

## Investigation of Group 12 Metal Complexes with a Tridentate SNS Ligand by X-ray Crystallography and $^1\text{H}$ NMR Spectroscopy

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Two series of zinc triad complexes containing the ligand 2,6-bis(methylthiomethyl)pyridine ( $\text{L}^1$ ) were synthesized and characterized by X-ray crystallography and solution-state  $^1\text{H}$  NMR spectroscopy. The distorted meridional octahedral  $\text{M}(\text{L}^1)_2(\text{ClO}_4)_2$  series includes the first structurally characterized Zn(II) and Cd(II) complexes with  $\text{N}_2(\text{SR}_2)_4$  coordination spheres. Coordination of  $\text{HgCl}_2$  and  $\text{ZnCl}_2$  with 1 equiv of ligand afforded mononuclear, five-coordinate species  $\text{Hg}(\text{L}^1)\text{Cl}_2$  and  $\text{Zn}(\text{L}^1)\text{Cl}_2$ , respectively, with distorted square-pyramidal and trigonal-bipyramidal geometries. With  $\text{CdCl}_2$ , the dimeric  $[\text{Cd}(\text{L}^1)\text{Cl}(\mu\text{-Cl})_2]$  complex was obtained. The distorted octahedral coordination geometry of each Cd(II) center in this complex is formed by one tridentate ligand, two bridging chloride ions, and one terminal chloride ion. NMR spectra indicate that the intermolecular ligand-exchange rate of  $[\text{M}(\text{L}^1)_2]^{2+}$  decreased in the order  $\text{Cd(II)} > \text{Zn(II)} > \text{Hg(II)}$ . Slow intermolecular ligand-exchange conditions on the chemical-shift time scale were found for 1:2 metal-to-ligand complexes of  $\text{L}^1$  with Hg(II) and Zn(II) but not Cd(II). Slow intermolecular ligand-exchange conditions in acetonitrile- $d_3$  solutions permitting detection of  $^3\text{-}^5J(^{199}\text{Hg}^1\text{H})$  were found for 1:1 and 1:2  $\text{Hg}(\text{ClO}_4)_2/\text{L}^1$  complexes, but not for the related  $\text{Cd}(\text{ClO}_4)_2$  complexes. The magnitudes of  $J(^{199}\text{Hg}^1\text{H})$  for equivalent protons were smaller in  $[\text{Hg}(\text{L}^1)_2]^{2+}$  than in  $[\text{Hg}(\text{L}^1)(\text{NCCCH}_3)_x]^{2+}$ . The relative intermolecular ligand-exchange rates of the zinc triad complexes investigated here suggest that the toxicity of Hg(II) is accentuated by the relative difficulty of displacing it from the coordination sites encountered.

### Introduction

The considerable differences between the bioactivities of the group 12 metal ions motivate parallel investigations of their coordination chemistry with biologically relevant ligands. In physiological systems, Zn(II) serves important catalytic and structural roles by selectively binding to sites of specific metalloproteins. On the other hand, Cd(II) and Hg(II) are toxic, and the molecular mechanisms for their toxicities are incompletely understood. The only beneficial role for Cd(II) is the recently discovered Cd(II)-specific carbonic anhydrase in the marine diatom *Thalassiosira weissflogii*, produced in the presence of Cd(II) under zinc-limited conditions.<sup>1</sup> Other than binding the transcription regulator of mercury detoxification proteins, no physiologi-

cally beneficial roles have been discovered for Hg(II). The transcriptional regulation and metal binding of metalloproteins are highly selective for a single physiologically essential metal ion under normal circumstances. However, trace nonessential metal ions interfere with normal function. The potential toxicological targets of Cd(II) and Hg(II) are extensive because of their low coordination geometry and number preferences. Clarification of the range of slow intermolecular exchange binding environments for divalent zinc triad metal ions is required to fully appreciate the intricate coordination of specific metal-binding events in biochemistry and the most detrimental physiological effects of heavy metal ions.

Investigating the coordination chemistry of the group 12 metal ions poses some unique challenges. The divalent forms of these metals are  $d^{10}$ . Therefore, their coordination number and geometry preferences are weak compared to those of transition metal ions with incomplete outer d shells. As a

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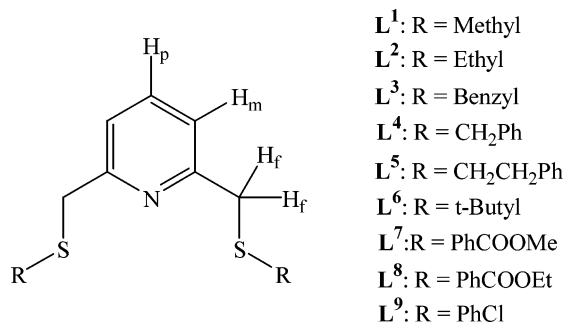


Figure 1. Pyridine-based dithioether ligands.

result, their coordination chemistry with simple ligands is typically plagued by rapid intermolecular ligand exchange between a variety of complexes. Furthermore, the divalent group 12 metal ions are diamagnetic, and few spectroscopies are available for studying their coordination. Perhaps the most versatile spectroscopic method for characterizing organic complexes of these metals is NMR spectroscopy, which can detect slow intermolecular ligand exchange on the chemical-shift time scale for Zn(II), Cd(II), and Hg(II) complexes and on the  $J(^{111/113}Cd^1H)$  and  $J(^{199}Hg^1H)$  time scales for Cd(II) and Hg(II) complexes, respectively.

Complexes of the group 12 metal ions with sulfur/nitrogen mixed donor ligands, such as thiolates or macrocyclic thioethers, have been widely investigated.<sup>2–6</sup> Complexes with acyclic thioether ligands, however, have been less well studied. We recently structurally characterized seven coordination complexes of group 12 metals with the NSN-donor ligand bis(2-methylpyridyl) sulfide ( $Py_2S$ ).<sup>7</sup> In the present article, X-ray crystallographic and solution NMR spectroscopic characterization of the coordination chemistry of divalent group 12 metal ions with the SNS-donor ligand 2,6-bis(methylthiomethyl)pyridine ( $L^1$ ) is reported. As summarized in Figure 1, several other dithioether-derivatized lutidyl ligands have been reported.<sup>8–16</sup> In crystallographically

characterized metal complexes, these ligands generally behave as tridentate chelating ligands, giving two five-membered rings.<sup>8,10,15,16</sup> Bidentate binding modes have been observed in  $[Pd(Me)(L^1)]^{12}$  and  $[Cu(L^3)Br(\mu-Br)]_2$ ,<sup>8</sup> where only the pyridine nitrogen and one thioether moiety bind the metal ions. The only group 12 metal ion complexes previously reported with this family of ligands are  $[Zn(L^2)Br_2]^{16}$  and  $[Cd(L^2)Cl(\mu-Cl)]_2$ .<sup>14</sup>

In this article, the synthesis and characterization of  $MCl_2$  and  $M(ClO_4)_2$  [ $M = Zn(II), Cd(II), Hg(II)$ ] complexes of  $L^1$  are reported. X-ray crystallographic structures are presented for nonhomologous chloride complexes with 1:1 metal-to-ligand stoichiometry and for a homologous  $[M(L^1)_2](ClO_4)_2$  series. These are the first complexes having the stoichiometry  $M(L)_2$  with this class of ligands. In addition, the Zn(II) and Cd(II) complexes with  $N_2(SR_2)_4$  coordination spheres are the first to be crystallographically characterized. Conditions for slowed intermolecular ligand exchange on the chemical-shift time scale in acetonitrile- $d_3$  solution were found for  $[Zn(L^1)_2]^{2+}$  and  $[Hg(L^1)_2]^{2+}$ , but not for  $[Cd(L^1)_2]^{2+}$ . In addition, slow intermolecular exchange conditions on the  $J(M^1H)$  time scale were found for  $[Hg(L^1)_2]^{2+}$  and  $[Hg(L^1)(CH_3CN)_x]^{2+}$ , but not for comparable Cd(II) complexes. The lowest intermolecular exchange rates for this SNS ligand were observed with Hg(II), followed by Zn(II) and finally Cd(II). This observation suggests that the relative difficulty of displacing Hg(II) from mixed nitrogen/thioether sulfur coordination environments contributes to its broad toxicological effects.

## Experimental Section

Solvents and reagents were of commercial grade and were used as received unless otherwise stated. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA. The proton labeling scheme is shown in Figure 1. Reported coupling constants are  $^3J(^1H^1H)$  unless otherwise noted. *Caution!* All of the perchlorate salts of metal complexes included in this work were stable for routine synthesis and purification procedures. However, organic perchlorates are potentially explosive and should be handled with care.<sup>17</sup>

**Synthesis of 2,6-Bis(methylthiomethyl)pyridine ( $L^1$ ).** The ligand was prepared by a variation of the procedure described by Canovese and co-workers.<sup>18</sup> Sodium methanethiolate (3.1 g, 44 mmol) was added to an ice-cooled solution of 2,6-bis(bromomethyl)pyridine<sup>19</sup> (5.3 g, 20 mmol) in DMF (50 mL). The mixture was brought to room temperature and stirred for 24 h. The solvent was removed by Kugelrohr distillation (50 °C, 0.5 mmHg). Continued Kugelrohr distillation (150 °C, 0.01 mmHg) of the yellow oily residue yielded  $L^1$  as a colorless oil (3.3 g, 83%).  $^1H$  NMR ( $CD_3CN$ , 20 °C):  $\delta$  7.70 (t, 1H,  $J = 8$  Hz,  $H_p$ ), 7.26 (d, 2H,  $J = 8$  Hz,  $H_m$ ), 3.75 (s, 4H,  $H_f$ ), 2.07 (s, 6H, Me). Anal. Calcd for  $C_9H_{13}NS_2$ : C, 27.09; H, 3.28; N, 3.51. Found: C, 27.09; H, 3.27; N, 3.53.

