

## Solid-State and Solution-State Coordination Chemistry of the Zinc Triad with the Mixed N,S Donor Ligand Bis(2-methylpyridyl) Sulfide

Steven M. Berry and Deborah C. Bebout\*

Department of Chemistry, The College of William and Mary, Williamsburg, Virginia 23187-8795

Raymond J. Butcher

Department of Chemistry, Howard University, Washington, D.C. 20059

Received August 7, 2004

The binding of group 12 metal ions to bis(2-methylpyridyl) sulfide (**1**) was investigated by X-ray crystallography and NMR. Seven structures of the chloride and perchlorate salts of Hg(II), Cd(II), and Zn(II) with **1** are reported. Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, Cd(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, and Zn(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>CN form mononuclear, six-coordinate species in the solid state with **1** binding in a tridentate coordination mode. Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> has a distorted trigonal prismatic coordination geometry while Cd(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and Zn(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·CH<sub>3</sub>CN have distorted octahedral geometries. With chloride anions, the 1:1 metal to ligand complexes Hg(1)Cl<sub>2</sub>, [Cd(1)Cl<sub>2</sub>]<sub>2</sub>, and Zn(1)Cl<sub>2</sub> are formed. A bidentate binding mode that lacks thioether coordination is observed for **1** in the four-coordinate, distorted tetrahedral complexes Zn(1)Cl<sub>2</sub> and Hg(1)Cl<sub>2</sub>. [Cd(1)Cl<sub>2</sub>]<sub>2</sub> is dimeric with a distorted octahedral coordination geometry and a tridentate **1**. Hg(1)Cl<sub>2</sub> is comprised of pairs of loosely associated monomers and Zn(1)Cl<sub>2</sub> is monomeric. In addition, Hg<sub>2</sub>(1)Cl<sub>4</sub> is formed with alternating chloride and thioether bridges. The distorted square pyramidal Hg(II) centers result in a supramolecular zigzagging chain in the solid state. The solution <sup>1</sup>H NMR spectra of [Hg(1)<sub>2</sub>]<sup>2+</sup> and [Hg(1)(NCCH<sub>3</sub>)<sub>x</sub>]<sup>2+</sup> reveal <sup>3–5</sup>J(<sup>199</sup>Hg<sup>1</sup>H) due to slow ligand exchange found in these thioether complexes. Implications for use of Hg(II) as a metalloprobe are discussed.

### Introduction

The involvement of group 12 elements in biology and the environment is diverse. Zinc is an essential trace element specifically utilized by many enzymes. On the other hand, cadmium and mercury are known for their detrimental effects on living organisms and their bioavailability resulting from natural and industrial processes warrants concern.<sup>1,2</sup> Studying the binding of Cd(II) and Hg(II) to heteroatoms may provide insight into their toxicological behavior,<sup>1,2</sup> their mode of detoxification by metallothionein<sup>3–6</sup> and phytochelatin,<sup>7</sup> and their presence in Hg<sup>8–12</sup> and Cd<sup>13–18</sup> binding proteins.

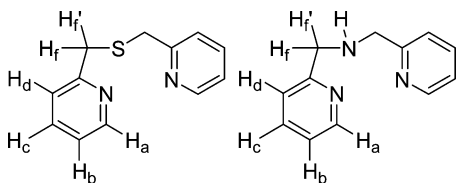
Understanding the solution-state behavior of these metal ions in biological environments is important to determining their activity.

The ligand bis(2-methylpyridyl) sulfide (**1**) (Figure 1, left) has previously been used to probe the biologically relevant coordination chemistry, the supramolecular chemistry, or the catalytic reactions of Cu(I/II),<sup>19–22</sup> Ag(I),<sup>23</sup> Ni(II),<sup>21</sup> Pt(II),<sup>24</sup>

\* Author to whom correspondence should be addressed. Phone: (757) 221-2558. Fax: (757) 221-2715. E-mail: dcbebo@wm.edu.

