N) 658 cm<sup>-1</sup>.

**2.4.6.** Synthesis of (5). A solution of hpp–H (137 mg, 1 mmol) in methanol (5 mL) was added to a solution of CdCl<sub>2</sub> (201 mg, 1 mmol) in methanol (40 mL), and the resultant solution was stirred magnetically for 10h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of **5** were obtained after 10 days. **Anal. Calcd** for C<sub>8</sub>H<sub>11</sub>CdCl<sub>2</sub>NO, (Mw = 320.48): C 29.64., H 3.43, N 4.28. Found: C 29.91, H 3.45, N 4.36. **IR** (KBr, cm<sup>-1</sup>): vC=N 1606 cm<sup>-1</sup> v(Cd–O) 763 cm<sup>-1</sup> v(Cd–N) 647 cm<sup>-1</sup>.

**2.4.7. X-ray Crystallography.** Single crystal X-ray structural studies of **1-5** were performed on a CCD Agilent technology supernova diffractometer equipped with a low temperature attachment. Data were collected at 150(2) K using graphite-monochromoated Mo K $\alpha$ . The

strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97, refining on F <sup>2</sup>.<sup>[11]</sup> Positions of all the atoms were obtained by direct methods. All nonhydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in the geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 x Ueq of their parent atoms. In 4 the disordered solvent molecule was observed, which was omitted by applying SQUEEZE option from Platon. All the H-bonding interactions, mean plane analyses, and molecular drawings were obtained using the program Diamond (ver 3.1d). The crystal and refinement data are summarized in Table A1 and A4. Selected bond distances and bond angles are shown in Table A2 and A5. Intermolecular and intramolecular hydrogen bond distances and bond angles are shown in Table A3 and A6. All the tables have been placed in Annexure 1

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# **CHAPTER 3**

# Acid-Driven Dimensionality Control of Cd(II) Complexes: From Discrete Double Open Cubane to 1D and 3D Networks

#### **3.1. Introduction**

Coordination polymers (CPs) are of great importance because of their significant role in combining synthetic chemistry and applied materials field, and provide broader perspective in the arrangement of molecules and their functions.<sup>[1]</sup> A rapid development has been made in designing and construction of CPs with varying dimensionalities, but the dimensionality control still remains the challenging task in the field of crystal engineering<sup>[2]</sup> and metallo-supramolecular chemistry.<sup>[3]</sup> The studies and synthesis of discrete polynuclear and polymeric systems of heavy metal ions were driven to a large extent by their specific structural features, and their promising applications in diverse areas such as ion exchange, absorption, separation, catalysis and host–guest chemistry.<sup>[4]</sup>

Recent trends show increasing interest in the fabrication of Cd(II)-based coordination polymers (CPs) due to their potential applications in optical properties, catalysis, biological activity and molecular metal wires.<sup>[5]</sup> Cd(II)-based one-, two and three-dimensional (1D, 2D, and 3D) CPs are in high demand because of their ability to form molecular-based materials with interesting magnetic and luminescent properties.<sup>[6]</sup>

Like Hg and Pb, Cd also has been known as biologically toxic metal ion, however, recent studies have emphasized the role of Cd(II) ion as the catalytic center in a newly discovered carbonic anhydrase.<sup>[7]</sup> Complexes of Cd(II) with nitrogen-containing ligands were found to be useful in ligand exchange chromatography.

The psudohalides complexes of Cd(II) specially Cd-N<sub>3</sub> are found to be of specific importance in the synthesis of polynuclear,<sup>[8]</sup> and polymeric compounds with different dimestionalities,<sup>[9]</sup> as well as in their ability to affect the emission wavelength.<sup>[10]</sup> Some of these compounds produced interesting structures with different alternative bonding modes of azide bridges.<sup>[11]</sup>

Development of dimensionality in the coordination polymers also necessitates the optimization of appropriate reaction conditions. An important functionality of CPs is less likelihood of occurrence of low dimensional structures.<sup>[12]</sup> Coordination of a terminal ligand is prohibited at a higher temperature therefore resulting in the formation of polymer frameworks with high dimensionality.<sup>[13]</sup> In general, the structural geometry and dimensionality of the CPs are controlled by employing appropriate bridging ligands or spacers along with the variation of metal to ligand ratio. The self-assembly of coordination complexes is largely dependent on suitable intra- and intermolecular interactions such as metal-ligand interactions and supramolecular contacts (hydrogen bonding and other weak interactions). The scope of manipulation in these interactions always exists to obtain self-assemblies of altered structures with improved properties. Such manipulations can be executed by tuning of metal ions : ligands ratio choice of solvents, temperature, and pH of the reaction medium.<sup>[14]</sup> Various other factors such, as the nature of the metal ions (co-ordination number and geometry) $^{[15]}$  and the counter anions (shape, size and charge)<sup>[16]</sup> may also influence the formation of one structure over the other.

In this chapter, we have discussed the systematic study of the effect of three different acids (HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) on molecular assemblies of Cd-pyridine alcohol complexes and report on (i) discrete double open cubane<sup>[17]</sup> tetramer complex and its acid induced transformations to diverse 1D polymeric chain and to 3D network with topology seh-4,6-C2/c net and (ii) transformation of the 1D polymeric

chain into another 1D polymeric chain with varying coordination of ligands. Moreover, we also studied the extended structures of all the complexes *via* supramolecular contacts. Although the acid driven supramolecular tuning of metal salts, particularly those of Co, Zn, Re, and Tc, are known, <sup>[18]</sup> hitherto, this is the first report on transformations of discrete Cd(II) complexes to polymeric species to the best of our knowledge.

#### 3.2. Results and discussion

**3.2.1. Synthesis and characterization.** Reaction of CdCl<sub>2</sub> with hep-H (hep-H = 2 - (2-hydroxyethyl)pyridine) in methanol at room temperature resulted the in formation the double open cubane  $[Cd_2(\mu-Cl)_2(\mu_3-Cl)(hep-H)_2Cl]_2$  (1), where hep-H was bonded to Cd(II) ion in a bidentate fashion through its N, O donor atoms. The effect of methanolic HCl on A led to protonation of pyridine N and addition of Cl<sup>-</sup>, which resulted in the transformation of a double open cubane tetramer to the 1D polymeric chain  $[Cd(\mu_2-Cl)_2(Cl)(hep-H_2)]_n$  (1). Use of methanolic HNO<sub>3</sub> afforded a 1D polymeric ribbon shape structure  $^{[19]}([Cd_5Cl_{12}(H_2O)_3](hep-H_2)_2)_n$  (2) in which each repeating unit contained a dianionic [Cd<sub>5</sub>Cl<sub>12</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub><sup>-</sup> and two pyridinium-2-ethanol  $[hep-H_2]^+$  as counter cations. Furthermore, treatment of methanolic H<sub>2</sub>SO<sub>4</sub> on A resulting into complete removal of hep-H and Cl<sup>-</sup> ligands and formed a seh-4,6-C2/c net of  $[Cd(SO_4)(H_2O)]_n$  (3) (Scheme 3.1). Similarly the treatment of methanolic HCl with Cd(II) complexes 4 and 5 reported in chapter 1 resulted isostructural 1D polymeric chains  $[Cd_2(\mu_2-Cl)_4-(Cl)_2(hmp-H_2)_2]_n$  (4A) and  $[Cd(\mu_2-Cl)_2(Cl)(hpp-H_2)]_n$ (5A) by addition of  $H^+$  and  $Cl^-$  as observed in 1 (Scheme 3.2). However, the reaction of 4 and 5 with methanolic  $HNO_3$  and  $H_2SO_4$  gave nonisolable products. A, 1 and 4A-5A were characterized by microanalytical, IR spectral studies, thermal analysis, and powder X-ray diffraction techniques. All were authenticated by their single crystal X-ray studies.



Scheme 3.1. Synthetic outline for A, and 1-3.

The different course of reactivities of HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> were attributed to different conjugate bases Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> presented in these acids. The empirical formulas of **1**, **4A**, and **5A** suggested that their formation resulted from a formal addition of HCl molecules to their respective parent complexes **A**, **4**, and **5**. This was perhaps feasible due to smaller Cl<sup>-</sup> ions from HCl occupying the vacant coordination site on Cd(II) generated by a change in coordination mode of pyridine alcohol from bidentate to monodentate as a result of protonation, which satisfied the octahedral coordination of Cd(II). However, in the case of HNO<sub>3</sub>, protonation of pyridine was not followed by subsequent addition of anion, probably because of its larger size.

This caused removal of the hep–H ligand and triggered rearrangement of  $Cl^{-}$  groups in the double open cubane structure of **A**, which through  $Cl^{-}$  bridging formed a cationic 1D ribbon structure of **2** having [hep–H<sub>2</sub>]<sup>+</sup> units as counter cation.



Scheme 3.2. Synthetic route for 4A-5A.

Effect of H<sub>2</sub>SO<sub>4</sub> on **A** led to complete removal of Cl<sup>-</sup> and hep–H ligands and afforded a seh-4,6-*C*2/c net of **3**. This prompted us to reinvestigate aforementioned transformation in the presence of other  $SO_4^{2^-}$  sources Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> instead of H<sub>2</sub>SO<sub>4</sub>. It was observed that either Na<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub> failed to transform **A** into **3**. This suggested that  $SO_4^{2^-}$  alone was unable to bring transformation, and the presence of H<sup>+</sup> was necessary to protonate the pyridine alcohol to weaken its binding with Cd(II) through disruption of its chelate, thereby allowing binding of  $SO_4^{2^-}$  to Cd(II). In order to study the fate of the detached hep–H ligand in the reaction of **A** with H<sub>2</sub>SO<sub>4</sub>, we extracted the organic product from neutralized reaction mixture whose <sup>1</sup>H NMR spectrum confirmed the presence of hep-H and thus corroborated that during the reaction hep–H did not undergo any chemical transformation.

In order to reach an optimum acid concentration, we also studied the effect of the varying concentration of three acids on these transformations. It was observed that the monobasic acids HCl and HNO<sub>3</sub> showed similar concentration dependence in their reactions. The optimum concentration for these two acids was found to be 1M, which completed the reaction in 3h (same time for 2–6 M solutions). However, dilute solutions 0.5 and 0.1 M take longer time 8h and 2 days, respectively, to complete the reaction. With the further dilution of HCl and HNO<sub>3</sub> solutions (0.01M), no observable transformation was seen. In the case of dibasic acid H<sub>2</sub>SO<sub>4</sub>, the optimum concentration of the acid was found to be 0.1M to complete the conversion of **A** to **3** in 3h (same time for 1–6M solutions). As observed, 0.01M solutions of HCl and HNO<sub>3</sub> were insufficient to bring any substantial transformation; at the same concentration, complete transformation was observed with H<sub>2</sub>SO<sub>4</sub> but in longer duration of 14h. However, no reaction was observed with 0.001M H<sub>2</sub>SO<sub>4</sub> solution.

3.2.2. Structural aspects of A. A crystallized into triclinic Pī space group with a crystallographically imposed inversion center (Table A7, **Figure 3.1**). A consisted of two dimeric  $[Cd(\mu-Cl)Cl]_2$  units that linked together to formed tetranuclear  $[Cd_2(\mu-Cl)_2(\mu_3-Cl)(hep-H)_2Cl]_2$  with double open cubane core (inset Figure 3.1). The Cd(II) ions in the core were linked through chloride bridges. The hep-H linked to the Cd(II) centers via N and O atoms in bidentate mode, creating six-membered rings around the metal centers with metal bite angles  $80.2^{\circ} \{ (N(1)-Cd(1)-O(1) \} \text{ and } 81.5^{\circ} \{ (N(2)-Cd(2)-O(2) \} (Table A8) \}$ 



Figure 3.1. Molecular structure of A (double open cubane core in inset).

Both the Cd(II) atoms were present in the hexacoordinated environment forming distorted octahedral geometry. In Cd(1), out of the six coordination sites, two were occupied by  $\mu_2$ –Cl and two by  $\mu_3$ –Cl, and the remaining two sites were occupied by N, O of the hep–H ligand. However, in Cd(2) two positions were occupied by  $\mu_2$ –Cl, two by N and O atoms of hep–H ligand, one by  $\mu_3$ –Cl, and the remaining one by terminal Cl. Cd(2) differed from Cd(1) due to the presence of one terminal Cl atom. Cd–Cl bond lengths were in the range of 2.537(2)–2.886(2) Å. The bond distance between Cd(2) and  $\mu_3$ –Cl was relatively larger 2.886(2) Å than Cd(2) and  $\mu_3$ –Cl 2.668(3) Å (**Table A8**).

**3.2.3. Structural aspects of 2. 2** crystallized in monoclinic  $P2_1/n$  space group with a crystallographically imposed inversion center (**Table A7**, **Figure 3.2**). Asymmetric unit in **2** consisted of dianionic  $[[Cd_5Cl_{12}(H_2O)_3](hep-H_2)_2]^{2-}$  and two protonated  $[hep-H_2]^+$  ligands in the lattice as counter cation, which on further expansion generated a ribbon shaped 1D polymeric chain.



Figure 3.2. Ribbon like molecular structure of 2.

The geometry around each Cd(II) atom was distorted octahedral with two different types of coordination environments. Cd(1), Cd(4), and Cd(5) were surrounded by three Cl atoms of  $\mu_3$ -Cl, two Cl atoms of

 $\mu_2$ -Cl, and one O atom of the coordinated water molecule. However, in Cd(2) and Cd(3), all the coordination sites were occupied by Cl atoms three by Cl atoms of  $\mu_3$ -Cl, two by Cl atoms of  $\mu_2$ -Cl, and one by terminal Cl atom. Cd-Cl distances were in the range of 2.515(7)-2.786(7) Å, whereas the Cd-O distances were Cd(1)-O(101) 2.352(15) Å, Cd(5)-O(102) 2.343(14) Å, Cd(4)-O(103) 2.313(17) Å (**Table A8**). The two [hep-H<sub>2</sub>]<sup>+</sup> cations present in the lattice were involved in strong hydrogen bonding for extension of supramolecular networks.

**3.2.4. Structural aspects of 3. 3** crystallized in monoclinic  $P2_1$ /n space group with crystallographically imposed inversion center (**Table A7**, **Figure 3.3**) as reported earlier.<sup>[20]</sup> We observed better refinement parameters and the topology of this 3D network which has not been discussed so far. Moreover, the synthetic route presented by us was also different. The Asymmetric unit of **3** consisted of Cd(II) metal ions with identical hexacoordinated (O6) environment. Cd–O bond distances were in the range of 2.240(4)–2.405(4) Å (**Table A8**). Each Cd(II) metal was linked through the O atoms of sulfate and H<sub>2</sub>O molecule in all directions yielding a seh-4,6-*C*2/c like 3D network.



**Figure 3.3.** (a) Structure of  $CdSO_4(H_2O)$  **3** and (b) the underlying net in standard representation.

The structure of  $CdSO_4(H_2O)$  (**3**) was formed by cations  $Cd^{2+}$  and two ligands  $SO_4^{2-}$  and  $H_2O$  (**Figure 3.3a**). The  $Cd^{2+}$  ion has coordination number 6, and the sulfate ion was coordinated by four

cadmium atoms. The water molecule was a bridging ligand coordinated by two cadmium atoms. The following simplified standard representation can be proposed. The cadmium and sulfur atoms were represented by 4- and 6-coordinated nodes, while the oxygen atoms of ligands H<sub>2</sub>O and  $SO_4^{2-}$  were represented by edges of the underlying net. The topological type of the underlying net for the structure in standard representation was seh-4,6-C2/c, which mean a 4,6coordinated binodal net of the maximal symmetry C2/c (Figure 3.3b) derived from the seh net according to the procedure described.<sup>[21]</sup> Moreover,  $Cd^{2+}$  ions and H<sub>2</sub>O molecules formed *zig-zag* like parallel chains arranged in hexagonal rod packing according to classification.<sup>[22]</sup> The seh-4,6-C2/c net was described by an isohedral natural tiling<sup>[23]</sup> with only one type of tile  $[3^2.4^2.6^4]$  (Figure 3.4) (each tile represents a cage in the structure). The symbol  $[3^2.4^2.6^4]$  meant that the tile consisted of two 3-rings, two 4-rings, and four 6-rings.



**Figure 3.4.** Natural tiling and a tile in the seh-4,6-*C*2/c underlying net. Red balls corresponding nodes of the underlying net.

The rings corresponding to the channel sections separated the cages (tiles). The transitivity of the tiling was [2561], where 2, 5, 6, and 1 were the numbers of in equivalent vertices, edges, faces (windows of channels) and tiles in the natural tiling, respectively.

The topological motif of the arrangement of tiles in the natural tiling was described by the net that originated from dualization of the tiling. The vertices of the dual net coincided with the centers of the tiles, and the edges passed through the faces of the tiles to link the center. Since tiles corresponded to cages, the dual net characterized the system of cages and channels. The dual net in the structure of  $CdSO_4$  (H<sub>2</sub>O) was 8-coordinated ecu (**Figure 3.5**) and had transitivity [1652] (the reverse of 2651).



Figure 3.5. Underlying net (blue) intertwined with the dual net (black) in the  $CdSO_4(H_2O)$  structure.

Table A. Composition of the structures	s isoreticular series	s with topology seh-	-4,6- <i>C</i> 2/c
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Types	Composition	Extra frame work Cations A	Framework metals M	Anions
Monohydr ated Salts	M <sup>2+</sup> XO <sub>4</sub> <sup>2-</sup> (H <sub>2</sub> O)		Mn, Mg, Cd, Ni, Co, Zn, Fe, Cu	$SeO_4^2$ $SO_4^{2-}$
	$M^{3+}, XO_4^{3-}(H_2O)$	-	V	PO <sub>4</sub> <sup>3-</sup>
Oxosalts	$M^{5+}O^{2-}(XO_4)^{3-}$	-	V, Sb	PO4 <sup>3-</sup>
	$A^+M^{5+}O^2(XO_4)^-$	Li, Na	Sb, Nb, Ta	SiO <sub>4</sub> <sup>4-</sup> GeO <sup>4-</sup>
	$Me^+Me^{4+}O^2(XO_4)^{3-}$	Li, Na	V, Ti	$PO_4^{3}$ AsO <sup>3-</sup>
	$Me^{2+}Me^{4+}O^2(XO_4)^{4-}$	Ca, Sr	Ti, Sn, Zr, V	SiO <sub>4</sub> <sup>4-</sup> GeO <sup>4-</sup>
	$Me^{2+}Me^{5+}O^{2}(XO_{4})^{5-}$	Ca	Та	AlO <sub>4</sub> <sup>-</sup>
Oxy salts	$Me^{3+}(OH)^{-}(XO_4)^{2-}$	-	Fe	SO4 <sup>2-</sup>
	$Me^{+}Me^{3+}(OH)(XO_4)^{3-}$	Li	Mn	$AsO^{3-}$ $PO_4^{-3-}$

According to the data from TTO collection, <sup>[24]</sup> the isoreticular series with topology seh-4,6-*C*2/c is presented by 89 inorganic structures. These structures were of three types: monohydrate salts (14 structures), oxo salts (69 structures), and oxy salts (6 structures). All inorganic frameworks of the isoreticular series were composed of six-coordinated metal atoms (Ti, Zr, V, Nb, Ta, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb), bridging ligand (molecules of water, hydroxide or oxygen ions), and 4- coordinated anion  $(SO_4^{2-}, SeO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, SiO_4^{4-}, GeO_4^{4-}, AlO_4^{5-})$  (**Table A**).

**3.2.5.** Structural aspects of 1, 4A, and 5A. Complexes 1, 4A and 5A crystallized in orthorhombic  $P2_12_12_1$ , Pna21 and  $P2_12_12_1$  space groups, respectively (Table A7, Figures 3.6–3.8). Each Cd(II) center exhibited distorted octahedral geometry. The six coordination sites were bound with the five Cl atoms and one O atom, where four were bridging Cl *i.e.*, Cl(1) and Cl(2), one was terminal Cl *i.e.*, Cl(3), and one is the alcoholic O atom of ligand. Due of unavailability of the N lone pair of protonated pyridine, in complexes 1, 4A, and 5A the ligands bonded to the metal in monodentate fashion through their alcoholic O atom.



Figure 3.6. Molecular structure of 1D polymeric chain of 1.

The Cd–O bond distances in 1, 4A, and 5A were 2.376(2) Å, 2.478(5) Å/2.529(4) Å and 2.463(6) Å, respectively. The Cd–O bond distance in 1 was shorter than 4A and 5A. In the case of 1, 4A, and 5A,

the O atom of alcoholic (OH) and terminal Cl atom were found to be quite close to each other, which were involved in the intramolecular Hbonding (see below)



Figure 3.7. Perspective view of 1D polymeric chain of 4A.



Figure 3.8. Perspective view of 1D polymeric chain of 5A.

# 3.3. Comparative structural motif in A, 1-3, 4A and 5A

It was interesting to mention here that when  $CdCl_2$  was treated with hmp–H, hep–H, and hpp–H, the ligand was bound to the metal in a bindentate manner *via* N and O atoms (complexes A, 4, and 5). But, when these complexes were treated with acids, either the binding mode of the ligand changed (monodentate in 1, 4A, and 5A, on treatment with HCl) or the ligands remained as counter cation  $[hep-H_2]^+$  (in complex 2 on treatment with HNO<sub>3</sub>) or got detached from the metal center (in complex 3, on treatment with H<sub>2</sub>SO<sub>4</sub>). Besides changes in bonding between pyridine alcohols and cadmium metals, the gradual increase in acid strength also affected a systematic increase in Cd–Cd separations in the acid treated products. The Cd–Cd separations before acid treatment in **A** was observed to be in the range 3.761(5)-3.992(4) Å, and after treating with HCl the Cd–Cd separations in **1**, was found to be in the range 3.750(1)-3.914(1) Å, which showed a slight decrease compared to HNO<sub>3</sub> in **2** where Cd–Cd separations were in the range of 3.796(9)-4.060(2) Å. In the case of the H<sub>2</sub>SO<sub>4</sub>-treated product **3**, the Cd–Cd separation ranges were found to be 4.077(3)-5.547(3)Å larger than others. An increase in Cd–Cd separations were observed by employing stronger acids from HCl to HNO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>.

#### **3.4.** Supramolecular expansion

The extended supramolecular interactions were observed in A, 1–3 and 4A–5A. The double open cubane tetramer A showed strong intermolecular H-bonding involving the alcoholic (OH) and terminal Cl atom of the adjacent tetramer leading to the formation of a H-bonded octamer, which further extended to form a linear 1D polymeric chain. The linear 1D chain was extended *via* the pyridine H-atom and terminal Cl atom forming a 2D network of two layers resembling a ribbon-shaped polymeric chain. The 2D network was further extended *via* the pyridine H atom and bridging Cl atom forming a hydrogen-bonded 3D network (Figure 3.9, 3.10 and Table A9).



Figure 3.9. Packing diagram showing the H-bonded 2D network of A.



**Figure 3.10.** Intermolecular H-bonding interactions between H(2) and H(3) of hep–H attached to Cd(1) and  $\mu$ –Cl(3),  $\mu$ –Cl(1), of layer C(2)–H(2) … $\mu$ –Cl(3) 2.845(2) Å, C(3)–H(3) … $\mu$ –Cl(1) 2.847(3) Å leading to the formation of, 3D polymeric network of **A** tilted along *a* axis.

Two ribbon shaped 1D polymeric chains of **2** were linked *via* intermolecular H-bonding involving the H atom of uncoordinated hep–H and  $\mu$ –Cl atoms of neighbor polymeric chains, which were further extended yielding a 3D network (**Table A9**, **Figures 3.11**).



**Figure 3.11.** (a) Hydrogen bonded 2D network of **2** through tilted *b* axis. (b) Packing diagram showing uncoordinated hep $-H_2$  trapped between two ribbon-shaped 1D polymeric chains in **2** forming a 3D network along the *a* axis.

The packing diagrams of 1D polymeric chains in 1, 4A, and 5A showed intramolecular O–H····Cl hydrogen bonding between the alcoholic (OH) and terminal Cl atom of neighboring Cd(II) ion. Each 1D polymeric chain was extended to form hydrogen bonding 2D network through the pyridine H atom of one layer to the terminal and bridging Cl atom of another layer. In 5A the extension of these supramolecular interactions involved  $\pi \cdots \pi$  stacking (3.371 Å) between two pyridine rings of adjacent two layers. This 2D network was further extended *via*  H-bonding forming H-bonded 3D network (Table A9, Figures 3.12, 3.13 and 3.14).

**(a)** 





(c)



**Figure 3.12.** (a) Intramolecular H-bonded 1D network of **1** was involving H(101), of alcoholic OH, H1N and H6B of hep–H ring and terminal Cl(3),  $\mu$ –Cl(1),  $\mu$ –Cl(2), Cl(3) O(1)–H(101)····Cl(3) 2.223(32) Å, N(1)-H(1N) ····Cl(1) 2.348(21) Å, C(6)–H(6B)····Cl(2) 2.901(1) Å, C(6)–H(6B)····Cl(3) 2.656(1) Å along with 1D polymeric chain. (b) Intermolecular H-bonding involves H(3) of one layer and terminal Cl(3) of another layer C(3)–H(3)····t–Cl(3) 2.721(1) Å yielding 2D polymeric chain of **1** along tilted *b* axis. (c) Packing diagram showing intermolecular H-bonded 3D-network of **1** along the *a* axis.







(c)

**Figure 3.13.** Intramolecular H-bonded 1D polymeric chain of **4A** involved H(101), H(102) of alcoholic (OH) and H(1N), H(2N) of hmp–H ring and terminal Cl(6), Cl(3) and  $\mu$ –Cl(5),  $\mu$ –Cl(1) of neighboring Cd(II) ion O(1)–H(101)····Cl(6) 2.027(30) Å, O(1)–H(102)····Cl(3) 2.067(37) Å, N(1)–H(1N)····Cl(5) 2.366(1) Å, N(2)–H(2N)····Cl(1) 2.677(1) Å along 1D polymeric chain. (**b**) Intermolecular interactions involved H(8), H(9) of pyridine ring of hmp-H ring of one layer and terminal Cl(6),  $\mu$ –Cl(2), of adjacent layer C(8)–H(8)···t–Cl(6) 2.597(1) Å, C(9)-H(9)···µ–Cl(2) 2.915(1) Å forming 2D polymeric chain of **4A** along tilted *c* axis. (**c**) Intermolecular H-bonded 3D network in **4A** through the *b* axis.



**Figure 3.14.(a)** Intramolecular H-bonded 1D polymeric chain of **5A** involved H(101), H(1N) of alcoholic (OH) and pyridine ring of hpp–H and terminal Cl(3),  $\mu$ –Cl(2) O(1)-H(101)…Cl(3) 2.199(65) Å, N(1)–H(1N)… $\mu$ –Cl(2) 2.854(2) Å of 1D polymeric chain. (b) Two adjacent 1D polymeric chains were linked through the intermolecular Hbonding interactions involved H(3) of pyridine ring of hpp-H of one layer and terminal Cl(3) C(3)–H(3)…t–Cl(3) 2.717(2) Å of other layer and  $\pi$ … $\pi$  interaction 3.371 Å were also found between pyridine ring of two layers of **5A** along tilted *c* axis.

# 3.5. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns of A, 1 and 4A–5A were consistent with the simulated PXRD pattern generated from single crystal data that imply the structural identity and phase purity of the bulk product.



Figure 3.15. PXRD pattern of A, 1, 4A and 5A.

#### 3.6. Thermal analysis and IR studies

In order to check the thermal stability of complexes, **A**, **1**, and **4A–5A** thermogravimetric analysis (TGA) was performed (**Figure 3.16**). All these complexes were stable until 210°C with two steps decomposition. The order of thermal stability in **A**, **1**, **4A–5A** was hmp–H > hep–H > hpp–H with the final end set temperature  $\approx 650$  °C. **A**, **1**, **4A** showed ~99% weight loss, while **5A** showed ~87% weight loss. The IR spectra of **A**, **1**, and **4A–5A** showed one new strong intensity vibration in the region 762–783 cm<sup>-1</sup> due to the formation of the Cd–O bond. The  $\nu$ (C=N) absorptions of pyridine appeared in the region 1603–1625 cm<sup>-1</sup>.



Figure 3.16. TGA of A-1, 4A-5A.

#### **3.7.** Conclusions

In present chapter, we have demonstrated the effect of three different acids (HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) on coordination behavior of discrete double open cubane tetramer and 1D chain formed by the complexation of pyridine alcohols with CdCl<sub>2</sub>. The three acids having different conjugate bases affect the intra- and intermolecular interactions of Cd(II) complexes in different ways and lead to their transformation into diverse 1D polymeric chains and 3D networks. In the case of HCl, transformation involved protonation of the pyridine nitrogen of the pyridine alcohol ligand causing a bidentate to monodentate change in its coordination mode, which was subsequently followed by addition of a  $Cl^-$  to the vacant coordination site on Cd(II). With HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, protonation of the pyridine nitrogen was accompanied by detachment of the hep-H ligand from Cd(II) in the case of HNO<sub>3</sub>, whereas in the case of H<sub>2</sub>SO<sub>4</sub>, complete removal of hep–H and all Cl<sup>-</sup> ligands and binding of SO<sub>4</sub><sup>2-</sup> were observed.
#### **3.8. Experimental Section**

**3.8.1.** Materials and Physical Measurements. The commercially available starting materials, CdCl<sub>2</sub>, 2- (2-hydroxyethyl)pyridine (hep–H), 2-(2-hydroxypropyl)pyridine (hpp–H), and reagent grade methanol were used as received. IR spectra [4000–400 cm<sup>-1</sup>] were recorded with a Bio-Rad FTS 3000MX instrument on KBr pellets. Thermogravimetric analyses were performed on Metler Toledo thermal analysis system. The measurements were done at a heating rate of 10°C/min from 25 to 900°C under flowing nitrogen environment. Elemental analyses were carried out with a Flash 2000 elemental analyzer. Powder X-ray diffraction for complexes was recorded on a Rigaku Smart Lab X-ray diffractometer using monochromated Cu K-alpha radiation (0.154 nm).

**3.8.2.** Synthesis of (A). A hep–H (123 mg, 1 mmol) solution in methanol (5 mL) was added to a CdCl<sub>2</sub> (201 mg, 1 mmol) solution in methanol (40 mL), and the resultant solution was stirred magnetically for 10h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of **A** were obtained after 10 d. **Anal. Calcd** for C<sub>28</sub>H<sub>36</sub>Cd<sub>4</sub>Cl<sub>8</sub>N<sub>4</sub>O<sub>4</sub>, (Mw = 1225.89): C 27.45, H 2.63, N 4.57. Found: C 27.77, H 2.96, N 4.69. **IR** (KBr, cm<sup>-1</sup>):  $\upsilon$  (C=N) 1603 cm<sup>-1</sup> $\upsilon$  (Cd–O) 783 cm<sup>-1</sup> $\upsilon$  (Cd–N) 641 cm<sup>-1</sup>.

**3.8.3.** Synthesis of (1). Compound A (1225 mg, 0.1 mmol) was dissolved in 1M solution of HCl in methanol (20 mL) and stirred magnetically for 3h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of 1 were obtained after two months. Anal.

Calcd for C<sub>7</sub>H<sub>10</sub>CdCl<sub>3</sub>NO·HCl, (Mw = 379.39): C 22.16, H 2.92, N 3.69. Found: C 21.82, H 2.81, N 3.55. **IR** (KBr, cm<sup>-1</sup>):  $\upsilon$  (C=N) 1620 cm<sup>-1</sup> $\upsilon$  (Cd–O) 762 cm<sup>-1</sup>.