**Preparation of  $Hg(L^1)_2(ClO_4)_2$  (1).** A solution of  $Hg(ClO_4)_2 \cdot 3H_2O$  (230 mg, 0.50 mmol) in 5 mL of methanol was added dropwise to a solution of  $L^1$  (100 mg, 0.5 mmol) in 5 mL of

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Table 1. Crystallographic Data for Complexes 1–3

	1	2	3
empirical formula	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> S <sub>4</sub> HgCl <sub>2</sub> O <sub>8</sub>	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> S <sub>4</sub> CdCl <sub>2</sub> O <sub>8</sub>	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> S <sub>4</sub> ZnCl <sub>2</sub> O <sub>8</sub>
fw	798.14	709.95	662.92
crystal system	orthorhombic	orthorhombic	monoclinic
space group	<i>Ibca</i>	<i>Pcca</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	13.5814(17)	14.2898(19)	11.982(6)
<i>b</i> , Å	14.184(3)	13.5492(17)	11.667(6)
<i>c</i> , Å	27.412(3)	27.536(4)	19.559(11)
$\alpha$ , deg	90	90	90
$\beta$ , deg	90	90	103.672(9)
$\gamma$ , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	5280.5(14)	5331.4(12)	2657(2)
<i>Z</i>	8	8	4
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	2.008	1.769	1.657
$\mu$ , mm <sup>-1</sup>	6.394	1.378	1.485
<i>T</i> , K	148(2)	103(2)	103(2)
R1, <sup>a</sup> wR2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0452, 0.1026	0.0234, 0.0582	0.0396, 0.0974
R1, <sup>a</sup> wR2 <sup>b</sup> (all data)	0.0597, 0.1115	0.0377, 0.0613	0.0605, 0.1080

$${}^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

methanol with stirring. A white precipitate formed. The solution was filtered, and the filtrate was diluted slowly with 10 mL of acetonitrile and set aside for slow evaporation. Colorless X-ray-quality crystals of **1** (91 mg, 46%) formed upon standing for 4 days. Mp: 170–171 °C (dec). <sup>1</sup>H NMR (2 mM, CD<sub>3</sub>CN, 20 °C):  $\delta$  8.15 [t, 1H, *J* = 8 Hz, <sup>3</sup>*J*(<sup>199</sup>Hg<sup>1</sup>H) = 15 Hz, H<sub>p</sub>], 7.54 [d, 2H, *J* = 8 Hz, <sup>4</sup>*J*(<sup>199</sup>Hg<sup>1</sup>H) = 15 Hz, H<sub>m</sub>], 4.15 [s, 4H, <sup>3</sup>*J*(<sup>199</sup>Hg<sup>1</sup>H) = 39, H<sub>f</sub>], 2.18 [s, 6H, <sup>3</sup>*J*(<sup>199</sup>Hg<sup>1</sup>H) = 49 Hz, Me]. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>-Cl<sub>2</sub>HgN<sub>2</sub>O<sub>8</sub>S<sub>4</sub>: C, 54.26; H, 6.53; N, 7.03. Found: C, 54.43; H, 6.64; N, 7.01%.

**Preparation of Cd(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2).** A solution of Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (210 mg, 0.50 mmol) in 5 mL of acetonitrile was added dropwise to a solution of L<sup>1</sup> (100 mg, 0.5 mmol) in 5 mL of methanol with stirring. A white precipitate formed. The solution was clarified by the addition of 5 mL of acetonitrile. The mixture was slowly diluted with 6 mL of toluene and set aside for slow evaporation. Colorless X-ray-quality crystals of **2** (100 mg, 60%) formed upon standing for 4 days. Mp: 248–250 °C (dec). <sup>1</sup>H NMR (2 mM, CD<sub>3</sub>CN, 20 °C):  $\delta$  8.01 (t, 1H, *J* = 8 Hz, H<sub>p</sub>), 7.54 (d, 2H, *J* = 8 Hz, H<sub>m</sub>), 4.15 (s, 4H, H<sub>f</sub>), 2.13 (s, 6H, Me). Anal. Calcd for C<sub>18</sub>H<sub>26</sub>CdCl<sub>2</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub>: C, 30.46; H, 3.66; N, 3.95. Found: C, 30.41; H, 3.63; N, 3.88.

**Preparation of Zn(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (3).** A solution of Zn(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (190 mg, 0.50 mmol) in 3 mL of acetone was added dropwise to a solution of L<sup>1</sup> (100 mg, 0.5 mmol) in 2 mL of acetone with stirring. Colorless crystals of **3** (26 mg, 15%) suitable for X-ray crystallography were obtained in 5-mm glass tubes after 5 days by slow diffusion of the mixture into toluene. Mp: 229–231 °C. <sup>1</sup>H NMR (2 mM, CD<sub>3</sub>CN, 20 °C):  $\delta$  7.99 (t, 1H, *J* = 8 Hz, H<sub>p</sub>), 7.51 (d, 2H, *J* = 7 Hz, H<sub>m</sub>), 4.07 (s, 4H, H<sub>f</sub>), 2.10 (s, 6H, Me). Anal. Calcd for C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>8</sub>S<sub>4</sub>Zn: C, 32.61; H, 3.95; N, 4.23. Found: C, 31.86; H, 4.04; N, 4.18.

**Preparation of Hg(L<sup>1</sup>)Cl<sub>2</sub> (4).** A solution of HgCl<sub>2</sub> (140 mg, 0.50 mmol) in 5 mL of methanol was added dropwise to a solution of L<sup>1</sup> (100 mg, 0.5 mmol) in 5 mL of acetonitrile with stirring. Slow evaporation of the solution resulted in the formation of colorless X-ray-quality crystals of **4** (90 mg, 40%) in 10 days. Mp: 132–133 °C. <sup>1</sup>H NMR (2 mM, CD<sub>3</sub>CN, 20 °C):  $\delta$  7.93 (t, 1H, *J* = 8 Hz, H<sub>p</sub>), 7.46 (d, 2H, *J* = 8 Hz, H<sub>m</sub>), 4.14 (s, 4H, H<sub>f</sub>), 2.05 (s, 6H, Me). Anal. Calcd for C<sub>9</sub>H<sub>13</sub>Cl<sub>2</sub>HgNS<sub>2</sub>: C, 22.96; H, 2.78; N, 2.98. Found: C, 23.05; H, 2.75; N, 2.91.

**Preparation of [Cd(L<sup>1</sup>)Cl(μ-Cl)]<sub>2</sub> (5).** A solution of CdCl<sub>2</sub> (90 mg, 0.5 mmol) in 10 mL of methanol was added dropwise to a solution of L<sup>1</sup> (100 mg, 0.5 mmol) in 5 mL of methanol with

stirring. The precipitate was filtered off and dried in vacuo (130 mg, 67%). Recrystallization from acetonitrile and toluene gave colorless X-ray-quality crystals of **5**. The complex decomposed at 205 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 20 °C):  $\delta$  7.96 (t, 1H, *J* = 8 Hz, H<sub>p</sub>), 7.48 (d, 2H, *J* = 8 Hz, H<sub>m</sub>), 4.15 (s, 4H, H<sub>f</sub>), 2.06 (s, 6H, Me). Anal. Calcd for C<sub>18</sub>H<sub>26</sub>Cd<sub>2</sub>Cl<sub>4</sub>N<sub>2</sub>S<sub>4</sub>: C, 28.25; H, 3.42; N, 3.66. Found: C, 28.32; H, 3.39; N, 3.61.

**Preparation of Zn(L<sup>1</sup>)Cl<sub>2</sub> (6).** A solution of ZnCl<sub>2</sub> (68 mg, 0.50 mmol) in 5 mL of acetone was added dropwise to a solution of L<sup>1</sup> (100 mg, 0.5 mmol) in 5 mL of acetone with stirring. The solution was slowly diluted with 10 mL of toluene and set aside for slow evaporation. Colorless X-ray-quality crystals of **6** (110 mg, 65%) formed upon standing for 3 days. Mp: 198–199 °C. <sup>1</sup>H NMR (2 mM, CD<sub>3</sub>CN, 20 °C):  $\delta$  7.96 (t, 1H, *J* = 7 Hz, H<sub>p</sub>), 7.48 (d, 2H, *J* = 7 Hz, H<sub>m</sub>), 4.05 (s, 4H, H<sub>f</sub>), 2.27 (s, 6H, Me). Anal. Calcd for C<sub>9</sub>H<sub>13</sub>Cl<sub>2</sub>NS<sub>2</sub>Zn: C, 32.21; H, 3.90; N, 4.17. Found: C, 32.30; H, 3.79; N, 4.19.

