Characterization of Novel d10 Metal Ion Complexes of Multidentate Ligands by X-ray Crystallography and 1H NMR Spectroscopy

Pei Wang

College of William and Mary
Characterization of Novel $d^{10}$ Metal Ion Complexes of Multidentate Ligands by X-ray Crystallography and $^1$H NMR Spectroscopy

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelor of Science with Honors in Chemistry from The College of William and Mary in Virginia

by

Pei Wang

Accepted for Honors

Deborah C. Bebout, Director, Chemistry

John C. Poutsma, Chemistry

Nicole M. Santiago, Art and Art History

Williamsburg, VA
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Abstract

Hg(II) complexes with tris (6-methyl-2-pyridylmethyl)-amine (L₁), 6-methyl-N(2-mercaptoethyl)picolylamine (HL₂) and 2,6-bis(pyridyl-2-methyliomethyl)pyridine (HL₃) have been synthesized and characterized by measurements of ¹H NMR. The molecular structures of [Hg(L₁)(NO₃)₂] (1) and [Hg₃(HL₂)₃](ClO₄)₃ (3) were determined by single-crystal X-ray structure analysis and a disordered crystal was obtained from crystallization of L₃ with CdCl₂. In complex 1, the Hg(II) metal center has three strong bonds to ligand nitrogen, a weak bond to the third pyridyl, and two bidentate nitrates. Complex 3 contains Hg(II) coordinated with the NN'S donor set from ligand HL₂ with the thiolates of each ligand bridging to a second metal center. 3 forms a novel trinuclear complex with a three-fold symmetric (HgS)₃ core. Variable temperature ¹H NMR of 3 showed slow intramolecular ligand exchange on the J(¹H¹H) time scale. Further analysis and additional studies at higher temperature of 3 are planned to study dissociation or alternative oligomers.
Characterization of Novel d\textsuperscript{10} Metal Ion Complexes of Multidentate Ligands by X-ray Crystallography and \textsuperscript{1}H NMR Spectroscopy
Introduction

Metals in trace amounts are essential to the well being of human life. Some of the essential metals include iron, zinc, copper, manganese, calcium, cobalt, molybdenum, sodium and potassium.¹ In physiological systems these usually exist in ion forms and coordinate with proteins for important biophysical functions that are vital to the functions of a cell such as various metabolic and signaling pathways in the organism. For example, iron porphyrin compounds such as hemoglobin and myoglobin are used in oxygen transfer and storage in the blood and muscle tissues.² Metal ions are often proteins cofactors that mediate redox reactions involved in cellular respiration. However, concentrations of these vital metals higher than the biological acceptable amount become detrimental to human and animals.

It is widely known that proteins are an essential part of life. Without them, the basic operations of life, such as metabolism and anabolism, could not be performed. Metals, especially the reactive transition metals, interact strongly with protein nitrogen, oxygen, sulfur and phosphate donor groups. A native protein adopts a specific structure for the function it is suppose to perform. As a result, the protein has a specific selectivity for binding substances tailored to the demands of its cellular location. It is therefore vital for proteins to retain their native tertiary structure for correct substrate-active site interaction to occur. Heavy metals, such as Cd(II) and Hg(II) in the zinc triad, change native proteins’ conformations and alter their reactivity to cause deleterious effects.

Therefore, a detailed investigation of how metals can bind to and interact with proteins is essential to understand both the toxicity of the metals and physiological impact of heavy metal poisoning. Studying protein metal coordination remains complicated because many factors influence the detrimental effect of heavy metal poisoning. Some of these factors include, concentration ratio of the metal to protein, exposure time of the heavy metal, the metal-containing species and the route of exposure.³

Humans and other organisms are exposed to a variety of chemical and physical forms of mercury. All forms of mercury are recognized as toxic, including elemental vapor mercury, inorganic mercurous (Hg(I)) and mercuric (Hg(II)) salts, and organic mercuric compounds.¹ Atmospheric deposition such as volcanoes and geologic deposits are the main source for mercury distribution and human activities such as coal burning and chemical factories are increasing the amount of mercury cycling in the environment.⁴ Mercurous and mercuric ions exhibit their toxicity through strong molecular interactions with reduced, soft and easily polarizable sulfur atoms. Although Hg(II)-thiolate bonds are extremely thermodynamically stable, their highly labile and fast ligand exchange causes dispersion in Hg(II) to other random thiol ligands causing widespread alterations to essential biochemical processes.⁵

The widespread dispersal of cadmium, either naturally or industrially, in the environment is also deleterious to higher organisms. Cadmium toxicity is closely linked

³ D. C. Bebout, personal communication.

with oxidative stress in mammalian cells.\textsuperscript{6} Cadmium also causes transition metal homeostasis deregulation and blocks the trace metal pathways.\textsuperscript{6} Both zinc and cadmium form divalent $d^{10}$ cations. Cadmium(II) can bind to a large diversity of bio-molecules with S, N, or O functional groups.

Further study of Cd(II) and Hg(II) in biologically relevant environments is necessary to improve chelation therapy agents and understanding of heavy metal toxicological profiles. Since proteins are complicated biopolymers whose behaviors are hard to predict, synthetic complexes of small organic molecules containing sites similar and parallel to protein metal-binding sites were used. These particular complexes can offer an orderly and systematic model of protein-ligand-like interactions. Complexes were grown as well-ordered crystals and then an array of spectroscopic and X-ray crystallographic techniques were used to obtain coordination geometry, ligation and other physical properties.