**3.8.4.** Synthesis of (2). Compound A (1225 mg, 0.1 mmol) was dissolved in 1M HNO<sub>3</sub> solution in methanol (20 mL) and stirred magnetically for 3h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, very low yield colorless single crystals of **2** were obtained after ~30 days. Anal. Calcd for  $C_{14}H_{20}Cd_5Cl_{12}N_2O_5$  (Mw = 1283.69): C 13.07, H 1.56, N 2.17. Found: C 13.46, H 1.77, N 2.33.

**3.8.5.** Synthesis of (3). Compound A (1225 mg, 0.1 mmol) was dissolved in 0.1M solution of  $H_2SO_4$  in methanol (20 mL) and stirred magnetically for 3h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, very low yield colorless single crystals of **3** were obtained after ~30 days. Anal. Calcd for [Cd(SO<sub>4</sub>)(H<sub>2</sub>O)], (Mw = 226.49): H 0.89, S 14.16 Found: H 0.95, S 14.99.

**3.8.6.** Synthesis of (4A). Compound 4 (58.4 mg, 0.1 mmol) was dissolved in 1M HCl solution in methanol (20 mL) and stirred magnetically for 3h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of 4A were obtained after 2 months. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>Cd<sub>2</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>2</sub>, (Mw = 657.77): C 21.84, H 2.75, N 4.25. Found: C 20.06, H 2.28, N 4.01. IR (KBr, cm<sup>-1</sup>):  $\upsilon$  (C=N) 1609 cm<sup>-1</sup>  $\upsilon$  (Cd–O) 765 cm<sup>-1</sup>.

**3.8.7.** Synthesis of (5A). Compound 5 (32.0 mg, 0.1 mmol) was dissolved in 1M HCl solution in methanol (20 mL) and stirred magnetically for 3h at room temperature. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of 5A were obtained after 2 months Anal. Calcd for C<sub>8</sub>H<sub>12</sub>CdCl<sub>3</sub>NO, (Mw = 356.94): C 26.92, H 3.39, N 3.92. Found: C 27.13, H 3.36, N 3.91. **IR** (KBr, cm<sup>-1</sup>):  $\upsilon$  (C=N) 1624 cm<sup>-1</sup> $\upsilon$  (Cd–O) 781 cm<sup>-1</sup>.

3.8.8. X-ray Crystallography. Single crystal X-ray structural studies of all the compounds were performed on a CCD Agilent technology supernova diffractometer equipped with a low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo Ka  $(\lambda \alpha = 0.71073 \text{ Å})$  and Cu K $\alpha$  ( $\lambda \alpha = 1.54814 \text{ Å}$ ). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F<sup>2</sup>.<sup>[25]</sup> Position of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally  $1.2 \times \text{Ueq}$  of their parent atoms. All the Hbonding interactions, mean plane analysis, and molecular drawings were obtained using the program Diamond (version 3.1d). In the case of 2 after many attempts the H atom of uncoordinated (OH) of hep-H and coordinated water molecule could not be located. The crystal and refinement data were summarized in Table A7, and selected bond distances and bond angles were shown in Table A8. All tables were placed in Annexure 1.

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## **CHAPTER 4**

# Isolation of Metastable Intermediate in Heterometallic Cu(II)-Hg(II) 1D Polymeric Chain: Synthesis, Crystal Structures and Photophysical Properties

## **4.1. Introduction**

Heterometallic transition-metal coordination polymers represent an actively pursued topic in modern coordination chemistry,<sup>[1]</sup> reflecting the fact that heterometallic complexes have significant applications in catalysis,<sup>[2]</sup> electrical conductivity,<sup>[3]</sup> sensing,<sup>[4]</sup> and magnetism.<sup>[5]</sup> Heterometallic catalysts, where multiple metal centers are present in close proximity to each other, exhibit better reactivity than equivalent mixtures of monometallic complexes.<sup>[2c,6]</sup> Moreover, heterometallic coordination polymers are also appealing from the crystallographic point of view owing to their diverse geometrical arrangements.<sup>[7]</sup>

Out of several approaches for the construction of heterometallic complexes, one is based on the idea that different metals show different affinities for a particular donor atom and, thus, the addition of a ligand possessing different donor atoms with a mixture of metals leads to self-assembled or well-ordered heterometallic systems.<sup>[8]</sup> In the 5d transition metals, Hg is known to be a good candidate for generating heterometallic complexes with various other metal ions.<sup>[9]</sup> It forms dinuclear, trinuclear, tetranuclear, and polynuclear complexes with different metals; however, it exhibits a better compatibility with Cu(II) metal.<sup>[10]</sup> These aspects extend the impetus to introduce newer routes for the construction of heterometallic complexes. Moreover, the isolation and structural characterization of a metastable intermediate is a formidable challenge. In the literature, there are only a few reports dealing with structurally characterized discrete metastable intermediates.<sup>[111]</sup>

In this chapter, we described isolation as well as structural characterization of a kinetically controlled metastable heterometallic 1D polymeric intermediate **1**, along with the thermodynamically driven Cu(II)–Hg(II) 1D polymeric chain **2** and a monomeric Cu(II) complex **3** obtained during recrystallization of **2** in methanol (MeOH). To the best of our knowledge, this was the first report dealing with the structural characterization of a heterometallic 1D polymer chain intermediate. Furthermore, we also synthesized and characterized eight new Hg(II) monomeric and polymeric complexes, with 2,2′–bipyridine and amino/hydroxy-benzoic acids, and studied their photo-physical properties.

#### 4.2. Results and discussion

4.2.1. Synthesis and characterization. Heterometallic polymer 2 was synthesized via the reaction of  $Hg(OAc)_2$ ,  $Cu(OAc)_2 \cdot H_2O$ , bpy, (bpy = 2,2'-bipyridine) and DIPSA (DIPSA = 3.5-diisopropylsalicylic acid) in acetonitrile (ACN) at room temperature. The initial reaction mixture was dark green after 3 h and turned to light green within 12 h. A fraction of the dark-green reaction mixture was therefore extracted after 3 h, and a single spot on the thin-layer chromatography (TLC) plate ensured the presence of only one component. Its subsequent crystallization established the isolation of the kinetically driven intermediate 1. The further extension of the same reaction up to 12 h led to the isolation of the thermodynamically stable form 2. Moreover, recrystallization of 2 in MeOH serendipitously resulted in the new Cu(II) monomer 3 via the breaking of the Cu(II)-Hg(II)-based polymer 2. The coordinated ACN molecule from the symmetric Cu(II) dimeric [Cu(bpy)(DIPSA)(CH<sub>3</sub>CN)]<sub>2</sub> unit in 2 was replaced by a MeOH molecule in **3** probably because of the formation of a stronger Cu-O bond (Scheme 4.1). 1-3 have been characterized by elemental analysis, Fourier transform infrared, UV-Vis spectroscopy, and single-crystal X-ray studies. The photophysical properties of 1-3complexes have also been discussed.



Scheme 4.1. Synthetic route of 1-3.

**4.2.2. Structural aspects of 1. 1** crystallized in the monoclinic space group  $P2_1/c$  with a crystallographically imposed inversion centre (**Table A10**). **1** consisted of alternating dimeric units of [Cu(bpy)(DIPSA)]<sub>2</sub> and [Hg(OAc)<sub>2</sub>(DIPSA)]<sub>2</sub>. These units were

connected via the same O atom of the carboxylic group of DIPSA, which generated a 1D polymeric chain (Figures 4.1). Each Cu(II) atom in the dimeric [Cu(bpy)(DIPSA)]<sub>2</sub> unit was in pentacoordinated (N<sub>2</sub>O<sub>3</sub>) environment. The Cu(II) atom was surrounded by two Natom donors of bpy, one carboxylic O atom, and two phenolic O atoms of DIPSA, creating a distorted square-pyramidal geometry. Phenolic O atoms bridge the neighboring Cu(II) atoms within the dimeric [Cu(bpy)(DIPSA)]<sub>2</sub> unit. The average Cu-N and Cu-O distances were in the ranges of 1.995(9)-2.013(8) and 1.921(7)-2.277(6) Å, respectively (Table A11), which were found to be identical with the reported analogous dimers.<sup>[12]</sup> Each Hg(II) atom in the dimeric [Hg(OAc)<sub>2</sub>(DIPSA)]<sub>2</sub> unit was in heptacoordinated O(7) environment. The Hg(II) atom was bonded to five O atoms from the acetate groups and two from the carboxylic groups of DIPSA, leading to a distorted pentagonal-bipyramidal geometry. Moreover, the chelated acetate groups bridged the adjacent Hg(II) atoms in the dimeric unit [Hg(OAc)<sub>2</sub>(DIPSA)]<sub>2</sub>. The dimeric units [Hg(OAc)<sub>2</sub>(DIPSA)]<sub>2</sub> consisted of two different sets of Hg–O distances; the shorter and longer range were 2.101(9)-2.402(7) and 2.606(8)-2.870(9) Å, respectively.<sup>[13]</sup>



Figure 4.1. Molecular structure of 1 (hydrogen atoms were omitted for clarity).

**4.2.3.** Packing features of 1. The packing diagram of 1 revealed the existence of intra- and intermolecular hydrogen bonding and CH··· $\pi$  interactions. The intramolecular hydrogen bonding involved C(1)–H(1)···O(7), 2.856(1) Å, and C(9)–H(9)···O(5), 2.551(1) Å, between the bpy ring and acetate group along the polymeric chain. Intermolecular hydrogen-bonding interactions were comprised of C(3)–H(3)···O(3), 2.681(8) Å, between bpy and DIPSA. Moreover, the CH··· $\pi$  interactions, involved the H(4) and H(7) atoms of bpy and the  $\pi$  electrons of the aromatic ring of DIPSA with a distance 3.06 Å,<sup>[14]</sup> forming a 2D-framework along the *b* axis (Figure 4.2 and Table A12).



**Figure 4.2.** Packing diagram of **1** showing the intra- and intermolecular hydrogenbonded 2D-network (H atoms were removed for clarity).

**4.2.4. Structural aspects of 2. 2** crystallized in the triclinic space group *P*<sup>T</sup> with a crystallographically imposed inversion center (**Table A10**). **2** consisted of two alternating dimeric units,  $[Cu(bpy)(DIPSA)(CH_3CN)]_2$  and  $[Hg(OAc)(DIPSA)_2]_2$ , linked *via* carboxylic O-atom donors of DIPSA. Unlike **1**, in **2** these Cu(II) and Hg(II) units were connected by different O atoms of the same carboxylic group of DIPSA. In contrast to **1**, in **2** each Cu(II) ion in dimeric  $[Cu(bpy)(DIPSA)(CH_3CN)]_2$  was in hexacoordinated (N<sub>3</sub>O<sub>3</sub>) environment. The basal plane consisted of two N atoms of bpy and one phenolic and one carboxylic O atom of DIPSA and

the axial positions were occupied by a phenolic O atom of DIPSA and N atom of the ACN molecule, leading to a distorted octahedral geometry (**Figures 4.3**). The adjacent Cu(II) atoms in the dimeric unit were connected *via* phenolic O atoms of different DIPSA molecules. The average Cu–N and Cu–O distances were between 2.005(10) and 2.007(12) and 1.888(9) and 1.938(9) Å, respectively (**Table A11**). In the dimeric [Hg(OAc)(DIPSA)<sub>2</sub>]<sub>2</sub> unit, coordination environment around Hg(II) was hexacoordinated where Hg(II) atom was bonded to two O atoms of the bidentate acetate group and four carboxylic groups of DIPSA, led to a distorted octahedral arrangement. The two O atoms of different DIPSA molecules were connected to the neighboring Cu(II) atoms, and another O atom of DIPSA was working as a bridge between Cu- and Hg-derived dimeric units. The remaining one O atom of DIPSA was coordinated to one Hg(II) atom only. The average Hg–O distances were in the range of 2.154(1)–2.589(1) Å.



Figure 4.3. Molecular structure of 2 (H atoms were omitted for clarity).

**4.2.5.** Packing features of 2. The packing diagram of 2 revealed the presence of intra- and intermolecular hydrogen-bonding interactions. Intramolecular interactions involved C(9)-H(9) $\cdots$ O(5), 2.527(1) Å, and C(9)-H(9) $\cdots$ O(6), 2.684(1) Å, between bpy and the acetate group. Further, it showed the presence of stronger O(8)-H(108) $\cdots$ O(7), 1.844(1) Å, nonbonding interaction between an H atom of the hydroxyl group of DIPSA and an O atom of the carboxylate group of the same DIPSA group.

The coordinated ACN molecule was trapped between the two adjacent layers of the 1D polymeric chain and developed the hydrogen-bonding interaction *via* C(4)–H(4)····N(333) with a distance of 2.459(6) Å, which indeed led to the formation of a 2D-network (**Figure 4.4**, **Table A12**).



**Figure 4.4.** Packing diagram of **2**, where ACN molecules were trapped between two 1D chains, formed a 2D polymeric framework (H atoms were removed for clarity).



Figure 4.5. Intramolecular H-bonding in 2 (H-atoms were omitted for clarity).

#### 4.2.6. Comparative discussion of 1 and 2

In **1** and **2**, all of the ligands were in the *trans* orientation. The transformation of **1** to **2** involved the replacement of two of the acetate groups in the Hg(II) dimer by bulky DIPSA molecules, followed by coordination of the ACN solvent to the Cu(II) center in the dimeric unit. The symmetric Cu<sub>2</sub>O<sub>2</sub> and Hg<sub>2</sub>O<sub>2</sub> rings in **1** and **2** were planar. In **1** and **2**, the Cu<sub>2</sub>O<sub>2</sub> ring was deviated from Hg<sub>2</sub>O<sub>2</sub> by angles of 71.85° and 72.43°,

respectively. The estimated dihedral angles between the bpy and DIPSA rings in the Cu(II) dimeric units of **1** and **2** were  $64.10^{\circ}$  and  $17.89^{\circ}$ , respectively.

#### 4.2.7. Mechanism for the transformation of 1 to 2

A plausible mechanism for the transformation of **1** to **2** was depicted in **Scheme 4.2**. The common feature in **1** and **2** was the presence of the stable Cu(II) dimeric unit  $[Cu(bpy)(DIPSA)]_2$ . However, the Hg(II)-derived dimeric unit  $[Hg(OAc)_2(DIPSA)]_2$  underwent the major transformation in the form of replacement of the bridging acetate groups<sup>[15]</sup> by DIPSA as acetic acid<sup>[16]</sup>. Moreover, the strong intramolecular hydrogen bonding between H-atom of the phenolic group O(8) and the carboxylic O(7) of DIPSA might have extended the necessary driving force towards stabilization of **2** (**Figure 4.5**).<sup>[17]</sup>



Scheme 4.2. Probable reaction pathway towards the transformation of 1 to 2.

**4.2.8. Structural aspects of 3.3** crystallized in the triclinic space group *P*<sub>1</sub> (Table A10). The Cu(II) ion in the monomer unit  $[Cu(bpy)(DIPSA)(CH_3OH)] \cdot CH_3OH$  was in pentacoordinated  $(N_2O_3)$ environment. The basal plane consisted of two N atoms of bpy and one phenolic and one carboxylic O atom of DIPSA, while the apical position was occupied by the O atom of the solvent molecule (MeOH). This in effect led to a distorted square-pyramidal geometry (Figure 4.6). The Cu-O and Cu-N bond distances were Cu(1)-O(1) 1.897(1) Å, Cu(1)–O(3) 1.877(1) Å, and Cu(1)–O(111) 2.544(4) and  $\approx 2.00$  Å, respectively (Table A11).



Figure 4.6. Molecular structure of 3.

**4.2.9.** Packing features of 3. The packing diagram of monomeric 11 revealed intermolecular hydrogen-bonding and  $\pi \cdots \pi$  interactions. Intermolecular hydrogen bonding interaction C(8)–H(8)…O(2), 2.523(1) Å, between bpy and DIPSA led to the formation of a 1D layer, which has been further extended *via* C(4)–H(4)…O(111), 2.466(2) Å, and C(7)–H(7)…O(111), 2.691(2) Å, interactions between bpy and coordinated MeOH. The  $\pi \cdots \pi$  interaction between two bpy rings of two monomeric units with a distance of 3.360 Å resulted in a 2D-network (Figure 4.7 and 4.8, Table A12).



Figure 4.7. Intermolecular H-bonded 1D chain of 3.



**Figure 4.8.** Packing diagram of **3** showing 2D polymeric chain formed *via* intermolecular H-bonding and  $\pi \cdots \pi$  interaction (Hydrogen atoms were removed for clarity).

Furthermore, we have extended our work on Hg(II) based complexes with the synthesis of heteroleptic complexes with different aromatic acids (amino and hydroxyl derivatives of benzoic acid) and bpy. Complexes **4–9** were obtained by the reaction of Hg(OAc)<sub>2</sub>, bpy and varying aromatic acids, *i.e.*, benzoic acid (BA) (**4**), 2–amino benzoic acid (2–ABA) (**5**), 3–amino benzoic acid (3–ABA) (**6**), 4–amino benzoic acid(4–ABA) (**7**), 2–hydroxy benzoic acid (2–HBA) (**8**), and 4–hydroxy benzoic acid (4–HBA) (**9**) in acetonitrile (ACN) at room temperature (**Scheme 4.3** and **4.4**). The progress of these reactions has been monitored by thin layer chromatography (TLC) and **4–9** were obtained in good yield. All these complexes were stable at room temperature with poor solubility in common organic solvents. **4**, **5**, **7–9** were monomers with hexa coordinated Hg(II) center whereas **6** was a *zig–zag* 1D-polymer with hepta-coordinated Hg(II) ion. Unlike other substituted benzoic acids, the 3–amino benzoic acid showed both –NH<sub>2</sub> and –COOH groups having

affinity towards Hg(II) centers, but the reaction of HgCl<sub>2</sub>/HgBr<sub>2</sub> with 3– amino benzoic acid it was observed that only –NH<sub>2</sub> group coordinated to Hg(II) center and –COOH group remained uncoordinated, yielding **10** and **11**. **4–9** have been characterized by elemental analysis, FT–IR, and UV–Vis spectroscopy as well as by their single-crystal X-ray structures.



Scheme 4.3. Synthetic pathway of 4–9.

**4.2.11. Structural aspects of 4**, **5**, **7**, **8** and **9**. Complexes **4**, **7**, **8** and **9** crystallized in monoclinic  $P2_1/n$ , and **5** crystallized in triclinic  $P\overline{1}$  space groups, respectively (**Table A13**). **4**–**5** and **7**–**9** were monomeric complexes where Hg(II) ion was present in N<sub>2</sub>O<sub>4</sub> environment. The Hg(II) ion was bonded to four O atoms of carboxylate groups of two BA and two N atoms of bpy, forming distorted octahedral geometry (**Figure 4.9**). Hg–O bond distances were in the range of 2.149(9)–2.316(4) Å, whereas Hg–

N bond distances were ranged from 2.288(4) Å to 2.500(4) Å (Table A14).



Figure 4.9. Perspective view of (a) 4 (b) 5 (c) 7 (d) 8 (e) 9.

**4.2.12. Packing features of 4.** Packing diagram of **4** revealed the presence of intermolecular hydrogen bonding interaction.

Intermolecular H–bonding interactions involved donor oxygen atom of BA unit and hydrogen atom of adjacent unit of another benzoic acid ring C(20)–H(20)···O(1) 2.430 Å, C(17)–H(17)···O(4) 2.445 Å, C(16)–H(16)···O(2) 2.344 Å, leading to the formation of a 1D polymeric chain which further extended *via* C(8)–H(8)···O(2) 2.677Å, C(9)–H(9)···O(3) 2.623 Å, forming 2D-network (**Figure 4.10, Table A15**).



**Figure 4.10.** 1D and 2D-network of **4** formed by intermolecular H-bonding interactions.

**4.2.13.** Packing features of 5. Packing diagram of 5 suggested the presence of intermolecular hydrogen bonding and C-H··· $\pi$  interaction. C-H··· $\pi$  interactions were involved C(1)-H(1)··· $\pi$  2.492 Å, C(2)-H(2)··· $\pi$  2.721 Å, yielding 1D-network which further

extended *via* C(7)–H(7)····O(4) 2.508 Å, C(9)–H(9)····O(1) 2.580 Å, and C(8)–H(8)····N(3)–C(18) 2.680 Å, generating a 2D-network (**Figure 4.11**).

**(a)** 



**Figure 4.11.** 1D and 2D-network in **5** formed *via* intermolecular H-bonding interactions (D represents centroid of the aromatic ring).

**4.2.14. Packing features of 7.** Packing diagram of **7** confirmed the presence of intermolecular hydrogen bonding and C–H··· $\pi$  interaction. Intermolecular H-bonding interactions were present between hydrogen atom of 4–ABA H(4)N, H(23) and oxygen atom of adjacent molecule of 4–ABA O(1), O(3) C(23)–H(23)···O(3) 2.584 Å, N(4)–NH(4)···O(3) 2.274 Å, C(24)–H(24)···O(1) 2.719 Å, yielded 1D–chain which was further extended *via* C(16)–H(16)··· $\pi$  2.789 Å, leading to the formation of a 2D-network (**Figure 4.12**).



**(b)** 



**Figure 4.12.** Intermolecular H-bonding interactions in **7**, 1D and 2D-network (D represents centroid of the aromatic ring).

**4.2.15. Packing features of 8.** Packing diagram of **8** revealed the presence of intermolecular hydrogen bonding interactions. Intermolecular H–bonding interaction involved hydrogen H(2) of bipyridine ring and O(6) of 2–HBA unit of adjacent molecule C(2)– $H(2)\cdots O(6)$  2.461 Å forming 1D–chain which was further extended *via* C(14)–H(14)···O(4) 2.408 Å, C(15)–H(15)···O(2) 2.634 Å, leading to the formation of 2D-network (**Figure 4.13**).

**4.2.16. Structural aspects of 8.** Packing diagram of **8** suggested the presence of intermolecular hydrogen bonding interactions. Intermolecular H–bonding interactions were present between oxygen and hydrogen atom of 4–HBA ring O(5), H(20) and H(16), O(3) with another 4–HBA unit of the adjacent molecule *via* C(16)– $H(16)\cdotsO(5)$  2.694 Å, C(20)– $H(20)\cdotsO(3)$  2.59 Å, leading the formation of a 1D-network which was further extended *via* C(3)– $H(3)\cdots\pi$  3.677 Å, generating a 2D-network (**Figure 4.14**). (a)



**(b)** 



**Figure 4.13.** 1D and 2D-network generated through intermolecular H-bonding interactions in **8**.



**Figure 4.14.** Intermolecular H-bonding interactions in **9**, (**a**) 1D and (**b**) 2D-network (D represents centroid of the aromatic ring).

**4.2.17.** Structural aspects of 6. 6 crystallized in triclinic *P*<sup>T</sup> space group with crystallographically imposed inversion center (**Table A13**). 6 revealed formation of a *zig-zag* 1D-polymeric chain. In the 1D polymeric chain of 6, Hg(II) was represented in a distorted pentagonal bipyramidal geometry where four coordination sites were occupied by four oxygen atoms of two units of 3–ABA, two by N–atoms of bipyridine and apical position by one N–atom of 3–ABA (**Figure 4.15**) Hg–N and Hg–O bond distances range between Hg–N 2.351(4) Å–2.500(4) Å and Hg–O 2.316(4)

Å –2.652(5) Å (**Table A14**). The 3–ABA molecule was coordinated to the Hg(II) ion by the carboxylate group in a bidentate manner whereas with amino group it was directly attached to the another Hg(II) ion, where 3–ABA acting as a bridging ligand between two Hg(II) ions leading to the formation of *zig-zag* 1D-polymeric chain. The two Hg(II) ions in successive monomeric unit were deviated from the mean plane by the angle of 60.31°. The dihedral angle between two 3–ABA coordinated to Hg(1) and Hg(2) through the carboxylate group were calculated as 87.47° and 75.04°.



Figure 4.15. Perspective view of 6.

**4.2.18.** Packing features of 6. Packing diagram of 6 revealed the presence of intermolecular hydrogen bonding interactions. Intermolecular H-bonding interaction involved C(39)–H(39)···O(7) 2.588 Å resulted in 1D-network which was further extended *via* C(31)–H(31)··· $\pi$  3.682 Å leading the formation of 2D-network (Figure 4.16).



**(b)** 



**Figure 4.16.** (a) Intermolecular H-bonding interactions in 6, 1D and (b) 2D-network (D represents centroid of the aromatic ring).



Scheme 4.4. Synthesis of 10-11.
**4.2.19. Structural aspects of 10 and 11.** Complex **10** and **11** crystallized in triclinic  $P_{\overline{1}}$  and monoclinic  $C_2/c$  space group, respectively. In both the complexes Hg(II) atom was surrounded by two halide atoms and two nitrogen atoms of amino groups of two acid molecules, creating a distorted tetrahedral geometry (**Figure 4.17, Table A13**). In **10–11** the carboxylic group remained uncoordinated. In **10** the N(1)–Hg–N(2) bond angle was found to be 107.7° which was observed to be 131.1° in **11**.



Figure 4 17. Perspective view of (a) 10 (b) 11.

**4.2.20.** Packing features of 10 and 11. Packing diagrams of 10 and 11 revealed the presence of intermolecular hydrogen bonding interaction (Figure 4.18).



Figure 4.18. Intermolecular H-bonding interactions in (a) 10 and (b) 11 1D-network.

### **4.3.** Absorption and emission spectroscopy

Electronic absorption and emission spectra of 1–3 and DIPSA have been recorded in MeOH. DIPSA showed a peak at 314 nm and a shoulder at 240 nm due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively.<sup>[18]</sup> Upon complexation with metal, the  $\pi \rightarrow \pi^*$  band was found to be blue-shifted by 8–10 nm and the  $n \rightarrow \pi^*$  band was disappeared. The blue shift of the  $\pi \rightarrow \pi^*$ transition might have taken place because of the destruction of hydrogen bonding between the phenolic and carboxyl functions of DIPSA during the complexation process.<sup>[19]</sup> The highly fluorescent DIPSA ligand exhibited an emission band at 412 nm upon excitation at 314 nm with a calculated quantum yield of 0.29. However, the emission intensity of the complexes was guenched appreciably with the red-shifted band at 424 nm. The estimated quantum yields of 1-3 were 0.11, 0.13, and 0.09, respectively were quite less compared to the pure ligand. The quenching of fluorescence of the free ligand upon complexation may be attributed to the presence of well-known fluorescent quencher Hg(II) and Cu(II) metal ions (Figures 4.19).<sup>[20]</sup>

The electronic absorption and emission spectra of compounds **4–9** were recorded in chloroform at room temperature, and are displayed in **Figure 4.20** and **4.21** The UV-Vis spectra of **4–9** showed three types of absorption bands. The first band in the region between 300-380nm showed weak absorption peak due to  $\pi \rightarrow \pi^*$  and another strong absorption band in the region of 280nm was observed which is due to intra ligand charge transfer (ILCT) from acid unit to pyridine unit.<sup>[21]</sup> Except **5** and **6**, other compounds showed another band in the region of 235 nm which corresponded to the  $\pi \rightarrow \pi^*$  transition. When the complexes **4–9** in chloroform and methanol were exposed to UV lamp, they exhibited blue fluorescence but remained colourless for the other solvent. Interestingly, polymer **6** showed different emission peaks in different solvents; here maximum fluorescence was observed in chloroform and minimum in THF.



**(b)** 



Figure 4.19. (a) Absorption and (b) emission spectra of 1-3.





Figure 4.21. Emission pattern of 6 in different solvents.

Compounds **4–9** showed emission peaks on excitation at 280nm. The maximum quantum yield (*i. e.* 0.089) was observed for polymer **6** and for **8** it was 0.075 whereas for **4**, **5**, **7** and **9** only ~0.007 quantum yield was calculated which was quiet less as compared to **6** and **8**. The higher quantum yield for 1D polymer **6** may be attributed to the higher degree of conjugation  $^{[22]}$  whereas no appropriate reason could be found for the high quantum yield of **8**.

### **4.4.** Conclusions

In this chapter, we have demonstrated the isolation and structural characterization of the first example of the kinetically driven intermediate. heterometallic polymeric 1 along with а thermodynamically controlled 1D polymeric chain, 2. The transformation of 1 to 2 essentially takes place via the partial replacement of the OAc group by the DIPSA ligand around the Hg centers, keeping the Cu centers unaltered. Strong intramolecular hydrogen bonding between the H atom of the phenolic group and the carboxylic O atom of DIPSA plays a vital role in stabilizing 2. To our surprise, 2 upon recrystallization from MeOH changes to the Cu(II)-based monomeric complex 3 via the ACN/MeOH exchange process. Furthermore eight new monomeric complexes of Hg(II) with different aromatic acids (with benzoic acid, 2- or 3-or 4amino/hydroxy benzoic acid) have been synthesized and thoroughly characterized.

### **4.5. Experimental Section**

4.5.1. Materials and physical instruments. The commercially available starting materials All chemicals and solvents were used as received. (CH<sub>3</sub>COO)<sub>2</sub>Hg, Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O HgCl<sub>2</sub>, HgBr<sub>2</sub>, 2,2'-bipyridine, benzoic acid, 2-aminobenzoic acid, 3-aminobenzoic acid, 4– aminobenzoic acid, 2-hydroxybenzoic acid, 4-hydroxybenzoic acid and diisopropylsalicylic acid (DIPSA) and reagent-grade solvents (MeOH and ACN) were purchased from sigma Aldrich. IR spectra ( $4000-400 \text{ cm}^{-1}$ ) were recorded with a Bio-Rad FTS 3000MX instrument on KBr pellets. Elemental analyses were carried out with a Flash 2000 elemental analyzer. UV spectra were recorded on a Cary-100 Bio UV-Vis spectrophotometer. Fluorescence spectra of all of the compounds were recorded on a Horiba Jobin-Yvon Floromax 4P spectrophotometer. Fluorescence quantum yields  $(\Phi_f)$  were calculated by comparing the total Single-crystal X-ray structural studies were performed on an Agilent Technology Supernova CCD diffractometer equipped with a low-temperature attachment.

# 4.5.2. Synthesis of heterometallic polymeric chains and Cu(II) monomer

**Synthesis of (1).** A solution of  $Hg(CH_3COO)_2$  (0.318 g, 1 mmol) and bpy (0.156 g, 1 mmol), and DIPSA (0.222 g, 1 mmol) in acetonitrile was stirred for 15 min, and then Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O (0.0497 g, 0.25 mmol) was added. The entire contents were stirred magnetically for 3h at room temperature. The color of the reaction mixture was dark green after 3h, so a fraction of the reaction mixture was extracted after 3h. In this mixture, we observed a single-spot TLC, ensuring the presence of only one component in the system, so it was left for crystallization and was characterized as intermediate **1**. When the reaction time was exceeded, the color of the solution turned to light green after 12h. Upon extension of the reaction time to more than 12h, no remarkable changes were observed. The progress of the reaction was monitored by TLC. The solution was then passed through filter paper (Whatman filter paper, 70 mm) in order to

remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. Upon slow evaporation of the solvent, light-green single crystals of **2** were obtained after 2 weeks. **Anal. Calcd** for **1**: C 42.79, H 3.99, N 3.68. Found: C 42.84, H 3.97, N 2.97. **Anal. Calcd.** for **2**: C 49.99, H 4.82, N 4.37. Found: C 49.55, H 4.79, N, 4.30. **IR** (KBr, cm<sup>-1</sup>): v 3419 (br), 1570 (s), 1442 (s), 1245 (w), 1168 (w), 887 (s), 768 (s).