**Solution-State NMR Spectroscopy.** NMR spectra were collected in 5-mm-o.d. NMR tubes on a Varian Mercury 400VX NMR spectrometer operating in the pulse Fourier transform mode. All solutions for low-temperature NMR measurements were prepared using calibrated autopipets by dilution of metal salt and L<sup>1</sup> stock solutions with CD<sub>3</sub>CN. The metal ion concentration in the solutions used in the NMR analysis was 2 mM. The sample temperature was maintained by blowing chilled nitrogen over the NMR tube in the probe. Proton chemical shifts were measured relative to internal solvent but are reported relative to tetramethylsilane (TMS).

**X-ray Crystallography.** Selected crystallographic data are reported in Tables 1 and 2, and the complete data are provided in CIF files as Supporting Information. Data were collected on a Bruker SMART 1K CCD four-circle diffractometer using graphite-monochromated Mo K $\alpha$  X-radiation ( $\lambda$  = 0.71073 Å). During data collection, 50 frames were measured at both the beginning and end of the data collection to monitor intensity decay. The structures were solved by direct methods and refined on *F*<sup>2</sup> by full-matrix least-squares using the SHELXTL97 program package.<sup>20</sup> All non-hydrogen atoms were fixed as anisotropic, the hydrogen atomic positions were fixed relative to the bonded carbons, and the isotropic thermal parameters were fixed.

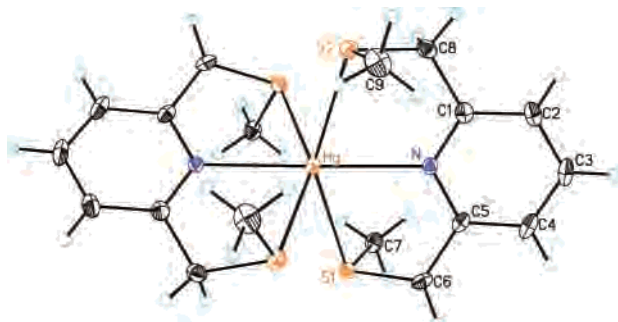
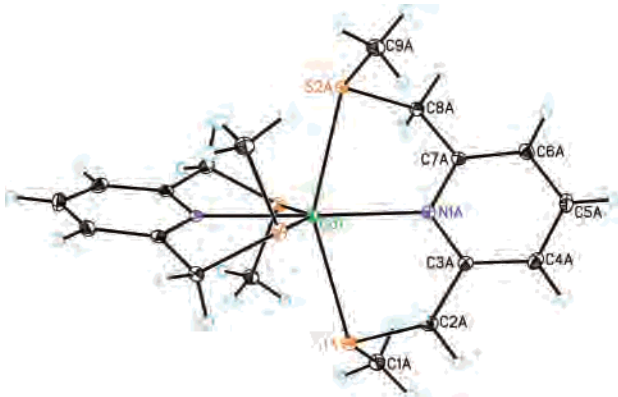
(20) Sheldrick, G. M. *SHELXL*, version 6.14; University of Göttingen: Göttingen, Germany, 1997.



**Table 2.** Crystallographic Data for Complexes 4–6

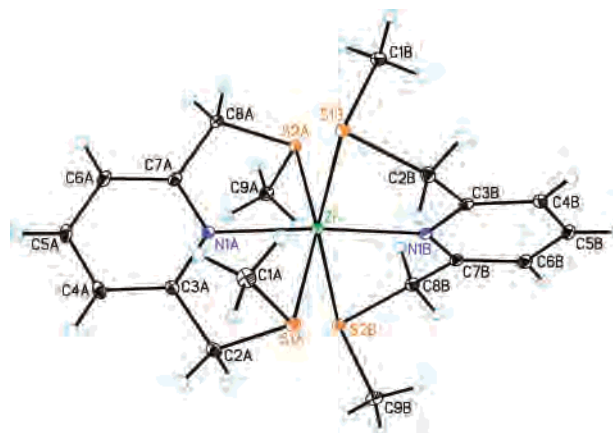
	4	5	6
empirical formula	C <sub>9</sub> H <sub>13</sub> NS <sub>2</sub> HgCl <sub>2</sub>	C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> S <sub>4</sub> Cd <sub>2</sub> Cl <sub>4</sub>	C <sub>9</sub> H <sub>13</sub> NS <sub>2</sub> ZnCl <sub>2</sub>
fw	470.81	765.25	335.59
crystal system	triclinic	monoclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> , Å	7.57(2)	7.8108(13)	15.090(6)
<i>b</i> , Å	7.84(2)	14.487(3)	15.121(6)
<i>c</i> , Å	11.67(3)	11.835(2)	11.663(5)
$\alpha$ , deg	87.92(5)	90	90
$\beta$ , deg	83.39(5)	103.095(3)	90
$\gamma$ , deg	81.87(5)	90	90
<i>V</i> , Å <sup>3</sup>	681(3)	1304.3(4)	2661.2(19)
<i>Z</i>	2	2	8
<i>d</i> <sub>calc.</sub> , g cm <sup>-3</sup>	2.297	1.948	1.675
$\mu$ , mm <sup>-1</sup>	11.975	2.371	2.529
<i>T</i> , K	148(2)	148(2)	103(2)
R1, <sup>a</sup> wR2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0820, 0.2255	0.0332, 0.0862	0.0172, 0.0405
R1, <sup>a</sup> wR2 <sup>b</sup> (all data)	0.0877, 0.2320	0.0340, 0.0869	0.0187, 0.0410

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

**Figure 2.** Structure of the cation of Hg(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (1). Thermal ellipsoids are shown at the 50% level. Anions are omitted for clarity.**Figure 3.** Structure of one of the two similar cations in the unit cell of Cd(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2). Thermal ellipsoids are shown at the 50% level. Anions are omitted for clarity.

## Results and Discussion

L<sup>1</sup> acts as a tridentate chelating ligand in the solid-state structures of complexes 1–6. Complexes 1–3 consist of the dications [Hg(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>, [Cd(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>, and [Zn(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup>, respectively (Figures 2–4), and well-separated perchlorate anions. Selected bond distances and angles for complexes 1–3 are given in Table 3. Complexes 1–3 are the first crystallographically characterized complexes of this class of ligands with 1:2 metal-to-ligand ratios. The structures of chloride complexes Hg(L<sup>1</sup>)Cl<sub>2</sub> (4), [Cd(L<sup>1</sup>)Cl( $\mu$ -Cl)]<sub>2</sub> (5), and Zn(L<sup>1</sup>)Cl<sub>2</sub> (6) are shown in Figures 5–7, respectively. Similar coordi-

**Figure 4.** Structure of the cation of Zn(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (3). Thermal ellipsoids are shown at the 50% level. Anions are omitted for clarity.

ination spheres have been observed in [Cu(L<sup>8</sup>)Cl<sub>2</sub>],<sup>13</sup> [Cu(L<sup>2</sup>)Cl<sub>2</sub>],<sup>15</sup> [Cu(L<sup>3</sup>)Br], [Ni(L<sup>3</sup>)Br<sub>2</sub>],<sup>8</sup> [Cd(L<sup>2</sup>)Cl( $\mu$ -Cl)]<sub>2</sub>,<sup>14</sup> and [Zn(L<sup>2</sup>)Br<sub>2</sub>].<sup>16</sup> Selected bond distances and angles for complexes 4–6 are given in Table 4.

**Crystal Structure of Hg(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (1).** As shown in Figure 2, the [Hg(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup> cation has a meridional octahedral structure with crystallographically imposed C<sub>2</sub> symmetry and a N–Hg–N bond angle of 174.7(2)°. The L<sup>1</sup> ligands are rotated by 73° relative to each other, with intraligand S–Hg–S and average N–Hg–S bond angles of 149.16(5)° and 74.6(7)°, respectively. The thioether methyl groups of both ligands are arranged trans with respect to the pyridyl planes. The 2.406(5) Å Hg–N distance is similar to the Hg–N<sub>pyridyl</sub> distances observed in other six-coordinate complexes such as [Hg(pyridine)<sub>6</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and Hg(BMPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> {BMPA = bis[(2-pyridyl)methyl]amine}.<sup>21,22</sup> The Hg–S distances of 2.676(2) and 2.754(2) Å are close to those [2.654(1) and 2.671(1) Å] recently reported for Hg(Py<sub>2</sub>S)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub><sup>7</sup> and comparable to those observed in six-coordinate Hg(II) complexes of macrocyclic thioethers.<sup>23,24</sup> Each of the five-membered chelate rings in 1 adopts an envelope conformation with the S atom 1.0 Å from the plane containing Hg, N, and two lutidyl C atoms. The Hg–O(perchlorate) distances (3.87–6.35 Å) are greater than the sum of the van der Waals radii for Hg and O [*r*<sub>vdw</sub>(Hg) = 1.70–2.00 Å, *r*<sub>vdw</sub>(O) = 1.54 Å].<sup>25</sup>