- (1) Vig, K.; Megharaj, M.; Sethunathan, N.; Naidu, R. *Adv. Environ. Res.* **2003**, *8*, 121.
- (2) Sigel, A.; Sigel, H. *Metal Ions in Biological Systems*; Dekker: New York, 1997; Vol. 34.
- (3) Lu, W.; Zelazowski, A. J.; Stillman, M. J. *Inorg. Chem.* **1993**, *32*, 919.
- (4) Nielson, K. B.; Atkin, C. L.; Winge, D. R. *J. Biol. Chem.* **1985**, *260*, 5342.
- (5) Furey, W. F.; Robbins, A. H.; Clancy, L. L.; Winge, D. R.; Wang, B. C.; Stout, C. D. *Science* **1986**, *231*, 704.

- (6) Robbins, A. H.; McRee, D. E.; Williamson, M.; Collett, S. A.; Xuong, N. H.; Furey, W. F.; Wang, B. C.; Stout, C. D. *J. Mol. Biol.* **1991**, *221*, 1269.
- (7) Matsumoto, S.; Shiraki, K.; Tsuji, N.; Hirata, K.; Miyamoto, K.; Takagi, M. *Sci. Technol. Adv. Mater.* **2004**, *5*, 377.
- (8) Fleissner, G.; Kozlowski, P. M.; Vargek, M.; Bryson, J. W.; O'Halloran, T. V.; Spiro, T. G. *Inorg. Chem.* **1999**, *38*, 3523.
- (9) Huffman, D. L.; Utschig, L. M.; O'Halloran, T. V. *Metal Ions in Biological Systems*; Dekker: New York, 1997; Vol. 34, p 503.
- (10) Utschig, L. M.; Bryson, J. W.; O'Halloran, T. V. *Science* **1995**, *268*, 380.
- (11) Hobman, J. L.; Brown, N. L. *Metal Ions in Biological Systems*; Dekker: New York, 1997; Vol. 34, p 527.
- (12) Watton, S. P.; Wright, J. G.; MacDonnell, F. M.; Bryson, J. W.; Sabat, M.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1990**, *112*, 2824.
- (13) Strasdeit, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 707.
- (14) Smirnova, I. V.; Bittel, D. C.; Ravindra, R.; Jiang, H.; Andrews, G. K. *J. Biol. Chem.* **2000**, *275*, 9377.



**Figure 1.** Bis(2-methylpyridyl) sulfide (**1**), left, and bis(2-methylpyridyl)amine (BMPA), right.

and Pd(0/II).<sup>25,26</sup> The ligand contains two pyridyl groups linked through a thioether, providing a model for commonly occurring coordinating amino acids. The ligand has been known to bind a single metal ion in either tridentate or bidentate fashion.<sup>20,22</sup> It also coordinates two or three metal ions with a bridging thioether S atom.<sup>19,23</sup> The structures and solution behavior of Zn(II), Cd(II), and Hg(II) complexes of **1** were previously unknown.

Our studies in the past have focused on the coordination of amine, pyridyl,<sup>27,28</sup> and imidazolyl<sup>29</sup> groups to Cd(II) and Hg(II). <sup>1</sup>H NMR studies of these complexes have yielded new information on their behavior in solution. Slow exchange conditions for coordination compounds of Hg(II) with nitrogen donors were identified with large <sup>3</sup>J, <sup>4</sup>J, and for the first time <sup>5</sup>J(<sup>199</sup>Hg<sup>1</sup>H).<sup>27</sup> Given the known thiophilicity of Hg(II) and Cd(II), as well as recent studies implicating the coordination of Hg(II) to protein cysteine residues,<sup>10,30</sup> the study of complexes with thiolate and thioether donating groups is a logical extension of this work.