Synthesis of (3). When complex 2 was kept for recrystallization in MeOH, compound 3 was obtained after 8 days. Anal. Calcd for 3: C 59.57, H 6.40, N 5.56. Found: C 59.55, H 6.79, N 5.30. IR (KBr, cm<sup>-1</sup>): v 3422 (br), 1605 (s), 1567 (s), 1443 (s), 1309 (w), 1248 (w), 1167 (w), 1027 (m), 768 (s).

#### 4.5.3. Synthesis of Hg(II) monomeric complexes

Synthesis of (4). To a solution of Hg(CH<sub>3</sub>COO)<sub>2</sub> (0.318 g, 1 mmol) in acetonitrile (20 ml) was added benzoic acid (0.244 g, 2 mmol) in acetonitrile (10 ml) and 2,2'-bipyridine (0.156g, 1 mmol). The mixture was stirred at room temperature for overnight resulting in the formation of colorless precipitate and then mixture was filtered. Filtrate was kept as such for crystallization at room temperature after 10-15 days needle shaped crystals formed. Anal Calcd. for 4, C 48.12, H 3.03, N 4.68 Found: C 47.80, H 3.30, N 4.98. IR (KBr cm<sup>-1</sup>)  $\nu$ (COO)= 1595 cm<sup>-1</sup> (asy), 1398 cm<sup>-1</sup> (sym), 731(Hg-O); UV-Vis (MeOH,  $\lambda_{max}$  (nm( $\epsilon$  M<sup>-1</sup> cm<sup>-1</sup>))): 230 (31000), 280 (26000).

Complexes **5–9** and were prepared by a similar method. Analysis for these complexes are given below-

Synthesis of (5). Anal- Calcd.: C 45.83, H 3.20, N 8.91, Found: C 46.06, H 3.15, N, 8.84, IR (KBr cm<sup>-1</sup>)  $\nu$ (COO)= 1532 cm<sup>-1</sup> (asy), 1391 cm<sup>-1</sup> (sym), 758<sub>(Hg-O)</sub>; UV-Vis (MeOH,  $\lambda_{max}$  (nm( $\xi$  M<sup>-1</sup> cm<sup>-1</sup>))): 332 (11000), 281 (29000).

Synthesis of (6). Anal- Calcd.: C 41.42, H 2.91, N 7.90, Found: C 41.88, H 3.14, N 8.24 **IR** (KBr cm<sup>-1</sup>)  $\upsilon$ (COO)= 1555 cm<sup>-1</sup> (asy), 1388 cm<sup>-1</sup> (sym), 763<sub>(Hg-O)</sub>, UV-Vis (MeOH,  $\lambda_{max}$ (nm( $\varepsilon M^{-1} cm^{-1}$ ))): 281 (25000).

Synthesis of (7). Anal- Calcd.: C 45.83, H 3.20, N 8.91, Found: C 45.03, H 3.69, N 8.44, IR (KBr cm<sup>-1</sup>)  $\nu$ (COO)= 1533cm<sup>-1</sup> (asy), 1343cm<sup>-1</sup> (sym), 721<sub>(Hg-O)</sub>, UV-Vis (MeOH  $\lambda_{max}$ (nm( $\epsilon M^{-1} cm^{-1}$ ))): 228 (12000), 282 (21000).

Synthesis of (8). Anal- Calcd.: C 45.68, H 2.88, N 4.44, Found: C 46.02 H 3.35, N, 4.92, IR (KBr cm<sup>-1</sup>)  $\nu$ (COO)= 1578 cm<sup>-1</sup> (asy), 1391cm<sup>-1</sup> (sym), 762<sub>(Hg-O)</sub>, UV-Vis (MeOH,  $\lambda_{max}$  (nm( $\xi$  M<sup>-1</sup> cm<sup>-1</sup>))): 232 (25000), 280 (22000).

Synthesis of (9). Anal- Calcd.: C 45.68, H 2.88, N 4.44, Found: C 45.19, H 2.91, N 4.95, IR (KBr cm<sup>-1</sup>)  $\nu$ (COO)= 1570 cm<sup>-1</sup> (asy), 1385 cm<sup>-1</sup> (sym), 731<sub>(Hg-O)</sub> ;UV-Vis (MeOH,  $\lambda_{max}$  (nm( $\xi$  M<sup>-1</sup> cm<sup>-1</sup>): 233 (32000), 280 (28000).

**4.5.3.** Synthesis complexes (10) and (11). Complexes 10 and 11 were prepared by the reaction of  $HgX_2$  (X=Cl, Br) with 3-aminobenzoic acid in methanol at room temperature.

**Synthesis of (10). Anal- Calcd.:** C 26.66, H 1.60, N 4.44, Found: C 27.12 H, 1.95, N 4.50.

**Synthesis of (11). Anal- Calcd.**: C 31.04, H 1.86, N 5.17. Found: C 31.39, H 2.04 N 4.99.

**4.5.4. X-ray Crystallography.** Data were collected at 150(2) K using graphite-monochromated Mo K $\alpha$  ( $\lambda \alpha = 0.71073$  Å) and Cu K $\alpha$  ( $\lambda \alpha = 1.54814$  Å). The strategy for data collection was evaluated using the CrysAlisPro CCD software. The data were collected by the standard  $\varphi - \omega$  scan techniques and scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares with SHELXL-97 on F<sup>2</sup>.<sup>[23]</sup> The positions of all of the atoms were obtained by direct methods. All non-H atoms were refined anisotropically. The remaining H atoms were placed in

geometrically constrained positions and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. All of the hydrogenbonding interactions, mean-plane analyses, and molecular drawings were obtained using the Diamond program (version 3.1d). The crystal and refinement data are summarized in **Table A10** and **Table A13**, and selected bond distances and angles are shown in **Table A11** and **A14**.

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## **CHAPTER 5**

# Varying Coordination Modes of Amide Ligand in Group 12 Hg(II) and Cd(II) Complexes: Synthesis, Crystal Structure and Nonlinear Optical Properties 5.1. Introduction

The carboxamide [C(O)–NH–] group is a basic structural unit in protein, and it also plays an important role as a building unit in coordination complexes.<sup>[1]</sup> Nitrogen rich aromatic and aliphatic groups such as pyridine carboxamide, containing the flexible --NH-CO-py-CO--NH core, have been recognized to be important in multifunctional materials,<sup>[2]</sup> azo dves,<sup>[3]</sup> asymmetric catalysts,<sup>[4]</sup> molecular receptors,<sup>[5]</sup> dendrimer synthons<sup>[6]</sup> and in antitumor agents with Pt(II)<sup>[7]</sup> owing to their varying The remarkable feature of N,N' -bis[2-(2structural motifs. pyridyl)methyl]pyridine-2,6-dicarboxamide ( $H_2L$ ) is its ability to entwine and to form double helical dimers, trimers and tetramers with d block metals.<sup>[1,8]</sup> This multi-function ligand has been chosen due to its capability to coordinate metal ions in various coordination modes. At a discrete molecular level it can bind metal ion in a monodentate  $^{[9a]}$  (IV), bidentate, <sup>[9b]</sup> tridentate<sup>[8, 10]</sup> (II, III), tetradentate<sup>[8]</sup> (I) and pentadentate mode<sup>[8,9c,d]</sup> as shown in Chart 1. The coordination mode representations of  $H_2L$  in I to IV involving pyridine/amido nitrogen are common. However, to date, coordination mode of H<sub>2</sub>L involving oxygen (V–VI) is rare, to the best of our knowledge.

Interest in inclusion of heavy metals, such as Zn(II), Cd(II) and Hg(II), in biomolecules has been growing rapidly in the field of medicinalinorgani chemistry due to their potential applications in biomedical research. <sup>[11-14]</sup> Although Cd(II) and Hg(II) are considered to be toxic, they have a wide variety of applications in industrial processes. <sup>[15-16]</sup> Cd(II) is often considered as a competitive candidate for its interaction with the available binding sites in the cell and other genetic control sites. Nonlinear optical properties of metal–ligand complexes are unique compared to standard inorganic materials. <sup>[17]</sup> The ligand is known to possess large third order nonlinearity, <sup>[18]</sup> and incorporation of metal might change the nonlinearity by metal–ligand charge transfer. <sup>[17,19]</sup> Dramatic enhancement in nonlinear refraction by incorporating Cd or Zn has been observed compared to the free ligand.<sup>[20a, b]</sup> These measurements, however, were carried out using longer laser pulses (either nanosecond or picosecond pulses). For measuring purely electronic contribution, ultrashort (few femtosecond) laser pulses are essential.





In this chapter, we discussed the synthesis and crystal structures of two new complexes, helical dimeric  $[Hg(L)]_2$  (1) and trimeric  $[Cd_3(H_2L)_4(Cl)_6]$  (2). Complexes 1 and 2 showed the contrasting electrochemical behavior arising due to different coordination modes of ligand and its rationalization by density functional calculations. We also reported on measurements of the real part of the third order optical nonlinearity  $\chi(3)$  of these complexes, for the first time, using 40 fs pulses, accessing purely the electronic response.

### 5.2. Results and discussion

**5.2.1.** Synthesis and characterization. Complexes 1 and 2 were synthesized by reaction of  $Hg(CH_3COO)_2$  and  $CdCl_2$  with  $H_2L$  in 1 : 1 molar ratio, in MeOH/CHCl<sub>3</sub> at room temperature (Scheme 5.1).





The ligand  $H_2L$  was synthesized by using previously reported method.<sup>[8]</sup> The number of earlier reports were there which show that  $H_2L$ was coordinating through the N-atoms only, while the O-atoms of carbonyl group were restricted to the coordination. The flexibility and presence of various nitrogen rich functionalities in  $H_2L$  has prompted us to explore the possible modes of binding towards the Group 12 Hg(II) and Cd(II) metal ions. Complexes **1** and **2** have been characterized by FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and their molecular structures have been established by single crystal X-ray studies.



Figure 5.1. Perspective view of 1, (all water molecules and H-atoms were removed for clarity). (Inset showed double helical skeleton of  $H_2L$ ).

**5.2.2. Structural aspects of 1. 1** crystallized in monoclinic  $P2_1/c$  space group with crystallographically imposed inversion center (Figure 5.1, Table A16). Coordination environment around each Hg(II) ion in 1 was hexa-coordinated (N6) mode where Hg(II) ion was bonded to six N-atoms from a pair of central pyridine rings Hg(1)-N(1) 2.694(4)Å, Hg(2)-N(6)2.698(4)Å, terminal pyridine rings Hg(1)-N(9) 2.494(4)Å, Hg(2)-N(8) 2.475(4)Å, Hg(1)–N(3) 2.522(4)Å, Hg(2)–N(5) 2.495(4)Å and amido groups Hg(1)–N(2) 2.118(4)Å, Hg(2)–N(4) 2.128(3)Å, Hg(2)–N(7) 2.121(3)Å, Hg(2)–N(1) 2.644(3)Å forming four 5-membered chelate rings around each Hg(II) ion, led to the formation of a distorted octahedral geometry (Table A17). The five lattice water molecules were present in the asymmetric unit, which were involved in hydrogen bonding. The central pyridine N-atoms connected to both Hg(II) atoms in 1 form an irregular quadrangular central Hg<sub>2</sub>N<sub>2</sub> ring with varying Hg-N bond distances. The Hg(II) ions in 1 were separated by 3.3483(10) Å with two ligands being helically enfolded around the Hg(II) centers The carbonyl O-atoms (O1, O2, O3, and O4) from amido groups remain uncoordinated

(Figure 5.2) and participate in hydrogen bonding interactions (Inset of Figure 5.1).



**Figure 5.2.** (a) Crystal structure of complex 1 showed five lattice water molecules. (b) 1D polymeric chain of 1 formed intermolecular hydrogen bonding.

**5.2.3.** Packing features of 1. The packing diagram of 1 revealed the existence of intermolecular H-bonding interactions. Intermolecular H-bonding interactions involve uncoordinated carbonyl O-atoms C(28)– $H(28)\cdots O(4) 2.476(1)$  Å and C(34)– $H(34)\cdots O(2) 2.541(3)$  Å between a terminal pyridine ring and uncoordinated carbonyl O-atoms of the amido group from one dimeric unit to another, led to the formation of a hydrogen bonded 1D polymeric chain, which extended further *via* C(32)– $H(32)\cdots\pi$  3.679 (1) Å interaction, leading to the formation of a single helical layer. Moreover, water molecules present in the lattice were involved in formation of an H-bonded chain of water tetramers (O111, O222, O333,

O444, and O555) with O–H···O distances in the range of 2.023(1)– 2.624(1) Å,<sup>[21]</sup> which hold adjacent helical layers and resulted in the formation of a 2D-network (**Figure 5.3**, **Table A18**).



**Figure 5.3.** (a) Space filling model showing water tetramers trapped between two helices *via* hydrogen bonding in **1**. (b) Packing of complex **1** represented water tetramer between two helical layers.

**5.2.4. Structural aspects of 2. 2** crystallized in orthorhombic *Pbca* space group with a crystallographically imposed inversion center (**Table A16**). An asymmetric unit contained two types of Cd(II) ion one in the center Cd(2) and two at the terminal Cd(1) positions. Each Cd(II) ion in **2** exhibited a hexacoordinated environment, firmly bonded by two O atoms of carbonyl groups Cd(1)–O(2) 2.410(4) Å and Cd(2)–O(1) 2.331(4) Å, two N atoms of the terminal pyridine ring, Cd(1)–N(5) 2.387(4) Å and Cd(2)–N(4) 2.341(4) Å, whereas the remaining two coordination sites were occupied by the terminal Cl atoms Cd(1)–Cl(1) 2.5271(12) Å and Cd(1)–Cl(2) 2.5185(12) Å, resulted in a distorted octahedral geometry (**Table A17**). The asymmetric unit also contained three lattice water molecules (**Figure 5.4a**). The three Cd(II) ions in **2** were arranged linearly with the central Cd(II) ion holding Cl atoms in *trans* fashion, and the two

terminal Cd(II) ions holding Cl atoms in *cis*-fashion, and the metal : ligand ratio is 3 : 4.



**Figure 5.4.** (a) Crystal structure of complex **2**. (b) Packing diagram of intermolecular hydrogen bonded 2D layer in **2** along *b*-axis.

**5.2.5.** Packing features of 2. The packing diagram of complex 2 revealed the existence of intermolecular C–H····Cl hydrogen bonding and C–H··· $\pi$  interactions. The intermolecular packing interactions involved C–H····Cl, H-bonding interactions between H(10) and H(17) of coordinated pyridine with terminal Cl(1) (2.884(1) Å and Cl(2) 2.672(1) Å, respectively, and C(16)–H(16)··· $\pi$ (py) (3.424 Å) interactions between terminal pyridine rings of adjacent molecules, led to the formation of a 2D-network (**Figure 5.4b**, Table A18).

### 5.3. Comparative discussion of 1 and 2

According to Cambridge Structural Database (CSD ver 1.15),  $H_2L$  bound to Ni,<sup>[8]</sup> Cu,<sup>[8]</sup> Fe, <sup>[22a]</sup> Co,<sup>[22b]</sup> Zn<sup>[9a]</sup> and Ag<sup>[9b]</sup> via N-atoms of amido and pyridine groups, and only one report was available on bonding of O atom of carbonyl to potassium in a bimetallic complex.<sup>[22b]</sup> However, to the best of our knowledge, there existed no report on the binding mode of such ligands involved coordination of both the carbonyl O-atoms to the transition metal center, which resulted in a rare seven membered metallacyclic ring (**Inset of Figure 5.4a**). The flexibility and contrast binding of  $H_2L$  has been observed in 1 and 2. In 1, the two terminal pyridine rings R1 and R2 were twisted to 41.44° and 16.98° with respect to the central pyridine ring R3 (green), whereas the other two terminal pyridine rings, R5 and R6, were twisted at 48.25° and 37.56° with respect to the central pyridine ring R4 (brown) (**Figure 5.5**).



**Figure 5.5.** Complex **1** showed dihedral angle between terminal and central pyridine rings.

In case of **2**, the dihedral angle between two coordinated terminal pyridine rings R1 and R2 bonded to Cd(1) was 74.84°, whereas the terminal pyridine rings R4 coordinated to Cd(2) were found to be in the same plane. Similarly, the dihedral angle between terminal pyridine ring R1 and uncoordinated central pyridine ring R3, as well as between uncoordinated central pyridine ring R5 and terminal pyridine ring R6, were also calculated as  $84.14^{\circ}$  and  $65.48^{\circ}$ , respectively (**Figure 5.6**). The central pyridine ring in **1** was coordinated to both the Hg(II) atoms, whereas in **2** it remained free.



**Figure 5.6.** Crystal structure of **2** shows dihedral angle between terminal and central pyridine rings. Dihedral angle between rings R1, R2 and R4, R4 were 78.84° and 0°. Other dihedral angles between rings R1, R3 and R5, R6 were found to be 84.14° and 65.48°.

Unlike 1, where both the terminal pyridines of each  $H_2L$  ligand participate in coordination, in 2, out of four  $H_2L$ , two were bonded through both terminal pyridines, whereas the remaining two coordinate through only one terminal pyridine with the other being pendant. Of the total eight terminal pyridine rings available on the four  $H_2L$ , six of these coordinated to the three Cd(II) atoms, the other two terminal pyridine rings remained free, and these act as head and tail of the Z-shaped complex 2 (Figure 5.7).

The O-atoms of amido carbonyl groups in 1 remained free as routinely observed for such ligands. However, in 2, a rare coordination of the amido O-atoms to Cd(II) has been observed. The unusual bonding of O-atoms of amido groups to Cd(II) in 2 leave six accessible vacant coordination sites (Chart B) providing an option for the complex to grow further.



Chart B. Showed six vacant coordination sites for further growth.



Figure 5.7. Z shaped structure of 2 (Hydrogen atoms were removed for clarity).

### **5.4. Electrochemical properties**

Previous studies on electrochemical behavior of N,N-bis[2-(2pyridyl)methyl]pyridine-2,6-dicarboxamide and its complexes have revealed solvent dependent ligand based two successive reductions ( $L^{0/-}$ ,  $L^{-/2^-}$ ), **1** which have been related to the reduction of carbonyl moieties of two carboxamide groups present in the ligand.<sup>[23]</sup> Contrary to this, the cyclic voltammogram of ligand **H**<sub>2</sub>**L**, recorded in DMSO solution using a Pt-working electrode with reference to a Ag/AgCl electrode, exhibited a single quasireversible reduction peak at -0.75 V (Table A). The differential pulse voltammetry experiment also showed only one peak suggested a concurrent two electron reduction of ligand ( $L^{0/-2}$ ) (**Figure 5.8**). The corresponding reduction in **1** and **2** exhibited a relative shift compared to that of the ligand with no redox event associated to metal centers (Hg<sup>2+</sup>/<sup>+</sup> and Cd<sup>2+</sup>/<sup>+</sup>).

The reduction wave of the Hg(II) complex **1** showed a cathodic shift ( $E^{o}_{red} = -0.86$  V) compared to the ligand, which indicated that after coordination, reduction of the ligand becomes more difficult, which was understandable for the dianionic nature of deprotonated ligand in **1**. In contrast, ligand reduction in Cd(II) complex **2** was observed with an

anodic shift at -0.65 V and can be attributed to its unique >C=O  $\rightarrow$  Cd(II) coordination conducive for stabilization of reduced carbonyl groups through charge delocalization. The complexation of Hg(II) and Cd(II) to **H**<sub>2</sub>**L** resulted in a greater cathodic and anodic peak separation ( $E_{pc} - E_{pa} = \Delta E_p = 272$  mV in **1** and 486 mV in **2**) and distortion in the anodic wave compared to that in free ligand possibly due to electro-adsorption or subsequent slow electrode reaction.<sup>[1,24]</sup>.



**Figure 5.8.** Cyclic voltammograms and Differential potentialvoltammograms of  $H_2L$  (a Complexes 1(b) 2(c) at 0.001M concentration in 0.1 MTBAPF<sub>6</sub> in DMSO recorded at a scan rate of 100 mV s<sup>-1</sup>.

### **5.5. Density functional calculation**

In recent years, correlation between the theoretically calculated LUMO energy and the experimental reduction potential of several quinines, polycyclic aromatic hydrocarbons (PAH), flexible aromatic molecules and heterocyclic amines have been extensively studied.<sup>[25]</sup> This prompted us to analyze the frontier molecular orbitals of our systems by density functional calculations, in order to rationalize the contrasting electrochemical behavior of 1 and 2. All the calculations were performed at B3LYP<sup>[26]</sup> level of theory using LANL2DZ<sup>[27]</sup> basis set as implemented in GAUSSIAN 09 suite of programs,<sup>[28]</sup> as the B3LYP/LANL2DZ model chemistry has a proven track record of predicting the correct structure for similar systems.<sup>[10]</sup> Geometry optimizations of ligand, 1 and 2 were carried out in gas phase without any symmetry constrain, and their optimized structures (Figure 5.9) were validated by frequency calculations, which did not show the presence of any imaginary frequency. The optimized structures also compared well with experimental geometrical parameters.

The frontier molecular orbitals of  $H_2L$ , 1 and 2 were depicted in Figure 5.9. The HOMO of the ligand mainly consisted of nonbonding lone pairs of central pyridine nitrogen and both carboxamide oxygens, whereas the LUMO was dispersed over  $\pi$ -orbitals of entire central pyridine and carbonyls of carboxamides. Complexation of Hg(II) and Cd(II) did not cause any significant redistribution of component atomic orbitals in frontier orbitals of resulting complexes 1 and 2, and they remained ligand based exclusively with no contribution from metal centers, except for HOMO of 2 having sole contribution from nonbonding lone pairs of the Cl atoms on the terminal Cd metals. The HOMO of 1 was located on O and N of carboxamide groups, and the LUMO is restricted to the  $\pi$ -orbitals of the central pyridine ring. The HOMO of 2 has exclusive Cl lone pair character, whereas its LUMO comprises central pyridine  $\pi$ orbitals extended to both carbonyl carbons. Overall, the frontier orbitals of **1** and **2** mainly possess characteristics of ligand and have no metal component. This indicated that the properties originating from frontier orbitals were expected to have an insignificant effect of metal type (Hg or Cd) in these complexes.

Compound	E <sup>o</sup> red.	ΔΕρ	HOMO energy	LUMO energy
	(V) <sup>[a]</sup>	(mV) <sup>[b]</sup>	(eV)	(eV)
$H_2L$	-0.75	194	-6.69	-1.60
1	-0.86	272	-5.50	-1.43
Cd analogue of $1^{[c]}$			-5.40	-1.51
2	-0.65	486	-5.61	-2.30
Hg analogue of $2^{[c]}$			-5.84	-2.28

**Table A.** Correlation of redox potential and LUMO energy of  $H_2L$ , 1 and 2. [a] Determined by DPV peak. [b]  $\Delta Ep = Ep_c \cdot Ep_a$ . [c] hypothetical system.

The calculated energies of HOMO and LUMO were given in Table A, which indicated that the varying coordination modes of ligand in 1 and 2 alter their LUMO energies in different ways. Ligand coordination to Hg(II) through only nitrogen led to the destabilization of LUMO (-1.43 eV) compared to that of ligand (-1.60 eV) and thus hardens its reduction, whereas that to Cd(II) through both nitrogen and oxygen stabilized the LUMO (-2.30 eV) and thus eases the reduction. Furthermore, to confirm the effect of coordination modes on the electrochemical behavior of our systems, we extended the frontier molecular orbital analysis to possible Cd and Hg analogues of 1 and 2 (optimized structures depicted in Figure 5.10).

The observed LUMO energies of these hypothetical systems (-1.51 eV for Cd analogue of 1 and -2.28 eV for Hg analogue of 2) revealed that despite metal exchange, coordination modes involved both nitrogen and oxygen stabilized the LUMO energy and therefore was conducive for reduction, in contrast to those having only nitrogen involved

in coordination. The DFT studies on these systems supported the fact that contrasting electrochemical behavior of 1 and 2 aroused due to varying coordination modes of  $H_2L$  and not because of two different metals present in them.



-1.51 eV

-5.40 eV



Figure 5.9. HOMO and LUMO of  $H_2L$ , 1, 2 and hypothetical Cd and Hg analogues of 1 and 2.



Figure 5.10. Optimized structures of  $H_2L(a)$ , 1 (b), 2 (c), Cd analogue of 1 (d) and Hg analogue of 2 (e).

### 5.6. Nonlinear optical properties

The third-order NLO properties of a similar ligand 2,6 dicarboxamido-2pyridylpyridine (H<sub>2</sub>dcapp) and its metal complexes  $[Ag_{10}(dcapp)_4] \cdot _2(OH) \cdot 12H_2O$ ,  $[Zn_4O(dcapp)_3] \cdot 6H_2O$  and  $[Hg_2(dcapp)_2]$ were reported by Hou *et al.*<sup>[10]</sup> which motivated us to examine the NLO behavior of  $H_2L$ , 1 and 2 by using ultrashort femtosecond laser pulses. We experimentally determined the nonlinear refractive indices,  $n_2$ , of the complexes using a femtosecond Z-scan technique that has been described recently.<sup>[29]</sup> Summary of nonlinear refractive index values was given in Table B. A typical trace of transmitted light through the complexes was shown in **Figure 5.12**. We deduced the nonlinear refractive index of the complex by measuring the maximum light transmittance, Tp as well as the minimum transmittance, Tv. The quantity  $\Delta$ Tpv was the change of normalized transmittance, from which we deduced the  $n_2$  value using the relation.<sup>[30]</sup>

 $n_2 = \frac{1/4 \Delta T_{pv} \lambda}{0.406 (1\text{-}S)^{0.27} 2 \pi I_0 L_{eff}}$ 

Here,  $\lambda$  denotes the laser's wavelength 800 nm, which was far from the absorption wavelength of H<sub>2</sub>L, 1 and 2 (Figure 5.11, 5.12), S was a measure of the fraction of input light transmitted by a circular 1 mm diameter aperture placed prior to the power energy meter used. Leff denotes the effective sample length while I<sub>0</sub> was the peak laser intensity. The real part of the third order nonlinearity  $\chi(3)$  can be deduced from the values of n<sub>2</sub>, which was a quantitative reflection of the optical nonlinearity exhibited by the two metal incorporated ligands.<sup>[20b]</sup> The origin of optical nonlinearity in transparent materials was due to their electronic and molecular response to intense pulses of light. The former result from distortion of the electronic charge cloud; it was expected to occur on considerably faster timescales than the molecular response to the applied optical field.



Figure 5.11. UV-Visible absorption of H<sub>2</sub>L, 1 and 2.

Theoretical estimates predict that molecular responses were typically in the ps regime, whereas electronic responses may be as fast as **1** fs.<sup>[31]</sup> Using ultra-short laser pulses of fs duration it was possible to separate the electronic and molecular responses. In contrast to conventional experiments, which use picosecond and nanosecond long laser pulses, in our experiments, use of a 40 fs pulse permits us to probe, for the first time, the pure electronic NLO response, precluding any contribution from the molecular response. Our results showed that the 20% enhancement in refractive indices value obtained in the case of **1** (and the 3% enhancement in the case of **2**) compared to the ligand was attributed solely to the electronic responses in these molecules. As observed in DFT calculations, the properties featuring frontier orbitals had very little effect of metal. The 20% enhancement in  $n_2$  value for **1** compared to that of 3% for **2** was attributed to different coordination modes of the ligand in these systems.

Compound	<b>n</b> <sub>2</sub>	$\chi^{(3)}$ (real part)	γ <sup>h</sup>
	$(\text{cm}^2/\text{W}) \ 10^{-14}$	(esu) 10 <sup>-11</sup>	(esu) $10^{-30}$
1	4.66	2.52	3.8
2	3.97	2.14	3.2
H <sub>2</sub> L	3.86	2.08	3.1
Neat DMSO	3.75	2.02	3.0

 Table B. Summary of nonlinear refractive index values obtained in the present measurements.



**Distance (mm) Figure 5.12.** Closed-aperture z-scan of complexes 1 and 2 obtained using a 40 fs laser pulse of 800 nm wavelength.
# **5.7.** Conclusions

In this chapter, we have demonstrated the varying coordination modes of N,N'-bis[2-(2-pyridyl)methyl]pyridine-2,6-dicarboxamide ( $H_2L$ ) ligand towards Hg(II) and Cd(II) metal ions. The arrangements of  $H_2L$  in 1 show all the terminal and central pyridine N-atoms being on the same side and are involved in coordination with Hg(II). However, in case of Cd(II) complex 2, a rare coordination mode of  $H_2L$  was observed, which features coordination of N as well as of O of pyridine and carboxamide groups, respectively, which is made accessible by the flipping of terminal pyridine rings by 180°. The Flipping of pyridine rings also provides availability of free coordination sites in 2, and thus makes it a suitable precursor for construction and design of new complexes. We have also demonstrated that the two complexes featuring different coordination modes of  $H_2L$ exhibit significantly different photophysical and electrochemical properties. Density functional calculations performed on these complexes suggest that the bonding patterns involving coordination of only N atoms of pyridine rings and amido groups destabilizes the LUMO and thus shows cathodic shift for its reduction, whereas that involving coordination of pyridine N and carboxamide O stabilizes the LUMO energy and causes the anodic shift.

# **5.8.** Experimental section

5.8.1. Materials and physical measurements. The commercially available starting materials  $Hg(CH_3COO)_2$ ,  $CdCl_2$  and reagent grade solvents were used as received. The ligand was synthesized in the lab by a previously reported method.<sup>[8]</sup> IR spectra [4000–400 cm<sup>-1</sup>] were recorded with a Bio-Rad FTS 3000MX instrument on KBr pellets. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded at 400 MHz using  $CDCl_3$  and  $DMSO-d_6$  as solvents, respectively. Tetramethylsilane (TMS) was used as reference for recording <sup>1</sup>H (of residual proton;  $\delta = 7.26$  ppm) and  ${}^{13}C$  ( $\delta = 77.0$  ppm) spectra in CDCl<sub>3</sub> and DMSO-d<sub>6</sub>. Cyclic voltammograms (CVs) were recorded with a CHI620D electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode with a scan rate of 100 mV s<sup>-1</sup> using solution of tetrabutylammoniumhexafluorophosphate  $(TBAPF_6)$  in DMSO (0.1 M) as supporting electrolyte. UV-visible absorption spectra were recorded using a Cary-100 Bio UV-visible spectrophotometer. Nonlinear optical measurements were carried out using 40 fs laser pulses centered at 800 nm wavelength obtained from a Ti:Sapphire amplifier system (Odin I, Quantronix) at a repetition rate of 1 kHz. Using a fused silica wedge, reflected beam (along with neutral density filter) was used to perform experiments at incident energy in the range of 0.1–0.4 µJ. These energy values were chosen to avoid any contribution from the fused silica cuvette. Moreover, the nonlinear absorption in the sample was insignificant. A 30 cm lens was used to focus this laser beam onto a 1mm cuvette containing the samples diluted in DMSO to 3 mM. The cuvette was placed on the motorized translation stage. Closed-aperture z-scan measurements were performed to measure the transmitted light on a shot-to-shot basis using a power-energy meter coupled to a laboratory computer.

**5.8.2.** Synthesis of (1). A solution of  $Hg(CH_3COO)_2$  (0.0318 gm, 0.1 mmol) in 30 mL methanol was stirred for 2h, and then a solution of  $H_2L$ 

ligand (0.0350 gm, 0.1 mmol) in 20 mL CHCl<sub>3</sub> was added. The resultant solution was stirred magnetically for 6h at room temperature. The reaction mixture was passed through the filter paper (Whatman filter paper, 70 mm) to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of **1** were obtained after 6 days. **IR** (KBr, cm<sup>-1</sup>):  $\nu$ C=N 1557 cm<sup>-1</sup>,  $\nu$ C=O 1661 cm<sup>-1</sup>. <sup>1</sup>H **NMR** [CDCl<sub>3</sub>, 400 MHz]  $\delta = 8.03$  (d, J = 8 Hz, 4 H), 7.72 (t, J = 8 Hz, 2 H) 7.50–7.55 (m, 8 H), 6.74–6.77 (m, 8 H), 4.59–5.14 (m, 8 H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>)  $\delta = 167.8$ , 157.3, 151.7, 146.4, 138.3, 137.4, 125.0, 123.8, 122.4, 50.3.