Unfortunately, solution-state coordination chemistry studies of the divalent $d^{10}$ metal ions of interest present many challenges. With simple ligands, complexes of Cd(II) and Hg(II) are plagued by rapid intermolecular ligand exchange, facile intramolecular isomerization and complex speciation. In contrast, multidentate ligands have been found to provide slow-exchange binding environments facilitating further studies of the coordination geometry of these divalent metals. A solution-state investigation of the complexation of Hg(II) by a tridentate ligand bis[(2-pyridy)methyl]amine (BMPA) showed a rapid equilibrium exchange between the isomeric trigonal prismatic and facial

octahedral forms of the complex.\textsuperscript{7} Significantly, d\textsuperscript{10} metal ions lack crystal field stabilization energy, paramagnetic, and d-d absorption spectra. However, since Hg(II) and Cd(II) are diamagnetic and possess a non-radioactive spin I=1/2 isotopes with high abundance, Nuclear Magnetic Resonance or NMR has emerged as one of the most important and versatile tools in characterization of their coordination complexes. NMR can provide \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{15}N, \textsuperscript{199}Hg and \textsuperscript{113}Cd chemical shifts as a function of magnetic environment as well as $J(\textsuperscript{199}Hg\textsuperscript{1}H)$ and $J(\textsuperscript{111/113}Cd\textsuperscript{1}H)$. Studies have shown that \textsuperscript{113}Cd NMR is a powerful structural probe of oxygen-rich zinc and calcium protein metal binding site.\textsuperscript{8} Table 1 contains the natural abundance, spin state and relative receptivity of Cd and Hg. Not only does NMR provide chemical shift information related to the magnetic environment of an NMR active nucleus, it also provides coupling constants, which documents interactions between specific nuclei and can often be related back to the complex’s geometric parameters.

As shown in Table 1, \textsuperscript{199}Hg and \textsuperscript{113}Cd have comparable natural abundances, but \textsuperscript{199}Hg has larger chemical shift dispersion with shorter relaxation times. Because of the relative better sensitivity and versatility of \textsuperscript{199}Hg, one-dimensional NMR structural characterization of Hg (II) compound could be potentially more successful. This tool has been successfully used as a probe for understanding the structural and molecular mechanism involved in the bacterial detoxification process using proteins such as MerR and MerP.\textsuperscript{5} The genes are only expressed in the presence of Hg(II). \textsuperscript{199}Hg chemical shift is sensitive of the to the coordination sphere such as the nature of the donor ligands,

coordination number and the geometry of the metal center. The MerR protein exists in a dimer form and its binding site contains a total of six cysteines. This provides a high binding affinity for Hg(II) for efficient transformation of the toxic Hg(II) to the significantly less toxic Hg(0) as a evolutionary way of bacterial mercury resistance.\(^5\)

\(^{199}\)Hg chemical shifts from \(\delta = -179\) to -320 ppm and from \(\delta = -830\) to -950 ppm indicate thiolate ligand to Hg(II) ratio of 3:1 and 2:1 respectively. This lead to the discovery of a \([\text{LHg}_2(\text{L-H})]\) that contains a dithiolated-Hg(II) metal center. Furthermore \(^{199}\)Hg combined with \(^{199m}\)Hg perturbed angular correlation (PAC) spectroscopy characterized the mechanistic steps of speciation of the complex under different pH conditions. As mentioned before, a novel dithiolate-Hg(II) complex was found at high pH conditions in the interior of a three-stranded coiled coil \(\text{L}_3\) and equilibrates into a trigonal thiolate-Hg(II) complex at even higher pH with the deprotonation of the third ligand. This gives crucial insights and can be extended to further understanding of the structural, kinetic, and thermodynamic details of the interaction between Hg(II) and proteins complex and the molecular basis of Hg(II) toxicity and the detrimental physiologically effects of Hg(II).\(^5\)

**Table 1:** Properties of NMR-active nuclei of Cd and Hg

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(^{111})Cd</th>
<th>(^{115})Cd</th>
<th>(^{199})Hg</th>
<th>(^{201})Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>3/2</td>
</tr>
<tr>
<td>Natural abundance</td>
<td>12.75</td>
<td>12.26</td>
<td>16.84</td>
<td>13.22</td>
</tr>
<tr>
<td>Relative receptivity</td>
<td>6.97</td>
<td>7.59</td>
<td>5.42</td>
<td>1.08</td>
</tr>
<tr>
<td>Chemical shift range (ppm)</td>
<td>900</td>
<td>5000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Characterization of potentially labile systems by NMR often requires variable temperature studies. If elevated temperatures cause a rapid exchange process, a mole fraction weighted average signal is detected. If the process occurs more slowly than the
NMR time scale at lower temperatures, different resonances for the nuclear environments become apparent.\textsuperscript{3} VT NMR therefore becomes an important tool for the detections of any intramolecular or intermolecular exchanges that might occur under normal physiological conditions.

Another common and straightforward way to study the coordination chemistry of metal-ligand complexes involves X-ray crystallography. While it is very difficult to obtain X-ray quality crystals of a protein-metal complex, it is feasible, under the right conditions, for a smaller organic molecule to crystallize with the heavy metal. The regularly repeating array of atoms or molecules in a crystal is required for X-ray crystallography. Using the principles of symmetry analysis, the smallest repeating unit cell can be analyzed and used to represent the larger 3-D crystal in repeating patterns. The single crystal is positioned within the X-ray beam and rotated to produce a series of diffraction images.\textsuperscript{9} Using sophisticated software, the diffraction images are converted to electron density maps, which allow determination of the mean atomic positions in the crystal.

Several multidentate ligands were synthesized and studied with heavy metals. The ligands provided nitrogen donors, sulfur donors or both for coordinating to heavy metals. \textbf{L}_1 or tris(6-methyl-2-pyridylmethyl)amine (Figure 1) can be a representative model of a protein metal binding site that consists of nitrogen containing residues such as lysine or histidine. A multidentate ligand such \textbf{L}_1 forms chelated complexes with much less potential to exchange. Coordination of \textbf{L}_1 with various other metals such as Cu(I),

\textsuperscript{9} R. D. Pike, personal communication.
Cu(II), and Fe(II) has been studied before.\textsuperscript{10} \textbf{L}_{1} coordinating with Cu(II) combined with the negative oxalate ion generates a six coordinated octahedron complex, which can easily dimerize by controlling the proper mole ratio of the complex squaric acid.\textsuperscript{11} Coordination of \textbf{L}_{1} with other counterions such as Cl was studied before.\textsuperscript{8} A potentially tetradentate ligand, 3- and 4-coordinate binding modes of \textbf{L}_{1} have been found in structurally characterized complexes of HgCl\textsubscript{2}.\textsuperscript{8} Two structures were characterized based on plausible information for the prevalence at high or low metal to ligand concentration. Hg(II) maybe unique in the ways it makes strong bonds to nitrogen and yet has facile ligand exchange.\textsuperscript{11}

![Diagram of \textbf{L}_{1}](image)

\textbf{Figure 1} Tris (6-methyl-2-pyridylmethyl)-amine (\textbf{L}_{1})

\textsuperscript{10} J. F. Bush. \textit{Honors Thesis}, The College of William and Mary \textbf{1998}.
The related potentially tridentate ligand 6-methyl-N-(2-mercaptoethyl)picolylamine (HL$_2$) was also investigated (Figure 2). This is a tridentate ligand containing one pyridyl group, an amino group and a thiol group, which can be deprotonated to form a thiolate. This ligand offers a cysteine-like metal binding group. The methyl group on the pyridyl ring provides additional steric hindrance for comparison with previous coordination studies of N-(2-mercaptoethyl)picolylamine (MEPA). A new mercuric perchlorate complex of HL$_2$ was structurally characterized and studied using Variable Temperature $^1$H NMR for investigation of possible intermolecular or intramolecular metal ligand exchange.