Furthermore, NMR of the naturally occurring spin-1/2 isotopes of Hg(II) and Cd(II) is possible, enabling their use as probes for protein active sites.<sup>10,31</sup> However, there are limited biologically relevant small molecule analogues providing mixed N,S-donor coordination environments<sup>32,33</sup> for chemical shift referencing. Furthermore, Zn(II) complexes with mixed N,S(thioether) coordination environments are

rare.<sup>34–44</sup> Therefore, determining the solution-state behavior and structure of Zn(II), Cd(II), and Hg(II) complexes with mixed N,S-heteroatom-containing ligands will expand the number of known coordination complexes and can yield insight to their different behavior in biological systems.

In this paper we report the coordination of **1**, a mixed N,S-heteroatom-containing ligand with potential thioether donation, to the chloride and perchlorate salts of Zn(II), Cd(II), and Hg(II). Solution-state <sup>1</sup>H NMR and <sup>199</sup>Hg NMR data for these complexes are presented with correlations to their solid-state structures. Under slow exchange conditions, complexes of Hg(ClO<sub>4</sub>)<sub>2</sub> and **1** displayed <sup>3</sup>J–<sup>5</sup>J(<sup>199</sup>Hg<sup>1</sup>H). The crystal structures of seven different complexes of **1** were determined. The structures of 1:2 complexes of M(ClO<sub>4</sub>)<sub>2</sub> displayed thioether coordination by **1**. Unexpectedly, the 1:1 MCl<sub>2</sub> complexes of **1** lack thioether coordination in the case of ZnCl<sub>2</sub> and HgCl<sub>2</sub>, while **1** is tridentate in the CdCl<sub>2</sub> complex.

## Experimental Section

Solvents and reagents were of commercial grade and used without further purification. 2-Picolyl chloride hydrochloride (Acros), thiourea (Mallinckrodt Baker, Inc), mercury(II) perchlorate trihydrate (Sigma-Aldrich Co.), anhydrous mercury(II) chloride (Sigma-Aldrich Co.), cadmium(II) perchlorate hydrate (Sigma-Aldrich Co.), anhydrous cadmium(II) chloride (Pfaltz and Bauer, Inc.), zinc(II) perchlorate hexahydrate (Sigma-Aldrich Co.), anhydrous zinc(II) chloride (Fisher), and acetonitrile-*d*<sub>3</sub> (Acros) were purchased from commercial sources. Reported coupling constants are interproton unless otherwise noted. **Caution!** *Extreme caution must be exercised when working with potentially explosive organic perchlorates.*

**Synthesis of 1.** Bis(2-methylpyridyl) sulfide (**1**) was synthesized by following analogous published procedures with minor changes.<sup>19,22</sup> 2-Picolyl chloride hydrochloride (24.90 g, 152 mmol) was added to a solution of thiourea (6.00 g, 80 mmol) and KOH (17.69 g, 315 mmol) in 150 mL of 1:1 benzene–absolute ethanol. The initial dark brown suspension was stirred and refluxed for 24 h. Rotary evaporation of solvent from the resulting bright red mixture produced a solid. Extraction with ether (4 × 100 mL), filtration, and solvent evaporation provided a yellow oil from the solid. Two distillations of the yellow oil (139–146 °C, 0.1 mmHg) with a vacuum-jacketed Claisen–Vigreux (22 cm) distillation head provided 7.22 g (46.1% yield) of pure product. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>S: 66.63, C; 5.59, H; 12.95, N. Found: 66.49, C; 5.76,