**5.8.3.** Synthesis of (2). A methanolic solution (30 mL) of  $CdCl_2 \cdot H_2O$  (0.0201 gm, 0.1 mmol) was stirred for 2h, and then a 20 mL CHCl<sub>3</sub> solution of **H**<sub>2</sub>L ligand (0.0350 gm, 0.1 mmol) was added. The resultant solution was stirred for 6h at room temperature. The reaction mixture was filtered and maintained room temperature for crystallization. On slow evaporation of the solvent, colorless single crystals of **2** were obtained after 11 days. **IR** (KBr, cm<sup>-1</sup>): vNH 3421.69 cm<sup>-1</sup>, vC=N 1539.60 cm<sup>-1</sup>, vC=O 1647cm<sup>-1</sup>. <sup>1</sup>H NMR [DMSO-d<sub>6</sub>, 400 MHz]  $\delta$  = 10.01 (t, J = 4 Hz, 8 H), 8.51–8.52 (m, 8 H), 8.19–8.27 (m, 8 H) 7.74–7.78 (m, 8 H), 7.35 (d, J = 8 Hz, 8 H), 7.26–7.29 (m, 8 H), 4.68–4.69 (16 H). <sup>13</sup>C (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  = 163.4, 158.4, 148.9, 148.6, 139.6, 136.8, 124.5, 122.2, 121.1, 44.3.

**5.8.4. X-ray crystallography.** Single crystal X-ray structural studies of **1** and **2** were performed on a CCD Agilent Technology Supernova diffractometer equipped with a low-temperature attachment. Data were collected at 150(2) K using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda \alpha = 0.71073$  Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. Data were collected by the standard phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-

97, refining on  $F^{2,[32]}$  Positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The distances and thermal parameters of hydrogen atoms for the five water molecules in **1** and the three water molecules in **2** were fixed at  $1.5 \times$  Ueq. of their parent atoms. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally  $1.2 \times$  Ueq of their parent atoms. All the H-bonding interactions, mean plane analysis, and molecular drawings were obtained using the program Diamond (ver 3.1d). The crystal and refinement data are summarized in **Table A16**, and selected bond distances and bond angles were shown in **Table A17**.

### **5.9. References**

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# **CHAPTER 6**

# Anthracene Derived Dinuclear Gold(I) Diacetylide Complexes: Synthesis, Photophysical Properties and Supramolecular Interactions

# **6.1. Introduction**

Polyaromatic hydrocarbons (PAHs) with extended conjugation have gained much attention in past decades due to their strong visible  $\pi \rightarrow \pi^*$ absorption, intense luminescence and high charge mobility in the solid state.<sup>[1]</sup> They have got applications in advanced materials for organic light-emitting diodes (OLEDs), field-effect transistors (FETs) and solar cells.<sup>[2]</sup> Connecting PAH to the metal center through the alkyne unit as a spacer introduces additional features to be used as molecular wires, nonlinear optical materials and molecular electronics.<sup>[3]</sup> It is well known that metallation of PAH ring system has the significant effect on its photophysical properties and structural dimensionalities.<sup>[4]</sup>

Alkynyl gold complexes have drawn considerable interest in recent years<sup>[5]</sup> because of their aurophilic properties, exciting photophysical properties and their ability to build a supramolecular array.<sup>[6]</sup> Recent reports on PAH linked with platinum(II) and gold(I) *via* the alkynyl spacer show interesting structural property, photophysical properties and their structural reactivity.<sup>[7]</sup> The organoAu(I) system shows enhanced luminescent properties for alkynylAu(I) phosphines complexes compared to other gold complexes.<sup>[8]</sup>

Non-covalent interactions are the primary driving force in constructing supramolecular architectures as well as in determining the constitution and conformation of molecules. Although, in gold chemistry, extensive literature are available to understand the aurophilic interaction (Au···Au),<sup>[9]</sup> however, the non-covalent Au···H–C interactions are less explored.<sup>[10]</sup> The Au···H–C interactions are mainly observed in Au(I)

phosphine and thione complexes where gold atoms are in almost linear geometry and leaving behind coordination site for gold hydrogen interactions. Usually, Au···H–C contacts in Au(I) complexes are intramolecular in nature and in case of intermolecular Au···H–C interactions they are restricted to supramolecular 1D-chain.<sup>[11]</sup>

In this chapter, we discussed the synthesis, characterization and photophysical properties of a series of three new anthryl Au(I) diacetylide, 1–3 complexes in which the Au(I) acetylide units were attached at 9,10-, 2,6- and 1,8-positions of anthracene. 1 display more red shift and stronger fluorescence with high quantum yield probably due to more perturbation of Au(I) on  $\pi$  system in 1 compared to 2 and 3. Additionally, the single crystal studies of 1–3 reveal that 1 showed rare noncovalent intermolecular Au···H–C interactions that leading to the formation of a supramolecular 2D-network, whereas, in 3 intramolecular Au···H–C interactions have been observed.

## **6.2. Results and discussion**

**6.2.1.** Synthesis and spectroscopic characterization of 1. 1 was synthesized by reaction of 2 mol equivalent of  $PPh_3AuCl$  with anthracene acetylene at 9,10-positions in the presence of NaOEt in ethanol (Scheme **6.1**). UV/Vis absorption and emission spectra of 1 revealed high fluorescence property with excellent quantum yield. Single crystal X-ray diffraction studies of 1, indicated the existence of intermolecular Au···H–C interactions creating a rare supramolecular 2D-network.



Scheme 6.1. Synthetic outline for 1.

**6.2.2.** Structural aspects of 1. 1 was crystallized in  $P2_1/n$  space group, with crystallographically imposed inversion center (Figure 6.1, Table A24). In 1, the C=CAuPPh<sub>3</sub> units were attached to the planar anthracene ring at the 9,10-positions. The Au–P and Au–C distances of 2.281(1) Å and 2.004(5) Å, respectively, were similar to that reported for aryl Au(I) phosphine complexes (Table A25).<sup>[12]</sup> The slight deviation from linearity has been observed in P–Au–C angle of 175.1(2)° in 1, consequently the C=C (C1–C2) bond lied 4° out of the anthracene plane.



Figure 6.1. Molecular structure of 1. (Solvent molecules were omitted for clarity).



Figure 6.2. Ladder like 1D polymeric chain of 1 showed CH<sup> $\cdots$ </sup> $\pi$  interactions.

6.2.3. Packing features of 1. It was interesting to note that the linear coordination geometry around Au(I) in **1** made it susceptible for additional non-covalent interactions. The packing diagram of 1 revealed that the coordination environment of Au(I) was extended further by an intermolecular Au···H-C interaction between the metal ion and one of the aromatic hydrogens of PPh<sub>3</sub> of adjacent molecule Au(1)···H(11)-C(11) 2.87(1) Å with the Au(1)···H(11)–C(11) bond angle of  $171.00(1)^{\circ}$ . It has been observed that neighboring molecules link together through these interactions along the *b*-axis, yielding one-dimensional polymeric chain. <sup>[13]</sup> This 1D chain further extended *via* the same Au···H–C interactions along the *c*-axis, forming herringbone like 2D-network. Thus, both the gold atoms in 1 were involved in Au-H-C supramolecular interactions (Figure 6.2, 6.3 and 6.4). The considerably short Au···H-C bond distance and larger Au···H-C bond angle develop regular directionality, which suggested that these interactions were hydrogen bonding in nature.<sup>[11f-h]</sup> To the best of our knowledge, 1 represented the first example of supramolecular 2D-network involving intermolecular Au-H-C noncovalent interactions.



Figure 6.3. Au-H-C bonded supramolecular 2D network of 1 through tilted a axis.



**Figure 6.4.** Supramolecular 2D extended network of **1** showing Au...HC interactions. (Solvent molecules are omitted for clarity).

The above interesting features showed the influence (if any) of the binding of C=CAuPPh<sub>3</sub> at the 9,10-positions of the anthracene moiety towards the formation of 2D-network *via* Au···H–C interactions. This prompted us to synthesized similar complexes by varying the position of the alkynyl group attached to anthracene such as 2,6- and 1,8-positions. In this regard, we obtained compounds **2** and **3** with the linkage of C=CAuPPh<sub>3</sub> at 2,6- and 1,8-positions (**Scheme 6.2**).

**6.2.4.** Synthesis and characterization of 2 and 3. Complexes 2 and 3 were synthesized by following the same procedure as of 1 and along with usual spectroscopic techniques analyzed by UV/Vis absorption/fluorescence spectra and were established to be fluorescent albeit less than 1. Both compounds were further analysed by single crystal X-ray diffraction studies ensuing the presence of  $\pi$ ··· $\pi$  and CH··· $\pi$  interactions in 2 while intramolecular Au···H–C interaction in 3.



Scheme 6.2. Synthetic outlines for 2 and 3.

6.2.5. Structural aspects of 2 and 3. 2 and 3 were crystallized in Pi and  $P2_12_12_1$  space group, respectively, (Figure 6.5, 6.6 and Table A24). 2 showed a planar anthracene ring on which C=CAuPPh<sub>3</sub> units were attached to its 2,6- position. Unlike 2, where substitutions were at trans positions, in 3, the C=CAuPPh<sub>3</sub> units were attached to its 1.8- position *i.e. cis*-position to the planar anthracene ring. The distance between Au–P and Au–C are 2.275(5) Å, 2.00(2) Å in **2**, and 2.271(7) Å, 2.282(6) Å, 1.94(3) Å, in **3** respectively (**Table A25**). Which were similar to the reported aryl Au(I) phosphine complexes. The P-Au-C and Au-C-C angles in 2 were found to be 176.9(4)° and 172.4(17)° which suggested slightly distorted geometry around Au(I) from linearity. The C=C (C1–C2) bonds in 2 and 3 were also slightly deviated from the anthracene plane by  $5^{\circ}$  and  $2^{\circ}$ , respectively. Compound **3** found to be highly strained due to the presence of bulky PPh<sub>3</sub> groups at *cis* position which resulted in both the Au(I) centers to move slightly outward and tilted from the anthracene plane (Table A25).



Figure 6.5. Molecular structure of view of 2.



Figure 6.6. Molecular structure of 3.



**Figure 6.7.** Wave like 1D polymeric chain of **2** showing CH $\cdots\pi$  and  $\pi\cdots\pi$  interactions.

**6.2.6.** Packing features of 2 and 3. The packing diagram of 2 revealed the existence of CH··· $\pi$  and  $\pi$ ··· $\pi$  interactions. CH··· $\pi$  interactions involved H(13) of the phenyl ring of PPh<sub>3</sub> unit and  $\pi$  electrons of the acetylenic bond, forming a wave like 1D polymeric chain (Figure 6.7). The packing features of 3 established intramolecular Au···H–C interactions involving hydrogens of PPh<sub>3</sub>, where Au···H–C bond distances and bond angles were

Au(2)-H(48) 3.01(1) Å, Au(2)-H(54) 2.86 (1) Å, Au(1)-H(20) 3.00 (1) Å and Au(2)-H(54)-C(54) 123.00(1)°, Au(2)-H(48)-C(48) 118.31(1)°, Au(1)-H(20)-C(20) 111.66(1)° (**Figure 6.8**).



Figure 6.8. Intramolecular Au<sup>...</sup>HC interactions in 3.

Unlike **1** or **2**, the observed intramolecular Au···H–C interactions in **3**, originated due to the *cis* orientation of C=CAuPPh<sub>3</sub> moieties. The steric repulsion between the two PPh<sub>3</sub> groups in the *cis* orientation facilitated the C–H of the phenyl ring to move closer to the gold. The packing of **3** is further extended by C–H··· $\pi$ , interactions C(4)–H(34)··· $\pi$ 3.359 Å, resulting in 1D polymeric chain (**Figure 6.9**). The synthesis of **3** found to be unique, as to the best of our knowledge there were no reports of 1,8-anthracenyl complexes with bulky PPh<sub>3</sub> group substitution at Au(I) center. So far only few reports of 1,8-anthracenyl substituted Pd(II) / Pt(II) complexes with less bulkier triethyl phosphine group at Pd(II) center have been reported.<sup>[14]</sup>



**Figure 6.9.** (a) 1D chain of 3 showing CH- $\pi$  interactions.(H-atoms omitted for clarity. (b) With H-atoms.

# 6.3. Photophysical properties of complexes of 1–3

The absorption and emission spectroscopic studies of complexes 1–3 were recorded in CH<sub>2</sub>Cl<sub>2</sub> (1.0 x 10<sup>-5</sup> M) at room temperature (**Figure 6.10-6.14**, **Table 1**). 1–3 complexes display two absorption bands (i) with a broad intense vibronic band between 320–470 nm (A), and (ii) very intense, band between 265–310 nm (B). Since the spectra of anthracene and diethynyl anthracene display similar absorption patterns, the absorption bands were assigned to  $\pi \rightarrow \pi^*$  transitions primarily localized in the anthracene. The absorption bands of anthracene were due to the LUMO←HOMO ( ${}^{1}B_{1u} \leftarrow {}^{1}Ag$ ), LUMO←HOMO-1 ( ${}^{1}B_{2u}^{+} \leftarrow {}^{1}Ag$ ), LUMO+1←HOMO ( ${}^{1}B_{2u}^{-} \leftarrow {}^{1}Ag$ ), The second and third transitions led to the two degenerate  ${}^{1}B_{2u}$  excited states, which undergo strong configuration interaction to gave the high-energy "plus" state  ${}^{1}B_{2u}^{+}$  and the low-energy "minus" state  ${}^{1}B_{2u}^{-}$ . The very intense band at around 250 nm corresponded to the  $({}^{1}B_{1u}^{+}\leftarrow {}^{1}Ag)$  transition. Whereas the transition  $({}^{1}B_{1u}^{-}\leftarrow {}^{1}Ag)$  was slightly higher in energy than the  $({}^{1}B_{1u}\leftarrow {}^{1}Ag)$  transition  $({}^{1}B_{1u}$  was lower than  ${}^{1}B_{2u}^{-}$  by ~1500 cm-<sup>1</sup>) was forbidden ( $\varepsilon \approx 10 \text{ M}^{-1} \text{ cm}^{-1}$ ) and hidden under the latter.<sup>[15]</sup>

Though the symmetries of the Au(I) complexes and anthracene were quite different, still there existed a similarity between absorption bands displayed by the complexes and the electronic transitions of anthracene. Band A in the spectra of the complexes corresponded to the LUMO $\leftarrow$ HOMO ( ${}^{1}B_{1u}\leftarrow{}^{1}Ag$ ) transition, which was also known as an S0 $\rightarrow$ S1 transition. The intense band B corresponded to the transition to the "plus" state  ${}^{1}B_{2u}$  ( ${}^{1}B_{2u}$  +  $\leftarrow{}^{1}Ag$ ).

S. No	Absorption $\lambda_{max}$ nm 10 <sup>-</sup> <sup>5</sup> / $\epsilon_{max}$ (cm <sup>-1</sup> , M <sup>-1</sup> )	Emission λ <sub>max</sub> (nm)	Emission Life Time (τ)ns	Quantum yield Φ
1	462(1.01), 434(0.781), 410(0.387), 275(1.87), 230(2.07)	499	4.06	0.89
2	412(1.17), 389(1.36), 366(0.897), 310(8.77), 238(4.30)	445	4.02	0.02
3	422(.976), 398(.936), 376(.583), 267(5.67), 228(4.69)	455	0.57	0.038

Table 1. Absorptions and emissions spectroscopic details of 1, 2 and 3.

The transition was significantly intensified in the spectra of the complexes, indicating that the electronic structure of the anthracenyl ring is significantly perturbed by the Au(I) ions and the ethynyl groups.<sup>[10, 16]</sup> Further, absorption bands of complexes **1**, **2** and **3** were found to be red

shifted compared to respective ligands. Absorption maxima of **1** showed red shifts of ~50 nm compare to **2** and **3**, which indicated that substituents have more perturbation on the anthracenyl rings when they were at 9,10 position. In case of **2** and **3** the bands were observed almost in the same range. In addition to this, complexes display intense absorption in near-UV region. **2** showed an intense absorption band at 310 nm whereas in **1** and **3** showed around 274 and 267 nm, similar to that of previously reported complexes.<sup>[4c]</sup>

Complexes 1–3 were found to be emissive in solution as their respective ligands. On excitation of complexes 1, 2 and 3 at 434 nm, 389 nm and 398 nm, respectively, they display similar emission pattern to their corresponding ligands. Emission spectra of 1 showed very strong fluorescence with the quantum yield of 0.89 compared to 2 and 3 (quantum yield = 0.02 for 2 and 0.04 for 3). 1 showed high fluorescence probably due to the substitution at 9,10 position which was in contrast with 2 and 3.<sup>[17]</sup> Complex 1 also showed emissive nature in solid-state (**Figure 6.10**).

# 6.4. Computational studies of 1–3

To get an insight into the nature of electronic transitions, densityfunctional theory (DFT) and time dependent density-functional theory (TDDFT) calculations were performed with the Gaussian09 program package.<sup>[18]</sup> All the calculations were performed at B3LYP <sup>[19]</sup> level of theory using the Stuttgart/Dresden effective core potential (SDD) basis set <sup>[20]</sup> for the gold atoms and 6-31G\*\* basis set <sup>[21]</sup> for remaining atoms. Geometries were optimized without imposed symmetry or other restraints. On the basis of the ground state optimized geometries, TD-DFT calculations were performed in the presence of dichloromethane using the conductive polarizable continuum model (CPCM).<sup>[22]</sup>



**Figure 6.10**. (a) Electronic absorption spectra of complexes (1–3) in CH<sub>2</sub>Cl<sub>2</sub>. (b) Emission spectra of complexes (1–3) in CH<sub>2</sub>Cl<sub>2</sub>. Inset shows the expanded emission spectra of **2** and **3** along the Y-axis. (c) Solid state luminescence of **1**.



Figure 6.11. HOMO and LUMO of complexes 1, 2 and 3 and their band gap.

In all three cases, the calculated bond distances for the optimized structures were in good agreement to those obtained in their crystal structures (**Figure A1, A2** and **A3 Annexure 1**). For all three complexes, the highest-occupied molecular orbitals (HOMOs) were  $\pi$ -type MOs while the lowest-occupied molecular orbitals (LUMOs) were  $\pi$ \*-type, delocalized on the anthracene unit. The TD-DFT predicted spectra were in good agreement with the experimental data and clearly suggested that the band observed in the visible range was dominated by HOMO to LUMO excitation (**Figure 6.12**). Further, in comparison to 2,6- and 1,8- derivative, there was red-shift in case of 9,10- anthracene derivative, which was supported by calculations as the calculated HOMO-LUMO gaps were 0.102 eV, 0.117 eV and 0.115 eV for 1, 2 and 3 respectively (**Figure 6.11**). Since perturbation on anthracene lowers the symmetry of the  $\pi$ -system which led to a bathochromic shift in HOMO to LUMO

transition, the result suggested that substituents have more perturbation on the anthracenyl rings when they were at 9,10 position.

# **TD-DFT data**











Figure 6.12. TD DFT details of complexes 1, 2 and 3.

# **6.5.** Conclusions

In this chapter we have reported a complex **1** with C=CAuPPh<sub>3</sub> moieties attached to the 9,10-positions of anthracene selectively yielded the strong fluorescent, rare 2D-network feature *via* intermolecular Au···H–C interactions. However, the analogous compounds **2** and **3** with C=CAuPPh<sub>3</sub> moieties attached to the 2,6- and 1,8- positions of anthracene resulted weakly fluorescent 1D-polymeric chain *via* C–H··· $\pi$  and  $\pi$ ··· $\pi$  interactions and intramolecular Au···H–C interactions, respectively. The present work thus highlights the Au···H–C interactions as well as the impact of linkage of Au(I) acetylide groups at the selective sites of the planar anthracene on the photophysical properties.

#### **6.6. Experimental section**

**6.6.1. General Methods.** All manipulations were carried out at room temperature under a nitrogen atmosphere. Solvents were predried, distilled and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. The starting materials 9,10-dibromoanthracene, 1,8-diiodoanthracene and AuPPh<sub>3</sub>Cl were commercially available. The starting material 2,6-diiodoanthracene was prepared by the procedures described in the literature. <sup>[23]</sup> 9,10-Bis-((trimethylsilyl)ethynyl) anthracene,<sup>[17b,24]</sup> 2,6-Bis((trimethylsilyl)ethynyl) anthracene,<sup>[17b,25]</sup> 1,8-Bis((trimethylsilyl)ethynyl) anthracene,<sup>[17b,26]</sup> and their corresponding acetylenes were synthesized by earlier reported method.<sup>[8d]</sup>

**6.6.2. Instruments.** Elemental analyses were carried out with a Flash 2000 elemental analyzer. UV/Vis absorption and emission spectra were recorded on a Cary-100 Bio UV–Vis spectrophotometer and a Horiba Jobin-Yvon Floromax 4P spectrophotometer respectively. 9,10-bis(phenylethynyl) anthracene was used as a standard in measuring the quantum yields. <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded on Bruker Avance(III) 400MHz spectrometer. HRMS was recorded on a Brucker-Daltonics, micrOTOF-Q II mass spectrometer. Single-crystal X-ray structural studies were performed on an Agilent Technology Supernova CCD diffractometer equipped with a low-temperature attachment.

**6.6.3.** Synthesis of  $(Ph_3PAu^I)_2$ -9,10-anthracenyldiacetylide 1. To a suspension of Ph<sub>3</sub>PAuCl (100 mg, 0.20 mmol) in ethanol (20 ml) NaOEt, freshly prepared from sodium (4.87 mg, 0.21 mmol) in ethanol (5 ml) and 9,10- bis (ethynyl anthracene) (22.6 mg, 0.10 mmol) were added. The solution was refluxed for 1 h, cooled and concentrated after which a yellow precipitate formed. The yellow colored solid was isolated by simple filtration method. The precipitate was further washed with ethanol and dried at room temperature to afford 1. X-ray quality crystals of 1 were obtained from CHCl<sub>3</sub>/ hexane at room temperature. Yield: 60% Anal

Calcd for **1** ( $C_{54}H_{38}Au_2P_2$ ) C 56.76, H 3.35. Found: C 56.81, H 3.05 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.86 (dd, J=3.2, 4H ant), 7.49-7.65(m, 34H anth and PPh<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 96.51, 125.73, 128.17, 129.14, 129.26, 131.58, 132.79, 134.36, 134.49, <sup>31</sup>P NMR (165.561 MHz, CDCl<sub>3</sub>) 42.38, ESI-MS: 1142[M].

**6.6.4.** Synthesis of  $(Ph_3PAu^I)_2$ -2,6-anthracenyldiacetylide 2. Complex 2 was synthesizes by following the same method as 1 using 2,6-bis( ethynylanthracene). Light yellow color crystals of 2 were grown in CH<sub>2</sub>Cl<sub>2</sub>/hexane at room temperature. Yield: 38% Anal Calcd for 2 (C<sub>54</sub>H<sub>38</sub>Au<sub>2</sub>P<sub>2</sub>) C 56.76, H 3.35. Found: C 57.12, H 2.89 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.22(s, 2H ant), 8.13( s, 2H ant), 7.85 (d, J= 10.28, 2H ant), 7.45-7.60(m, 32H ant and PPh<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 91.92, 125.56, 127.71, 129.13, 129.24, 129.35, 130.72, 131.58, 131.93, 134.29, 134.43, <sup>31</sup>P NMR (165.561 MHz, CDCl<sub>3</sub>) 42.31, ESI-MS: 1142[M].

**6.6.5.** Synthesis of  $(Ph_3PAu^I)_2$ -1,8-anthracenyldiacetylide 3. Complex 3 was synthesizes by following the method described above for 1 using 1,8bis( ethynyl anthracene). Golden yellow color crystals of 3 were grown in CHCl<sub>3</sub>/hexane at room temperature. Yield: 48% Anal Calcd for 3 (C<sub>54</sub>H<sub>38</sub>Au<sub>2</sub>P<sub>2</sub>) C 56.76, H 3.209. Found: C 57.01, H 3.508 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.83(s 1H anthracene), 8.35 (s 1H anthracene) 7.86 (d, J= 8.5, 2H ant), 7.80 (d, J= 6.7, 2H ant), 7.54-7.47(m, 32H ant and PPh<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 87.56, 124.96, 126.90, 127.22, 129.01, 129.12, 130.35, 131.34, 131.57, 132.07, 134.33, 134.46, <sup>31</sup>P NMR (165.561 MHz, CDCl<sub>3</sub>) 42.19, ESI-MS: 1165[M + 23].

#### 6.6.6. X-ray Crystallography

Data were collected at 150 K for **2** and at 293 K for **1** and **3** using graphite-monochromated Mo K $\alpha$  ( $\lambda \alpha = 0.71073$  Å) and Cu K $\alpha$  ( $\lambda \alpha = 1.54814$  Å). The strategy for data collection was evaluated using the CrysAlisPro CCD software. The data were collected by the standard  $\varphi-\omega$  scan techniques and scaled and reduced using CrysAlisPro RED software.

The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares with SHELXL-97 on  $F^{2,[27]}$  The positions of all of the atoms were obtained by direct methods. All non-H atoms were refined anisotropically. In **3** SQUEEZE was applied by using platon programme to remove **3** disorder chloroform solvent molecules. All Hydrogen atoms were placed in geometrically constrained position and refined with isotropic temperature factors, generally 1.2 X U<sub>eq</sub> of their parent atoms. Moreover, despite several attempts, we could not get better quality of crystals for **2** and **3**. All the short contacts and interactions, mean-plane analyses, and molecular drawings were obtained using the Diamond program (version 3.1d) and Mercury (v 3.5.1). The crystal and refinement data are summarized in **Table A24**, and selected bond distances and angles are shown in **Table A25**.



Figure 6.13. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1.



**Figure 6.14.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2**.





Figure 6.15. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3.

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# **ANNEXURE 1**

**Tables A1-A25** 

## Chapter 2

### Table A1. Crystallographic Parameters for 1 and 2

Identification code	1	2
Empirical formula	$C_{12}H_{14}Cl_4Hg_2N_2O_4$	$C_{12}H_{12}Cl_4Hg_2N_2O_2$
Formula weight	793.23	759.22
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, C2/c	Triclinic, Pī
	Unit Cell Parameter	
a/Å	11.6344(5)	7.2184(6)
b/Å	11.0503(5)	7.3924(9)
c/Å	15.0011(14)	9.4701(9)
α/°	90	107.253(10)
β/ <sup>°</sup>	96.075(6)	92.442(7)
γ/°	90	112.812(10)
V/Å <sup>3</sup>	1917.8(2)	437.66(8)
$Z, d_{\text{calcd}}(\text{mg/m}^3)$	4, 2.747	1, 2.881
μ/ mm <sup>-1</sup>	16.567	18.133
F(000)	1440	342
Crystal size (mm <sup>3</sup> )	0.23 x 0.18 x 0.13	0.26 x 0.22 x 0.18
θ range	2.98 to 24.98 deg.	3.11 to 25.00 deg.
Reflections collected / unique	5737 / 1687 [R(int) = 0.0262]	3937 / 1543 [R(int) = 0.0560]
Max. and min. transmission	0.2220 and 0.1150	0.1388 and 0.0883
Data / restraints / parameters	1687 / 2 / 11	1543 / 0 / 100
GOF, F <sup>2</sup>	1.045	1.116
R1, wR2 [I>2σ(I)]	0.0451, 0.0984	0.0501, 0.1427
R1, wR2 (all data)	R1 = 0.0526, wR2 = 0.1033	R1 = 0.0553, wR2 = 0.1467
Largest diff. peak and hole	2.039 and -1.529e.A <sup>-3</sup>	4.569 and -2.303 e.A^- <sup>3</sup>

Bond distance	1	2	3
Hg(1)-N(1)	2.207(8)	2.178(12)	2.231(11)
Hg(1)-Cl(1)	2.351(3)	2.352(4)	2.510(3)
Hg(1)-Cl(2)	2.682(3)	2.760(3)	2.354(4)
Hg(1)-Cl(2)#1	2.763(3)	2.805(4)	
Hg(1)-O(1)	2.740 9(2)	2.612(10)	
Hg(1)-Cl(3)			2.772(4)
Hg(2)-N(2)			2.245(10)
Hg(2)-Cl(1)			2.815(4)
Hg(2)-Cl(3)			2.513(3)
Hg(2)-Cl(4)			2.338(4)
Selected b	ond angles $(^{\circ})$ for <b>1</b> , <b>2</b> a	nd <b>3</b>	
N(1)-Hg(1)-Cl(1)	149.7(2)	162.2(3)	104.6(3)
N(1)-Hg(1)-Cl(2)	96.6(2)	96.9(3)	133.7(4)
Cl(1)-Hg(1)-Cl(2)	105.94(11)	98.31(13)	
N(1)-Hg(1)-Cl(2)#1	101.5(2)	91.5(3)	
Cl(1)-Hg(1)-Cl(2)#1	100.81(10)	97.69(12)	
Cl(2)-Hg(1)-Cl(2)#1	84.10(9)	89.53(10)	
Hg(1)-Cl(2)Hg(1)#1	93.57(9)	90.47(10)	
C(1)-N(1)-Hg(1)	118.0(7)	116.3(9)	
C(5)-N(1)-Hg(1)	122.2(6)	125.0(11)	
N(1)-Hg(1)-O(1)		68.0(4)	
Cl(1)-Hg(1)-O(1)		94.3(3)	
O(1)-Hg(1)-Cl(2)		150.4(2)	
O(1)-Hg(1)-Cl(2)#1		115.3(2)	
C(6)-O(1)-Hg(1)		107.0(8)	
Cl(2) Hg(1) Cl(1)			118.01(14)
Cl(2) Hg(1) Cl(3)			96.08(13)

Table A2. Bond distances and bond angles of 1-3

Cl(1) Hg(1) Cl(3)	 	96.16(11)
Cl(4) Hg(2) Cl(3)	 	119.72(14)
Cl(4) Hg(2) Cl(1)	 	96.39(14)
Cl(3) Hg(2) Cl(1)	 	93.72(11)
N(1)-Hg(1)-Cl(3)	 	96.6(3)
N(2)-Hg(2)-Cl(4)	 	137.5(3)
N(2)-Hg(2)-Cl(3)	 	101.0(3)
N(2) Hg(2) Cl(1)	 	92.4(3)
Hg(1) Cl(1) Hg(2)	 	99.63(13)
Hg(2) Cl(3) Hg(1)	 	97.99(12)

-										
	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)					
	1									
1	C(1)-H(1)Cl(2) #(1)	0.95(.010)	2.758(.003)	3.495(.012)	135.00(0.67)					
2	O(101)H(111)O(1) # (1)	1.102(0.68)	1.727(.294)	2.672(.016)	140.57(21.3)					
3	C(2)-H(2)O(1) #(2)	0.950(.011)	2.594(.008)	3.263(.015)	127.73(0.73)					
4	C(3)-H(3)O(1) #(2)	0.950(.012)	2.997(.008)	3.459(.014)	111.42(0.71)					
5	C(3)-H(3)O(101) #(2)	0.950(.012)	2.947(.013)	3.578(.017)	124.98( 0.74)					
6	O(101)-H(222)Cl(1) #( 3)	1.101(.245)	2.465(.234)	3.517(.013)	159.41(17.27)					
7	O(101)-(H222)Cl(2) #( 4)	1.101(.245)	2.827(.251)	3.255(.014)	102.88(15.10)					
	<u>.</u>	2								
1	C(1)-H(1)Cl(2) #( 0)	0.95(2)	2.746(4)	3.501(2)	137.01(9)					
2	C(2)-H(2)Cl(1) # (1)	0.95(2)	2.740(4)	3.515(2)	139.26(10)					
3	C(3)-H(3)Cl(2) # (2)	0.95(2)	2.764(4)	3.649(2)	155.42(9)					
4	C(6)-H(6B) Cl(1)#(3)	0.990(2)	2.717(4)	3.682(2)	164.97(10)					