![Figure 2 6-methyl-N-(2-mercaptoethyl)picolylamine (HL$_2$)](image)

The third ligand studied was 2,6-bis[[2-pyridylmethyl]thio]methyl]pyrdine or N3S2 (Figure 3). This ligand, which contains three pyridine groups and two thioether groups, is unbranched and potentially pentadentate. More similar to an actual protein,
this could be modeled after proteins that contains an active center with methionine. A CdCl$_2$ complex of $L_3$ was isolated.

![Image of $L_3$]

**Figure 3** 2,6-Bis(pyridyl-2-methylthiomethyl)pyridine ($L_3$)

Reported here are the syntheses of the three ligands with Hg and Cd metal complexes as well as the results of spectroscopic studies, and the metal complexes. The novel complexes and their coordination were also compared with the coordination of other similar molecules. The complexes isolated have potential implications for investigation of mercury coordination in environmental and physiological systems.
Experimental

Methods and Materials

Solvents and reagents were of commercial grade and used as received unless otherwise stated. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, Georgia. Reported coupling constants are interproton unless otherwise noted. All the mercury(II) perchlorate compounds were stable for the synthesis and crystal growth. However, organic perchlorate could be potentially explosive and should be handled with extreme caution.\(^\text{12}\)

Instrumental Procedures

General X-ray Crystallography

Selected crystallographic data are provided in Tables (2-5). Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo K\(\alpha\) X-radiation (\(\lambda = 0.71073 \text{ Å}\)). The data were corrected for Lorentz and polarization effects and absorption using SADABS. The structures were solved by use of direct methods or Patterson map and refined on \(F^2\) by full-matrix least squares using the SHELXTL97 program package.\(^\text{13}\) All the non-hydrogen atoms were fixed as anisotropic. The hydrogen atoms, which are lighter atoms and possess little electron density, were assigned in theoretical positions in the final structure. The final structure was then assessed by

\(^{12}\text{K. N. Raymon. Chemical & Engineering News 1983. 61, 4.}\)
\(^{13}\text{G. M. Sheldrick. SHELXL, version 6.14; university of Göttingen: Göttingen, Germany, 1997.}\)
examining the residual unassigned electron density and a percentage match was determined.

**General NMR procedures**

All NMR experiments were performed on a General Electric QE-300 operating in the pulse Fourier transform mode. Solutions were prepared using acetonitrile-d$_3$ and DMSO-d$_6$ unless otherwise stated. Spectra for the sample were recorded in 5 mm-o.d. NMR tube. The chemical shifts were measured relative to internal solvent. All coupling constants are reported in Hz and $J(^1$H$^1$H) unless otherwise noted. For VT NMR experiments, the sample for analysis by NMR for the metal coordination with ligands was prepared by making a 3mM solution of the metal complex in CDCl$_3$. Spectra were taken at -40°C, -20°C, 0°C and 20°C respectively. The lower temperatures were maintained by blowing liquid nitrogen the sample tube in the NMR probe.

**Organic Synthesis**

**Synthesis of L$_1$**

Crude L$_1$ obtained from Kate Stephenson was purified by recrystallization from hexanes until the melting temperature was satisfactory. Light yellow crystals obtained after 10 filtrations and purifications were vacuum dried. M.p. 105-106 °C.

**Synthesis of HL$_2$**

This synthesis was based on that reported by Fuentes and Paudler$^{14}$ and James

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Bush (II). 6-Methyl-2-pyridine-carboxaldehyde (9.49 g, 78.3 mmol) was dissolved in 20 mL deionized water. A solution of hydroxylamine hydrochloride (10.89 g, 156.6 mmol) in 40 mL of deionized water was added. Saturated K$_2$CO$_3$ solution (16.7 mL, 8.10 M) was added drop wise via addition funnel over a period of two hours to neutralize the hydrochloric acid, producing a frothy pink suspension with pH 10.0. The suspension was refluxed for three hours. The reaction vessel was cooled in an ice bath and the salt removed through vacuum filtration. 6-Methyl-2-pyridinecarboxaldehyde oxime was dried under vacuum to give 10.38 g (97% yield) of an off-white solid. M.p 168-169 °C.

The solid (0.369 mL, 2.71 mmol), 1.2g 10% Pd/C and 337 mL methanol were hydrogenated for 3.5 hours in a Parr hydrogenation apparatus at room temperature with 35 psi H$_2$ initially. The product was isolated by vacuum filtration through Celite, removal of methanol by rotary evaporation and fractional vacuum distillation (1.5 mm, 41 °C) to give 4.62 g of a colorless oil (48% yield). $^1$H NMR (CDCl$_3$, 20°C) (Appendix 1): δ 2.50 (s, 3 H, CH$_3$Py), 3.89 (s, 2 H, -CH$_2$-), 6.67 (d, $J = 8$, 1 H, PyH), 7.04 (d, $J = 7.8$, 1 H, PyH), 7.49 (t, $J = 8$, 1H, PyH) ppm.

The synthesis was completed by modification of a procedure reported by Brand and Vahrenkamp.$^{15}$ 6-Methyl 2-(aminomethyl)pyridine (MAMP) (7.44 mL, 60.4 mmol) and 18 mL toluene were added to a round bottom equipped with condenser and additional funnel then flushed with argon. The solution was brought to a boil and ethylene sulfide (2.15 mL, 36.1 mmol) in 32 mL of toluene was added dropwise using an additional funnel producing a yellow mixture. The system was then insulated with glass wool and refluxed overnight to produce a clear solution. The product was fractionated

via vacuum distillation (0.5 mm, 109°C) to give 3.54 g of colorless oil (53.4% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 20°C) (Appendix 2): δ 2.51 (s, 3 H, CH\textsubscript{3}-Py), 2.67 (t, J = 6, 2 H, -CH\textsubscript{2}-), 2.84 (t, J = 6, 2 H, -CH\textsubscript{2}-), 3.86 (s, 2 H, CH\textsubscript{2}-Py), 7.00 (d, J = 8, 1 H, PyH), 7.09 (d, J = 8, 1 H, PyH), 7.51 (t, J = 8, 3 H, PyH) ppm.