- (15) Bittel, D.; Dalton, T.; Samson, S. L. A.; Gedamu, L.; Andrews, G. K. *J. Biol. Chem.* **1998**, *273*, 7127.  
 (16) Palmiter, R. D. *Proc. Natl. Acad. Sci.* **1994**, *91*, 1219.  
 (17) Radtke, F.; Heuchel, R.; Georgiev, O.; Hergersberg, M.; Gariglio, M.; Dembic, Z.; Schaffner, W. *EMBO J.* **1993**, *12*, 1355.  
 (18) Andersen, R. D.; Taplitz, S. J.; Oberbauer, A. M.; Calame, K. L.; Herschman, H. R. *Nucleic Acids Res.* **1990**, *18*, 6049.  
 (19) Caradoc-Davies, P. L.; Hanton, L. R.; Hodgkiss, J. M.; Spicer, M. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1581.  
 (20) Caradoc-Davies, P. L.; Gregory, D. H.; Hanton, L. R.; Turnbull, J. M. *J. Chem. Soc., Dalton Trans.* **2002**, 1574.  
 (21) Uhlig, E.; Heinrich, G. Z. *Anorg. Allg. Chem.* **1964**, *330*, 40.  
 (22) Diebold, A.; Kyritsakas, N.; Fischer, J.; Weiss, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *C52*, 632.  
 (23) Caradoc-Davies, P. L.; Hanton, L. R.; Lee, K. *Chem. Commun.* **2000**, 783.  
 (24) Pitteri, B.; Marangoni, G.; Cattalini, L. *Polyhedron* **1995**, *14*, 2331.  
 (25) Canovese, L.; Visentin, F.; Chessa, G.; Niero, A.; Uguagliati, P. *Inorg. Chim. Acta* **1999**, *293*, 44.  
 (26) Canovese, L.; Visentin, F.; Chessa, G.; Gardenal, G.; Uguagliati, P. *J. Organomet. Chem.* **2001**, *622*, 155.  
 (27) Bebout, D. C.; Bush, J. F., II; Crahan, K. K.; Bowers, E. V.; Butcher, R. J. *Inorg. Chem.* **2002**, *41*, 2529.  
 (28) Bebout, D. C.; Stokes, S. W.; Butcher, R. J. *Inorg. Chem.* **1999**, *38*, 1126.  
 (29) Bebout, D. C.; Garland, M. M.; Murphy, G. S.; Bowers, E. V.; Abelt, C. J.; Butcher, R. J. *J. Chem. Soc., Dalton Trans.* **2003**, 2578.  
 (30) Harris, H. H.; Pickering, I. J.; George, G. N. *Science* **2003**, *301*, 1203.  
 (31) Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43.  
 (32) Breiting, D. K. *Compr. Coord. Chem.* **2004**, *6*, 1253.  
 (33) Wright, J. G.; Natan, M. J.; MacDonnell, F. M.; Ralston, D. M.; O'Halloran, T. V. *Prog. Inorg. Chem.* **1990**, *38*, 323.

- (34) Helm, M. L.; Combs, C. M.; VanDerveer, D. G.; Grant, G. J. *Inorg. Chim. Acta* **2002**, *338*, 182.  
 (35) Garner, D. K.; Allred, R. A.; Tubbs, K. J.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2002**, *41*, 3533.  
 (36) Nekola, H.; Rehder, D. *Inorg. Chim. Acta* **2002**, *337*, 467.  
 (37) Hammes, B. S.; Carrano, C. J. *Inorg. Chem.* **2001**, *40*, 919.  
 (38) Jubert, C.; Mohamadou, A.; Marrot, J.; Barbier, J.-P. *J. Chem. Soc., Dalton Trans.* **2001**, 1230.  
 (39) Chiou, S.-J.; Innocent, J.; Riordan, C. G.; Lam, K.-C.; Liable-Sands, L.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 4347.  
 (40) Ghosh, P.; Parkin, G. *Chem. Commun.* **1998**, 413.  
 (41) Bruce, J. I.; Donlevy, T. M.; Gahan, L. R.; Kennard, C. H.; Byriel, K. A. *Polyhedron* **1996**, *15*, 49.  
 (42) Chakraborty, P.; Chandra, S. K.; Chakravorty, A. *Inorg. Chim. Acta* **1995**, *229*, 477.  
 (43) Goodman, D. C.; Tuntulani, T.; Farmer, P. J.; Darensbourg, M. Y.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69.  
 (44) Drew, M. G. B.; Rice, D. A.; Timewell, C. W. *J. Chem. Soc., Dalton Trans.* **1975**, 144.