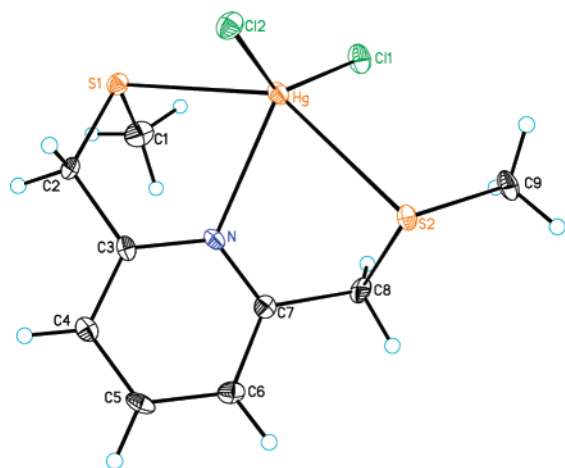
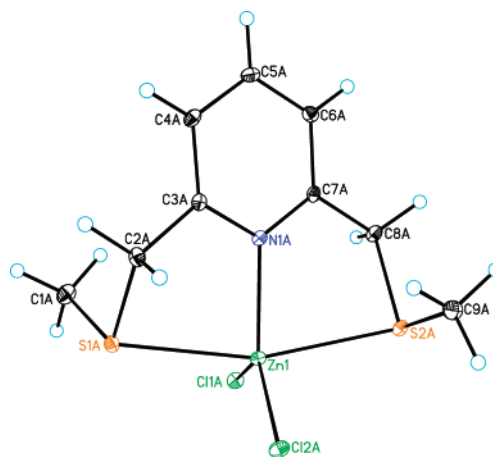
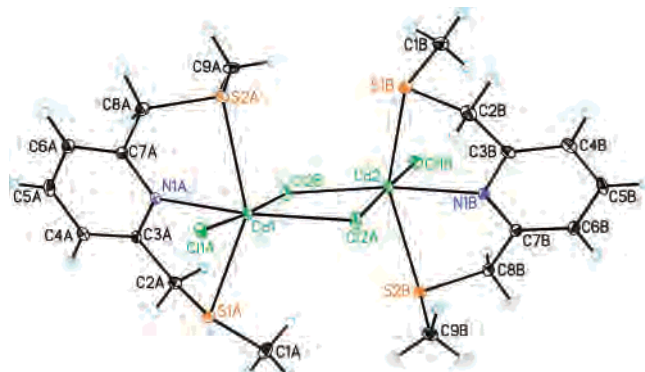
The only other structurally characterized Hg(II) complex with a N<sub>2</sub>(SR)<sub>4</sub> metal coordination sphere is the Hg(PF<sub>6</sub>)<sub>2</sub> complex of 1,4,10,13-tetrathia-7,16-diazacyclo-octadecane (TDO).<sup>26</sup> This complex crystallized in a distorted octahedral coordination geometry. The average Hg–S distance for the four sulfur donors in the equatorial plane of the TDO

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**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 1–3

Hg(L <sup>1</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> (1) <sup>a</sup>		Cd(L <sup>1</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> (2) <sup>b</sup>		Zn(L <sup>1</sup> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> (3)	
Hg–N	2.406(5)	Cd(1)–N(1A)	2.3558(14)	Zn–N(1A)	2.125(3)
Hg–S(1)	2.6763(16)	Cd(1)–S(1A)	2.7077(5)	Zn–S(1A)	2.5730(14)
Hg–S(2)	2.7538(17)	Cd(1)–S(2A)	2.7356(6)	Zn–S(2A)	2.5519(13)
		Cd(2)–N(1B)	2.3673(15)	Zn–N(1B)	2.119(3)
		Cd(2)–S(1B)	2.6819(5)	Zn–S(1B)	2.5300(11)
		Cd(2)–S(2B)	2.7359(5)	Zn–S(2B)	2.6508(14)
N–Hg–S(1)	75.28(13)	N(1A)–Cd(1)–S(1A)	75.69(4)	N(1A)–Zn–S(1A)	79.56(7)
N–Hg–S(2)	73.88(13)	N(1A)–Cd(1)–S(2A)	75.41(4)	N(1A)–Zn–S(2A)	80.06(8)
N–Hg–N#1	174.7(2)	N(1A)–Cd(1)–N(1A)#1	178.02(7)	N(1A)–Zn–N(1B)	175.23(9)
N–Hg–S(1)#1	107.95(12)	N(1A)–Cd(1)–S(1A)#1	105.57(4)	N(1A)–Zn–S(1B)	102.76(8)
N–Hg–S(2)#1	102.85(12)	N(1A)–Cd(1)–S(2A)#1	103.36(4)	N(1A)–Zn–S(2B)	97.20(8)
S(1)–Hg–S(2)	149.16(5)	S(1A)–Cd(1)–S(2A)	151.077(14)	S(1A)–Zn–S(2A)	159.61(3)
S(1)–Hg–S(1)#1	107.87(7)	S(1A)–Cd(1)–S(1A)#1	104.51(2)	S(1A)–Zn–N(1B)	98.10(7)
S(1)–Hg–S(2)#1	81.20(5)	S(1A)–Cd(1)–S(2A)#1	82.353(17)	S(1A)–Zn–S(1B)	92.15(4)
S(2)–Hg–S(2)#1	106.37(8)	S(2A)–Cd(1)–S(2A)#1	105.37(2)	S(1A)–Zn–S(2B)	88.66(4)
		N(1B)–Cd(2)–S(1B)	76.10(4)	N(1B)–Zn–S(2A)	102.19(8)
		N(1B)–Cd(2)–S(2B)#2	75.15(4)	S(1B)–Zn–S(2A)	92.83(4)
		N(1B)–Cd(2)–N(1B)#2	175.05(7)	S(2A)–Zn–S(2B)	93.39(4)
		N(1B)–Cd(2)–S(1B)#2	106.99(4)	N(1B)–Zn–S(1B)	81.41(8)
		N(1B)–Cd(2)–S(2B)	101.84(4)	N(1B)–Zn–S(2B)	78.53(8)
		S(1B)–Cd(2)–S(2B)	151.168(14)	S(1B)–Zn–S(2B)	159.84(3)
		S(1B)–Cd(2)–S(1B)#2	106.28(2)		
		S(1B)–Cd(2)–S(2B)#2	80.299(17)		
		S(2B)–Cd(2)–S(2B)#2	107.72(2)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $-x, -y + 1/2, z; x, -y + 1, -z + 1/2; -x - 1/2, y, -z$ . <sup>b</sup> Symmetry transformations used to generate equivalent atoms:  $-x + 3/2, -y + 1, z; -x + 1/2, -y, z; -x + 1, y, -z + 3/2; -x + 2, y, -z + 3/2$ .

**Figure 5.** Structure of Hg(L<sup>1</sup>)Cl<sub>2</sub> (4). Thermal ellipsoids are shown at the 50% level.**Figure 7.** Structure of one of the two similar complexes in the unit cell of Zn(L<sup>1</sup>)Cl<sub>2</sub> (6). Thermal ellipsoids are shown at the 50% level.**Figure 6.** Structure of [Cd(L<sup>1</sup>)Cl(μ-Cl)]<sub>2</sub> (5). Thermal ellipsoids are shown at the 50% level.

complex was 2.695(5) Å, which is very similar to the equatorial plane distance of complex 1. The aliphatic nitrogens in the axial positions had a Hg–N distance of

2.472(2) Å, slightly longer than the Hg–N<sub>pyridyl</sub> distance in 1.

**Crystal Structure of Cd(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2).** Complex 2 crystallizes in the orthorhombic *Pcca* space group with eight formula units per cell. The unit cell contains two similar but crystallographically independent [Cd(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup> cations (Figure 2). Both meridional octahedral [Cd(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup> cations have crystallographically imposed *C*<sub>2</sub> symmetry. The N–M–N bond angles of 175.05(7)° and 178.02(7)° in 2 are closer to linear than are those in 1. The L<sup>1</sup> pyridyl planes are rotated by 77° relative to each other. The average M–N [2.362(7) Å] and M–S [2.7153(3) Å] bond lengths of 2 are slightly shorter and nearly identical, respectively, to those in 1. The thioether methyl groups of both ligands are arranged trans with respect to the pyridyl planes, and the average intraligand S–M–S and N–M–S bond angles of 151.12(6)° and 75.591(5)° in 2 are similar to those observed