**Synthesis of L\textsubscript{3}**

This synthesis was based on that reported by Darbre, Tamis. et, al.\textsuperscript{16} and Newkome, George R. et, al.\textsuperscript{17} 2,6-pyridine dimethanol (4.11 g, 29.5 mmol) was dissolved in 40 mL of 48% hydrobromic acid and refluxed under Argon over 12 hours. An additional 20 mL of HBr was added and the solution was refluxed for another 7 hours. The solution was cooled and neutralized by adding 53 mL of 10 M sodium hydroxide to obtain a white precipitate. The solution was filtered and washed 3X with ionized water. 2,6-Bis(bromomethyl)pyridine was vacuum dried to give a white solid (3.69 g, 52.5% crude yield, 14.1 mmol). M.p. 60-62°C. The powder was chromatographed on neutral alumina, by elution with hexanes/EtOAc (1:1); Rf = 0.8. (47.8% yield, 2.71 mmol). M.p. 80-81°C. \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 20°C) (Appendix 1): δ 4.69 (s, 4 H, CH\textsubscript{2}Py), 7.48 (d, J = 8, 2 H, 3-pyH), 7.83 (t, J = 8, 1 H, 4-pyH) ppm.

2,6-Bis(bromomethyl)pyridine (1.28 g, 4.86 mmol) and thiourea (0.74 g, 9.73 mmol) were dissolved in ethanol (15 mL). This solution was refluxed overnight and the reaction was cooled in an ice bath and rotovaped to remove excess solvent. A pinkish powder was obtained and vacuum dried (\textsuperscript{1}H NMR Appendix 4). The pink powder and


\textsuperscript{17} GR Newkome, VK Gupta, FR Fronczek. *Inorg. Chem* 1984. 16, 23.
NaHCO$_3$ (0.81 g, 9.72 mmol) were refluxed in H$_2$O (25 mL) for 2 hours. The solution was then extracted with CH$_2$Cl$_2$ (3 x 15 mL), dried over Na$_2$SO$_4$ and rotovaped to obtain a yellowish oil residue. Kugelrohr distillation of the oil produced a clear oil product (70 $^\circ$C to 135 $^\circ$C, 0.01 mmHg, 41.7% yield). $^1$H NMR (DMSO-d$_6$, 20 $^\circ$C) (Appendix 5): $\delta$ 1.01 (t, $J = 7$, 2 H), 3.31-3.42 (m, 4 H, CH$_2$Py), 7.46 (d, $J = 8$, 2 H, 3-pyH), 7.89 (t, $J = 8$, 1H, 4-pyH) ppm.

2,6-Pyridinedimethanethiol (0.35 g, 2.03 mmol), NaOH (0.33 g, 8.13 mmol) and 2-picolychloride HCl (0.67 g, 4.07 mmol) were dissolved in EtOH (10 mL). The solution was refluxed for 3 hours under argon. The residue was cooled, rotovaped and extracted with CHCl$_3$ (3 x 15 mL). The solution was dried over Na$_2$SO$_4$ and rotovaped to obtain a yellow oil residue. The crude oil was chromatographed on neutral alumina, by elution with hexanes/EtOAc (1:1); $R_f = 0.35$; $^1$HNMR (CDCl$_3$, 20$^\circ$C) (Appendix 6): $\delta$ 3.80 (s, 4 H, CH$_2$Py), 3.84 (s, 4 H, CH$_2$Py), 7.15 (t, $J = 6$, 2 H, 4-pyH), 7.24 (d, $J = 8$, 2 H, 2-pyH), 7.39 (d, $J = 8$, 2 H, 2-pyH), 7.58 (t, $J = 8$, 1 H, 3-pyH), 7.62 (dt, $J = 8$, 2 H, 2-pyH), 8.54 (d, $J= 6$, 2 H, 4-pyH) ppm.

**Recrystallization of compounds**

**Recrystallization of [Hg(L$_1$)(NO$_3$)$_2$] via slow evaporation**

$\textbf{L}_1$ (0.179 g, 0.539 mmol) was dissolved in 6 mL of acetonitrile. Hg(NO$_3$)$_2$ (0.354 g, 0.539 mmol) dissolved in 5 mL of acetonitrile added to the $\textbf{L}_1$ solution slowly with stirring. The precipitate was removed by filtering through glass wool, celite and sand. The solution of Hg(NO$_3$)$_2$ and $\textbf{L}_1$ was mixed with 48% toluene and capped loosely with
and the solvent allowed evaporation. After several days, many colorless crystals of varying shapes and sizes formed (0.072 g, 20% yield). M.p. 171-172 °C. $^1$H NMR (CDCl$_3$, 20°C) (Appendix 7): δ 2.72 (s, 2 H), 4.06 (s, 2 H), 7.10 (d, 2 H), 7.46 (d, 2 H), 7.60 (t, 2 H) ppm. Elemental Analysis: C, 38.37; H, 3.68; N, 12.79, Found: C, 38.25; H, 3.75; N, 12.57.

**Recrystallization of [Hg$_3$(HL)$_2$](ClO$_4$)$_3$**

HL$_2$ (0.54 g, 2.94 mmol) was dissolved in 500mL MeOH with TEA (410 µL, 2.94 mmol) and stirred under Argon. HgClO$_4$·3H$_2$O (1.34 g, 2.94 mmol) was dissolved in 50 mL of MeOH. After both solutions became clear, the metal salt solution was added to the ligand solution drop-wise with stirring, forming a white precipitate. The suspension was cooled on ice with stirring and vacuum filtered through a medium pore sintered glass funnel. The off-white powder was dried under vacuum (0.39 g, 27% yield). M.p. 185-187 °C (dec.). Elemental Analysis: C, 22.54; H, 2.72; N, 5.82. Found: C, 22.98; H, 2.74; N, 6.05.