H; 13.08, N.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 21 °C): 8.55 (2H, dm,  $J = 4.9$  Hz,  $\text{H}_a$ ), 7.64 (2H, td,  $J = 7.8$  and 1.9 Hz,  $\text{H}_c$ ), 7.38 (2H, d,  $J = 7.7$  Hz,  $\text{H}_d$ ), 7.16 (2H, dd,  $J = 7.4$  and 4.9 Hz,  $\text{H}_b$ ), 3.83 (4H, s,  $\text{H}_f$ ).  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , -20 °C): 8.51 (2H, ddd,  $J = 4.9$ , 1.9 and 0.8 Hz,  $\text{H}_a$ ), 7.72 (2H, td,  $J = 7.8$  and 1.8 Hz,  $\text{H}_c$ ), 7.41 (2H, dt,  $J = 7.7$  and 1.0 Hz,  $\text{H}_d$ ), 7.24 (2H, ddd,  $J = 7.6$ , 4.8 and 1.2 Hz,  $\text{H}_b$ ), 3.77 (4H, s,  $\text{H}_f$ ).

**Synthesis of  $\text{Hg}(\text{I})_2(\text{ClO}_4)_2$ .** A solution (10 mL) of 0.05 M  $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  in methanol was added slowly with stirring to a 10 mL solution of 0.05 M **1** in methanol. A fine white precipitate formed. The solution was clarified with the addition of 5 mL of acetonitrile. Aliquots of this solution were mixed with 0.25 or 0.5 parts (v/v) toluene. Slow evaporation of the solvent resulted in formation of clear, colorless crystals in 1 week. Mp: 139–142 °C. Anal. Calcd for  $\text{HgCl}_2\text{O}_8\text{C}_{24}\text{H}_{24}\text{N}_4\text{S}_2$ : 34.64, C; 2.91, H; 6.73, N. Found: 34.61, C; 2.85, H; 6.60, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, -20 °C): 8.07 (2H, d,  $J = 4.8$  Hz,  $J(\text{Hg}-\text{H}) = 23.5$  Hz,  $\text{H}_a$ ), 7.97 (2H, td,  $J = 7.7$  and 1.7 Hz,  $\text{H}_c$ ), 7.62 (2H, d,  $J = 7.8$  Hz,  $J(\text{Hg}-\text{H}) = 5.2$  Hz,  $\text{H}_d$ ), 7.39 (2H, dd,  $J = 7.7$  and 5.0 Hz,  $\text{H}_b$ ), 4.43 (4H, s,  $J(\text{Hg}-\text{H}) = 56.3$  Hz,  $\text{H}_f$ ).

**Synthesis of  $\text{Hg}(\text{I})\text{Cl}_2$  and  $\text{Hg}_2(\text{I})\text{Cl}_4$ .** A solution (5 mL) of 0.1 M  $\text{HgCl}_2$  in methanol was added slowly with stirring to a 5 mL solution of 0.1 M **1** in methanol. A fine white precipitate formed. The solution was clarified with the addition of acetonitrile (~70 mL) and heat. The clear solution was allowed to cool slowly to room temperature and then stored at -20 °C. After 2 days, yellow needle-shaped crystals formed, and after 1 week, additional square, colorless crystals formed. The two different crystal forms were physically separated and analyzed. Colorless crystals: mp 125–130 °C. Anal. Calcd for  $\text{HgCl}_2\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$ : 29.55, C; 2.48, H; 5.74, N. Found: 29.66, C; 2.38, H; 5.58, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, -20 °C): 8.67 (2H, dm,  $J = 4.9$  Hz,  $\text{H}_a$ ), 7.91 (2H, td,  $J = 7.7$  and 1.7 Hz,  $\text{H}_c$ ), 7.52 (2H, d,  $J = 7.8$  Hz,  $\text{H}_d$ ), 7.48 (2H, td,  $J = 6.6$  and 0.9 Hz,  $\text{H}_b$ ), 4.08 (4H, s,  $\text{H}_f$ ). Yellow crystals: mp 155–157 °C. Anal. Calcd for  $\text{Hg}_2\text{Cl}_4\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$ : 18.98, C; 1.59, H; 3.69, N. Found: 19.57, C; 1.57, H; 3.73, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, -20 °C): 8.69 (2H, dt,  $J = 4.9$  and 1.3 Hz,  $\text{H}_a$ ), 7.97 (2H, t,  $J = 7.7$  Hz,  $\text{H}_c$ ), 7.55 (2H, d,  $J = 7.6$  Hz,  $\text{H}_d$ ), 7.54 (2H, t,  $J = 7.6$  Hz,  $\text{H}_b$ ), 4.17 (4H, s,  $\text{H}_f$ ).