**Table 4.** Selected Bond Distances (Å) and Bond Angles (deg) for Complexes 4–6

Hg(L <sup>1</sup> )Cl <sub>2</sub> (4)		[Cd(L <sup>1</sup> )Cl(μ-Cl)] <sub>2</sub> (5)		Zn(L <sup>1</sup> )Cl <sub>2</sub> (6)	
Hg–Cl(1)	2.383(7)	Cd(1)–N(1A)	2.395(4)	Zn(1)–N(1A)	2.0785(15)
Hg–Cl(2)	2.409(6)	Cd(1)–Cl(2A)	2.5301(12)	Zn(1)–Cl(2A)	2.2333(8)
Hg–N	2.454(11)	Cd(1)–Cl(1A)	2.5355(11)	Zn(1)–Cl(1A)	2.2548(7)
Hg–S(1)	2.777(7)	Cd(1)–Cl(2B)	2.7050(11)	Zn(1)–S(1A)	2.5741(9)
Hg–S(2)	2.854(7)	Cd(1)–S(1A)	2.7060(12)	Zn(1)–S(2A)	2.5814(9)
		Cd(1)–S(2A)	2.7342(12)	Zn(2)–N(1B)	2.0828(15)
		Cd(2)–N(1B)	2.356(4)	Zn(2)–Cl(1B)	2.2190(8)
		Cd(2)–Cl(1B)	2.5192(13)	Zn(2)–Cl(2B)	2.2326(8)
		Cd(2)–Cl(2B)	2.5279(11)	Zn(2)–S(1B)	2.6168(9)
		Cd(2)–S(1B)	2.7080(13)	Zn(2)–S(2B)	2.6318(8)
		Cd(2)–S(2B)	2.7359(12)		
		Cd(2)–Cl(2A)	2.7477(12)		
Cl(1)–Hg–Cl(2)	139.31(17)	N(1A)–Cd(1)–Cl(2A)	168.48(9)	N(1A)–Zn(1)–Cl(2A)	117.21(4)
Cl(1)–Hg–N	116.7(3)	N(1A)–Cd(1)–Cl(1A)	93.51(10)	N(1A)–Zn(1)–Cl(1A)	113.15(4)
Cl(2)–Hg–N	103.9(3)	Cl(2A)–Cd(1)–Cl(1A)	97.43(4)	Cl(2A)–Zn(1)–Cl(1A)	129.62(2)
Cl(1)–Hg–S(1)	101.97(13)	N(1A)–Cd(1)–Cl(2B)	84.45(10)	N(1A)–Zn(1)–S(1A)	81.78(4)
Cl(2)–Hg–S(1)	93.20(16)	Cl(2A)–Cd(1)–Cl(2B)	84.48(4)	Cl(2A)–Zn(1)–S(1A)	88.89(3)
N–Hg–S(1)	71.3(3)	Cl(1A)–Cd(1)–Cl(2B)	177.01(4)	Cl(1A)–Zn(1)–S(1A)	97.09(3)
Cl(1)–Hg–S(2)	94.89(15)	N(1A)–Cd(1)–S(1A)	73.09(10)	N(1A)–Zn(1)–S(2A)	79.79(4)
Cl(2)–Hg–S(2)	95.27(18)	Cl(2A)–Cd(1)–S(1A)	109.93(4)	Cl(2A)–Zn(1)–S(2A)	95.82(2)
N–Hg–S(2)	71.4(3)	Cl(1A)–Cd(1)–S(1A)	92.26(4)	Cl(1A)–Zn(1)–S(2A)	93.96(3)
S(1)–Hg–S(2)	142.70(10)	Cl(2B)–Cd(1)–S(1A)	89.23(4)	S(1A)–Zn(1)–S(2A)	161.101(16)
		N(1A)–Cd(1)–S(2A)	73.79(9)	N(1B)–Zn(2)–Cl(1B)	119.52(5)
		Cl(2A)–Cd(1)–S(2A)	103.11(4)	N(1B)–Zn(2)–Cl(2B)	117.61(4)
		Cl(1A)–Cd(1)–S(2A)	86.93(4)	Cl(1B)–Zn(2)–Cl(2B)	122.87(2)
		Cl(2B)–Cd(1)–S(2A)	90.40(4)	N(1B)–Zn(2)–S(1B)	79.12(5)
		S(1A)–Cd(1)–S(2A)	146.76(4)	Cl(1B)–Zn(2)–S(1B)	98.68(2)
		N(1B)–Cd(2)–Cl(1B)	91.26(10)	Cl(2B)–Zn(2)–S(1B)	92.08(3)
		N(1B)–Cd(2)–Cl(2B)	169.95(9)	N(1B)–Zn(2)–S(2B)	79.96(5)
		Cl(1B)–Cd(2)–Cl(2B)	97.33(4)	Cl(1B)–Zn(2)–S(2B)	91.63(3)
		N(1B)–Cd(2)–S(1B)	76.62(10)	Cl(2B)–Zn(2)–S(2B)	97.55(3)
		Cl(1B)–Cd(2)–S(1B)	101.50(4)	S(1B)–Zn(2)–S(2B)	159.083(18)
		Cl(2B)–Cd(2)–S(1B)	106.56(4)		
		N(1B)–Cd(2)–S(2B)	74.00(9)		
		Cl(1B)–Cd(2)–S(2B)	88.98(4)		
		Cl(2B)–Cd(2)–S(2B)	100.84(4)		
		S(1B)–Cd(2)–S(2B)	148.98(4)		
		N(1B)–Cd(2)–Cl(2A)	87.66(10)		
		Cl(1B)–Cd(2)–Cl(2A)	178.38(4)		
		Cl(2B)–Cd(2)–Cl(2A)	83.64(4)		
		S(1B)–Cd(2)–Cl(2A)	79.43(4)		
		S(2B)–Cd(2)–Cl(2A)	89.56(4)		
		Cd(1)–Cl(2A)–Cd(2)	95.02(4)		
		Cd(2)–Cl(2B)–Cd(1)	96.13(4)		

in complex **1**, indicating that the ligands are in a similar conformation. No other structurally characterized Cd(II) complex with a N<sub>2</sub>(SR)<sub>2</sub> metal coordination sphere has been reported.

**Crystal Structure of Zn(L<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (3).** As shown in Figure 4, the [Zn(L<sup>1</sup>)<sub>2</sub>]<sup>2+</sup> cation in complex **3** has a more ideally meridional octahedral structure than the cations of complexes **1** and **2**. Unlike for **1** and **2**, there is no crystallographically imposed symmetry for **3**. The 175.23(9)° N–M–N bond angle in **3** is comparable to those observed in **1** and **2**. The L<sup>1</sup> pyridyl planes are rotated by 87° relative to each other. The two methyl groups in the thioether moieties are placed in a trans fashion with respect to the pyridyl rings, as observed in complexes **1** and **2**. The Zn–N<sub>pyridyl</sub> distances of 2.119(3) and 2.125(3) Å are similar to those observed in six-coordinate Zn(II) complexes<sup>6,27–30</sup> and

also compare well with the Zn–N(His) distance in proteins,<sup>31–35</sup> but they are significantly smaller than the M–N bond lengths in **1** and **2**. The Zn–S bond distances ranging from 2.530(1) to 2.651(1) Å are comparable to those in six-coordinate Zn(II) complexes,<sup>2,36</sup> but also significantly shorter than all of the M–S bond lengths in **1** and **2**. The average intraligand S–M–S and N–M–S bond angles of 159.72(8) and 79.89(8)°, respectively, in complex **3** are somewhat larger than those in complex **1** and **2** because of the shorter Zn–N bond lengths. No other structurally characterized Zn(II) complex with a N<sub>2</sub>(SR)<sub>2</sub> metal coordination sphere has been reported.

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**Table 5.** Comparison of M–N<sub>aliphatic</sub>, M–N<sub>aromatic</sub>, and M–S Bond Length Ranges for Known Complexes with N<sub>2</sub>(SR<sub>2</sub>)<sub>4</sub> Coordination Spheres

metal ion	M–N <sub>aliphatic</sub> (Å)	M–N <sub>aromatic</sub> (Å)	M–S (Å)	ref(s)
Fe(II)	2.022(4)–2.038(4)		2.248(1)–2.2674(15)	46, 47
Co(II)		2.100(3)	2.460(1)–2.486(1)	45
Co(III)	1.9993(4), 1.994(4)		2.249(1)–2.268(1)	42
Ni(II)	2.065(13)–2.126(13)	2.053(2)–2.091(5)	2.389(2)–2.440(2)	39–44
Cu(II)	2.007(13)–2.191(17)		2.487(5)–2.578(5)	36–38
Zn(II)		2.119(3)–2.125(3)	2.5300(11)–2.6508(14)	this work
Cd(II)		2.3558(14)–2.3673(15)	2.6819(5)–2.7359(5)	this work
Hg(II)	2.472(17), 2.473(11)	2.406(5)	2.6764(17)–2.7538(17)	this work, 25

**Comparisons of Complexes 1–3 to Related Complexes of Physiologically Essential Metal Ions.** Although no metal complexes of L-type ligands with a 1:2 metal-to-ligand ratio have been previously structurally characterized, a handful of structurally characterized complexes of the physiologically essential divalent metal ions with N<sub>2</sub>(SR<sub>2</sub>)<sub>4</sub> coordination spheres are available. The metal complexes of type M[N<sub>2</sub>(SR<sub>2</sub>)<sub>4</sub>]<sup>2+</sup> [M = Cu(II),<sup>37–39</sup> Ni(II),<sup>40–45</sup> Co(II),<sup>46</sup> Co(III),<sup>43</sup> and Fe(II)<sup>47,48</sup>] with noncoordinating counterions all exhibit a distorted meridional C<sub>2v</sub> or trans facial D<sub>2h</sub> coordination geometry. Table 5 indicates the range of M–N and M–S bond lengths observed in these complexes. The Cu–N<sub>aliphatic</sub> bond has the largest range of 2.01(1)–2.19(2) Å, and all other divalent first-row transition metal bond distances M(II)–N fall into this range. As might be expected, the average for M–N bond distances increases as one moves down the group 12 family (Zn–N < Cd–N < Hg–N), consistent with the increased metal ion radius. Inspection of Table 5 also indicates that the range of M(II)–S bond distances follows the nearly periodic trend Fe < Ni < Co < Cu < Zn for the first-row transition metal ions. The group 12 metal ions present the feature Zn–S < Cd–S ≈ Hg–S, which was also observed in the six-coordinate group 12 metal crown thioether complexes [M(10S3)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>NO<sub>3</sub> [10S3 = bis(1,4,7-trithiacyclodecane)].<sup>36</sup>