[Hg(L$_2$)]ClO$_4$ powder (0.15 g, 0.311 mmol) was dissolved in minimal amount of acetonitrile. Recrystallizations in diffusion tubes with toluene, mestilyene and m-xylene cosolvents were prepared. After one week, promising crystals were recovered from the Me$_3$CN/toluene mixture following solvent removal and air drying (0.084 g, 56% yield). M. p. 224-226 °C. $^1$H NMR (CDCl$_3$, 20°C) (Appendix 8): δ 2.73 (s, 9 H, CH$_3$Py), 3.36-3.37 (m, 6 H), 4.19 (d, $J = 16$ Hz, 3 H), 4.59 (d, $J = 6$ Hz, 6 H), 4.55 (d, $J = 6$ Hz, 6 H), 4.66-4.73 (m, 6 H), 7.37 (dd, $J = 8$, 3 H, 3-PyH), 7.891 (t, $J= 8$, 6 H, 6-PyH) ppm. Elemental Analysis: C, 22.45; H, 2.72; N, 8.52. Found: C, 22.67; H, 2.60; N, 5.76.
Recrystallization of $[\text{Cd}_2(\text{L}_3)\text{Cl}_4]$ via slow evaporation

$\text{L}_3$ (45 mg, 0.13 mmol) was dissolved in 6 mL of MeOH and CdCl$_2$ (45 mg, 0.26 mmol) was dissolved in 10 mL of MeOH. The metal solution was added to the ligand solution slowly to minimize precipitation. Recrystallizations were set up in 8 ml vials with 30% toluene, 30% m-xylene, and 50% toluene and 50% m-xylene cosolvent systems. A few weeks later, crystals were harvested (0.03 g, 32% yield). M.p. 249-250 °C. NMR. Elemental Analysis of precipitate: C, 31.68; H, 2.66; N, 5.84. Found: C, 31.57; H, 2.56; N, 5.81.

X-ray Diffraction of $[\text{Hg}(\text{L}_1)](\text{NO}_3)_2$

A colorless cut block measuring 0.33 x 0.70 x 0.20 mm collected from CH$_3$CN/p-xylene solvents was glued to the end of a glass fiber of similar width. The data were collected using the $\omega$ scan type due to rapid degradation in the X-ray beam at -173 °C. XPREP= P2$_1$/c.

X-ray Diffraction of $[\text{Hg}_3(\text{L}_2)_3](\text{ClO}_4)_3$

A colorless cut block measuring 0.168 x 0.258 x 0.438 mm collected from CH$_3$CN/toluene via slow diffusion was glued to the end of a glass fiber of similar width. The data were collected using the $\theta$ scan type X-ray beam at -173 °C. XPREP= P2$_1$/3.
X-ray Diffraction of [Cd$_2$(L$_3$)]Cl$_4$

A colorless block measuring 0.25 x 0.16 x 0.14 mm collected from CH$_3$CN/toluene via slow diffusion was glued to the end of a glass fiber of similar width.

The data were collected using the $\theta$ scan type X-ray beam at -173 $^\circ$C. XPREP= c2/c.
Results and Discussion

Synthesis of $[\text{Hg(L}_1\text{)(NO}_3\text{)}_2]$ (1)

The reaction of $\text{L}_1$ with 1 mole ratio one of $\text{Hg(NO}_3\text{)}_2$ in $\text{Me}_3\text{CN}$ to produce a solution with a trace amount of precipitant. After filtration to remove the unwanted precipitant, solutions with 30-50% toluene, p-xylene and mesitylene cosolvents were loosely capped for slow evaporation. The 48% toluene:$\text{Me}_3\text{CN}$ solution yielded the most crystals of 1.

Scheme 1  Synthesis of complex 1.

Crystal Structure of $[\text{Hg(L}_1\text{)(NO}_3\text{)}_2$

$L_1$ (Figure 1) has three lutidyl and one amino nitrogen and it is a potential tetradequate ligand. A thermal ellipsoid diagram of $[\text{Hg(L}_1\text{)(NO}_3\text{)}_2$ is presented in Figure 4, general crystallographic information summarized in Table 2, selected bond lengths are included in Table 3 and selected bond angles are included in
Table 4. In $[\text{Hg}(L_1)(\text{NO}_3)_2]$ (Figure 4), two of the $\text{N}_{\text{lutidyl}}$ are coordinated to Hg(II) with Hg-N bond lengths of 2.35 and 2.41 Å. The amino nitrogen is also strongly bound with an Hg-N bond length of 2.36 Å. In contrast, the third $\text{N}_{\text{lutidyl}}$ is located 3.09 Å from the metal center, which is just within the sum of the van der Waals radii (1.55 Å for Hg and 1.60 Å for N). Furthermore, the third lutidyl is pointing downward in relation to the central N(4) like the more strongly coordinated lutidyl groups suggesting it should be considered part of the coordinating system. In addition to four $L_1$ nitrogen atoms, two of the oxygen from each NO$_3$ are bonded to Hg(II) at 2.95 Å, 2.40 Å and 2.29 Å, 2.92 Å respectively. The two chelated rings both have similar nearly planar conformation forming a 145° angle with respect to the center Hg(II). The plane of the other non-bonded lutidyl nearly parallels with one of the coordinated lutidyl. Packing of the crystal $[\text{Hg}(L_1)(\text{NO}_3)_2]$ is shown in Appendix 12.

There are two similar $L_1$ complexes coordinating chloride salts that contain one pendant lutidyl ring. Both $[\text{Hg}(L_1)\text{Cl}_2]$ and $[\text{Cu}(L_1)\text{Cl}_2]$ have a distorted trigonal bipyramidal geometry, the former more than the latter. Interestingly, the nitrogen of the pendant lutidyl ring is directed away from the metal center in $[\text{Hg}(L_1)\text{Cl}_2]$ (Figure 5). The mercuric chloride complex has a slightly shorter Hg-$\text{N}_{\text{amine}}$ distance of 2.36 Å than the nitrate complex, possibly related to reducing the metal coordination number to five from eight. Similarly, 138.9° N(1)-Hg-N(3) angle observed in the chloride complex compared with the 145.19° observed in the nitrate complex suggest that the chelating

---

nitrates impose a flatter binding conformation on the organic ligand than the monodentate chlorides.