# Table A3. Hydrogen bonding parameters for 1-2 [Å and ()]

#### **Symmetry Positions**

**For 1** #(1) x,y,z, #(2) -x+1/2+2, +y+1/2, -z+1/2, #(3) -x+1/2+1,+y+1/2,-z+1/2, #(4) x-1/2,+y+1/2,+z **For 2** #(0) x,y,z, # (1) x,+y-1,+z-1, # (2) x,+y,+z-1, # (3) -x, -y+2, -z

Identification code	3	4	5
Empirical formula	C <sub>8</sub> H <sub>11</sub> Cl <sub>2</sub> HgNO	$C_{12}H_{14}Cd_2Cl_4N_2O_2$	C <sub>8</sub> H <sub>11</sub> CdCl <sub>2</sub> NO
Formula weight	408.67	584.85	320.48
Wavelength	0.71073	0.71073	0.71073
Crystal system, space	Triclinic, Pī	Orthorhombic, <i>P b c n</i>	Monoclinic, $P 2_1/c$
group			
a/Å	7.7359(17)	9.5274(2)	6.5278(3)
b/Å	9.2243(16)	7.1161(2)	15.3457(6)
c/Å	16.077(3)	26.9956(6)	11.3396(4)
α/°	101.303(15)	90	90
β/	97.136(18)	90	105.729
γ/°	90.733(17)	90	90
V/Å <sup>3</sup>	1115.5(4)	1830.25(8)	1093.39(8)
$Z, d_{\text{calcd}}(\text{mg/m}^3)$	4, 2.443	4, 2.122	4, 1.947
μ/ mm	14.239	2.912	2.446
F(000)	752	1120	624
Crystal size (mm <sup>3</sup> )	0.20 x 0.14 x 0.11	0.23 x 0.17 x 0.12	0.33 x 0.26 x 0.21
θ range	3.09 to 25.00	3.02 to 24.99	3.24 to 24.99
Reflections collected /	7743 / 3921 [R(int) =	1608 / 1608 [R(int) =	8146 / 1927 [R(int) =
unique	0.0776]	0.0000]	0.0302]
Max. and min.	1.000 and 0.6651	0.7214 and 0.5540	0.6276 and 0.4990
transmission			
Data / restraints /	3921 / 0 / 235	1608 / 7 / 104	1927 / 1 / 122
parameters			
GOF, F <sup>2</sup>	1.007	1.089	1.158
R1, wR2 [I>2σ(I)]	0.0502, 0.0967	0.0188, 0.0452	0.0261, 0.0593
R1, wR2 (all data)	0.0862, 0.1204	0.0198, 0.0457	0.0307, 0.0621
Largest diff. peak and hole	0.947 and -1.664 e.A <sup><math>-3</math></sup>	0.781 and -0.939 e.A <sup><math>^{-3}</math></sup>	0.734 and -0.590 e.A <sup><math>^{-3}</math></sup>

### Table A4. Crystallographic Parameters for 3, 4 and 5

Bond distance	4	5
Cd(1)-N(1)	2.294(2)	2.331(3)
Cd(1)-O(1)	2.411(2)	2.432(3)
Cd(1)-Cl(2)	2.5352(7)	2.5767(9)
Cd(1)-Cl(1)	2.5484(6)	2.6748(9)
Cd(1)-Cl(1)#1	2.6656(6)	2.6015(9)
Cd(1)-Cl(2)#2	2.7129(7)	2.6444(9)
Selected	bond angles $(^{\circ})$ for <b>4</b> and <b>5</b>	
N(1)-Cd(1)-O(1)	70.22(8)	89.30(11)
N(1)-Cd(1)-Cl(2)	152.58(6)	170.65(9)
O(1)-Cd(1)-Cl(2)	85.59(6)	81.36(7)
N(1)-Cd(1)-Cl(1)	98.53(5)	95.83(9)
O(1)-Cd(1)-Cl(1)	159.07(6)	168.06(7)
Cl(2)-Cd(1)-Cl(1)	108.37(30)	93.26(3)
N(1)-Cd(1)Cl(1)#1	87.68(5)	91.26(8)
O(1)-Cd(1)-Cl(1)#1	101.19(6)	101.63(7)
Cl(2)-Cd(1)-Cl(1)#1	84.48(2)	91.09(3)
Cl(1)-Cd(1)-Cl(1)#1	95.75(2)	89.06(3)
N(1)-Cd(1)-Cl(2)#2	96.26(6)	90.23(8)
O(1)-Cd(1)-Cl(2)#2	80.62(6)	81.04(7)
Cl(2)-Cd(1)-Cl(2)#2	92.18(2)	87.86(3)
Cl(1)-Cd(1)-Cl(2)#2	83.27(2)	88.15(3)
Cl(1)#1-Cd(1)-Cl(2)#2	176.04(2)	176.96(3)
Cd(1)-Cl(1)-Cd(1)#2	96.48(2)	90.94(3)
Cd(1)-Cl(2)-Cd(1)#1	95.62(2)	92.14(3)

 Table A5. Selected bond distances and angles for 4 and 5.

	3								
1	C(9)-H(9)-Cl(3)#(0)	0.930(1)	2.960(.004)	3.625(1)	129.69(1)				
2	C(7)-H(7)Cl(4)#(4)	0.970(1)	2.895(.004)	3.749(.012)	147.45( 0.75)				
3	C(12)-H(12)-Cl(4)#(6)	0.930(.018)	2.845(.005)	3.647(.019)	145.13( 1.04)				
4	C(11)-H(11)-Cl(3)#(6)	0.930(.015)	2.930(.004)	3.823(.016)	161.52(1.03)				
5	C(4)-H(4)Cl(2)#(3)	0.930(.013)	2.833(.004)	3.604(.013)	141.09( 0.88)				
6	C(3)-H(3)Cl(1)#(3)	0.930(.015)	2.940(.004)	3.826(.016)	159.70( 0.93)				
			4						
1	C(3)-H(3)Cl(1)#(1)	0.950(3)	2.941(1)	3.636(3)	131.02( 0.17)				
2	C(3)-H(3)Cl(2)#(2)	0.990(3)	2.871(1)	3.701(3)	141.90( 0.18)				
			5						
1	C(1)-H(1)Cl(1)#(0)	0.950(5)	2.873(1)	3.578(4)	131.84( 0.27)				
2	C(3)-H(3)Cl(2)#(1)	0.950(5)	2.928(1)	3.839(5)	161.25( 0.30)				
3	C(6)H(6A)Cl(1)#(3)	0.990(4)	2.861(1)	3.751(4)	149.98( 0.27)				
4	O()-H(101)Cl(1)#(5)	0.881(5)	2.433(5)	3.305(3)	170.48( 4.20)				

**Table A6.** Hydrogen bonding parameters for **3-5** [Å and  $\stackrel{\circ}{()}$ ]

#### **Symmetry Positions**

 $\label{eq:For 3 #(0) x,y,z, #(3) x,+y+1,+z, #(4) x-1,+y,+z, #(6) x,+y-1,+z} \\$ 

**For 4** #(1) x+1,+y,+z, )#(2) x+1/2,+y+1/2,-z+1/2,

**For 5** #(0) x,y,z, (1) x,+y,+z-1, #(3) -x+1,-y+1,-z+2 )#(5) -x,-y+1,-z+2.

## Chapter 3

Table A7. Crystallographic details of A, 1-3,4A and 5A

Identification code	Α	1	2	3	4A	5A
Empirical	C20H2cCd4Cl0N4O4	C <sub>7</sub> H <sub>10</sub> CdCl <sub>2</sub> NO	C14H20Cd5Cl12N2O5	CdOrS	CuaHuCdaCleNOa	C <sub>8</sub> H <sub>12</sub> CdCl <sub>2</sub> NO
formula	028113600401811404	0/11/000013110	0141120003011211203	04030		0,1120001,110
Formula	1225.00	241.00	1202.00	224.46		255.02
weight	1225.89	341.90	1283.69	224.46	655./5	355.93
Wavelength Å	0.71073	0.71073	1.5418	1.5418	1.54180	1.54180
Crystal system,	Triclinic,	Orthorhombic,	Monoclinic,	Monoclinic,	Orthorhombic,	Orthorhombic,
space group	Pī	$P 2_1 2_1 2_1$	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /n	P n a 21	$P 2_1 2_1 2_1$
a/Å	9.513(2)	7.7819(4)	9.8733(5)	7.6262(5)	22.4932(4)	7.5743(3)
b/Å	10.681(4)	11.6662(5)	20.4901(11)	7.4531(3)	7.51190(10)	11.1535(4)
c/Å	10.952(2)	12.4557(8)	17.2559(8)	7.6295(5)	11.9686(2)	13.5879(5)
α/	98.71(2)	90	90	90	90	90
β/	98.47(2)	90	94.890	115.423(8)	90	90
γ/°	115.03(3)	90	90	90	90	90
V/Å <sup>3</sup>	968.5(5)	1130.79(10)	3478.2(3)	391.66(4)	2022.29(6)	1147.91(7)
$Z, d_{\text{calcd}}(\text{mg/m}^3)$	1, 2.102	4, 2.008	4, 2.444	4, 3.807	4, 2.154	4, 2.060
$\mu/\text{ mm}^{-1}$	2.757	2.601	32.834	49.012	24.226	21.404
F(000)	592	660	2392	416	1256	692

	$\theta$ range (deg)	3.06 to 24.99	3.09 to 32.45	3.36 to 40.00	6.87 to 66.60	3.93 to 72.22	5.13 to 44.79
	Reflections collected / unique	7428 / 3398 [R(int) = 0.0612]	12443 / 3765 [R(int) = 0.0330]	7569 / 2100 [R(int)= 0.0515]	1857 / 689 [R(int) = 0.0175]	13239 / 3743 [R(int) = 0.0291]	2267 / 770 [R(int) = 0.0208]
	Max. and min. transmission	0.6826and 0.5697	0.6810 and 0.5741	0.1000 and 0.0494	0.0346and 0.0219	0.0974 and 0.0562	0.1833 and 0.0794
	Data / restraints / parameters	3398 / 0 / 218	3765 / 0 / 122	2100 / 15 / 343	689 / 0 / 60	3743 / 3 / 229	770 / 0 / 132
	GOF, F <sup>2</sup>	1.085	1.044	1.120	1.117	1.027	1.156
Tabl	R1, wR2 [I>2σ(I)]	0.0595, 0.1832	0.0252, 0.0478	0.1143, 0.2738	0.0399, 0.1049	0.0469, 0.1258	0.0229, 0.0620
е А8.	R1, wR2 (all data)	0.0664, 0.1996	0.0320, 0.0504	0.1274, 0.2964	0.0400, 0.1050	0.0471, 0.1262	0.0229, 0.0620
Sele	Largest diff.	2.112 and -3.978	0.603 and -0.478	5.237 and -1.418	1.764 and -2.538	0.763 and -1.012	0.574 and -0.574
cted	peak and hole	e.A^-3	e.A^-3	e.A^-3	e.A^-3	e.A^-3	e.A^-3
bond	CCDC No	1002558	1002563	1002559	1002560	1002564	1002565

lengths (Å) an	d bond angle	s (°) of A,	1-3, 4A	and 5A.

Bond distance	Α	1	2	3	4A	5A
Cd(1)-N(1)	2.341(7)					
Cd(1)-O(1)	2.388(6)	2.3790(18)			2.530(4)	2.462(6)
Cd(1)-Cl(2)	2.668(3)	2.6254(6)			2.6092(12)	2.6530(18)
Cd(1)-Cl(1)	2.562(2)	2.6800(6)			2.6135(16)	2.6201(19)

Cd(1)-Cl(1)#1		2.6729(6)		 	2.5989(18)
Cd(1)-Cl(2)#2		2.6135(6)		 	2.6467(18)
Cl(2)-Cd(1)#1	2.673(2)			 	
Cd(2)-Cl(3)#1	2.537(2)			 	
Cd(1)-Cl(3)	2.582(2)	2.5306(7)		 2.4994(18)	2.5525(19)
Cd(2)-Cl(4)#1	2.558(2)			 	
Cd(2)-Cl(4)				 2.6314(12)	
Cd(2)-Cl(1)	2.656(3)			 	
Cd(2)-Cl(2)	2.886(2)			 	
Cd(2)-N(2)	2.317(7)			 	
Cd(2)-O(2)	2.348(6)			 2.477(5)	
Cd(1)-Cl(4)			2.540(6)	 2.6060(14)	
Cd(1)-Cl(5)			2.577(6)	 2.6384(13)	
Cd(2)-Cl(6)				 2.5258(18)	
Cd(1)-Cl(7)			2.644(7)	 	
Cd(1)-Cl(9)			2.666(6)	 	
Cd(1)-Cl(9)#1			2.719(7)	 	
Cd(2)-Cl(1)			2.529(6)	 	
Cd(2)-Cl(6)			2.609(6)	 	
Cd(2)-Cl(8)			2.676(6)	 	
Cd(2)-Cl(5)			2.570(6)	 2.6437(15)	
Cd(2)-Cl(10)			2.741(6)	 	

Cd(2)-Cl(7)	 	2.786(7)			
Cd(3)-Cl(2)	 	2.515(7)			
Cd(3)-Cl(6)	 	2.601(6)			
Cd(3)-Cl(8)	 	2.663(6)			
Cd(3)-Cl(11)	 	2.713(6)			
Cd(3)-Cl(11)#2	 	2.764(7)			
Cd(4)-Cl(12)	 	2.559(6)			
Cd(4)-Cl(3)	 	2.567(6)			
Cd(4)-Cl(10)	 	2.653(6)			
Cd(4)-Cl(11)	 	2.662(7)			
Cd(4)-Cl(8)	 	2.723(6)			
Cd(5)-Cl(12)	 	2.553(6)			
Cd(5)-Cl(4)	 	2.560(6)			
Cd(5)-Cl(7)	 	2.656(6)			
Cd(5)-Cl(10)	 	2.679(7)			
Cd(5)-Cl(9)	 	2.712(6)			
Cl(1)-Cd(2)#2	 			2.6462(15)	
Cl(2)-Cd(2)#2	 			2.5699(14)	
Cd(1)-O(101)	 	2.352(15)			
Cd(4)-O(103)	 	2.313(17)			
Cd(5)-O(102)	 	2.343(14)			
Cd(1)-O(1)#1	 		2.240(4)		

Cd(1)-O(2)		 	2.247(6)	 
Cd(1)-O(4)#3		 	2.304(5)	 
Cd(1)-O(3)#4		 	2.323(4)	 
Cd(1)-O(5)#2		 	2.246(5)	 
Cd(1)-O(3)		 	2.405(4)	 
Bond angle				
N(1)-Cd(1)-O(1)	80.2(2)	 		 
N(1)-Cd(1)-Cl(2)	93.0(2)	 		 
O(1)-Cd(1)-Cl(2)	172.68(16)	 		 
N(1)-Cd(1)-Cl(1)	98.86(18)	 		 
O(1)-Cd(1)-Cl(1)	95.53(16)	 		 
Cl(2)-Cd(1)-Cl(1)	88.08(8)	 		 
N(1)-Cd(1)-Cl(1)#1		 		 
O(1)-Cd(1)-Cl(1)#1		 		 88.27(12)
Cl(2)-Cd(1)-Cl(1)#1	92.41(7)	 		 
Cl(1)-Cd(1)-Cl(1)#1		 		 
N(1)-Cd(1)-Cl(2)#2		 		 
O(1)-Cd(1)-Cl(2)#2		 		 
Cl(2)-Cd(1)-Cl(2)#2		 		 
Cl(1)-Cd(1)-Cl(2)#2		 		 
Cl(1)#1-Cd(1)-Cl(2)#2		 		 
Cd(1)-Cl(1)-Cd(1)#2		 		 

Cd(1)-Cl(2)-Cd(1)#1	90.42(7)		 		
N(1)-Cd(1)-Cl(3)	84.16(18)		 		
O(1)-Cd(1)-Cl(3)	81.88(16)	177.53(5)	 	176.65(10)	168.95(13)
Cl(1)-Cd(1)-Cl(3)	175.67(7)		 		
Cl(3)-Cd(1)-Cl(2)	94.88(7)	97.49(2)	 		
N(1)-Cd(1)-Cl(2)#1	168.51(18)		 		
O(1)-Cd(1)-Cl(2)#1	96.61(15)	89.71(5)	 		
Cl(3)-Cd(1)-Cl(2)#1	84.46(7)	91.17(2)	 		
Cl(2)-Cd(1)-Cl(2)#1	89.58(7)	170.580(8)	 		
N(2)-Cd(2)-O(2)	81.5(3)		 		
N(2)-Cd(2)-Cl(3)#1	165.36(19)		 		
O(2)-Cd(2)-Cl(3)#1	87.18(17)		 		
N(2)-Cd(2)-Cl(4)	99.02(18)		 		
O(2)-Cd(2)-Cl(4)	98.88(17)		 		
Cl(3)#1-Cd(2)-Cl(4)	91.89(7)		 		
N(2)-Cd(2)-Cl(1)	94.5(2)		 		
O(2)-Cd(2)-Cl(1)	163.71(17)		 		
Cl(3)#1-Cd(2)-Cl(1)	93.74(8)		 		
Cl(4)-Cd(2)-Cl(1)	97.35(8)		 		
N(2)-Cd(2)-Cl(2)	88.19(18)		 		
O(2)-Cd(2)-Cl(2)	82.17(17)		 		
Cl(3)#1-Cd(2)-Cl(2)	81.02(6)		 		

Cl(4)-Cd(2)-Cl(2)	172.79(7)	 	 	
Cl(1)-Cd(2)-Cl(2)	81.91(7)	 	 	
Cd(1)-Cl(1)-Cd(2)	98.94(8)	 	 	
Cd(1)-Cl(2)-Cd(1)#1	90.42(7)	 	 	
Cd(1)-Cl(2)-Cd(2)	91.05(7)	 	 	
Cd(1)#1-Cl(2)-Cd(2)	91.71(6)	 	 	
Cd(2)#1-Cl(3)-Cd(1)	102.50(7)	 	 	
Cl(3)-Cd(1)-Cl(4)		 	 96.88(5)	
O(1)-Cd(1)-Cl(4)		 	 82.07(10)	
Cl(3)-Cd(1)-Cl(2)		 	 96.77(7)	
O(1)-Cd(1)-Cl(2)		 	 84.20(9)	
Cl(4)-Cd(1)-Cl(2)		 	 166.22(7)	
Cl(3)-Cd(1)-Cl(1)		 	 96.68(5)	
O(1)-Cd(1)-Cl(1)		 	 86.56(11)	
Cl(4)-Cd(1)-Cl(1)		 	 93.26(6)	
Cl(2)-Cd(1)-Cl(1)		 	 86.98(4)	
Cl(3)-Cd(1)-Cl(5)		 	 96.56(6)	
O(1)-Cd(1)-Cl(5)		 	 80.19(10)	
Cl(4)-Cd(1)-Cl(5)		 	 84.88(3)	
Cl(2)-Cd(1)-Cl(5)		 	 91.74(4)	
Cl(1)-Cd(1)-Cl(5)		 	 166.76(7)	
O(2)-Cd(2)-Cl(6)		 	 177.65(13)	

O(2)-Cd(2)-Cl(2)#1	 	 	83.63(11)	
Cl(6)-Cd(2)-Cl(2)#1	 	 	98.09(5)	
O(2)-Cd(2)-Cl(4)	 	 	83.25(10)	
Cl(6)-Cd(2)-Cl(4)	 	 	95.04(6)	
Cl(2)#1-Cd(2)-Cl(4)	 	 	166.86(7)	
O(2)-Cd(2)-Cl(5)	 	 	85.46(12)	
Cl(6)-Cd(2)-Cl(5)	 	 	95.99(4)	
Cl(2)#1-Cd(2)-Cl(5)	 	 	94.01(5)	
Cl(4)-Cd(2)-Cl(5)	 	 	84.27(4)	
O(2)-Cd(2)-Cl(1)#1	 	 	81.46(12)	
Cl(6)-Cd(2)-Cl(1)#1	 	 	97.00(7)	
Cl(2)#1-Cd(2)-Cl(1)#1	 	 	87.10(4)	
Cl(4)-Cd(2)-Cl(1)#1	 	 	91.63(5)	
Cl(5)-Cd(2)-Cl(1)#1	 	 	166.67(7)	
Cd(1)-Cl(1)-Cd(2)#2	 	 	90.96(5)	
Cd(2)#2-Cl(2)-Cd(1)	 	 	92.79(5)	
Cd(1)-Cl(4)-Cd(2)	 	 	94.89(5)	
Cd(1)-Cl(5)-Cd(2)	 	 	93.84(5)	
O(1)-Cd(1)-Cl(2)	 81.79(5)	 		91.18(13)
O(1)-Cd(1)-Cl(1)#2	 84.13(5)	 		
Cl(3)-Cd(1)-Cl(1)#2	 93.44(2)	 		
Cl(3)-Cd(1)-Cl(1)#1	 	 		98.81(7)

Cl(2)#1-Cd(1)-Cl(1)#2	 100.003(18)	 	 
Cl(2)-Cd(1)-Cl(1)#2	 83.225(18)	 	 
O(1)-Cd(1)-Cl(1)	 86.51(5)	 	 
Cl(3)-Cd(1)-Cl(1)	 95.89(2)	 	 93.19(6)
Cl(2)#1-Cd(1)-Cl(1)	 83.311(18)	 	 
Cl(2)-Cd(1)-Cl(1)	 92.092(18)	 	 
Cl(1)#2-Cd(1)-Cl(1)	 170.040(12)	 	 
Cd(1)#1-Cl(1)-Cd(1)	 93.985(18)	 	 
Cl(1)#1-Cd(1)-Cl(2)	 	 	 89.69(5)
Cl(1)#1-Cd(1)-Cl(1)	 	 	 167.41(2)
Cd(1)#2-Cl(1)-Cd(1)	 	 	 94.41(6)
Cd(1)#2-Cl(2)-Cd(1)	 96.690(18)	 	 92.55(6)
O(1)-Cd(1)-Cl(2)#1	 	 	 76.62(13)
Cl(3)-Cd(1)-Cl(2)#1	 	 	 95.37(7)
Cl(1)#1-Cd(1)-Cl(2)#1	 	 	 85.53(6)
Cl(1)-Cd(1)-Cl(2)#1	 	 	 97.20(6)
Cl(3)-Cd(1)-Cl(2)	 	 	 97.30(7)
Cl(1)-Cd(1)-Cl(2)	 	 	 84.98(6)
Cl(2)#1-Cd(1)-Cl(2)	 	 	 167.00(3)
O(1)#1-Cd(1)-O(5)#2	 	 175.37(14)	 
O(1)#1-Cd(1)-O(2)	 	 101.53(16)	 
O(5)#2-Cd(1)-O(2)	 	 82.57(16)	 

O(1)#1-Cd(1)-O(4)#3	 		86.23(18)	 
O(5)#2-Cd(1)-O(4)#3	 		89.23(18)	 
O(2)-Cd(1)-O(4)#3	 		162.1(2)	 
O(1)#1-Cd(1)-O(3)#4	 		87.45(15)	 
O(5)#2-Cd(1)-O(3)#4	 		92.52(15)	 
O(2)-Cd(1)-O(3)#4	 		117.94(18)	 
O(4)#3-Cd(1)-O(3)#4	 		78.14(16)	 
O(1)#1-Cd(1)-O(3)	 		89.83(15)	 
O(5)#2-Cd(1)-O(3)	 		88.74(15)	 
O(101)-Cd(1)-Cl(4)#1	 	87.9(4)		 
Cl(4)#1-Cd(1)-Cl(5)	 	98.8(2)		 
Cl(4)#1-Cd(1)-Cl(7)	 	170.9(2)		 
Cl(5)-Cd(1)-Cl(7)	 	88.7(2)		 
O(101)-Cd(1)-Cl(9)	 	173.3(4)		 
Cl(4)#1-Cd(1)-Cl(9)	 	98.77(18)		 
Cl(5)-Cd(1)-Cl(9)	 	91.5(2)		 
Cl(7)-Cd(1)-Cl(9)	 	86.22(19)		 
O(101)-Cd(1)-Cl(9)#1	 	97.1(4)		 
Cl(4)#1-Cd(1)-Cl(9)#1	 	85.39(19)		 
Cl(5)-Cd(1)-Cl(9)#1	 	173.77(19)		 
Cl(7)-Cd(1)-Cl(9)#1	 	87.6(2)		 
Cl(9)-Cd(1)-Cl(9)#1	 	83.3(2)		 

Cl(1)-Cd(2)-Cl(5)	 	94.6(2)	 	
Cl(1)-Cd(2)-Cl(6)	 	101.07(19)	 	
Cl(5)-Cd(2)-Cl(6)	 	98.9(2)	 	
Cl(1)-Cd(2)-Cl(8)	 	92.34(18)	 	
Cl(6)-Cd(2)-Cl(8)	 	85.2(2)	 	
Cl(1)-Cd(2)-Cl(10)	 	167.8(2)	 	
Cl(5)-Cd(2)-Cl(10)	 	89.16(19)	 	
Cl(6)-Cd(2)-Cl(10)	 	89.8(2)	 	
Cl(8)-Cd(2)-Cl(10)	 	82.95(18)	 	
Cl(1)-Cd(2)-Cl(7)	 	87.34(18)	 	
Cl(5)-Cd(2)-Cl(7)	 	85.8(2)	 	
Cl(6)-Cd(2)-Cl(7)	 	169.98(19)	 	
Cl(8)-Cd(2)-Cl(7)	 	89.1(2)	 	
Cl(10)-Cd(2)-Cl(7)	 	81.38(19)	 	
Cl(2)-Cd(3)-Cl(6)	 	96.2(2)	 	
Cl(2)-Cd(3)-Cl(3)#2	 	93.4(2)	 	
Cl(6)-Cd(3)-Cl(3)#2	 	98.9(2)	 	
Cl(2)-Cd(3)-Cl(8)	 	96.23(18)	 	
Cl(6)-Cd(3)-Cl(8)	 	85.6(2)	 	
Cl(3)#2-Cd(3)-Cl(8)	 	168.93(19)	 	
Cl(2)-Cd(3)-Cl(11)	 	171.8(2)	 	
Cl(6)-Cd(3)-Cl(11)	 	92.07(19)	 	

Cl(3)#2-Cd(3)-Cl(11)	 	85.2(2)	 	
Cl(8)-Cd(3)-Cl(11)	 	84.52(19)	 	
Cl(2)-Cd(3)-Cl(11)#2	 	88.7(2)	 	
Cl(6)-Cd(3)-Cl(11)#2	 	173.57(18)	 	
Cl(3)#2-Cd(3)-Cl(11)#2	 	85.0(2)	 	
Cl(8)-Cd(3)-Cl(11)#2	 	89.7(2)	 	
Cl(11)-Cd(3)-Cl(11)#2	 	83.07(19)	 	
O(103)-Cd(4)-Cl(12)	 	89.0(4)	 	
O(103)-Cd(4)-Cl(3)	 	97.4(4)	 	
Cl(12)-Cd(4)-Cl(3)	 	93.6(2)	 	
O(103)-Cd(4)-Cl(10)	 	92.3(4)	 	
Cl(12)-Cd(4)-Cl(10)	 	86.9(2)	 	
Cl(3)-Cd(4)-Cl(10)	 	170.27(19)	 	
O(103)-Cd(4)-Cl(11)	 	89.3(4)	 	
Cl(12)-Cd(4)-Cl(11)	 	177.9(2)	 	
Cl(3)-Cd(4)-Cl(11)	 	87.8(2)	 	
Cl(10)-Cd(4)-Cl(11)	 	92.0(2)	 	
O(103)-Cd(4)-Cl(8)	 	172.3(4)	 	
Cl(12)-Cd(4)-Cl(8)	 	97.25(19)	 	
Cl(3)-Cd(4)-Cl(8)	 	86.59(19)	 	
Cl(10)-Cd(4)-Cl(8)	 	83.71(19)	 	
Cl(11)-Cd(4)-Cl(8)	 	84.34(19)	 	

O(102)-Cd(5)-Cl(12)	 	97.9(4)	 	
O(102)-Cd(5)-Cl(4)	 	87.1(4)	 	
Cl(12)-Cd(5)-Cl(4)	 	93.9(2)	 	
O(102)-Cd(5)-Cl(7)	 	166.6(4)	 	
Cl(12)-Cd(5)-Cl(7)	 	93.44(19)	 	
Cl(4)-Cd(5)-Cl(7)	 	99.29(19)	 	
O(102)-Cd(5)-Cl(10)	 	88.5(4)	 	
Cl(12)-Cd(5)-Cl(10)	 	86.5(2)	 	
Cl(4)-Cd(5)-Cl(10)	 	175.68(19)	 	
Cl(7)-Cd(5)-Cl(10)	 	85.0(2)	 	
O(102)-Cd(5)-Cl(9)	 	83.7(4)	 	
Cl(12)-Cd(5)-Cl(9)	 	178.1(2)	 	
Cl(4)-Cd(5)-Cl(9)	 	85.1(2)	 	
Cl(7)-Cd(5)-Cl(9)	 	85.08(19)	 	
Cl(10)-Cd(5)-Cl(9)	 	94.6(2)	 	
Cd(4)-Cl(3)-Cd(3)#2	 	95.6(2)	 	
Cd(1)#1-Cl(4)-Cd(5)	 	98.3(2)	 	
Cd(2)-Cl(5)-Cd(1)	 	95.5(2)	 	
Cd(3)-Cl(6)-Cd(2)	 	95.9(2)	 	
Cd(1)-Cl(7)-Cd(5)	 	95.2(2)	 	
Cd(1)-Cl(7)-Cd(2)	 	89.0(2)	 	
Cd(5)-Cl(7)-Cd(2)	 	96.5(2)	 	

Cd(3)-Cl(8)-Cd(2)	 	92.9(2)	 	
Cd(3)-Cl(8)-Cd(4)	 	95.45(19)	 	
Cd(2)-Cl(8)-Cd(4)	 	96.60(18)	 	
Cd(1)-Cl(9)-Cd(5)	 	93.38(19)	 	
Cd(1)-Cl(9)-Cd(1)#1	 	96.7(2)	 	
Cd(5)-Cl(9)-Cd(1)#1	 	90.5(2)	 	
Cd(4)-Cl(10)-Cd(5)	 	90.8(2)	 	
Cd(4)-Cl(10)-Cd(2)	 	96.72(18)	 	
Cd(5)-Cl(10)-Cd(2)	 	97.1(2)	 	
Cd(4)-Cl(11)-Cd(3)	 	95.7(2)	 	
Cd(4)-Cl(11)-Cd(3)#2	 	89.8(2)		
Cd(3)-Cl(11)-Cd(3)#2	 	96.93(19)		
Cd(5)-Cl(12)-Cd(4)	 	95.9(2)		