**Crystal Structure of Hg(L<sup>1</sup>)Cl<sub>2</sub> (4).** As shown in Figure 5, complex 4 has a nearly square-pyramidal Hg(II) coordination geometry ( $\tau = 0.06^{49}$ ). The square plane is defined by the S(1), S(2), Cl(1), and Cl(2) donor atoms. The sulfur atoms are 0.861 Å from the mean least-squares plane, and the chloride atoms are positioned, on average, a comparable

distance from the opposite side. The Hg(II) ion is displaced 0.03 Å from the mean least-squares plane toward the chlorides. The largest angles between atoms in the basal plane of the complex are 142.7(1)° for S(1)–Hg–S(2) and 139.3(2)° for Cl(1)–Hg–Cl(2). Five-coordinate Hg(II) complexes exhibiting similar square-pyramidal structures are known,<sup>50,51</sup> as are complexes with more trigonal-bipyramidal character.<sup>52–54</sup> With L-type ligands, a distorted square-pyramidal geometry is observed in [Ni(L<sup>3</sup>)Br<sub>2</sub>] and [Cu(L<sup>2</sup>)Cl<sub>2</sub>], with the nitrogen atom, two sulfur atoms and one halide atom occupying the four basal positions of the square pyramid.<sup>8</sup> However, distorted trigonal-bipyramidal geometries have also been observed in the complexes [Cu(L<sup>8</sup>)Cl<sub>2</sub>] and [Zn(L<sup>2</sup>)Br<sub>2</sub>].<sup>13,16</sup>

Inspection of Tables 3 and 4 shows that the 2.45(1) Å Hg–N and 2.82(5) Å average Hg–S bond lengths in 4 are essentially identical and only 0.10 Å longer, respectively, than their counterparts in complex 1. The intraligand S–Hg–S and N–Hg–S bond angles of 142.7(1)° and 71.4(3)° are ~4.5% smaller than those in complex 1. The most distinct difference between the ligand conformations in 4 and 1 is the cis and trans orientations, respectively, of the two methyl groups bonded to the two sulfur atoms. The Hg–Cl distances of 2.383(7) and 2.409(6) Å are comparable to the observed range of 2.310–2.428 Å in five-coordinate complexes.<sup>51,52,55,56</sup>

**Crystal Structure of [Cd(L<sup>1</sup>)Cl(μ-Cl)]<sub>2</sub> (5).** Complex 5 exists in the solid state as a dimer asymmetrically bridged by two chloride ligands (Figure 6). Each of the Cd(II) centers adopts a distorted octahedral geometry, with one tridentate L<sup>1</sup> ligand, two bridging chlorides, and one terminal chloride atom occupying the six positions. The ligand L<sup>1</sup> is bound to Cd(II) in an approximately meridional fashion, with one bridging chloride atom in the same plane and the terminal and the other bridging chloride ligand in the axial positions. It is interesting to note that the two L<sup>1</sup> moieties are arranged in different configurations. In the dimer, the two methyl groups of one L<sup>1</sup> ligand are found cis about the pyridyl plane, but those of the other ligand are trans, resembling Hg(L<sup>1</sup>)–

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Cl<sub>2</sub> and Zn(L<sup>1</sup>)Cl<sub>2</sub>, respectively [see the following section for Zn(L<sup>1</sup>)Cl<sub>2</sub>]. Moreover, the dimeric structure of complex **5** indicates the greater tendency of Cd(II) toward octahedral coordination relative to Hg(II) and Zn(II) and the flexible ligation capacity of halide ligands.<sup>57</sup> A similar dimeric structure is common in CdCl<sub>2</sub> complexes, such as [Cd(L<sup>2</sup>)Cl(μ-Cl)]<sub>2</sub>,<sup>14</sup> Cd<sub>2</sub>(Py<sub>2</sub>S)<sub>2</sub>Cl<sub>4</sub>,<sup>7</sup> and Cd<sub>2</sub>(L)<sub>2</sub>Cl<sub>4</sub> [L = 1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-oxapropane].<sup>57</sup>

The average Cd–Cl<sub>bridge</sub> bond distance of 2.628(9) Å and Cd–Cd distance of 3.894 Å are comparable to those in chloride-bridged Cd(II) dimers and polymers.<sup>58,59</sup> The average Cd–Cl<sub>terminal</sub> bond distance is 2.527(6) Å, similar to those found in six-coordinate Cl-bridged Cd(II) complexes.<sup>10,59</sup> The average Cd–S distance of 2.721(4) Å and Cd–N distance of 2.375(9) Å are close to the corresponding 2.713(6) and 2.3803 Å values observed in complex [Cd(L<sup>2</sup>)Cl(μ-Cl)]<sub>2</sub>.<sup>14</sup> The intraligand N–Cd–S bond angles range from 73.09(10)° to 76.62(10)°. The axial Cl<sub>bridge</sub>–Cd–Cl<sub>terminal</sub> bond angles of 177.01(4)° and 178.38(4)° are slightly smaller than the ideal for an octahedral geometry.

**Crystal Structure of Zn(L<sup>1</sup>)Cl<sub>2</sub> (6).** Complex **6** contains two similar but crystallographically independent Zn(II) centers (Figure 7) in the crystal structure. Each Zn(II) ion is located in a coordination environment consisting of one tridentate L<sup>1</sup> and two chloride ligands with slightly more trigonal-bipyramidal character than square-pyramidal {τ = 0.525 [Zn(1)], 0.604 [Zn(2)]<sup>49</sup>}. The Zn, N, Cl(1), and Cl(2) atoms are coplanar, defining the equatorial plane, and the two sulfur atoms occupy axial positions. The structure closely resembles that of Hg(L<sup>1</sup>)Cl<sub>2</sub>, except for the trans conformation of the two methyl groups with respect to the pyridine plane and a pseudo-C<sub>2</sub> axis along the Zn–N bond. The S–Zn–S bond angles of 161.10(2)° and 159.08(2)° deviate significantly from linearity. However, the angles between the atoms in the equatorial plane are approximately ideal, ranging from 113.15(4)° to 129.62(2)°. The average Zn–S bond distance of 2.60(3) Å and Zn–N bond length of 2.081(3) Å are typical for five-coordinate Zn(II) complexes<sup>60,61</sup> and comparable to Zn–S(Cys) and Zn–N(His) distances, respectively, in proteins.<sup>31–35,62–64</sup> Teixidor et al.<sup>16</sup> previously reported the structurally similar complex [Zn(L<sup>2</sup>)-Br<sub>2</sub>], which has similar Zn–S and Zn–N bond distances. The R groups in complex [Zn(L<sup>2</sup>)Br<sub>2</sub>] were found to be trans to each other, as observed in **6**. The intraligand S–Zn–S bond angle of 157.0(1)° and N–Zn–S angle of 78.5(7)° also compare well with those in **6**.

**Comparisons of Complexes 4–6 to Related Complexes of Physiologically Essential Metal Ions.** The crystal structures of [Cu(L<sup>8</sup>)Cl<sub>2</sub>],<sup>13</sup> [Cu(L<sup>2</sup>)Cl<sub>2</sub>],<sup>15</sup> [Cu(DAHT)Cl<sub>2</sub>] {DAHT = 3,10-dithia-16-azabicyclo[10.3.1]hexadeca-1(16), 12,14-triene},<sup>15</sup> [Ni(L<sup>3</sup>)Br<sub>2</sub>],<sup>8</sup> and [Ni(L<sup>3</sup>)Br(μ-Br)]<sub>2</sub><sup>9</sup> have been previously reported. [Cu(L<sup>8</sup>)Cl<sub>2</sub>] resembles complex **6** with a distorted trigonal-bipyramidal geometry.<sup>13</sup> The Cu–S bond distances range from 2.338(3) to 2.431(1) Å [average 2.366(7) Å],<sup>13</sup> which are shorter than the Zn–S distances observed in complex **6**. The average Cu–N distance of 2.045(6) Å<sup>13</sup> is comparable to the average Zn–N distance of 2.080(7) Å in **6**. The average S–Cu–S bond angles of 158.7(8)° is also comparable to the S–Zn–S angle of 160.09(2)° observed in complex **6**.

The complexes [Cu(L<sup>2</sup>)Cl<sub>2</sub>],<sup>15</sup> [Cu(DAHT)Cl<sub>2</sub>],<sup>15</sup> and [Ni(L<sup>3</sup>)Br<sub>2</sub>]<sup>8</sup> exist in the solid state as monomers adopting distorted square-pyramidal coordination geometries much like **6**. The complex [Ni(L<sup>3</sup>)Br<sub>2</sub>]<sup>8</sup> has an average Ni(II)–S distance of 2.383(7) Å and a Ni(II)–N distance of 2.057(5) Å that compares well with the above Cu(II) complexes. However, a cis arrangement of the R groups of the ligand was observed, as in complex **4**. The R groups of the ligands in complexes [Cu(L<sup>2</sup>)Cl<sub>2</sub>]<sup>15</sup> and [Cu(L<sup>8</sup>)Cl<sub>2</sub>]<sup>13</sup> are both arranged in trans fashion as observed in complex **6**. The dimeric complex [Ni(L<sup>3</sup>)Br(μ-Br)]<sub>2</sub><sup>9</sup> has a distorted octahedral coordination geometry for Ni(II), which is similar to those of **5** and [Cd(L<sup>2</sup>)Cl(μ-Cl)]<sub>2</sub>.<sup>14</sup> The average Ni–N and Ni–S bond distances are 2.0557(5) and 2.443(7) Å, respectively, and their R groups are both trans to each other.