**Figure 4** Thermal ellipsoid representation of [Hg(L₁)(NO₃)₂] at 50% probability.
Figure 5  Thermal ellipsoid representation of Hg(L₁)Cl₂ at 50% probability
### Table 2 Crystallographic data for [Hg(L1)(NO3)2] (I)

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</thead>
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<td><strong>R2(^b)</strong></td>
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\(^a\) \text{R1} = \Sigma \left| \frac{F_o - |F_c|}{\Sigma |F_o|} \right|. \quad \text{\(^b\) R2} = \left[ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \right]^{1/2}.}
Table 3 Selected bond length (Å) for [Hg(L₁)(NO₃)₂] (1)

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<td>Hg(1)-O(6)</td>
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Table 4 Selected bond angles [Hg(L₁)(NO₃)₂] (1)

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Synthesis of Methyl-N-(2-mercaptoethyl) picolylamine (HL$_2$) (Scheme 2)

Three main steps were required to synthesize HL$_2$. The first two steps were based on the methods of Fuentes and Paudler.\textsuperscript{14} Reaction of 6-methyl-2-pyridine-carboxaldehyde with hydroxylamine provided 2-formaldoximo-6-methylpyridine in 97% yield (Scheme 2, step 1 and 2). The oxime was then reduced by catalytic hydrogenation to form a primary amine (Scheme 2, step 3), which was isolated as a colorless oil by fractional distillation in vacuum. Working on a ten gram scale under optimal vacuum conditions, amine yields approached 50%. Recovery was drastically compromised by working on significantly smaller scales or allowing the vacuum to fall below 1.5 mm Hg.

The final step in the preparation of HL$_2$ was based on the method of Brand and Vahrenkamp.\textsuperscript{15} Ethylene sulfide was added dropwise to excess 6-methyl-2-(aminomethyl)pyridine (MAMP) in boiling toluene (Scheme 2, step 4). Under these conditions, undesirable byproducts, such as ethylene sulfide oligomers and multiple ethylene sulfide additions to MAMP, are minimized. Fractional distillation under full vacuum provided HL$_2$ as a higher boiling point fraction in 53% yield.
Scheme 2  Synthesis of 6-methyl-N-(2-mercaptopeth)picolylamine (HL₂)
Crystal Structure of [Hg$_3$(L$_2$)$_3$(ClO$_4$)$_3$] (3)

The reaction of L$_2$H (Scheme 3) with one equivalent each of triethylamine (TEA) and Hg(ClO$_4$)$_2$•3H$_2$O in MeOH produced a precipitate that was analyzed as HgL$_2$ClO$_4$ (2). An acetonitrile solution of the powder was layered over toluene, m-xylene and mesitylene in 5 mM diffusion tubes. Crystals of comparable quality were produced with toluene/Me$_3$CN and m-xylene/Me$_3$CN solvent mixtures after one week of slow diffusion. Colorless X-ray quality crystals of [Hg$_3$(L$_2$)$_3$](ClO$_4$)$_3$ were taken mainly from the toluene/Me$_3$CN mixture. A thermal ellipsoid diagram of the complex is shown in Figure 6. General crystallographic information is summarized in Table 2. Selected bond lengths and angles are given in Table 6 and Table 7.

![Scheme 3](image_url)  

**Scheme 3** Synthesis of complex 3.
This complex is part of the cubic crystal system P2₁₃ and the symmetry elements include 2- and 3-fold screw axes and 3-fold rotation axes. Each L₂ binds a single Hg(II) with its NN'S donor set. The thiolate of each ligand also bridges to a second metal. The trinuclear complex has a (HgS)₃ core with three fold symmetry and rotor-like flanking aromatic ligands. The perchlorate ions are well separated from the metal centers. A closer examination was taken of the complex angles and bond lengths. The Hg-N bond lengths are 2.319 Å and 2.378 Å, for the pyridyl and amino nitrogen atoms, respectively. The Hg-S bond length is 2.639 Å when the associated mercury is bound to the nitrogens of the same tridentate ligand and 2.373 Å when bridged to an adjacent metal.

The mixed donor ligands represented among the ten structurally characterized complexes with cyclic (HgS)ₙ (n ≥ 3) components have generated isolable (HgS)₄ monocycles²⁰ and Hg₄S₆²¹ tricyclic complexes. The one known compound containing a (HgS)₃ cycle is shown in (Figure 7).²¹ It contains doubly solvated perchlorate ion where the anion is bracketed in a linear fashion by the hydrogen atoms of the chloroform molecules. This complex also contains an adamantine-like cage skeleton composed of six-membered (Hg(μ-S))₃ ring in the approximate chair conformation. The mercury atoms, each with a terminal triphenylphosphine ligand, are located at the bridge vertices, with phenylthiolate ligands bridging the six edges.²¹ In the cage conformation, all the ring bond angles are significantly smaller than the angles found in [Hg₃(L₂)₃](ClO₄)₃ (3). The inter-cyclic angles for 3 (Figure 6) are 120.2° for S-Hg-S and 100.25° Hg-S-Hg compared to the related angles in the published compound (Figure 7) 102.55° and 85.75°. Not only does this show that Hg(II) has a variety of bonding orientation ranging from having an

²⁰ Cambridge Structural Database. 2009. v. 5.31.
almost a linear coordination to a tetrahedral coordination geometry. Packing of the cells can be seen in Appendix 13.

Figure 6  Thermal ellipsoid representation of [Hg₃(L₂)₃](ClO₄)₃ at 50% probability
Figure 7  Thermal ellipsoids plot of \([(\mu\text{-SPh})_6(\text{HgPPh}_3)_4](\text{ClO}_4)_2\cdot2\text{CHCl}_3\) at 50\% probability.\textsuperscript{21}
Table 5 Crystallographic data for [Hg₃(L₂)₃](ClO₄)₃ (3)

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<tr>
<td>R2&lt;sup&gt;b&lt;/sup&gt;</td>
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<sup>a</sup> R1 = \( \sum |F_o| - |F_c| / \sum |F_o| \)

<sup>b</sup> R2 = \( \left[ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right]^{1/2} \).
Table 6  Selected bond distance (Å) for [Hg₃(L₂)₃(ClO₄)₃] (3)

<table>
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<th>Distance (Å)</th>
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<td>Hg(1)-N(1)</td>
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<td>Hg(1)-S(1)</td>
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Table 7  Selected bond angles for [Hg₃(L₂)₃(ClO₄)₃] (3)