**Table A9.** Hydrogen Bonding in A, 1-3, 4A-5A [ $\mathring{A}$  and  $(\degree)$ ].

	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)					
	Α									
1	O(1)-H(101)Cl(4)#(1)	0.950(6)	2.592(3)	3.168(8)	119.39(39)					
2	O(2)-H(102)Cl(4)#(2)	0.950(7)	2.400(3)	3.212(8)	143.30(40)					
3	C(2)-H(2)Cl(3)#(3)	0.950(9)	2.845(2)	3.738(8)	157.13(65)					

4	C(3)-H(3)Cl(1)#(4)	0.950(12)		2.847(3)	3.565(11)	133.12(73)
5	C(4)-H(4)Cl(4)#(5)	0.950(9)	, ,	2.834(2)	2.834(2)	156.83(58)
			1		·	
1	N(1)-H(1N)Cl(1)#(0)	0.893(2) 2.348(2)			3.230(2)	169.08(1.70)
2	C(1)-H(1)Cl(3)#(1)	0.950(3)	2.861(1)		3.796(3)	168.05( 0.17)
3	C(2)-H(2)Cl(1)#(1)	0.950(3)	2.929(1)		3.671(3)	135.91( 0.17)
4	C(1)-H(1)Cl(3)#(1)	0.950(3)	2.862(1)		3.795(3)	167.47( 0.16)
5	C(3)-H(3)Cl(3)#(2)	0.950(3)	2.7	721(1)	3.528(3)	143.20( 0.18)
6	C(6)-H(6B)Cl(2)#(3)	0.990(3)	2.901(1)		3.691(3)	137.40( 0.16)
7	C(6)-H(6B)Cl(3)#(4)	0.990(3)	2.656(1)		3.418(3)	133.89( 0.15)
8	O(1)-H(101)Cl(3)#(6)	0.816(3)	2.223(3)		3.030(2)	169.83( 3.02)
			2			
1	N(2)-H(2A)Cl(2) #(0)	0.880(3)		2.387(6)	3.255(2)	169.15( 1.54)
2	C(1)-H(1)Cl(6)#(0)	0.950(3)		2.892(6)	3.830(3)	169.77( 1.92)
3	C(4)-H(4)Cl(1)#(0)	0.950(3)		2.767(6)	3.550(3)	140.18( 1.68)
4	C(2)-H(2)Cl(12)#(1)	0.950(3)		2.902(5)	3.551(3)	126.57(1.83)
5	N(1)-H(1A)Cl(11) #(3)	0.880(3)		2.923(7)	3.646(3)	140.67( 1.52)
6	C(8)-H(8)Cl(10)#(5)	0.950(4)		2.858(7)	3.521(4)	127.77( 2.25)
7	C(13)-H(13A)Cl(3)#(7)	0.990(2)		2.792(6)	3.517(2)	130.54( 1.29)
8	C(10)-H(10)Cl(8)#(2)	0.950(3)		2.814(7)	3.648(3)	147.06( 1.69)
			4A			

1	O(1)-H(101)Cl(6) #(0)	0.998(3)	2.02	27(3)		3.017(4)	171.27( 2.03)			
2	N(1)-H(1N)Cl(5)#(0)	0.880(4)	2.36	2.366(1)		3.201(4)	158.38( 0.27)			
3	N(2)-H(2N)Cl(1)#(1)	0.880(8)	2.677(1)		3.534(8)		164.96( 0.48)			
4	C(4)-H(4)Cl(5)#(3)	0.950(1)	2.89	2.893(1)		3.715(1)	145.50( 0.61)			
5	C(7)-H(7)Cl(3)#(6)	0.950(1)	2.60	)0(2)		3.444(1)	148.19( 0.79)			
6	C(8)-H(8)Cl(6)#(6)	0.950(2)	2.59	2.597(1)		3.515(2)	162.56( 1.03)			
7	C(9)-H(9)Cl(2)#(7)	0.950(1)	2.91	2.915(1)		3.805(9)	156.43( 0.52)			
8	O(1)-H(102)Cl(3)#(9)	0.993(3)	2.06	2.067(4)		3.058(4)	175.81( 2.45)			
9	C(10)-H(10)Cl(4)#(9)	0.950(8)	2.61	11(2) 3		3.502(8)	156.37( 0.49)			
	5A									
1	N(1)-H(1N)Cl(2)#(1)	0.880(7)	)	2.854(2)		3.459(7)	127.30( 0.45)			
2	O(1)-H(101)Cl(3)#(1)	0.896(3)		2.173(3)		3.058(5)	169.45( 2.35)			
3	C(1)-H(1)Cl(3)#(2)	0.950(9)	)	2.8	76(2)	3.552(8)	129.07( 0.45)			
4	C(3)-H(3)Cl(3)#(3)	0.950(10	)	2.7	17(2)	3.611(10)	155.25( 0.59)			

#### **Symmetry Positions**

**For A.** #(1) x,+y-1,+z, #(2) -x,-y+2,-z+1, #(3) -x+1,-y+1,-z+1, #(4) x+1,+y,+z, #(5) -x,-y+1,-z

For 1. #(0) x, y, z, #(1) -x+1/2+1,-y+1,+z-1/2, #(2) x,+y,+z-1, #(3)-x+1,+y+1/2,-z-1/2, #(4) -x+2,+y+1/2,-z-1/2, #(6) x-1/2,-y+1/2+1,-z. For 2. #(0) x,y,z, #(1)-x+1/2+1,+y+1/2,-z+1/2, #(2)-x+1/2,+y+1/2,-z+1/2, #(3)x-1,+y,+z, #(5)x-1,+y,+z, #(7)-x+1,-y,-z.

**For 4A.** #(0) x, y, z, #(1) x,+y+1,+z, #(3) -x+1/2+1,+y-1/2,+z-1/2, #(6) x-1/2,-y+1/2+2,+z, #(7) x-1/2,-y+1/2+1,+z, #(9) x,+y+1,+z. **For 5A**#(1) x-1/2,-y+1/2,-z+1, #(2) -x,+y+1/2,-z+1/2+1, #(3) x,+y+1,+z.

## Chapter 4

### Table A10. Crystallographic parameters of 1-3

Identification code	1	2	3
Empirical formula	C <sub>27</sub> H <sub>30</sub> CuHgN <sub>2</sub> O <sub>7</sub>	C40H47CuHgN3O8	$C_{25}H_{32}CuN_2O_5$
Formula weight	758.66	961.96	504.07
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073	0.71073	1.5418
Crystal system, space	Monoclinic <i>P</i> 2 <sub>1</sub> /c	Triclinic <i>P</i> ī	Triclinic <i>P</i> ī
group			
Unit Cell Parameter			
a/Å	12.8050(11)	10.3212(9)	10.7914(5)
b/Å	21.5075(16)	13.1358(13)	10.9401(4)
c/Å	10.2905(7)	16.0182(17)	11.7748(5)
α/°	90	66.804(10)	90.658(3)
β/°	105.406(8)	79.650(8)	109.259(4)
γ/°	90	87.942(7)	113.692(4)
V/Å <sup>3</sup>	2732.2(4)	1962.2(3)	1184.93(9)
$Z, d_{\text{calcd}}(\text{mg/m}^{3})$	4, 1.844	2, 1.628	2, 1.413
μ/ mm <sup>-1</sup>	6.438	4.504	1.621
F(000)	1484	962	530
θ range	3.10 to 25.00	3.05 to 25.00	4.03 to 72.08
Reflections collected /	20148 / 4803 [R(int) =	14767 / 6899 [R(int) =	7697 / 4555 [R(int) =
unique	0.0891]	0.0763]	0.0127]
Max. and min.	0.7390 and 0.4882	0.3653 and 0.2939	0.7271 and 0.6087
Transmission			
Refinement method	Full-matrix least-squares on	Full-matrix least-squares on	Full-matrix least-squares on
	F^2	F^2	F^2
Data / restraints /	4803 / 0 / 349	6899 / 0 / 488	4555 / 0 / 312
parameters			
GOF, F <sup>2</sup>	1.055	1.055	1.033
R1, wR2 [I>2σ(I)]	R1 = 0.0628, wR2 = 0.1537	R1 = 0.0852, wR2 = 0.2284	R1 = 0.0344, wR2 = 0.0943
R1, wR2 (all data)	R1 = 0.0831, wR2 = 0.1699	R1 = 0.1162, wR2 = 0.2785	R1 = 0.0352, wR2 = 0.0952
CCDC No	1014845	1014846	1014847

Bond distance(Å)		1	
Hg(1)-O(6)	2.101(9)	Cu(1)-O(2)	1.921(7)
Hg(1)-O(4)	2.104(10)	Cu(1)-O(1)	1.937(6)
Hg(1)-O(3)	2.402(7)	Cu(1)-N(2)	1.995(9)
Hg(1)-O(6)#1	2.606(8)	Cu(1)-N(1)	2.013(8)
Bond angle(°)			
O(6)-Hg(1)-O(4)	165.8(4)	O(2)-Cu(1)-N(2)	163.4(3)
O(6)-Hg(1)-O(3)	93.7(3)	O(1)-Cu(1)-N(2)	93.0(3)
O(4)-Hg(1)-O(3)	95.4(3)	O(2)-Cu(1)-N(1)	92.6(3)
O(6)-Hg(1)-O(6)#1	74.8(3)	O(1)-Cu(1)-N(1)	169.0(3)
O(4)-Hg(1)-O(6)#1	117.9(4)	N(2)-Cu(1)-N(1)	80.4(4)
O(2)-Cu(1)-O(1)	77.8(2)	O(2)-Cu(1)-O(1)#2	93.3(2)
O(2)-Cu(1)-O(1)	91.4(3)	O(1)-Cu(1)-O(1)#2	86.3(3)
N(2)-Cu(1)-O(1)#2	103.0(3)		
Bond distance(Å)		2	
Hg(1)-O(5)	2.154(1)	Hg(1)-O(4)	2.589(1)
Hg(1)-O(3)	2190(10)	Cu(1)-O(1)	1 888(9)
	2.170(10)	84(1) 8(1)	1.000())
Hg(1)-O(6)#1	2.347(12)	Cu(1)-O(2)	1.938(9)
Hg(1)-O(6)#1 Hg(1)-O(7)	2.347(12) 2.519(14)	Cu(1)-O(2) Cu(1)-N(2)	1.938(9) 2.005(10)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6)	2.347(12) 2.519(14) 2.587(10)	Cu(1) O(1)           Cu(1)-O(2)           Cu(1)-N(2)           Cu(1)-N(1)	1.938(9)       2.005(10)       2.007(12)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°)	2.347(12) 2.519(14) 2.587(10)	Cu(1)-O(2) Cu(1)-N(2) Cu(1)-N(1)	1.938(9)         2.005(10)         2.007(12)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°) O(5)-Hg(1)-O(3)	2.347(12) 2.519(14) 2.587(10) 129.1(6)	Cu(1)-O(2) Cu(1)-N(2) Cu(1)-N(1) O(5)-Hg(1)-O(6)	1.000(7)         1.938(9)         2.005(10)         2.007(12)         85.3(4)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°) O(5)-Hg(1)-O(3) O(5)-Hg(1)-O(6)#1	2.1750(10) 2.347(12) 2.519(14) 2.587(10) 129.1(6) 136.2(5)	Cu(1)-O(2) Cu(1)-N(2) Cu(1)-N(1) O(5)-Hg(1)-O(6) O(3)-Hg(1)-O(6)	1.000(7)         1.938(9)         2.005(10)         2.007(12)         85.3(4)         83.8(3)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°) O(5)-Hg(1)-O(3) O(5)-Hg(1)-O(6)#1 O(3)-Hg(1)-O(6)#1	2.1750(16) 2.347(12) 2.519(14) 2.587(10) 129.1(6) 136.2(5) 90.9(4)	Cu(1)-O(2) Cu(1)-N(2) Cu(1)-N(1) O(5)-Hg(1)-O(6) O(3)-Hg(1)-O(6) O(6)#1-Hg(1)-O(6)	1.938(9)         2.005(10)         2.007(12)         85.3(4)         83.8(3)         82.0(3)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°) O(5)-Hg(1)-O(3) O(5)-Hg(1)-O(6)#1 O(3)-Hg(1)-O(6)#1 O(5)-Hg(1)-O(7)	2.347(12) $2.519(14)$ $2.587(10)$ $129.1(6)$ $136.2(5)$ $90.9(4)$ $97.4(5)$	Cu(1)-O(2)         Cu(1)-N(2)         Cu(1)-N(1)         O(5)-Hg(1)-O(6)         O(3)-Hg(1)-O(6)         O(6)#1-Hg(1)-O(6)         O(7)-Hg(1)-O(6)	1.938(9)         2.005(10)         2.007(12)         85.3(4)         83.8(3)         82.0(3)         116.7(4)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°) O(5)-Hg(1)-O(3) O(5)-Hg(1)-O(6)#1 O(3)-Hg(1)-O(6)#1 O(5)-Hg(1)-O(7) O(3)-Hg(1)-O(7)	2.347(12) $2.519(14)$ $2.587(10)$ $129.1(6)$ $136.2(5)$ $90.9(4)$ $97.4(5)$ $131.6(4)$	Cu(1)-O(2)         Cu(1)-N(2)         Cu(1)-N(1)         O(5)-Hg(1)-O(6)         O(6)#1-Hg(1)-O(6)         O(7)-Hg(1)-O(6)         O(5)-Hg(1)-O(4)	1.938(9)         2.005(10)         2.007(12)         85.3(4)         83.8(3)         82.0(3)         116.7(4)         52.4(4)
Hg(1)-O(6)#1 Hg(1)-O(7) Hg(1)-O(6) Bond angle(°) O(5)-Hg(1)-O(3) O(5)-Hg(1)-O(6)#1 O(3)-Hg(1)-O(6)#1 O(5)-Hg(1)-O(7) O(3)-Hg(1)-O(7) O(6)#1-Hg(1)-O(7)	2.136(10) $2.347(12)$ $2.519(14)$ $2.587(10)$ $129.1(6)$ $136.2(5)$ $90.9(4)$ $97.4(5)$ $131.6(4)$ $53.6(4)$	Cu(1) O(1)         Cu(1)-O(2)         Cu(1)-N(2)         Cu(1)-N(1)         O(5)-Hg(1)-O(6)         O(6)#1-Hg(1)-O(6)         O(7)-Hg(1)-O(6)         O(5)-Hg(1)-O(4)         O(3)-Hg(1)-O(4)	$   \begin{array}{r}     1.000(7) \\     1.938(9) \\     2.005(10) \\     2.007(12) \\     \\     85.3(4) \\     83.8(3) \\     82.0(3) \\     116.7(4) \\     52.4(4) \\     103.7(5) \\   \end{array} $

Table A11. Selected bond lengths (Å) and bond angles (°) of 1-3.

O(6)-Hg(1)-O(4)	131.3(4)	O(7)-Hg(1)-O(4)	94.1(6)
Bond distance(Å)		3	
Cu(1)-O(3)	1.8776(12)	Cu(1)-N(2)	1.9953(14)
Cu(1)-O(1)	1.8969(12)	Cu(1)-N(1)	2.0143(15)
Bond angle(°)			
O(3)-Cu(1)-O(1)	94.74(5)	O(3)-Cu(1)-N(1)	172.73(5)
O(3)-Cu(1)-N(2)	92.19(6)	O(1)-Cu(1)-N(1)	92.50(6)
O(1)-Cu(1)-N(2)	170.75(6)	N(2)-Cu(1)-N(1)	80.53(6)

	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)							
	1											
1	C(1)-H(1)O(7)#(0)	0.950(1)	2.856(1)	3.662(1)	143.33(1)							
2	C(3) -H(3)O(3)#(2)	0.950(1)	2.681(1)	3.483(1)	142.47(8)							
3	C(9)-H(9)O(5)#(3)	0.950(1)	2.551(1)	3.145(2)	120.82(9)							
	2											
1	C(1)-H(1)O(7)#(0)	0.950(1)	2.625(1)	3.393(1)	138.22(1)							
2	O(8)H(108)O(7)#(0)	0.840(1)	1.844(1)	2.576(2)	144.71(1)							
3	C(4) -H(4)N(111)#(1)	0.950(1)	2.459(1)	3.368(1)	160.16(1)							
4	C(9)-H(9)O(5)#(2)	0.950(1)	2.527(1)	3.256(1)	133.57(1)							
5	C(9)-H(9)O(6)#(2)	0.950(1)	2.684(1)	3.494(1)	143.56(1)							
		3										
1	C(4)-H(4)O(111)#(2)	0.950(1)	2.466(1)	3.360(1)	156.83(1)							
2	C(7)-H(7)O(111)#(2)	0.950(1)	2.691(1)	3.577(1)	155.49(1)							
3	C(8)-H(8)O(2)#(3)	0.950(1)	2.523(1)	3.361(1)	147.06(1)							
	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)							

### Table A12. Hydrogen Bonding in 1, 2 and 3 [Å and (°)]

#### Symmetry positions.

For 1 #(0) x,y,z, #(2) x,+y,+z-1, #(2) x+1,+y,+z, For 2 #(0) x,y,z, #(1) -x+1,-y+2,-z, #(2) x,+y+1,+z, For 3 #(2) -x-1,-y+1,-z, #(3) x-1,+y-1,+z.

Identificati		-	6	-	0	0	10	11
on code	4	5	0		8	9	10	11
Empirical	C H H-NO	C U U-N O		C H H-NO	C II II-N O	C H H-N O	C II CIII-NO	C II Dr HaN O
formula	$C_{24}H_{18}HgN_2O_4$	$C_{24}H_{20}HgN_4O_4$	$C_{48}H_{38}Hg_2N_8O_8$	$C_{24}H_{20}HgN_4O_5$	$C_{24}H_{18}HgN_2O_6$	$C_{24}H_{18}HgN_2O_6$	$C_{14}H_{10}C_{12}HgN_2O_4$	$C_{14}H_{10}Br_2HgN_2O_4$
Formula	508.00	(20.04	1256.04	(45.02	(20.00	(20.00	541 72	(20.65
weight	598.99	629.04	1256.04	043.03	030.99	030.99	541.75	030.05
emperature(	150(2)	150(2)	150(2)	150(2)	150(2)	203(2)	150(2)	150(2)
K)	130(2)	130(2)	130(2)	150(2)	150(2)	293(2)	130(2)	130(2)
Wavelength	0.71072	0.71072	0.71072	0.71072	0.71072	0.71072	0.71072	0 71072
(Å)	0.71075	0.71075	0.71075	0.71075	0.71075	0.71075	0.71075	0.71073
Crystal	Monoalinia	Triclinia	Trialinia	Monoslinio	Monoalinia	Monoalinia	Trialinia	Mongolinia
system	Monochinic			Wionochinic	Wonochine	Wionochinic		Monochnic
Space group	$P2_{l}/n$	Pī	Pī	$P2_{l}/n$	$P2_{l}/n$	$P2_{l}/n$	Pī	$C_2/c$
a/Å	7.7105(8)	7.8245(9)	11.5864(3)	7.9627(2)	12.4757(14)	11.3077(13)	6.2070(8)	29.1428(9)
b/Å	16.2556(13)	10.4766(11)	11.8687(7)	16.7257(5)	13.484(3)	16.3645(10)	7.7447(12)	4.46370(10)
c/Å	17.0219(18)	13.5760(15)	17.3326(7)	16.9844(5)	12.781(2)	12.433(3)	16.5968(18)	12.9398(4)
α/°	90	97.274(9)	91.704(4)	90	90	90	83.778(10)	90
β/°	97.615(10)	91.611(9)	90.802(3)	102.626(2)	95.031(12)	106.63(2)	83.512(9)	99.134(3)
γ/°	90	103.039(9)	109.579(4)	90	90	90	86.169(11)	90
V/Å <sup>3</sup>	2114.7(4)	1073.6(2)	2243.97(18)	2207.31(11)	2141.7(6)	2204.4(6)	786.85(18)	1661.93(8)
$Z, d_{calcd}$ mg/m	4, 1.881	2, 1.946	2, 1.859	4, 1.941	4, 1.957	4, 1.901	2, 2.286	4, 2.520

## Table A13. Crystallographic parameters of 4-11.

μ/ mm	7.312	7.209	6.898	7.018	7.232	7.026	10.140	14.089
F(000)	1152	608	1212	1248	1216	1216	508	1160
θ range	2.95 to 25.00	3.00 to 25.00	2.923 to 25.000	3.13 to 25.00	3.20 to 25.00	3.289 to 25.00	3.04 to 25.00	3.690 to 24.992
	-9<=h<=9,	-9<=h<=9,	-13<=h<=13,	-9<=h<=9,	-14<=h<=14,	-13<=h<=8,	-7<=h<=7,	-33<=h<=34,
Index ranges	-18<=k<=19,	-12<=k<=12,	-14<=k<=10,	-19<=k<=18,	-15<=k<=16,	-19<=k<=19,	-9<=k<=8,	-5<=k<=5,
	-20<=l<=18	-16<=l<=16	-19<=l<=20	-20<=l<=20	-15<=l<=14	-14<=l<=14	-19<=l<=19	-15<=l<=15
Reflections	15258 / 3714	8877 / 3773	17623 / 7895	15997 / 3888	16854 / 3760	15490 / 3879	5948 / 2773	4775 / 1465
collected	[R(int)=0.2153]	[R(int)= 0.1431]	[R(int) = 0.0401]	[R(int)= 0.0437]	[R(int)=0.0967]	[R(int)=0.0270]	[R(int) = 0.0729]	[R(int)=0.0509]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least- squares on F <sup>2</sup>	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least- squares on F <sup>2</sup>	Full-matrix least- squares on F <sup>2</sup>
Data /restraints / parameters	3714 / 0 / 280	3773 / 0 / 306	7895 / 0 / 595	3888 / 0 / 323	3760 / 0 / 307	3879 / 0 / 298	2773 / 0 / 208	1465 / 0 / 105
GOF, F <sup>2</sup>	1.137	1.066	1.061	1.309	0.974	1.083	1.119	1.072
R1, wR2	R1 = 0.0611,	R1 = 0.0538,	R1 = 0.0327, wR2	R1 = 0.0471,	R1 = 0.0514,	R1 = 0.0273,	R1 = 0.0731, wR2	R1 = 0.0457, wR2
[I>2σ(I)]	wR2 = 0.1569	wR2 = 0.1215	= 0.0608	wR2 = 0.1075	wR2 = 0.1257	wR2 = 0.0758	= 0.1865	= 0.1237
R1, wR2	R1 = 0.0856,	R1 = 0.0839,	R1 = 0.0426, wR2	R1 = 0.0593,	R1 = 0.0598,	R1 = 0.0352,	R1 = 0.0791, wR2	R1 = 0.0480, wR2
(all data)	wR2 = 0.1844	wR2 = 0.1587	= 0.0658	wR2 = 0.1105	wR2 = 0.1303	wR2 = 0.0773	= 0.1935	= 0.1259
CCDC No.	1415542	1415543	1415540	1415539	1415541	1415546	1415544	1415545

Bond Distances	4	5	6	7	8	9	10	11
Hg(1)-O(1)	2.149(9)	2.591(9)	2.652(5)	2.130(6)	2.433(6)	2.393(4)	-	-
Hg(1)-O(2)	-	2.257(8)	2.388(4)	-	2.638(7)	2.652(4)	-	-
Hg(1)-O(3)	2.457(10)	2.488(9)	2.442(4)	-	-	2.155(3)	-	-
Hg(1)-O(4)	2.373(9)	2.256(10)	2.537(4)	2.139(7)	2.157(5)	-	-	-
Hg(2)-O(5)	-	-		-	-	-	-	-
Hg(2)-O(6)	-	-	2.453(4)	-	-	-	-	-
Hg(2)-O(7)	-	-	2.546(4)	-	-	-	-	-
Hg(2)-O(8)	-	-	2.316(4)	-	-	-	-	-
Hg(1)-N(1)	2.348(10)	2.369(11)		2.416(9)	2.241(7)	2.228(4)	2.299(14)	2.293(6)
Hg(1)N(1)#1	-	-		-	-	-	-	2.293(6)
Hg(1)-N(2)	2.350(8)	2.370(9)	2.403(5)	2.369(10)	2.282(7)	2.356(5)	2.253(13)	-
Hg(1)-N(3)	-	-	2.358(4)	-	-	-	-	-
Hg(1)-N(4)	-	-	2.439(4)	-	-	-	-	-
Hg(2)-N(5)	-	-	2.500(4)	-	-	-	-	-
Hg(2)-N(6)	-	-	2.373(5)	-	-	-	-	-
Hg(2)-N(7)	-	-	2.351(4)	-	-	-	-	-
Hg(1)-Cl(1)	-	-	-	-	-	-	2.557(4)	-
Hg(1)-Cl(2)	-	-	-	-	-	-	2.422(4)	-
Hg(1)-Br(1)	-	-	-	-	-	-	-	2.6155(8)

### Table A14. Bond distanced and Bond angles of 4-11.
## Bond Angles

O(1)-Hg(1)-N(1)	120.5(3)	150.6(4)		104.7(3)	114.2(2)	117.18(13)	-	-
O(1)-Hg(1)-N(2)	113.9(3)	96.4(3)	149.76(15)	104.5(3)	107.8(2)	102.39(14)	-	-
N(1)-Hg(1)-N(2)	70.1(4)	70.2(3)	-	68.6(3)	73.0(3)	72.49(17)	107.7(5)	-
O(1)-Hg(1)-O(4)	142.7(3)	101.6(3)	-	147.5(3)	88.7(2)	-	-	-
N(1)-Hg(1)-O(4)	93.4(3)	105.7(4)	-	100.9(3)	137.9(2)	-	-	-
N(2)-Hg(1)-O(4)	90.8(3)	96.3(3)	78.69(15)	103.3(3)	135.3(2)	-	-	-
O(1)-Hg(1)-O(3)	100.3(3)	119.4(3)	101.57(15)	-	-	86.84(13)	-	-
N(1)-Hg(1)-O(3)	101.7(3)	85.7(3)		-	-	143.43(17)	-	-
N(2)-Hg(1)-O(3)	144.3(4)	136.4(3)	98.87(15)	-	-	131.99(13)	-	-
O(4)-Hg(1)-O(3)	54.2(3)	55.1(3)	52.84(14)	-	-	-	-	-
O(4)-Hg(1)-O(2)	-	144.4(3)	83.30(15)	-	91.2(2)	-	-	-
O(2)-Hg(1)-N(1)	-	104.8(4)		-	78.9(2)	85.55(13)	-	-
O(2)-Hg(1)-N(2)	-	111.0(3)	152.98(16)	-	131.8(2)	132.45(13)	-	-
O(2)-Hg(1)-O(3)	-	110.0(3)	85.81(14)	-		90.00(12)	-	-
O(2)-Hg(1)-O(1)		54.4(3)	51.41(14)	-	51.29(19)	51.45(12)	-	-
N(1)-Hg(1)-N(1)#1	-	-	-	-	-	-	-	131.1(3)
N(1)-Hg(1)-Br(1)	-						-	104.98(17)
N(1)#1-Hg(1)-Br(1)	-	-	-	-	-	-	-	104.41(16)
N(1)-Hg(1)-Br(1)#1	-	-	-	-	-	-		104.41(16)

N(1)#1Hg(1)Br(1)#1	-	-	-	-	-	-	-	104.98(17)
Br(1)-Hg(1)-Br(1)#1	-	-	-	-	-	-	-	104.32(3)
N(3)-Hg(1)-O(2)	-	-	136.26(17)	-	-	-	-	-
N(3)-Hg(1)-N(2)	-	-	69.48(17)	-	-	-	-	-
N(3)-Hg(1)-N(4)	-	-	97.11(15)	-	-	-	-	-
O(2)-Hg(1)-N(4)	-	-	85.21(14)	-	-	-	-	-
N(2)-Hg(1)-N(4)	-	-	82.73(15)	-	-	-	-	-
N(3)-Hg(1)-O(3)	-	-	99.75(14)	-	-	-	-	-
N(4)-Hg(1)-O(3)	-	-	162.51(15)	-	-	-	-	-
N(3)-Hg(1)-O(4)		-	134.03(14)	-	-	-	-	-
N(4)-Hg(1)-O(4)	-	-	111.10(15)	-	-	-	-	-
N(3)-Hg(1)-O(1)	-		85.20(15)				-	
N(4)-Hg(1)-O(1)	-	-	84.37(16)	-	-	-	-	-
O(4)-Hg(1)-O(1)	-	-	131.54(13)	-	-	-	-	-
O(8)-Hg(2)-N(7)	-	-	129.55(18)	-	-	-	-	-
O(8)-Hg(2)-N(6)	-	-	159.66(17)	-	-	-	-	-
N(7)-Hg(2)-N(6)	-	-	69.50(19)	-	-	-	-	-
O(8)-Hg(2)-O(6)	-	-	83.74(13)	-	-	-	-	-
N(7)-Hg(2)-O(6)	-	-	97.47(15)	-	-	-	-	-
N(6)-Hg(2)-O(6)	-	-	102.18(15)	-	-	-	-	-
O(8)-Hg(2)-N(5)	-	-	86.12(13)	-	-	-	-	-
N(7)-Hg(2)-N(5)	-	-	103.75(15)	-	-	-	-	-

N(6)-Hg(2)-N(5)	-	-	81.50(15)	-	-	-	-	-
O(6)-Hg(2)-N(5)	-	-	158.32(15)	-	-	-	-	-

	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)				
	4								
1	C(20)-H(20)O(1)#(6)	0.950(.013)	2.430(.009)	3.317(.016)	155.42( 0.79)				
2	C(17) -H(17)O(4)#(5)	0.950(.013)	2.445(.009)	3.323(.017)	153.55(0.81)				
3	C(16)-H(16)O(2)#(5)	0.950(.015)	2.344(.011)	3.265(.019)	163.14( 0.90)				
4	C(8)-H(8)O(2)#(3)	0.950(.013)	2.677(.011)	3.436(.017)	137.29( 0.82)				
5	C(9)-H(9)O(3)#(3)	0.950(.016)	2.623(.009)	3.547(.018)	164.53( 0.94)				
		5							
1	C(7)-H(7)O(4)#(3)	0.950(.014)	2.508(.010)	3.326(.018)	144.30( 0.85)				
2	C(8)-H(8)N(3)#(4)	0.950(.013)	2.680(.010)	3.513(.016)	146.69( 0.88)				
3	C(9)-H(9)O(1)#(4)	0.950(.013)	2.580(.008)	3.452(.015)	152.79( 0.87)				
	6								
1	C(39)-H(39)O(7)#(0)	0.950(.000)	2.588(.000)	3.195(.000)	122.02( 0.01)				
		7	1						
1	C(23)-H(23)O(3)#(7)	0.950(.011)	2.584(.007)	3.292(.013)	131.58( 0.70)				
2	C(24)-H(24)O(1)#(7)	0.950(.011)	2.719(.007)	3.225(.013)	114.09( 0.66)				
3	N(4)-NH(4)O(3)#(7)	0.814(.127)	2.274(.121)	2.974(.013)	144.43(11.47)				
		8	3						
1	C(2)-H(2)O(6)#(1)	0.950(.000)	2.461(.000)	3.279(.000)	144.22( 0.02)				
2	C(14)-H(14)O(4)#(4)	0.950(.000)	2.408(.000)	3.352(.000)	172.20( 0.02)				
3	C(15)-H(15)O(2)#(4)	0.950(.000)	2.634(.000)	3.436(.000)	142.43( 0.01)				
		9							
1	C(16)-H(16)O(4)#(1)	0.930(.000)	2.695(.000)	3.342(.000)	127.35( 0.02)				
2	C(20)-H(20)O(5)#(7)	0.930(.000)	2.589(.000)	3.469(.000)	158.07( 0.01)				
		1	0						
1	C(13)-H(13)O(1)#(3)	0.950(.018)	2.403(.012)	3.280(.021)	153.39(1.10)				
		1	1						
1	C(4)-H(4)O(1)#(3)	0.950(.000)	2.665(.000)	3.573(.000)	159.95( 0.00)				