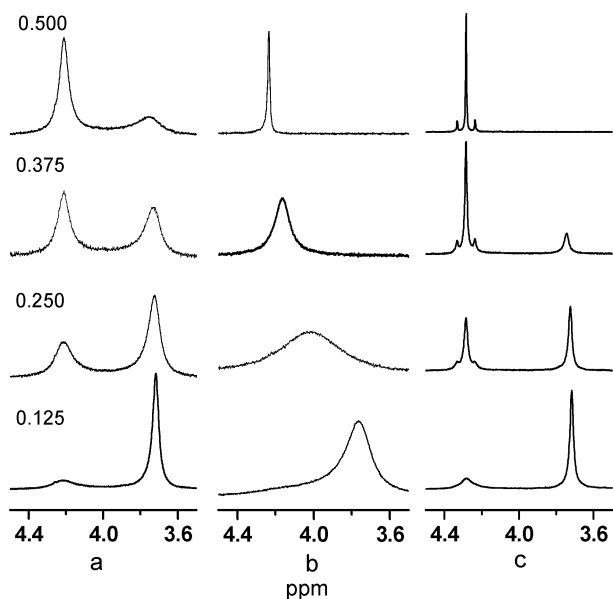
Crystallographic database searches revealed four other, non-L-based Cu(II)<sup>65–68</sup> complexes and one Zn(II)<sup>69</sup> complex with a N(SR)<sub>2</sub>X<sub>2</sub> coordination sphere. The Cu–S bond distances in these complexes range from 2.313(2) to 2.369(2) Å with an average of 2.334(9) Å, which falls in the observed range of the above Cu(II)–L complexes. The average Cu–N<sub>pyridyl</sub> and Cu–N<sub>aliphatic</sub> bond distances are 2.025(9) and 2.174(4) Å, respectively. The average Zn–S and Zn–N bond distances are 2.618(1) and 2.080(3) Å, which are comparable to the corresponding 2.686(7) and 2.083(5) Å values observed in the complex [Zn(L<sup>2</sup>)Br<sub>2</sub>].<sup>16</sup>

As discussed above, the halide salts used to study the coordination chemistry of the L-type ligands are limited to CuX<sub>2</sub>, NiX<sub>2</sub> and ZnX<sub>2</sub>, with only a few cases of heavy metal salts. Also, with only a few exceptions, such ligands are found coordinated to metal ions in a tridentate fashion. The mononuclear complexes M[N(SR)<sub>2</sub>X<sub>2</sub>] with tridentate coordination all adopt distorted square-pyramidal or trigonal-bipyramidal coordination geometries. Furthermore, the halide counterions are found in the primary coordination sphere, which could prevent a second ligand from binding.

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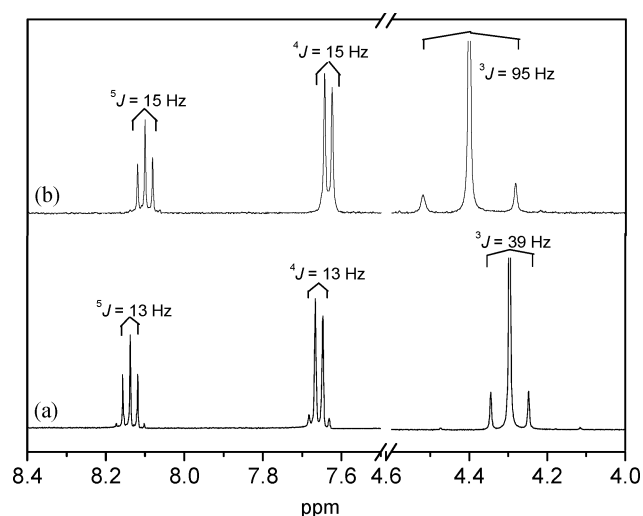




**Figure 8.** Methylene ( $H_f$ ) region of the  $^1H$  NMR spectra for  $L^1$  at  $-40$  °C in acetonitrile- $d_3$  as a function of added  $Zn(ClO_4)_2$  (left),  $Cd(ClO_4)_2$  (middle) and  $Hg(ClO_4)_2$  (right) with nominal  $[M^{2+}]/[L^1]$  ratios of 0.125, 0.250, 0.375, and 0.500. The nominal total  $M^{2+}$  concentration was 2 mM.

**Solution-State  $^1H$  NMR Spectroscopy.** Metal ion binding to  $L^1$  with the perchlorate and chloride salts of divalent zinc triad metals was studied in the solution state using  $^1H$  NMR spectroscopy. The room-temperature acetonitrile- $d_3$  solution  $^1H$  chemical shifts for complexes **1–6** are generally downfield of equivalent resonances for the free ligand. Downfield shifts are often observed upon complexation to metal ions and are attributed to the deshielding influence of  $\sigma$  donation to the metal center. Acetonitrile- $d_3$  solutions of the two series of complexes **1–3** and **4–6** exhibited similar  $^1H$  chemical shifts with no apparent periodic trends. Furthermore, the asymmetric ligand binding observed in all six crystal structures was not observed in solution. Each complex had a single resonance for each symmetry-related proton in the free ligand. The small differences between  $M(II)$ –S bond lengths ( $<0.12$  Å) and the ease of rearrangements of the coordination sphere of  $d^{10}$  metal ions facilitate ligand reorganization in the absence of crystal restraints. In addition, the inversion of thioether sulfur is rapid in solution even at  $-40$  °C.<sup>7</sup>

The coordination chemistry of  $L^1$  binding to divalent group 12 metal perchlorates in acetonitrile- $d_3$  solutions was investigated by  $^1H$  NMR spectroscopy at room temperature and  $-20$  and  $-40$  °C, with nominal  $[M(ClO_4)_2]/[L^1]$  molar ratios between 0.125 and 1.750 and a total  $M(ClO_4)_2$  concentration of 2 mM. Spectroscopic trends indicate that the formation of  $M(L^1)_2^{2+}$  was favored thermodynamically over the formation of  $M(L^1)(NCCH_3)_x^{2+}$  for  $[M(ClO_4)_2]/[L^1] < 0.5$  with all three metal ions [Figures 8 and S1–S3 (Supporting Information)]. At  $-40$  °C, sharp peaks for the free ligand gradually lost intensity as  $[Hg(ClO_4)_2]/[L^1]$  was increased to 0.5, and a new set of sharp peaks increased in intensity. This indicates that  $Hg(L^1)_2^{2+}$  and free ligand were in slow exchange on the chemical-shift time scale and coupling-constant time scale at low  $[Hg(ClO_4)_2]/[L^1]$ . In contrast, a



**Figure 9.** Selected  $^1H$  NMR spectra in  $CD_3CN$  with a total  $Hg(II)$  concentration of 2 mM at  $-20$  °C: (a)  $[Hg(L^1)_2]^{2+}$ , (b)  $[Hg(L^1)(NCCH_3)_2]^{2+}$ . The methyl protons with  $J(^{199}Hg^1H) = 49$  Hz for  $[Hg(L^1)_2]^{2+}$  and 105 Hz for  $[Hg(L^1)(NCCH_3)_2]^{2+}$  are omitted because of overlap with water protons.

single set of shifting-broadened ligand resonances was observed as a function of  $[Cd(ClO_4)_2]/[L^1]$  under similar conditions, indicating behavior approaching rapid intermolecular exchange on the chemical-shift time scale. Interestingly, two sets of slightly broadened ligand resonances with invariable chemical shifts were observed as a function of  $[Zn(ClO_4)_2]/[L^1]$  under similar conditions, revealing behavior approaching slow intermolecular exchange on the chemical-shift time scale. Our investigation of zinc triad binding to the NSN donor ligand bis(2-methylpyridyl) sulfide also provided some examples of  $Zn^{2+}$  coordination behavior being more similar to  $Hg^{2+}$  than  $Cd^{2+}$  coordination behavior.<sup>7</sup>

Complexes **1** and **2** were also examined for evidence of slow intermolecular exchange on the  $J(M^1H)$  time scale. For complex **1**,  $^3$ – $^5J(^{199}Hg^1H)$  couplings were observed in acetonitrile- $d_3$  at  $-40$  °C (Figure 9a), and an invariant NMR spectrum was obtained over 1 week at room temperature, indicating **1** was stable in acetonitrile- $d_3$  solution. The large magnitude of  $J(^{199}Hg^1H)$  to the methyl protons indicates that the thioether sulfur is bound to the metal center. The  $J(^{199}Hg^1H)$  to  $H_p$  is likely a five-bond coupling. Because neither  $J(^{199}Hg^1H)$  for a bidentate nitrogen and/or sulfur ligand nor  $^6J(^{199}Hg^1H)$  for a coordination compound have ever been reported, the pyridyl nitrogens are likely bound to  $Hg^{2+}$  in solution, as observed in the crystal structure of **1**. However, there are nine isomeric forms of bis-tridentate chelates.<sup>21</sup> The NMR spectrum observed has a single environment for all ligand protons and is consistent with either a meridional structure as observed in the solid state but with ligands bound symmetrically on average or rapid isomerization between all nine isomeric forms. Interconversion of the isomeric forms requires rotation about pseudo- $C_3$  axes of the trigonal-prismatic and pseudo-octahedral cores of ligating atoms. The energy differences between different isomeric forms are particularly small when all  $M$ – $L$  bond distances are equal. In **1**, the  $Hg$ – $N$  bond lengths are shorter than the  $M$ – $S$  bond lengths by 0.27 and 0.35 Å. These differences are somewhat greater than the 0.2

Å range between Hg–N of Hg(BMPA)<sup>2+</sup>, which was determined to exist as an equilibrium mixture of all but the meridional isomer.<sup>21</sup> Although a time invariant NMR spectrum was also obtained for complex **2**, conditions for detection of  $J(^{111/113}\text{Cd}^1\text{H})$  could not be found in acetonitrile-*d*<sub>3</sub> solution, even under conditions with excess metal ion. Stronger bonding, the typically larger magnitude of  $J(^{199}\text{Hg}^1\text{H})$  than  $J(^{111/113}\text{Cd}^1\text{H})$ ,<sup>70</sup> or a combination of the two might have permitted the observation of slow intermolecular exchange of **L**<sup>1</sup> on the coupling-constant time scale with Hg(II) but not Cd(II).