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Symmetry transformation used to generate equivalent atoms:

#1 –y+1, z+1/2, -x+1/2
#2 –z+1/2, -x+1, y-1/2
#3 y, z, x
#4 z, x, y
#5 –y+1, z-1/2, -x+3/2
#6 –z+3/2, -x+1, y+1/2
Tridentate ligand N-(2-pyridymethyl)-N-(2-ethylthiolate)-amine (MEPA) is a ligand with similar structure to L₂. Complexes of MEPA coordinated with Hg(II), Zn(II), Re(II) and Tc(I) have been characterized.²²,²³,²⁴,²⁵ Similar to L₂, MEPA has an {NN'S} donor set, but with less steric hinderance because of the lack of a methyl group on the pyridyl ring. The Zn₃ core of [Zn(MEPA)]₃(ClO₄)₂ formed a nearly equilateral triangle. The cation contained a (ZnS)₃ ring with distorted tetrahedral ZnS₂N₂ units (Figure 8).²⁵

In contrast to the chair (HgS)₃ ring conformation with all three Hg-S bonds on the same face of the ring observed in 3, the (ZnS)₃ has a boat conformation with one ZnS directed in the opposite direction as the other two (Figure 6). In general the Hg-S and Hg-N bond lengths are longer in 3 than in the Zn(II)-MEPA as expected for a larger metal ion. The (MS)₃ ring is very interesting because the same structural feature is found in metallothioneins. Zn- and Cd-containing metallothioneins bind metals in α and β domains with M₄S₁₁ and M₃S₉ clusters, respectively, having an M₃S₃ ring.²⁵

Recently, an Hg(II) complex of MEPA with unprecedented bicyclo[3.3.3] core structure was structurally characterized (Figure 9).²² In this complex, each ligand binds to one Hg(II) metal with its NN'S donor atoms. The thiolate of each ligand also bridges to a second Hg(II) metal to form one octahedral, two square pyramidal, and two seesaw metal centers with coordination environments Hg(NN'S)₂, HgNN'S₃ and HgNN'S₂, respectively. Interestingly, the core structure of the Hg(II) complex has (HgS)₄ rings.

---

Solution studies of the Hg(II) complex by NMR and ESI-MS indicated that the pentanuclear complex was a minor component of the equilibrium mixture.

**Figure 8** Thermal ellipsoids of [Zn₃(MEPA)₃](ClO₄)₃·CH₃OH at 35% probability.²⁵
Linear trinuclear complexes of the tridentate NN’S ligand MEPA with zinc triad metal ions have also been structurally characterized. Both Zn₃(MEPA)₄(ClO₄)₂ (Figure 10) and Zn₂Hg(MEPA)₄(ClO₄)₂ (Figure 11) had terminal metal ions with N₄S₂ environment and a central metal ion with S₄ coordination. The thiolates in both complexes served as a bridging ligand between the metals. It is interesting to note that with the more steric hinderance of L₂, a cyclic trinuclear complex was isolated instead of the linear ones.
Figure 10  Thermal ellipsoids of Zn$_3$(MEPA)$_4$(ClO$_4$)$_2$ at 50% probability.$^{24}$

Figure 11  Thermal ellipsoids of Zn$_2$Hg(MEPA)$_4$(ClO$_4$)$_2$ at 50% probability.$^{24}$
Organic synthesis of 2,6-Bis(pyridyl-2-methythiomethyl)pyridine (L₃)

A variation of the four-step synthesis reported by Newkome et al. was used to prepare L₃ (Scheme 4). ²⁶ 2,6 pyridine dimethanol was reacted with hydrobromic acid to obtain 2,6-bis(bromomethyl)pyridine (Scheme 4, step 1). The yield was improved from approximately 40% to 65% by adding an excess of HBr to the reaction. ¹⁶ Following neutralization of excess HBr with 10M NaOH, crude 2,6-bis(bromomethyl)pyridine was obtained by CH₂Cl₂ extraction and rotary evaporation. Purification by alumina chromatography provided 2,6-bis(bromomethyl)pyridine in 47.8% yield.

The second step (Scheme 4, step 2) in preparing L₃ involved reacting 2,6-bis(bromomethyl)pyridine with two equiv of thiourea in refluxing ethanol. Treatment with NaHCO₃ produced 2,6 pyridine dimethanethiol, which was purified by careful vacuum Kugelrohr distillation. To minimize opportunities for air oxidation, distilled 2,6 pyridine dimethanethiol was promptly reacted with 2 equiv of picoyl chloride•hydrochloride in the presence of a base to form the final product (Scheme 4, step 4 and 3). Following alumina chromatography, L₃ was obtained in 40.5% yield.

²⁶ GR Newkome; VK Gupta; FR Fronczek. Inorg. Chem, 1984, 23 (16)
Scheme 4 Synthesis of 2,6-Bis(pyridyl-2-methylthiomethyl)pyridine (L₃)
Crystals of Cd$_2$(L$_3$)Cl$_4$ were isolated from toluene/MeOH by slow evaporation. Unfortunately, the structure was too disordered to solve.

**VT $^1$H NMR study of [Hg$_3$(L$_2$)$_3$](ClO$_4$)$_3$ (3)**

Variable temperature NMR studies were performed on an acetonitrile-$d_3$ solution of [Hg$_3$(L$_2$)$_3$](ClO$_4$)$_3$ for comparison with previous NMR studies of [Hg$_5$(MEPA)$_6$](ClO$_4$)$_4$. A single L$_2$ environment was observed over the temperature range of -40 to 20 °C (Appendix 8-11). Changes in the chemical shifts of ligand protons over this temperature were less than 0.30 ppm, as expected for a single complex in slow intermolecular exchange on the chemical shift time scale. A broader peak at ~3.5 ppm, assigned to the exchangeable amine N-H, drifted 0.20 ppm over this temperature range.

The most conclusive evidence for slow intermolecular ligand exchange of an Hg(II) complex is detection of $J$(Hg$^{199}$H$_1$H). Although heteronuclear coupling between $^{199}$Hg and ligand protons has not been observed, to the best of our knowledge, for an Hg(II) complex of any thiolate ligand including [Hg$_5$(MEPA)$_6$](ClO$_4$)$_4$, ligands with enhanced steric demands have been observed to increase the magnitudes of $J$(Hg$^{199}$H$_1$H)$^{8,27}$

Despite the additional methyl group present in L$_2$, $J$(Hg$^{199}$H$_1$H) satellites were not in the NMR spectrum of [Hg$_3$(L$_2$)$_3$](ClO$_4$)$_3$ (3).