Table A15 H-bonding table of 4-11

#### **Symmetry Positions**

For 4 #(3) -x+1/2,+y-1/2,-z+1/2, #(5) x+1,+y,+z, #(6) x-1,+y,+z, For 5 #(3) -x,-y+1,-z+1, #(4) -x,-y,-z+1 For 6 #(0) x,y,z, For 7 #(7) x-1,+y,+z For 8 #(1) x-1,+y,+z, # ( 4) -x+1/2+1,+y+1/2,-z+1/2+1 For 9#(1) x-1,+y,+z #(7) x+1,+y,+z, For 10 #(3) x+1,+y,+z

**For 11** #(3) -x+1/2+1,+y-1/2,-z+1/2+1.

### Chapter 5

Identification code	1	2
Empirical formula	$C_{38}H_{30}Hg_2N_{10}O_9$	$C_{76}H_{68}Cd_3Cl_6N_{20}O_{14}$
Formula weight	1171.90	2035.40
Temperature	150(2) K	150(2) K
Wavelength	0.71073	1.5418
Crystal system, space group	Monoclinic P 2 <sub>1</sub> /c	Orthorhombic, P b c a
Unit Cell Parameter		
a/Å	11.7067(2)	18.6234(3)
b/Å	15.4042(4)	13.9776(2)
c/Å	22.2277(8)	32.2052(7)
α/°	90	90
β/ <sup>°</sup>	91.038(3)	90
γ/°	90	90
V/Å <sup>3</sup>	4007.72(19)	8383.3(3)
$Z, d_{\text{calcd}}(\text{mg/m}^3)$	4, 1.942	4, 1.613
μ/ mm <sup>-1</sup>	7.720	8.423
F(000)	2240	4088
θ range	3.05 to 25.00	3.63 to 72.42
Reflections collected /	22499 / 7026 [R(int) =	17929 / 8096 [R(int) =
unique	0.0515]	0.0363]
Max. and min.	0.5434 and 0.2698	0.4314 and 0.2475
transmission		
Data / restraints /	7026 / 0 / 532	8096 / 0 / 538
parameters		
GOF, F <sup>2</sup>	1.075	0.936
R1, wR2 [I>2σ(I)]	R1 = 0.0321, wR2 = 0.0774	R1 = 0.0625, wR2 = 0.1759
R1, wR2 (all data)	R1 = 0.0367, wR2 = 0.0804	R1 = 0.0638, wR2 = 0.1772
CCDC Number	1006217	1006218

 Table A16. Crystallographic parameters of complexes 1-2

Bond distance	1 (Å)	Bond distance	2 (Å)
Hg(1)-N(2)	2.117(4)	Cd(1)-O(4)	2.374(4)
Hg(1)-N(9)	2.491(4)	Cd(1)-N(5)	2.391(4)
Hg(1)-N(3)	2.522(4)	Cd(1)-N(10)	2.391(4)
Hg(1)-N(1)	2.688(4)	Cd(1)-O(2)	2.411(4)
Hg(1)-Hg(2)	3.3483(3)	Cd(1)-Cl(2)	2.5167(13)
Hg(2)-N(7)	2.116(4)	Cd(1)-Cl(1)	2.5276(12)
Hg(2)-N(4)	2.122(4)	Cd(2)-O(1)	2.337(4)
Hg(2)-N(8)	2.473(5)	Cd(2)-N(4)	2.336(4)
Hg(2)-N(5)	2.497(4)	Cd(2)-Cl(3)	2.5979(14)
Bond angle	(º)	Bond angle	(º)
N(2)-Hg(1)-N(10)	168.18(15)	N(5)-Cd(1)-N(10)	71.55(14)
N(2)-Hg(1)-N(9)	111.43(16)	O(4)-Cd(1)-O(2)	88.63(14)
N(10)-Hg(1)-N(9)	74.15(15)	N(5)-Cd(1)-O(2)	155.45(14)
N(2)-Hg(1)-N(3)	73.00(15)	N(10)-Cd(1)-O(2)	79.62(15)
N(10)-Hg(1)-N(3)	112.98(15)	O(4)-Cd(1)-Cl(2)	90.70(14)
N(9)-Hg(1)-N(3)	124.91(14)	N(5)-Cd(1)-Cl(2)	71.07(14)
N(2)-Hg(1)-N(1)	69.75(14)	N(10)-Cd(1)-Cl(2)	94.70(13)
N(10)-Hg(1)-N(1)	102.65(14)	O(2)-Cd(1)-Cl(2)	96.58(11)
N(9)-Hg(1)-N(1)	75.85(13)	O(4)-Cd(1)-Cl(1)	99.43(11
N(3)-Hg(1)-N(1)	142.22(13)	N(5)-Cd(1)-Cl(1)	168.88(10)
N(2)-Hg(1)-Hg(2)	81.25(11)	N(10)-Cd(1)-Cl(1)	164.25(12)
N(10)-Hg(1)-Hg(2)	86.93(11)	O(2)-Cd(1)-Cl(1)	96.03(10)
N(9)-Hg(1)-Hg(2)	117.29(10)	Cl(2)-Cd(1)-Cl(1)	100.53(10)
N(3)-Hg(1)-Hg(2)	117.60(10)	O(1)#1-Cd(2)-O(1	91.18(10)
N(1)-Hg(1)-Hg(2)	50.59(8)	O(1)#1-Cd(2)-N(4)	96.37(5)
N(7)-Hg(2)-N(4)	172.22(17)	O(1)-Cd(2)-N(4)	180.00(15)
N(7)-Hg(2)-N(8)	73.80(15)	N(4)-Cd(2)-N(4)#1	85.95(14)

Table A17. Selected bond lengths (Å) and bond angles(°) of  $1 \mbox{ and } 2$ 

N(4)-Hg(2)-N(8)	113.99(15)	O(1)#1-Cd(2)-Cl(3)	94.05(14)
N(7)-Hg(2)-N(5)	102.68(15)	O(1)-Cd(2)-Cl(3)	180.00(10)
N(4)-Hg(2)-N(5)	73.47(14)	N(4)-Cd(2)-Cl(3)	87.07(11)
N(8)-Hg(2)-N(5)	121.67(14)	O(1)#1-Cd(2)-Cl(3)#1	92.93(11)
N(7)-Hg(2)-N(1)	112.81(14)	N(4)-Cd(2)-Cl(3)#1	90.17(11)
N(4)-Hg(2)-N(1)	70.45(14)	O(1)#1-Cd(2)-Cl(3)#1	92.93(11)
N(8)-Hg(2)-N(1)	76.66(13)	N(4)-Cd(2)-Cl(3)#1	89.83(11)
N(5)-Hg(2)-N(1)	143.82(13)		
N(7)-Hg(2)-N(6)	69.92(14)		
N(4)-Hg(2)-N(6)	102.57(14)		
N(8)-Hg(2)-N(6)	140.99(13)		
N(5)-Hg(2)-N(6)	80.61(13)		
N(1)-Hg(2)-N(6)	104.64(12)		
N(7)-Hg(2)-Hg(1)	89.63(11)		
N(4)-Hg(2)-Hg(1)	87.19(10)		
N(8)-Hg(2)-Hg(1)	113.82(10)		
N(5)-Hg(2)-Hg(1)	124.46(10)		
N(1)-Hg(2)-Hg(1)	51.67(9)		
N(6)-Hg(2)-Hg(1)	53.11(8)		

	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)		
		1					
1	C(28)-H(28)O(4)#(7)	0.950(1)	2.476(1)	3.251(1)	138.74(3)		
2	C(34) -H(34)O(2)#(8)	0.950(1)	2.541(1)	3.417(1)	153.29(4)		
	2						
1	C(10)-H(10)Cl(1)#(2)	0.950(1)	2.884(1)	3.797(1)	161.58(1)		
2	C(17) -H(17)Cl(2)#(2)	0.950(1)	2.672(1)	3.570(1)	157.97(1)		
Sy Fo Fo	Symmetry Positions For 1 #(7) -x,-y+2,-z+1, #(8) -x,-y+2,-z+2 For 2 #(2) x-1/2,+y,-z+1/2						

# Table A18. Hydrogen Bonding in 1 and 2 [Å and (°)].

Table A19: Cartesian coordinates (	(Å) for calculated geometry of <b>H</b> <sub>2</sub> <b>L</b> .
	(1) for calculated geometry of H <sub>2</sub> L.

0	-2.740400	-3.494600	0.769100	C	1.463400	-3.237900	-0.053400
0	-2.742700	3.492900	-0.768900	С	2.441100	-4.256300	-0.061300
Ν	-2.215600	-0.000700	0.000000	Н	2.187800	-5.255700	0.282900
Ν	-0.794900	-2.344200	0.284500	С	3.732600	-3.956200	-0.522900
Н	-0.350100	-1.471200	0.004200	Н	4.501700	-4.723900	-0.542300
Ν	-0.796500	2.343900	-0.284300	C	4.015300	-2.647000	-0.964900
Н	-0.351000	1.471200	-0.003900	Н	4.999400	-2.375400	-1.334500
Ν	1.737000	-1.978100	-0.473600	C	2.985900	-1.691900	-0.920000
Ν	1.735500	1.979300	0.474000	Н	3.149400	-0.670000	-1.251700
С	-2.909600	-1.144600	0.225000	C	0.049200	3.520000	-0.433700
С	-4.317700	-1.187900	0.242500	Н	0.075500	3.844200	-1.486100
Н	-4.803100	-2.137300	0.439400	Н	-0.386500	4.361000	0.124700
С	-5.031300	-0.001600	-0.000300	C	1.461200	3.238800	0.053600
Н	-6.117700	-0.002000	-0.000400	C	2.438500	4.257700	0.061000
С	-4.318500	1.185100	-0.242900	Н	2.184800	5.256900	-0.283300
Н	-4.804500	2.134200	-0.439800	C	3.730300	3.958300	0.522400
С	-2.910400	1.142800	-0.225200	Н	4.499000	4.726300	0.541500
С	-2.140800	-2.423100	0.455300	C	4.013700	2.649300	0.964700
С	-2.142400	2.421800	-0.455200	Н	4.998000	2.378200	1.334100
С	0.051600	-3.519800	0.434300	C	2.984700	1.693700	0.920200
Н	0.078300	-3.843500	1.486800	Н	3.148700	0.671900	1.252000
Н	-0.383700	-4.361200	-0.123700				

#### Table A20. Cartesian coordinates (Å) for calculated geometry of $\mathbf{1}$

00	Ν	3.260100	1.596700	1.310400	
00	Ν	0.000900	-0.006700	2.141800	
00	Ν	1.583100	-2.057300	0.901100	
00	Ν	3.262000	-1.595300	-1.309500	
00	Ν	-3.262500	1.604100	-1.299400	
00	Ν	-1.580900	2.051500	0.912400	
00	С	0.418200	1.111400	-2.822500	
00	С	0.390400	1.162500	-4.229500	
00	Н	0.681000	2.085000	-4.719100	
00	С	-0.000800	0.014800	-4.942100	

Hg	-1.792900	-0.000300	-0.000300
Hg	1.791900	0.000300	0.000000
0	-0.707100	3.466600	2.566100
0	0.708600	3.482600	-2.546800
0	-0.705200	-3.467300	-2.565600
0	0.708900	-3.482800	2.545600
Ν	0.001000	0.006400	-2.142000
Ν	-1.580400	-2.052100	-0.912700
Ν	-3.262600	-1.604900	1.298600
Ν	1.582500	2.057700	-0.901600

Η	-0.001500	0.018100	-6.029200	Н	-0.684200	2.055300	4.730800
С	-0.391100	-1.137100	-4.235900	C	-0.002000	-0.016000	4.941900
Н	-0.682300	-2.056600	-4.730700	Н	-0.003000	-0.019500	6.028900
С	-0.417000	-1.094400	-2.828600	C	0.389800	-1.163300	4.229000
С	-0.914700	-2.306100	-2.060900	Н	0.680500	-2.085900	4.718400
С	-2.052600	-3.221800	-0.168900	С	0.418000	-1.111800	2.822000
Н	-1.204900	-3.753100	0.299000	C	0.917300	-2.318500	2.047600
Н	-2.507900	-3.951100	-0.857500	С	2.057200	-3.222200	0.151100
С	-3.047600	-2.895200	0.935800	Н	1.210200	-3.753000	-0.318700
С	-3.718700	-3.948500	1.598800	Н	2.514700	-3.954000	0.835500
Н	-3.523400	-4.974400	1.299400	С	3.050500	-2.887800	-0.952800
С	-4.614800	-3.657500	2.635800	С	3.723600	-3.936200	-1.621600
Н	-5.133900	-4.459400	3.154200	Н	3.531200	-4.964000	-1.327200
С	-4.832100	-2.311200	2.999400	С	4.618000	-3.637800	-2.658100
Н	-5.516300	-2.041100	3.797400	Н	5.138600	-4.435700	-3.180900
С	-4.132000	-1.317400	2.304200	C	4.831400	-2.289100	-3.015300
Н	-4.255000	-0.265700	2.547600	Н	5.514200	-2.013500	-3.812600
С	0.917000	2.318500	-2.048300	С	4.129600	-1.300500	-2.314500
С	2.056100	3.223000	-0.151800	Н	4.249600	-0.247300	-2.552800
Н	1.208800	3.754600	0.316400	С	-4.131500	1.316500	-2.305300
Η	2.514800	3.954000	-0.836200	Н	-4.254200	0.264800	-2.548900
С	3.047900	2.889100	0.953700	С	-4.831500	2.310200	-3.000700
С	3.719000	3.938000	1.623700	Н	-5.515400	2.040100	-3.799000
Н	3.526100	4.965700	1.329200	С	-4.614700	3.656500	-2.636900
С	4.612200	3.640200	2.661400	Н	-5.133700	4.458300	-3.155400
Н	5.131300	4.438500	3.185200	С	-3.718900	3.947600	-1.599500
С	4.826300	2.291700	3.018600	Н	-3.524000	4.973500	-1.300000
Н	5.508200	2.016500	3.816900	C	-3.048000	2.894300	-0.936300
С	4.126400	1.302600	2.316600	C	-2.053400	3.221100	0.168800
Н	4.247000	0.249400	2.554900	Н	-1.205800	3.752900	-0.298700
С	-0.417900	1.093700	2.828500	Н	-2.509300	3.950000	0.857400
С	-0.392400	1.136000	4.235800	C	-0.915800	2.305400	2.061000

## **Table A21.** Cartesian coordinates (Å) for calculated geometry of 2

Cd	6.750700	5.298000	-7.157000	Cl	7.782500	3.788900	-8.955500
Cd	0.000000	0.000000	0.000000	Cl	7.034400	7.839800	-7.533200

Cl	-2.251200	1.278200	-0.292600
0	1.132200	1.457400	-1.446600
0	6.193700	3.133000	-5.998300
Ν	3.376900	1.826100	-4.185200
Ν	0.786500	0.849600	-3.651000
Н	1.238900	0.712300	-4.548900
Ν	4.118300	2.447800	-6.766700
Н	3.216100	2.089800	-6.468100
Ν	-0.619700	-1.370200	-1.954800
Ν	4.482700	5.262900	-8.167100
С	3.021600	1.495000	-2.918400
С	3.946600	1.376600	-1.861700
Н	3.597100	1.045800	-0.888700
С	5.297000	1.661400	-2.128800
Η	6.041900	1.566600	-1.344600
С	5.666500	2.076600	-3.419700
Н	6.684400	2.345900	-3.678600
С	4.677200	2.138500	-4.420200
С	1.568600	1.263600	-2.623600
С	5.057800	2.611700	-5.798600
С	-0.653900	0.552600	-3.498000
Н	-1.162100	0.845200	-4.422900
Н	-1.052300	1.158300	-2.674300
С	-0.928700	-0.915900	-3.202600
С	-1.495200	-1.766800	-4.169800
Н	-1.736800	-1.377700	-5.155100
С	-1.758200	-3.110000	-3.840200
Η	-2.209700	-3.778600	-4.568300
С	-1.435300	-3.576100	-2.553900
Η	-1.650200	-4.596800	-2.251800
С	-0.856000	-2.671100	-1.646100
Η	-0.583400	-2.975900	-0.641400
С	4.355900	2.800100	-8.180600
Η	3.903600	2.022900	-8.806400
Η	5.439000	2.802900	-8.360800
С	3.783400	4.158500	-8.557100
С	2.583800	4.270300	-9.286300

Н	2.060100	3.372100	-9.601600
С	2.087700	5.546300	-9.612300
Н	1.167900	5.651600	-10.181700
С	2.808700	6.678600	-9.197700
Н	2.472300	7.683200	-9.433000
С	4.004200	6.496400	-8.479400
Н	4.621800	7.333700	-8.164600
0	2.899800	6.312000	1.480300
0	5.428700	5.814200	-5.177200
Ν	4.570600	6.349900	-1.721900
Ν	4.949800	7.180000	0.850100
Н	5.613800	7.362700	0.099000
Ν	6.678300	6.676700	-3.418700
Н	6.636500	6.891300	-2.425600
Ν	7.275300	8.461100	0.928800
Ν	8.580400	5.051800	-5.543700
С	3.542900	6.189000	-0.851500
С	2.289300	5.685500	-1.248900
Н	1.506200	5.581300	-0.506700
С	2.096700	5.341800	-2.597800
Н	1.138400	4.957000	-2.933500
С	3.161100	5.500100	-3.502100
Н	3.075500	5.253200	-4.554100
С	4.383900	6.002900	-3.019000
С	3.770500	6.564400	0.593000
С	5.549600	6.161700	-3.964400
С	5.325700	7.629500	2.182400
Η	5.409000	6.771900	2.867500
Η	4.538000	8.273600	2.598900
С	6.647100	8.383100	2.130000
С	7.184100	8.973700	3.292900
Η	6.653700	8.893300	4.238100
С	8.402500	9.666000	3.205600
Η	8.835000	10.131700	4.086900
С	9.053000	9.751700	1.957800
Η	9.993600	10.281700	1.845500
С	8.451600	9.133800	0.849200

Η	8.914400	9.177800	-0.133100
С	7.888000	7.006500	-4.201800
Н	8.428400	7.782100	-3.649200
Н	7.585600	7.425500	-5.170800
С	8.811100	5.817300	-4.440000
С	9.880900	5.532700	-3.567500
Н	10.050500	6.165000	-2.700400
С	10.724000	4.439400	-3.837900
Н	11.557500	4.210000	-3.178900
С	10.477300	3.658400	-4.980800
Н	11.108300	2.813400	-5.237500
С	9.394500	3.996500	-5.810500
Н	9.164900	3.442700	-6.717200
Cd	-6.750700	-5.298000	7.157000
Cl	-7.782500	-3.788900	8.955500
Cl	-7.034400	-7.839800	7.533200
Cl	2.251200	-1.278200	0.292600
0	-1.132200	-1.457400	1.446600
0	-6.193700	-3.133000	5.998300
Ν	-3.376900	-1.826100	4.185200
Ν	-0.786500	-0.849600	3.651000
Н	-1.238900	-0.712300	4.548900
Ν	-4.118300	-2.447800	6.766700
Н	-3.216100	-2.089800	6.468100
Ν	0.619700	1.370200	1.954800
Ν	-4.482700	-5.262900	8.167100
С	-3.021600	-1.495000	2.918400
С	-3.946600	-1.376600	1.861700
Η	-3.597100	-1.045800	0.888700
С	-5.297000	-1.661400	2.128800
Η	-6.041900	-1.566600	1.344600
С	-5.666500	-2.076600	3.419700
Η	-6.684400	-2.345900	3.678600
С	-4.677200	-2.138500	4.420200
С	-1.568600	-1.263600	2.623600
С	-5.057800	-2.611700	5.798600
С	0.653900	-0.552600	3.498000

Η	1.162100	-0.845200	4.422900
Н	1.052300	-1.158300	2.674300
С	0.928700	0.915900	3.202600
С	1.495200	1.766800	4.169800
Н	1.736800	1.377700	5.155100
С	1.758200	3.110000	3.840200
Н	2.209700	3.778600	4.568300
С	1.435300	3.576100	2.553900
Н	1.650200	4.596800	2.251800
С	0.856000	2.671100	1.646100
Н	0.583400	2.975900	0.641400
С	-4.355900	-2.800100	8.180600
Н	-3.903600	-2.022900	8.806400
Н	-5.439000	-2.802900	8.360800
С	-3.783400	-4.158500	8.557100
С	-2.583800	-4.270300	9.286300
Н	-2.060100	-3.372100	9.601600
С	-2.087700	-5.546300	9.612300
Н	-1.167900	-5.651600	10.181700
С	-2.808700	-6.678600	9.197700
Н	-2.472300	-7.683200	9.433000
С	-4.004200	-6.496400	8.479400
Н	-4.621800	-7.333700	8.164600
0	-2.899800	-6.312000	-1.480300
0	-5.428700	-5.814200	5.177200
Ν	-4.570600	-6.349900	1.721900
Ν	-4.949800	-7.180000	-0.850100
Η	-5.613800	-7.362700	-0.099000
Ν	-6.678300	-6.676700	3.418700
Н	-6.636500	-6.891300	2.425600
Ν	-7.275300	-8.461100	-0.928800
Ν	-8.580400	-5.051800	5.543700
С	-3.542900	-6.189000	0.851500
С	-2.289300	-5.685500	1.248900
Н	-1.506200	-5.581300	0.506700
С	-2.096700	-5.341800	2.597800
Н	-1.138400	-4.957000	2.933500

С	-3.161100	-5.500100	3.502100	C	-8.451600	-9.133800	-0.849200
Н	-3.075500	-5.253200	4.554100	Н	-8.914400	-9.177800	0.133100
С	-4.383900	-6.002900	3.019000	С	-7.888000	-7.006500	4.201800
С	-3.770500	-6.564400	-0.593000	Н	-8.428400	-7.782100	3.649200
С	-5.549600	-6.161700	3.964400	Н	-7.585600	-7.425500	5.170800
С	-5.325700	-7.629500	-2.182400	C	-8.811100	-5.817300	4.440000
Н	-5.409000	-6.771900	-2.867500	C	-9.880900	-5.532700	3.567500
Н	-4.538000	-8.273600	-2.598900	Н	-10.050500	-6.165000	2.700400
С	-6.647100	-8.383100	-2.130000	С	-10.724000	-4.439400	3.837900
С	-7.184100	-8.973700	-3.292900	Н	-11.557500	-4.210000	3.178900
Н	-6.653700	-8.893300	-4.238100	C	-10.477300	-3.658400	4.980800
С	-8.402500	-9.666000	-3.205600	Н	-11.108300	-2.813400	5.237500
Η	-8.835000	-10.131700	-4.086900	С	-9.394500	-3.996500	5.810500
С	-9.053000	-9.751700	-1.957800	Н	-9.164900	-3.442700	6.717200
Η	-9.993600	-10.281700	-1.845500				

## Table A22. Cartesian coordinates (Å) for calculated geometry of Cd analogue of ${\bf 1}$

С	-0.362100	4.161300	-1.109200
Н	-0.636100	4.662000	-2.031000
С	-0.390900	2.754400	-1.079300
С	-0.889700	1.996200	-2.297500
С	-2.064400	0.100800	-3.164400
Н	-1.230400	-0.340000	-3.738300
Н	-2.590800	0.759300	-3.874400
С	-2.991000	-1.035100	-2.755900
С	-3.673800	-1.777300	-3.746000
Н	-3.532600	-1.521100	-4.792100
С	-4.509600	-2.836400	-3.368300
Н	-5.037100	-3.415300	-4.121800
С	-4.653800	-3.144400	-1.998500
Н	-5.289000	-3.957700	-1.662500
С	-3.945300	-2.374200	-1.068900
Н	-4.010700	-2.573000	-0.002800
С	0.904000	1.946200	2.344000
С	2.078200	0.031200	3.167000
Н	1.244600	-0.411100	3.740100

0	-0.672200	-2.498200	3.458800
0	0.690100	2.422400	3.516600
0	-0.672900	2.496900	-3.459200
0	0.684900	-2.421600	-3.518100
Ν	0.006900	2.053300	0.024200
N	-1.565100	0.863100	-2.018800
N	-3.135500	-1.344700	-1.439000
Ν	1.577500	0.818800	2.039500
N	3.124100	-1.390600	1.406900
N	0.005300	-2.053700	-0.024800
N	1.575500	-0.819800	-2.041000
N	3.124400	1.388200	-1.408700
N	-3.131100	1.347800	1.442000
N	-1.564600	-0.863500	2.019700
С	0.403000	2.730400	1.143300
С	0.370800	4.136100	1.204700
Η	0.643800	4.616600	2.137500
С	0.003600	4.858800	0.055700
Н	0.002400	5.945900	0.067900

Η	2.617400	0.671300	3.884300	С	3.668000	1.874400	-3.703600
С	2.989500	-1.106700	2.730500	Н	3.534200	1.638700	-4.755400
С	3.668100	-1.877100	3.701700	С	4.490400	2.934500	-3.300200
Н	3.534900	-1.641000	4.753600	Н	5.015000	3.534600	-4.039100
С	4.489300	-2.938200	3.298200	С	4.625000	3.215800	-1.923600
Н	5.013400	-3.538700	4.037000	Н	5.249500	4.029000	-1.568000
С	4.623000	-3.219800	1.921600	С	3.921000	2.418600	-1.013500
Н	5.246500	-4.033600	1.565900	Η	3.979700	2.595800	0.056800
С	3.919500	-2.422000	1.011700	С	-3.938500	2.379600	1.072900
Η	3.977500	-2.599400	-0.058700	Н	-4.004500	2.578900	0.006900
С	-0.392100	-2.755000	1.078700	С	-4.644000	3.151400	2.003400
С	-0.364400	-4.161900	1.107900	Н	-5.277400	3.966500	1.668300
Η	-0.637900	-4.662800	2.029600	С	-4.499300	2.842700	3.373000
С	-0.000300	-4.859200	-0.057700	Н	-5.024400	3.422800	4.127200
Н	-0.002300	-5.946300	-0.070400	С	-3.665900	1.781200	3.749500
С	0.366500	-4.136300	-1.206700	Н	-3.524300	1.524400	4.795500
Н	0.638100	-4.616500	-2.140000	С	-2.986100	1.037500	2.758600
С	0.399900	-2.730600	-1.144700	С	-2.062300	-0.101200	3.165900
С	0.900500	-1.946300	-2.345400	Н	-1.227400	0.336900	3.740600
С	2.076000	-0.032000	-3.168500	Н	-2.590500	-0.759100	3.875100
Н	1.242200	0.411600	-3.740400	С	-0.889600	-1.997000	2.297400
Н	2.613700	-0.672200	-3.886800	Cd	1.748400	-0.000900	-0.000700
С	2.988900	1.104700	-2.732300	Cd	-1.749900	0.000300	0.000700

#### Table A23. Cartesian coordinates (Å) for calculated geometry of Hg analogue of ${\bf 2}$

CI CI CI O N N H N H

7.859700	3.952800	-9.111900	Ν	4.362600	5.193700	-8.215000
6.687000	8.043200	-7.384700	С	3.075600	1.530400	-2.975800
-2.317600	1.204500	-0.293600	С	3.985600	1.443000	-1.903500
1.148900	1.628500	-1.548100	Н	3.620400	1.165100	-0.920500
6.335500	2.926700	-6.098700	С	5.344600	1.689000	-2.165200
3.453600	1.805900	-4.249300	Н	6.077600	1.614300	-1.367600
0.853800	0.849800	-3.711200	С	5.738600	2.039500	-3.468000
1.330300	0.643100	-4.583000	Н	6.764700	2.276200	-3.726300
4.199900	2.380600	-6.825000	С	4.762700	2.083100	-4.481800
3.282200	2.089300	-6.501600	С	1.612700	1.337200	-2.694400
-0.605700	-1.389200	-2.101100	С	5.168200	2.496500	-5.873700

С	-0.592100	0.577000	-3.586500
Н	-1.086600	0.904200	-4.508000
Н	-0.984400	1.170700	-2.752700
С	-0.902500	-0.892900	-3.334400
С	-1.492300	-1.703300	-4.322900
Н	-1.724800	-1.283500	-5.297900
С	-1.789700	-3.047500	-4.026600
Н	-2.258100	-3.685000	-4.771700
С	-1.481900	-3.555300	-2.752100
Н	-1.724700	-4.576500	-2.473100
С	-0.879800	-2.687900	-1.821600
Н	-0.622200	-3.022900	-0.821900
С	4.416600	2.727400	-8.240700
Н	4.015000	1.920400	-8.864800
Н	5.497100	2.792800	-8.416700
С	3.754900	4.043600	-8.622700
С	2.557600	4.075200	-9.364100
Н	2.104800	3.144700	-9.695200
С	1.970100	5.315100	-9.678200
Н	1.050300	5.358500	-10.255600
С	2.597500	6.493700	-9.240300
Н	2.185800	7.472800	-9.463600
С	3.797800	6.392100	-8.513500
Н	4.345200	7.269200	-8.177300
0	2.924700	6.277700	1.634800
0	5.369200	5.640100	-5.045800
Ν	4.540900	6.263200	-1.596100
Ν	4.951200	7.156500	0.947700
Η	5.600600	7.326100	0.181100
Ν	6.603000	6.617600	-3.331300
Η	6.556100	6.868100	-2.347000
Ν	7.276200	8.443000	0.962800
Ν	8.577600	5.098600	-5.543900
С	3.531900	6.101300	-0.704200
С	2.285700	5.555700	-1.066400
Н	1.517300	5.452400	-0.309200
С	2.080300	5.168500	-2.401400