**Synthesis of  $\text{Cd}(\text{I})_2(\text{ClO}_4)_2$ .** A solution (10 mL) of 0.05 M  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in methanol was added slowly with stirring to a 10 mL solution of 0.1 M **1** in methanol. A fine white precipitate formed. The solution was clarified with the addition of 5 mL of acetonitrile. Aliquots of this solution were mixed with 0.5 parts (v/v) *m*-xylene. Slow evaporation of the solvent resulted in formation of clear colorless crystals over 1 month. Mp: 209–215 °C. Anal. Calcd for  $\text{CdCl}_2\text{O}_8\text{C}_{24}\text{H}_{24}\text{N}_4\text{S}_2$ : 38.75, C; 3.25, H; 7.53, N. Found: 38.89, C; 3.26, H; 7.58, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, -20 °C): 8.04 (2H, td,  $J = 7.7$  and 1.5 Hz,  $\text{H}_c$ ), 7.96 (2H, m,  $\text{H}_a$ ), 7.67 (2H, d,  $J = 7.8$  Hz,  $\text{H}_d$ ), 7.38 (2H, t,  $J = 6.4$  Hz,  $\text{H}_b$ ), 4.36 (4H, s,  $\text{H}_f$ ).

**Synthesis of  $[\text{Cd}(\text{I})\text{Cl}_2]_2$ .** A solution (10 mL) of 0.05 M  $\text{CdCl}_2$  in methanol was added slowly with stirring to a 5 mL solution of 0.1 M **1** in methanol. A fine white precipitate formed. The solution was clarified with the addition of 30 mL of acetonitrile. Aliquots of this solution were mixed with 0.2 or 0.33 parts (v/v) *m*-xylene. Slow evaporation of the solvent resulted in formation of clear colorless crystals over 1 month. Mp: 218–224 °C. Anal. Calcd for  $\text{CdCl}_2\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$ : 36.07, C; 3.03, H; 7.01, N. Found: 36.21, C; 3.00, H; 6.89, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, -20 °C): 8.98 (2H, d,  $J = 4.8$  Hz,  $\text{H}_a$ ), 7.87 (2H, td,  $J = 7.7$  and 1.4 Hz,  $\text{H}_c$ ), 7.45 (2H, t,  $J = 6.4$  Hz,  $\text{H}_b$ ), 7.42 (2H, d,  $J = 7.8$  Hz,  $\text{H}_d$ ), 4.13 (4H, s,  $\text{H}_f$ ).

**Synthesis of  $\text{Zn}(\text{I})_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ .** A solution (10 mL) of 0.1 M  $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in acetonitrile was added slowly with stirring to a 20 mL solution of 0.1 M **1** in acetonitrile. Aliquots of this solution were mixed with equal parts (v/v) benzene. Slow evaporation of the solvent resulted in formation of clear colorless crystals in 1 week. Mp: 227–228 °C. Anal. Calcd for  $\text{ZnCl}_2\text{O}_8\text{C}_{24}\text{H}_{24}\text{N}_4\text{S}_2$  ( $\text{CH}_3\text{CN}$  evaporated): 41.36, C; 3.47, H; 8.04, N. Found: 41.38, C; 3.47, H; 8.04, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, -20 °C): 8.44 (2H, d,  $J = 4.6$  Hz,  $\text{H}_a$ ), 7.91 (2H, td,  $J = 7.6$  and 1.0,  $\text{H}_c$ ), 7.50 (2H, d,  $J = 7.7$  Hz,  $\text{H}_d$ ), 7.41 (2H, dd,  $J = 7.5$  and 4.6 Hz,  $\text{H}_b$ ), 4.40 (4H, s,  $\text{H}_f$ ).