Less direct means of documenting slow intermolecular ligand exchange in solution include finding conditions that allow detection of discrete ligand environment or diasteriotopic methylene proton environment. The solution dynamics of Hg$_5$(MEPA)$_6^4$ were explored by NMR at 60 °C and -40 °C in CD$_3$CN.$^{22}$ At a higher temperature, there

---

$^{27}$ W. Lai; S. M. Berry; D.C. Bebout. *Inorganic Chemistry*. **2006.** 45, 571-581
appeared to be a single peak for each ligand proton, but at lower temperature three ligand environments in slow exchange were observed consistent with the solid state structure. Diasteriotopic proton environments and minimal chemical shift changes were observed in Variable temperature NMR studies of 3, indicating slow ligand exchange on the $J(^1\text{H}^1\text{H})$ time scale between metal ions. Dissociation of 3 to form three mononuclear [Hg(L₂)] may occur in solution with preservation of metal ligand bonds.

Further analysis of the NMR data, and perhaps additional studies at higher temperature, are planned to look for evidence of (Hg L₂)$_3^{3+}$ dissociation to three equivalents of (Hg L₂)$^+$ or reorganization to alternative oligomers.
**Conclusion**

This study investigated heavy metal bonding to three synthetic models of protein metal binding sites. The two newly characterized complexes 1 and 3 possessed cations with a 1:1 and 3:3 ratio between the metals and the ligands intended to model the binding or active site of a protein. The complexes had novel structural features.

The potentially tetradeinate ligand L4 formed three strong Hg-N bonds in 1 and a fourth very weak Hg-N. This binding mode is intermediate between that observed in related complexes where the Hg-N bond distances are comparable or one pyridyl ring is truly pendant with nitrogen oriented so as to preclude binding (Figure 4). The observed nitrate complex (1) has a nearly linear N(1)-Hg-N(3) angle suggesting the chelating nitrates are imposing a flatter binding conformation on the organic ligand.

The crystal structure of 3, ([Hg₃(L₂)₃](ClO₄)₃), was part of cubic system P2₁3 and displayed one cyclic (HgS)₃ in chair conformation that was completely unique to mercury. 3 was similar to a previously studied Zn(II)-MEPA complex (Figure 8) which appeared to be in a more strained boat conformation. Complex 3 has tetrahedral HgS₂N₂ units. The (MS)₃ ring is biologically relevant and important because the same structural feature was found in metallothioneins bound to heavy metals. More recently, another Hg(II)-(MEPA) complex was found with an unprecedented bicyclo[3.3.3] core structure. The core of the complex has (HgS)₄ rings. These studies suggest multidentate thiolate ligands offer a route to Hg(II) complexes with unusual structural feature.

NMR studies of the [Hg₅(MEPA)₅](ClO₄)₄ complex inspired variable temperature ¹H NMR studies of 3. Although there was a clear indication of intermolecular exchange
in [Hg$_5$(MEPA)$_6$](ClO$_4$)$_4$, minimal chemical shift changes were observed in 3, indicating that there was slow ligand exchange on the $J(\text{H}^1\text{H})$ time scale between the metal ions. Further analysis of NMR data and studies at higher temperatures are planned for 3 to look for evidence of complex dissociation to three equivalents of Hg(L$_2$)$^+$ complex or of alternative oligomers.

Ligand L$_3$ was studied because of its potential pentadentate binding mode. Cd(II)-L$_3$Cl$_2$ crystals were obtained, however the final structure could not be solved due to disorder. The structure appears to be dimeric. Further studies are planned to recrystallize the complex and to obtain a complete structure of ML$_3$.

Trace metals are essential to the well being of a human’s life. However, heavy metals such as Hg(II) and Cd(II) accumulate in higher organisms, bind to the proteins, change their native conformation and render them non-functional. It is therefore important to study the coordination chemistry of these heavy metals in biologically relevant environments. Although extensive study has been done on the subject of heavy metal toxicity via metal ligand coordination, the detailed mechanisms of toxicology involving heavy metals remain largely unsolved. The novel of Hg(II) coordination complexes characterized provide additional information that will inform efforts to better understand the toxicological effects of Hg(II).
Appendix 1  $^1$H NMR (CDCl$_3$, 20ºC, 2mM) of 6-Methyl 2-(aminomethyl)pyridine (MAMP)
Appendix 2 $^1$H NMR (CDCl$_3$, 20°C, 2mM) of MeMEPA (L$_2$)
Appendix 3 $^1$H NMR (CDCl$_3$, 20°C, 2mM) of 2,6 pyridine dimethanebromide
Appendix 4 $^1$H NMR (DMSO-$d_6$, 20$^\circ$C, 2mM) of intermediate (pink powder).
Appendix 5 ¹H NMR (DMSO-d₆, 20°C, 2mM) of 2,6-pyridinedimethanethiol
Appendix 6 $^1$H NMR (DMSO-$d_6$, 20°C, 2mM) of L₃
Appendix 7 $^1$H NMR (CDCl$_3$, 20°C, 2mM) of L$_3$
Appendix 8 VT $^1$H NMR (CDCl$_3$, 20°C, 3mM) of [Hg$_3$ (MeMEPA)$_3$(ClO$_4$)$_3$] (3)
Appendix 9 VT $^1$H NMR (CDCl$_3$, 0°C, 3mM) of [Hg$_3$ (MeMEPA)$_3$(ClO$_4$)$_3$] (3)
Appendix 10 VT $^1$H NMR (CDCl$_3$, 20°C, 3mM) of [Hg$_3$ (MeMEPA)$_3$ (ClO$_4$)$_3$] (3)
Appendix 11 VT \(^1\)H NMR (CDCl\(_3\), 40\(^\circ\)C, 3mM) of [Hg\(_3\) (MeMEPA)\(_3\)(ClO\(_4\))\(_3\)] (3)
Appendix 12 Packing images of [Hg(TLA)NO$_3$]$_2$ (I)
Appendix 13 Packing images of $[\text{Hg}_{3} (\text{MeMEPA})_{3}] (\text{ClO}_4)_3$ (3)