C         3.125600         5.327400         -3.3273           H         3.030100         5.046200         -4.3693           C         4.342800         5.874500         -2.8796           C         3.776100         6.519000         0.7253           C         5.489300         6.038700         -3.8493           C         5.344100         7.640900         2.2623           H         5.432300         6.801800         2.9693           H         4.563800         8.299000         2.6713           C         6.667000         8.388600         2.1750           C         7.224300         8.998500         3.3184           H         6.708900         8.998500         3.194           H         8.70100         10.164800         4.0653           C         9.074200         9.746000         1.9402           H         10.014500         10.270700         1.803           C         8.453200         9.110400         0.8526           H         8.900400         9.135400         -0.1373           C         7.794800         6.966500         -4.1303           H         8.331600         7.747700         -3.8517<	Η	1.127600	4.747600	-2.707400
H         3.030100         5.046200         -4.3694           C         4.342800         5.874500         -2.8796           C         3.776100         6.519000         0.7257           C         5.489300         6.038700         -3.8492           C         5.344100         7.640900         2.2625           H         5.432300         6.801800         2.9693           H         4.563800         8.299000         2.6713           C         6.667000         8.388600         2.1750           C         7.224300         8.998500         3.3184           H         6.708900         8.936600         4.2733           C         8.443300         9.684900         3.1994           H         8.891100         10.164800         4.0653           C         9.074200         9.746000         1.9402           H         10.014500         10.270700         1.803           C         8.453200         9.110400         0.8526           H         8.900400         9.135400         -0.1373           C         7.794800         5.789500         -4.3816           C         9.734200         5.435100         -3.4557	С	3.125600	5.327400	-3.327300
C       4.342800       5.874500       -2.8796         C       3.776100       6.519000       0.7257         C       5.489300       6.038700       -3.8492         C       5.344100       7.640900       2.2623         H       5.432300       6.801800       2.9693         H       4.563800       8.299000       2.6713         C       6.667000       8.388600       2.1750         C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2732         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0655         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1375         C       7.794800       6.966500       -4.1305         H       8.331600       7.747700       -3.5817         H       9.845600       6.005800       -2.5378         C       9.734200       5.435100       -3.45557	Н	3.030100	5.046200	-4.369800
C       3.776100       6.519000       0.7257         C       5.489300       6.038700       -3.8492         C       5.344100       7.640900       2.2625         H       5.432300       6.801800       2.9693         H       4.563800       8.299000       2.6713         C       6.667000       8.388600       2.1750         C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2733         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       9.845600       6.005800       -2.5373         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5373	С	4.342800	5.874500	-2.879600
C       5.489300       6.038700       -3.8492         C       5.344100       7.640900       2.2623         H       5.432300       6.801800       2.9693         H       4.563800       8.299000       2.6713         C       6.667000       8.388600       2.1750         C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2733         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       7.473400       7.389300       -5.090         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       9.734200       5.435100       -3.037         C       10.413700       3.646500       -4.943	С	3.776100	6.519000	0.725700
C       5.344100       7.640900       2.2623         H       5.432300       6.801800       2.9693         H       4.563800       8.299000       2.6713         C       6.667000       8.388600       2.1750         C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2733         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       9.074200       9.110400       0.8522         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       7.473400       7.389300       -5.090         C       9.734200       5.435100       -3.4553         H       9.845600       6.005800       -2.5373         C       10.584400       4.350600       -3.037         H       11.366300       4.067400       -3.037         H       11.366300       4.067400       -3.037	С	5.489300	6.038700	-3.849200
H       5.432300       6.801800       2.9693         H       4.563800       8.299000       2.6713         C       6.667000       8.388600       2.1750         C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2733         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5373         C       10.584400       4.350600       -3.037         H       11.366300       4.067400       -3.037         H       11.366300       4.067400       -3.037	С	5.344100	7.640900	2.262500
H4.5638008.2990002.6713C6.6670008.3886002.1750C7.2243008.9985003.3184H6.7089008.9366004.2732C8.4433009.6849003.1994H8.89110010.1648004.0653C9.0742009.7460001.9402H10.01450010.2707001.803C8.4532009.1104000.8526H8.9004009.135400-0.1373C7.7948006.966500-4.1303H7.4734007.389300-5.0907C8.7315005.789500-4.3816C9.7342005.435100-3.4557H9.8456006.005800-2.5373C10.5844004.350600-3.737H11.3663004.067400-3.037C10.4137003.646500-4.943H9.2168003.551700-5.8234H9.2168003.551700-5.8234H9.2168003.551700-6.7720CI-7.859700-3.9528009.1119CI-6.687000-8.0432007.3844CI2.317600-1.2045000.2936O-1.148900-1.6285001.548O-6.335500-2.9267006.098N-3.453600-1.8059004.2493	Н	5.432300	6.801800	2.969300
C       6.667000       8.388600       2.1750         C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2732         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.090         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.037         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234	Н	4.563800	8.299000	2.671300
C       7.224300       8.998500       3.3184         H       6.708900       8.936600       4.2732         C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.037         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234 <t< td=""><td>С</td><td>6.667000</td><td>8.388600</td><td>2.175000</td></t<>	С	6.667000	8.388600	2.175000
H6.7089008.9366004.2732C8.4433009.6849003.1994H8.89110010.1648004.0653C9.0742009.7460001.9402H10.01450010.2707001.803C8.4532009.1104000.8526H8.9004009.135400-0.1373C7.7948006.966500-4.1303H8.3316007.747700-3.5817H7.4734007.389300-5.0907C8.7315005.789500-4.3816C9.7342005.435100-3.4557H9.8456006.005800-2.5373C10.5844004.350600-3.737H11.3663004.067400-3.037C10.4137003.646500-4.943H9.2168003.551700-5.8234H9.2168003.551700-6.7720CI-7.859700-3.9528009.1119CI-6.687000-8.0432007.384CI2.317600-1.2045000.2936O-1.148900-1.6285001.548O-6.335500-2.9267006.098N-3.453600-1.8059004.2493	С	7.224300	8.998500	3.318400
C       8.443300       9.684900       3.1994         H       8.891100       10.164800       4.0653         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844	Н	6.708900	8.936600	4.273200
H       8.891100       10.164800       4.0657         C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8522         H       8.900400       9.135400       -0.1375         C       7.794800       6.966500       -4.1305         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.037         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.384	С	8.443300	9.684900	3.199400
C       9.074200       9.746000       1.9402         H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1375         C       7.794800       6.966500       -4.1305         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.384         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548	Н	8.891100	10.164800	4.065300
H       10.014500       10.270700       1.803         C       8.453200       9.110400       0.8526         H       8.900400       9.135400       -0.1375         C       7.794800       6.966500       -4.1305         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5376         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548 <td>С</td> <td>9.074200</td> <td>9.746000</td> <td>1.940200</td>	С	9.074200	9.746000	1.940200
C       8.453200       9.110400       0.8524         H       8.900400       9.135400       -0.1373         C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5373         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7724         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987 </td <td>Н</td> <td>10.014500</td> <td>10.270700</td> <td>1.803500</td>	Н	10.014500	10.270700	1.803500
H       8.900400       9.135400       -0.1375         C       7.794800       6.966500       -4.1305         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3847         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       3.7117	С	8.453200	9.110400	0.852600
C       7.794800       6.966500       -4.1303         H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5376         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       3.7117	Н	8.900400	9.135400	-0.137500
H       8.331600       7.747700       -3.5817         H       7.473400       7.389300       -5.0907         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3847         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       3.7117	С	7.794800	6.966500	-4.130500
H       7.473400       7.389300       -5.090         C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.037         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       3.7112	Н	8.331600	7.747700	-3.581700
C       8.731500       5.789500       -4.3816         C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5373         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.384         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.098         N       -3.453600       -1.805900       3.7112	Н	7.473400	7.389300	-5.090100
C       9.734200       5.435100       -3.4557         H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3847         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2492	С	8.731500	5.789500	-4.381600
H       9.845600       6.005800       -2.5378         C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0984         N       -3.453600       -1.805900       3.7112	С	9.734200	5.435100	-3.455700
C       10.584400       4.350600       -3.737         H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2492	Н	9.845600	6.005800	-2.537800
H       11.366300       4.067400       -3.037         C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         Cl       -7.859700       -3.952800       9.1119         Cl       -6.687000       -8.043200       7.3844         Cl       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       3.7112	С	10.584400	4.350600	-3.737800
C       10.413700       3.646500       -4.943         H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2497	Н	11.366300	4.067400	-3.037700
H       11.051700       2.808800       -5.206         C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3844         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2492	С	10.413700	3.646500	-4.943700
C       9.395200       4.050700       -5.8234         H       9.216800       3.551700       -6.7720         Cl       -7.859700       -3.952800       9.1119         Cl       -6.687000       -8.043200       7.3844         Cl       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2492         N       -0.853800       -0.849800       3.7112	Н	11.051700	2.808800	-5.206700
H       9.216800       3.551700       -6.7720         CI       -7.859700       -3.952800       9.1119         CI       -6.687000       -8.043200       7.3847         CI       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2497	С	9.395200	4.050700	-5.823400
Cl-7.859700-3.9528009.1119Cl-6.687000-8.0432007.3847Cl2.317600-1.2045000.2936O-1.148900-1.6285001.548O-6.335500-2.9267006.0987N-3.453600-1.8059004.2497N-0.853800-0.8498003.7117	Н	9.216800	3.551700	-6.772000
Cl       -6.687000       -8.043200       7.384'         Cl       2.317600       -1.204500       0.2936'         O       -1.148900       -1.628500       1.548'         O       -6.335500       -2.926700       6.098'         N       -3.453600       -1.805900       4.249'         N       -0.853800       -0.849800       3.711'	Cl	-7.859700	-3.952800	9.111900
Cl       2.317600       -1.204500       0.2936         O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.0987         N       -3.453600       -1.805900       4.2497         N       -0.853800       -0.849800       3.7117	Cl	-6.687000	-8.043200	7.384700
O       -1.148900       -1.628500       1.548         O       -6.335500       -2.926700       6.098         N       -3.453600       -1.805900       4.2493         N       -0.853800       -0.849800       3.7112	Cl	2.317600	-1.204500	0.293600
O         -6.335500         -2.926700         6.098''           N         -3.453600         -1.805900         4.249'           N         -0.853800         -0.849800         3.711'	0	-1.148900	-1.628500	1.548100
N-3.453600-1.8059004.2493N-0.853800-0.8498003.7112	0	-6.335500	-2.926700	6.098700
N -0.853800 -0.849800 3.7112	Ν	-3.453600	-1.805900	4.249300
	Ν	-0.853800	-0.849800	3.711200

Н	-1.330300	-0.643100	4.583000	C	-3.797800	-6.392100	8.513500
Ν	-4.199900	-2.380600	6.825000	Н	-4.345200	-7.269200	8.177300
Н	-3.282200	-2.089300	6.501600	0	-2.924700	-6.277700	-1.634800
Ν	0.605700	1.389200	2.101100	0	-5.369200	-5.640100	5.045800
Ν	-4.362600	-5.193700	8.215000	Ν	-4.540900	-6.263200	1.596100
С	-3.075600	-1.530400	2.975800	Ν	-4.951200	-7.156500	-0.947700
С	-3.985600	-1.443000	1.903500	Н	-5.600600	-7.326100	-0.181100
Н	-3.620400	-1.165100	0.920500	Ν	-6.603000	-6.617600	3.331300
С	-5.344600	-1.689000	2.165200	Н	-6.556100	-6.868100	2.347000
Н	-6.077600	-1.614300	1.367600	Ν	-7.276200	-8.443000	-0.962800
С	-5.738600	-2.039500	3.468000	Ν	-8.577600	-5.098600	5.543900
Н	-6.764700	-2.276200	3.726300	C	-3.531900	-6.101300	0.704200
С	-4.762700	-2.083100	4.481800	C	-2.285700	-5.555700	1.066400
С	-1.612700	-1.337200	2.694400	Н	-1.517300	-5.452400	0.309200
С	-5.168200	-2.496500	5.873700	C	-2.080300	-5.168500	2.401400
С	0.592100	-0.577000	3.586500	Н	-1.127600	-4.747600	2.707400
Н	1.086600	-0.904200	4.508000	C	-3.125600	-5.327400	3.327300
Н	0.984400	-1.170700	2.752700	Н	-3.030100	-5.046200	4.369800
С	0.902500	0.892900	3.334400	C	-4.342800	-5.874500	2.879600
С	1.492300	1.703300	4.322900	C	-3.776100	-6.519000	-0.725700
Н	1.724800	1.283500	5.297900	C	-5.489300	-6.038700	3.849200
С	1.789700	3.047500	4.026600	C	-5.344100	-7.640900	-2.262500
Н	2.258100	3.685000	4.771700	Н	-5.432300	-6.801800	-2.969300
С	1.481900	3.555300	2.752100	Н	-4.563800	-8.299000	-2.671300
Н	1.724700	4.576500	2.473100	C	-6.667000	-8.388600	-2.175000
С	0.879800	2.687900	1.821600	C	-7.224300	-8.998500	-3.318400
Н	0.622200	3.022900	0.821900	Н	-6.708900	-8.936600	-4.273200
С	-4.416600	-2.727400	8.240700	C	-8.443300	-9.684900	-3.199400
Н	-4.015000	-1.920400	8.864800	Н	-8.891100	-10.164800	-4.065300
Н	-5.497100	-2.792800	8.416700	C	-9.074200	-9.746000	-1.940200
С	-3.754900	-4.043600	8.622700	Н	-10.014500	-10.270700	-1.803500
С	-2.557600	-4.075200	9.364100	C	-8.453200	-9.110400	-0.852600
Н	-2.104800	-3.144700	9.695200	Н	-8.900400	-9.135400	0.137500
С	-1.970100	-5.315100	9.678200	C	-7.794800	-6.966500	4.130500
Н	-1.050300	-5.358500	10.255600	Н	-8.331600	-7.747700	3.581700
С	-2.597500	-6.493700	9.240300	Н	-7.473400	-7.389300	5.090100
Н	-2.185800	-7.472800	9.463600	C	-8.731500	-5.789500	4.381600

Η	-4.345200	-7.269200	8.177300
0	-2.924700	-6.277700	-1.634800
0	-5.369200	-5.640100	5.045800
N	-4.540900	-6.263200	1.596100
Ν	-4.951200	-7.156500	-0.947700
Η	-5.600600	-7.326100	-0.181100
N	-6.603000	-6.617600	3.331300
Н	-6.556100	-6.868100	2.347000
Ν	-7.276200	-8.443000	-0.962800
N	-8.577600	-5.098600	5.543900
С	-3.531900	-6.101300	0.704200
С	-2.285700	-5.555700	1.066400
Η	-1.517300	-5.452400	0.309200
С	-2.080300	-5.168500	2.401400
Η	-1.127600	-4.747600	2.707400
С	-3.125600	-5.327400	3.327300
Η	-3.030100	-5.046200	4.369800
С	-4.342800	-5.874500	2.879600
С	-3.776100	-6.519000	-0.725700
С	-5.489300	-6.038700	3.849200
С	-5.344100	-7.640900	-2.262500
Η	-5.432300	-6.801800	-2.969300
Η	-4.563800	-8.299000	-2.671300
С	-6.667000	-8.388600	-2.175000
С	-7.224300	-8.998500	-3.318400
Η	-6.708900	-8.936600	-4.273200
С	-8.443300	-9.684900	-3.199400
Η	-8.891100	-10.164800	-4.065300
С	-9.074200	-9.746000	-1.940200
Η	-10.014500	-10.270700	-1.803500
С	-8.453200	-9.110400	-0.852600
Η	-8.900400	-9.135400	0.137500
С	-7.794800	-6.966500	4.130500
Η	-8.331600	-7.747700	3.581700
Η	-7.473400	-7.389300	5.090100
С	-8.731500	-5.789500	4.381600

С	-9.734200	-5.435100	3.455700
Η	-9.845600	-6.005800	2.537800
С	-10.584400	-4.350600	3.737800
Η	-11.366300	-4.067400	3.037700
С	-10.413700	-3.646500	4.943700
Η	-11.051700	-2.808800	5.206700
С	-9.395200	-4.050700	5.823400
Η	-9.216800	-3.551700	6.772000
Hg	6.740400	5.409700	-7.258800
Hg	0.000000	0.000000	0.000000

### Chapter 6

Identification code	1	2	3
Empirical formula	$C_{56}H_{40}Au_2Cl_6P_2$	$C_{54}H_{38}Au_2P_2$	$C_{57}H_{38}Au_2P_2$
Formula weight	1381.45	1142.71	1142.78
Temperature	293(2) K	150(2) K	293(2) K
Wavelength	0.71073	0.71073	1.54184
Crystal system, space group	Monoclinic P 2 <sub>1</sub> /c	Triclinic, Pī	Orthorhombic, P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Unit Cell Parameter			
a/Å	8.6562(3)	6.9132(4)	11.2233(5)
$b/{ m \AA}$	16.4717(6)	11.3888(7)	16.4071(7)
c/Å	18.2662(7)	14.3364(9)	31.2057(17)
α/	90	75.119(5)	90
β/°	102.713(4)	84.566(5)	90
γ/ <sup>°</sup>	90	81.231(5)	90
V/Å <sup>3</sup>	2540.59(16)	1076.32(12)	5746.3(5)
$Z, d_{\text{calcd}}(\text{mg/m}^3)$	2, 1.806	1, 1.763	4, 1.321
$\mu/ \mathrm{mm}^{-1}$	6.184	6.918	10.194
F(000)	1332	550	2884
θ range	3.14 to 32.26	2.945 to 24.998	3.04 to 71.40
Reflections collected /	29270 / 8436	9150 / 9150	15036 / 9356
unique	[R(int) = 0.0545]	[R(int) = 0.0640]	[R(int) = 0.1141]
Max. and min.	1.00000 and 0.58516	1.00000 and	1.00000 and 0.60839
transmission		0.66180	
Data / restraints /	8436 / 0 / 298	9150 / 0 / 262	9356 / 348 / 511
parameters			
GOF, F <sup>2</sup>	1.072	1.194	0.897
R1, wR2 [I>2σ(I)]	R1 = 0.0416,	R1 = 0.0789	R1 = 0.0849
	wR2 = 0.0938	wR2 = 0.2336	wR2 = 0.1859
R1, wR2 (all data)	R1 = 0.0664,	R1 = 0.1009,	R1 = 0.1270,
	wR2 =0.1055	wR2 = 0.2629	wR2 = 0.2122
CCDC Number	1405508	1405509	1405510

**Table A24.** Crystallographic parameters of complexes 1, 2 and 3.

Bond Distances	1	2	3		
Au(1)-P(1)	2.2808(12)	2.277(5)	2.271(7)		
Au(1)-C(1)	2.004(5)	2.03(3)	1.94(3)		
Au(2)-C(3)			1.94(3)		
Au(2)-P(2)			2.282(6)		
C(1)-C(2)	1.199(6)	1.26(3)	1.21(3)		
C(3)-C(4)			1.23(3)		
	Bond Angles				
C(1)-Au(1)-P(1)	175.12(15)	176.8(6)	173.0(6)		
C(3)-Au(2)-P(2)			175.7(9)		
C(2)-C(1)-Au(1)	173.7(4)	172.4(17)	168.1(19)		
C(4)-C(3)-Au(2)			169(2)		

Table A25. Bond distances and Bond angles of complexes 1, 2 and 3.



#### DFT optimized structure

Figure A1. Optimized structure of 1.

#### **Optimized Cartesian coordinates**

Au	-0.40983605	-0.34426229	0.00000000
Р	-0.48137405	-2.69181029	-0.03063600
С	-0.30748405	4.29629271	-0.01639200
С	-0.30690505	5.02546371	1.20560900
С	2.29742895	-2.81866829	0.20520700
Н	2.27515995	-1.85092629	-0.28819000
С	-1.73178405	-2.66441129	-2.52495200
Н	-2.15890405	-1.72724229	-2.17873700
С	-0.32304005	4.35786271	2.46770800
Н	-0.33450305	3.27300771	2.46815000
С	-0.84344905	-3.37369029	-1.69972000
С	-3.69731405	-4.41001529	2.84161200
Н	-4.44660805	-4.80032529	3.52417900
С	-0.28385405	4.30149571	-2.50144600
Н	-0.29533305	3.21694471	-2.47753300
С	-0.27441405	-4.56649329	-2.17013100
Н	0.42838095	-5.11640429	-1.55231400
С	-0.35651505	1.64602371	0.00702600
С	1.09369195	-3.48196429	0.49339700
С	2.35707095	-5.28240529	1.51809400

Н	2.37695395	-6.23654329	2.03675400
С	-0.33146805	2.87450371	-0.00153000
С	-0.28755705	4.99752871	-1.25468600
С	-0.30809605	6.48308071	3.62855300
Н	-0.30877005	7.03309371	4.56579500
С	1.13253495	-4.71677029	1.15861600
Н	0.20947295	-5.23171229	1.40575700
С	-1.77168405	-3.39750529	1.07322500
С	-0.32342305	5.06185971	3.64449600
Н	-0.33532405	4.53321771	4.59388900
С	-3.42738105	-5.07644129	1.64511500
Н	-3.96565805	-5.98574329	1.39369700
С	-0.59862705	-5.04604729	-3.44082300
Н	-0.14904005	-5.96813129	-3.79775700
С	-3.01054905	-3.23502829	3.15458700
Н	-3.22485305	-2.70624829	4.07853600
С	3.55010795	-4.62194329	1.21916000
Н	4.50119395	-5.06196229	1.50466700
С	-2.05613905	-2.72690529	2.27379700
Н	-1.53786405	-1.80180029	2.51054400
С	3.51859695	-3.38977729	0.56283600
Н	4.44300195	-2.86612029	0.33823100
С	-2.46932805	-4.57429929	0.76245200
Н	-2.27428805	-5.09319229	-0.17083800
С	-1.49067005	-4.34157129	-4.25068800
Н	-1.73778005	-4.71476029	-5.24030600
С	-2.05660505	-3.15037129	-3.79092300
Н	-2.74249405	-2.59214129	-4.42114000
С	-0.27541505	7.16543571	-0.04871600
С	-0.27169405	6.43618371	-1.27082700
С	-0.25375405	7.10369971	-2.53295400
Н	-0.24256605	8.18851671	-2.53339900
С	-0.29252905	7.16025071	2.43621500
Н	-0.28089005	8.24484171	2.41231200
С	-0.26680605	9.81601271	-0.08398800
С	-0.26800905	8.58738471	-0.06570600
С	-0.29092905	6.46418771	1.18947400

C	-0.26561605	4.97857071	-3.69379900
Н	-0.26246705	4.42847171	-4.63099400
С	-0.25055105	6.39972971	-3.70975100
Н	-0.23648805	6.92839071	-4.65911400
Au	-0.29528405	11.80646671	-0.12151400
Р	-0.35508405	14.15398371	-0.16944600
С	-3.14160805	14.12855871	-0.02440300
Н	-2.99480305	13.20959471	0.53640100
С	1.14856895	14.29587071	2.17751000
Н	1.57781595	13.36000871	1.83045600
С	0.14906795	14.92814471	1.42011700
С	2.38951495	15.94010771	-3.45874200
Н	3.02823395	16.34581171	-4.23791900
С	-0.41908005	16.12068371	1.89275200
Н	-1.20510705	16.61133671	1.32738200
С	-2.02998405	14.82296771	-0.52934200
С	-3.52786605	16.46087771	-1.50962000
Н	-3.67531505	17.36348871	-2.09557000
С	-2.23342505	15.99109671	-1.27893500
Н	-1.38580405	16.52884171	-1.69167500
С	0.75029595	14.88869071	-1.44167200
С	2.20016395	16.64876071	-2.27105600
Н	2.69102195	17.60631671	-2.12300200
С	0.01446895	16.67534571	3.09839200
Н	-0.43466805	17.59643871	3.45845600
С	1.76587395	14.70369771	-3.63897000
Н	1.91922295	14.14262871	-4.55597500
С	-4.62717305	15.77130471	-0.99560100
Н	-5.63317705	16.13657771	-1.18056300
С	0.95411495	14.17663871	-2.63479100
Н	0.48623495	13.20531671	-2.76958200
С	-4.43215805	14.60496171	-0.25263800
Н	-5.28409805	14.05788071	0.13991600
С	1.38483695	16.12745671	-1.26488100
Н	1.25292895	16.68032871	-0.34007600
С	1.01535795	16.04646071	3.84081200
Н	1.34734595	16.47790071	4.78066900

С	1.58155995	14.85634871	3.37880900
Н	2.35272695	14.35701971	3.95776600
Н	2.35272695	14.35701971	3.95776600



Figure A2. Optimized structure of 2.

#### **Optimized Cartesian coordinates**

С	-0.90163931	0.57377048	0.00000000
С	-3.71999431	1.02268148	0.00156400
С	-4.07744531	-1.40361252	0.03667100
Н	-3.67869231	-2.41572952	0.04984900
С	-3.18530531	-0.31999952	0.01901400
С	-1.77281531	-0.50160952	0.01761200
Н	-1.37344231	-1.51149552	0.03076000
С	-2.79738431	2.11680748	-0.01623000
Н	-3.19419531	3.12904148	-0.02922300
С	0.51200469	0.39085548	-0.00139100
С	-1.44767931	1.90720348	-0.01704700
Н	-0.75644831	2.74376648	-0.03051400
Au	3.71166469	0.04690048	-0.00029300
Au P	3.71166469 6.04926169	0.04690048 -0.18290452	-0.00029300 0.00701100
Au P C	3.71166469 6.04926169 1.73187669	0.04690048 -0.18290452 0.25630748	-0.00029300 0.00701100 -0.00278800
Au P C C	3.71166469 6.04926169 1.73187669 6.88484569	0.04690048 -0.18290452 0.25630748 0.89993548	-0.00029300 0.00701100 -0.00278800 -1.22201000
Au P C C C	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500
Au P C C C H	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469 6.50443169	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748 4.01073648	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500 -2.56418300
Au P C C C H C	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469 6.50443169 6.64072169	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748 4.01073648 0.24187048	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500 -2.56418300 4.04584100
Au P C C C H C H	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469 6.50443169 6.64072169 6.07161869	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748 4.01073648 0.24187048 0.02341248	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500 -2.56418300 4.04584100 4.94451600
Au P C C C H C H C	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469 6.50443169 6.64072169 6.07161869 6.33251869	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748 4.01073648 0.24187048 0.02341248 2.16700148	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500 -2.56418300 4.04584100 4.94451600 -1.47147500
Au P C C C H C H C H	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469 6.50443169 6.64072169 6.07161869 6.33251869 5.41972269	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748 4.01073648 0.24187048 0.02341248 2.16700148 2.46722948	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500 -2.56418300 4.04584100 4.94451600 -1.47147500 -0.96438500
Au P C C C H C H C H C H	3.71166469 6.04926169 1.73187669 6.88484569 6.94212469 6.50443169 6.64072169 6.07161869 6.33251869 5.41972269 6.62068269	0.04690048 -0.18290452 0.25630748 0.89993548 3.03470748 4.01073648 0.24187048 0.02341248 2.16700148 2.46722948 -1.88822752	-0.00029300 0.00701100 -0.00278800 -1.22201000 -2.37703500 -2.56418300 4.04584100 4.94451600 -1.47147500 -0.96438500 -0.37472200

Н	4.96365069	-2.23598152	-1.71738900
С	6.81398569	0.24041348	1.62446000
С	8.04643169	0.51128348	-1.90590200
Н	8.47541669	-0.47145752	-1.73759900
С	8.10140969	2.64339948	-3.05031100
Н	8.57073369	3.31659248	-3.76179900
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С	7.77327169	-2.44461552	0.19969100
Н	8.35319669	-1.87463452	0.91858100
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Н	7.74004469	-5.49289052	-1.31511300
С	8.65002269	1.38158448	-2.81570700
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С	7.91001869	0.81645948	4.13989400
Н	8.33316869	1.04401448	5.11397900
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С	-8.28179831	-0.76909952	0.03730400
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Н	-7.81022631	1.31624748	0.00699500
С	-6.38592931	-2.31199352	0.05505500
Н	-5.98899731	-3.32417752	0.06833600
С	-9.69560931	-0.58746452	0.03661100
С	-7.73562031	-2.10251352	0.05495200
Н	-8.42684031	-2.93909452	0.06793300
С	-10.91587031	-0.45646652	0.03541200

Au	-12.89737831	-0.26413252	0.02643700
Р	-15.23778631	-0.06368452	0.00855700
С	-16.02188631	-0.56407352	1.59438300
С	-15.99386731	-2.02822752	3.53061200
Н	-15.52042731	-2.82583252	4.09531800
С	-15.92583631	-2.05431052	-3.51229500
Н	-15.38606431	-2.19945652	-4.44331300
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Н	-14.50517431	-2.05503252	1.97504600
С	-15.82673031	1.64919948	-0.30850200
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Н	-14.15756431	2.51304548	0.75813600
С	-16.03601631	-1.10196652	-1.28173700
С	-17.19051831	0.04023248	2.08193900
Н	-17.65418031	0.85273648	1.53136800
С	-17.16017631	-1.42602852	4.00728700
Н	-17.59918231	-1.75642352	4.94419100
С	-15.35177531	-1.29521952	-2.49290400
Н	-14.36555431	-0.86049752	-2.63036400
С	-16.99204431	1.92414048	-1.03948000
Н	-17.57403431	1.11196148	-1.46348500
С	-16.65467031	4.29799048	-0.70896800
Н	-16.97349631	5.32399648	-0.86808400
С	-17.75526131	-0.39124252	3.28355800
Н	-18.65743631	0.08585948	3.65532500
С	-17.29517331	-1.69425752	-1.10315000
Н	-17.82817831	-1.57003352	-0.16575700
С	-17.18213531	-2.63623752	-3.32983700
Н	-17.62478631	-3.23415252	-4.12117900
С	-17.40198231	3.24409948	-1.23714000
Н	-18.30313431	3.44695948	-1.80857000
С	-17.86351431	-2.45749552	-2.12472900
Н	-18.83682931	-2.91583752	-1.97518600
С	-15.49051531	4.03168348	0.01510600
Н	-14.89911431	4.84809248	0.41878000



Figure A3. Optimized structure of 3.

#### **Optimized Cartesian coordinates**

Au	-3.55305464	0.41800642	0.00000000
Au	2.71055636	0.07971042	0.35663200
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Р	-4.52425164	-1.68248358	0.40424300
С	-2.45859664	4.85085142	-0.72866000
С	-3.57422564	5.61923242	-1.02722700
Н	-4.53836164	5.12708542	-1.10319600
С	-3.48299264	7.01928942	-1.22631000
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Н	-2.19994364	8.73429242	-1.26748400
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Н	4.67669536	7.31875142	0.08322100
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С	2.48052836	4.69995742	0.03720700
С	0.15193736	7.56190342	-0.70282700
Н	0.20610236	8.63975742	-0.84086000

С	0.01126736	4.78421042	-0.34603800
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С	2.48979536	3.28209142	0.17605100
С	2.55572336	2.06129542	0.27944000
С	2.99660736	-2.98007458	2.07528100
С	2.33087836	-2.31798058	3.12032500
Н	1.80818036	-1.38607258	2.92191200
С	2.35681636	-2.84005458	4.41434900
Н	1.84454536	-2.31549658	5.21550300
С	3.05482136	-4.02048358	4.67966200
Н	3.08277536	-4.42076558	5.68897100
С	3.72926136	-4.67680058	3.64861200
Н	4.28319136	-5.58849558	3.85300400
С	3.70316436	-4.16013358	2.35178400
Н	4.24300236	-4.66953258	1.55948300
С	4.39041936	-2.87863458	-0.49024100
С	5.57550236	-2.13268258	-0.37827300
Н	5.57876736	-1.20584258	0.18869700
С	6.74294536	-2.56778458	-1.00425900
Н	7.65215236	-1.98101858	-0.91331500
С	6.73787336	-3.74422858	-1.75707900
Н	7.64558536	-4.07752558	-2.25164600
С	5.56147736	-4.48444658	-1.88234900
Н	5.55017136	-5.39481058	-2.47471800
С	4.39110936	-4.05593358	-1.25250400
Н	3.47918636	-4.63349058	-1.36507200
С	1.46837136	-3.09324158	-0.41732000
С	1.04315836	-4.38118158	-0.05615900
Н	1.54349236	-4.91589958	0.74530300
С	-0.03285264	-4.97682258	-0.71612600
Н	-0.35715864	-5.97194258	-0.42559300

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Н	-1.53805664	-4.75324158	-2.24504600
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С	0.79155536	-2.40790958	-1.43979200
Н	1.09645836	-1.40045158	-1.70861800
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Н	-0.57588564	-3.26310658	2.92082000
С	-2.31663664	-2.58787058	1.85303400
Н	-1.75202564	-1.93063458	1.19780300
С	-4.56893364	-2.78335758	-1.06995500
С	-4.58461964	-4.18243458	-0.96538500
Н	-4.53761364	-4.65505458	0.01076500
С	-4.64942964	-4.97312558	-2.11448600
Н	-4.66543764	-6.05552458	-2.02285900
С	-4.69229964	-4.37552558	-3.37647200
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Н	-4.69169664	-2.51346358	-4.46696700
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Н	-4.56872364	-1.10795658	-2.43195400
С	-6.27689164	-1.51639458	0.94114800
С	-7.28133464	-2.41532758	0.55361200
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Н	-9.36248364	-2.94283858	0.69697400
С	-8.90879964	-1.17742158	1.84921300
Н	-9.92911464	-1.04411558	2.19682200
С	-7.91461664	-0.27567258	2.23536100
Н	-8.15781464	0.56282442	2.88109500

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Н -5.84133564 0.27718842 2.06597600