Examination of the <sup>1</sup>H NMR spectra of M(ClO<sub>4</sub>)<sub>2</sub> with **L**<sup>1</sup> at [M(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] molar ratios greater than 0.5 also revealed differences in behavior. With Hg<sup>2+</sup>, downfield shifts of 0.10 and 0.17 ppm for the methylene (H<sub>f</sub>) and methyl protons, respectively, and upfield shifts of 0.02 and 0.03 ppm for H<sub>m</sub> and H<sub>p</sub>, respectively, occurred in a linear fashion between [Hg(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] molar ratios of 0.5 and 1.0 (Figure S1). The chemical-shift changes were smaller in magnitude than the differences in chemical shift between the free ligand and Hg(**L**<sup>1</sup>)<sub>2</sub><sup>2+</sup>. In addition, the magnitudes of  $J(^{199}\text{Hg}^1\text{H})$  to all the ligand protons increased (Figure 9). These changes indicate that Hg(**L**<sup>1</sup>)(NCCH<sub>3</sub>)<sub>x</sub><sup>2+</sup> was thermodynamically more stable than Hg(**L**<sup>1</sup>)<sub>2</sub><sup>2+</sup> between [Hg(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] ratios of 0.5 and 1.0. The ligand proton chemical shifts remained constant at [Hg(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] > 1, but the <sup>199</sup>Hg coupling satellites (Figure 9b) became exchange-broadened, indicating ligand exchange between solvated Hg<sup>2+</sup> and Hg(**L**<sup>1</sup>)(NCCH<sub>3</sub>)<sub>x</sub><sup>2+</sup>. In contrast, the proton NMR spectra of Cd(**L**<sup>1</sup>)<sub>2</sub><sup>2+</sup> and Zn(**L**<sup>1</sup>)<sub>2</sub><sup>2+</sup> remained essentially invariant in solutions with [M(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] > 0.625. This suggests that M(**L**<sup>1</sup>)<sub>2</sub><sup>2+</sup> is more thermodynamically stable than M(**L**<sup>1</sup>)(NCCH<sub>3</sub>)<sub>x</sub><sup>2+</sup> for M = Cd<sup>2+</sup> and Zn<sup>2+</sup> over the range of [M(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] ratios examined (Figure S4). However, the changes in  $J(^{199}\text{Hg}^1\text{H})$  are more definitive than the changes in proton chemical shift for the interconversion of Hg(**L**<sup>1</sup>)<sub>2</sub><sup>2+</sup> and Hg(**L**<sup>1</sup>)(NCCH<sub>3</sub>)<sub>x</sub><sup>2+</sup>. Because  $J(^{111/113}\text{Cd}^1\text{H})$  was never detected for the Cd<sup>2+</sup> complexes and zinc does not have a favorable isotope for NMR detection, the M/**L**<sup>1</sup> stoichiometry of the Cd<sup>2+</sup> and Zn<sup>2+</sup> complexes at [M(ClO<sub>4</sub>)<sub>2</sub>]/[**L**<sup>1</sup>] > 0.5 is ill-defined in solution.

Comparable solution equilibria have been reported for the Hg(II) coordination chemistry of related tridentate ligands.<sup>7,21</sup> The observed <sup>3</sup> $J(^{199}\text{Hg}^1\text{H})$  values for Hg(**L**<sup>1</sup>)(NCCH<sub>3</sub>)<sub>x</sub><sup>2+</sup> of 105 and 95 Hz are among the largest coupling constants reported for thioether-ligand-containing Hg(II) complexes.<sup>7,71</sup> Reports of longer-range  $J(^{199}\text{Hg}^1\text{H})$  couplings in Hg(II) coordination compounds are rare. Those <sup>4–5</sup> $J(^{199}\text{Hg}^1\text{H})$  couplings reported here fall in the known range of 8–30 Hz for coupling between <sup>199</sup>Hg and <sup>1</sup>H separated by four or five bonds.<sup>7,21,53,72–74</sup>

The coordination chemistry of **L**<sup>1</sup> binding to divalent group 12 metal chlorides was also investigated by <sup>1</sup>H NMR spectroscopy. Although **5** had a different structure than **4** and **6** in the solid state, the <sup>1</sup>H NMR spectra of the three complexes were strikingly similar. The observed proton chemical-shift differences for **4** and **5** in acetonitrile-*d*<sub>3</sub> were less than 0.02 ppm, and resonances for **6** were within 0.22 ppm of those for the other chloride complexes. The chemical-shift differences between these complexes when recorded in DMSO-*d*<sub>6</sub> solutions were even smaller ( $\Delta\delta \leq 0.08$  ppm, data not shown). These data suggest that the complexes are structurally similar in solution. In this context, dimeric and monomeric structures are likely extremes in a continuum that reflect subtle differences in packing constraints in the solid state or solubility differences. Furthermore, no  $J(\text{M}^1\text{H})$  couplings were found for complexes **4** and **5** at accessible temperatures with [M<sup>2+</sup>] ≤ 2 mM in either solvent. Previous work suggests that intermolecular ligand exchange of d<sup>10</sup> metal ions with coordinating counterions such as chloride ions occurs particularly rapidly because of reductions in the available charge density. Precedent for the detection of <sup>199</sup>Hg–<sup>1</sup>H couplings in coordination compounds of HgCl<sub>2</sub> is limited to tetradentate chelating ligands.<sup>51,53,54</sup>

## Conclusion

Solid-state characterization of six divalent group 12 metal complexes of **L**<sup>1</sup> revealed tridentate binding modes with comparable ligand geometries except for the relative orientation of the thioether methyl groups. The binding of two ligands to the same metal center was first observed for the pyridine-based dithioether ligands in complexes M(**L**<sup>1</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (M = Hg, Cd, Zn). The three complexes all display distorted octahedral structures in the solid state with the two ligands in similar conformations. Complexes Hg(**L**<sup>1</sup>)Cl<sub>2</sub> and Zn(**L**<sup>1</sup>)Cl<sub>2</sub> exist in the solid state as monomers with distorted square-pyramidal and trigonal-bipyramidal geometries, respectively. [Cd(**L**<sup>1</sup>)Cl(μ-Cl)]<sub>2</sub> exists in the solid state as a dimer of Cd(II) centers with a distorted octahedral coordination geometry.

The slight ligand binding asymmetry observed in the solid state for these six complexes was not observed in solution because of the ease of rearranging the coordination sphere of d<sup>10</sup> metal ions in the absence of crystal restraints and the low energy barrier to thioether inversion. Furthermore, the differences between the proton NMR spectra of **4–6** were negligible, suggesting that the different structures in the solid state were artifacts associated with crystallization. There were, however, interesting differences between the solution-state coordination chemistries of zinc triad perchlorate complexes of **L**<sup>1</sup>. The relative rates of intermolecular ligand exchange for ions of type ML<sub>2</sub><sup>2+</sup> decreased in the order Cd(II) > Zn(II) > Hg(II). Both 1:1 and 1:2 complexes of Hg(II) with **L**<sup>1</sup> were in slow exchange on the coupling-constant time scale below –20 °C, but slow exchange conditions could not be found for the equivalent Cd(II) complexes.

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Despite intense study, the detailed molecular mechanisms for the toxicology of heavy metals remain largely unresolved. Although it is generally appreciated that Hg(II) has different toxicological effects than Cd(II), the solution-state research described here offers the fundamental insight that slow intermolecular exchange of Hg(II) between multidentate coordination sites encountered relative to Cd(II) might contribute to the differences in their toxicological profiles. Similarly, physiologically essential Zn(II) is bound more transiently to the ligand investigated, suggesting that Zn(II) can be more readily displaced when bound to inappropriate sites. Comparisons of the solution-state behavior of complexes **1–3** suggest that Hg(II) might compete more effectively for the native metal-binding sites of some proteins than Cd(II) or even Zn(II). Furthermore, slow intermolecular ligand exchange for the lower-coordination-number 1:1 Hg<sup>2+</sup>/L<sup>1</sup> complex suggests that Hg(II) might not require preformed metal-binding sites with high coordination numbers to have toxic effects. Adventitious coordination of Hg(II) to arrangements of metal-binding amino acids on the surface of a protein might allosterically interfere with native functions or misdirect the folding of specific proteins. Differences in Hg(II), Cd(II), and Zn(II) binding to native metal-binding

sites and adventitious sites might contribute to their vastly different physiological impacts. Further examination of group 12 metal coordination to multidentate ligands should provide further insight regarding the differences between their bioactivities.

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**Supporting Information Available:** X-ray crystallographic data (CIF), additional NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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