**Synthesis of  $\text{Zn}(\text{I})\text{Cl}_2$ .** A solution (10 mL) of 0.1 M  $\text{ZnCl}_2$  in methanol was added slowly with stirring to a 20 mL solution of 0.05 M **1** in methanol. A fine white precipitate formed. The solution was clarified with the addition of 40 mL of acetonitrile. Clear colorless crystals formed in <24 h at 4 °C. Mp: 238–240 °C. Anal. Calcd for  $\text{ZnCl}_2\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}$ : 40.88, C; 3.43, H; 7.95, N. Found: 40.96, C; 3.39, H; 7.88, N.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 2 mM, +20 °C): 8.93 (2H, d,  $J = 5.6$  Hz,  $\text{H}_a$ ), 8.17 (2H, td,  $J = 7.9$  and 1.6 Hz,  $\text{H}_c$ ), 7.72 (2H, dt,  $J = 8.0$  and 0.9 Hz,  $\text{H}_d$ ), 7.67 (2H, dd,  $J = 5.6$  and 1.3 Hz,  $\text{H}_b$ ), 3.89 (4H, s,  $\text{H}_f$ ).

**Solution-State NMR Spectroscopy.** NMR data was obtained in 5 mm o.d. NMR tubes on a Varian Mercury 400VX NMR spectrometer operating in the pulse Fourier transform mode. 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). The samples with different M(II):**1** ratios were prepared by mixing fresh stocks of 10 mM metal salt with 20 mM **1** in  $\text{CD}_3\text{CN}$  to a total volume of 650  $\mu\text{L}$ . The final metal ion concentration was fixed at 2 mM, and the ligand concentration was varied from 16 mM (0.125 M(II):lig ratio) to 1.3 mM (1.5 M(II):lig ratio). The  $^{199}\text{Hg}$  NMR spectra were obtained on 20 mM samples. Resonances were referenced using the ratio (0.179 108 97) of the TMS resonance frequency [determined from the  $^1\text{H NMR}$  of the  $\text{CD}_3\text{CN}$  solvent peak (1.94 ppm)] to the 0 ppm resonance frequency of  $^{199}\text{Hg}$  [determined using 0.5 M phenyl mercuric acetate in DMSO (-1439.5 ppm vs  $\text{Hg}(\text{CH}_3)_2^{45,46}$ )].<sup>47</sup> All data were obtained at -20 °C unless otherwise indicated.

**X-ray Crystallography.** Selected crystallographic data are given in Tables 1 and 2, and complete data are given in the CIF file (Supporting Information). Data were collected on a Siemens P4 four-circle diffractometer using a graphite-monochromated Mo  $K\alpha$  X-radiation ( $\lambda = 0.710 73 \text{ \AA}$ ). During data collection three standard reflections were measured after every 97 reflections. All mercury complex crystals turned light gray in the beam, but the decay in the intensity of the standards was less than random error so no decay correction was performed on the data. The structures were solved by direct methods<sup>48</sup> and refined on  $F^2$  by full-matrix least squares using the SHELXTL97 program package.<sup>49</sup> All non-hydrogen atoms were refined as anisotropic, the hydrogen atomic positions were constrained in an idealized geometry relative to the bonded carbons, and the isotropic thermal parameters were fixed.

(45) Wrackmeyer, B.; Contreras, R. *Annu. Rep. NMR Spectrosc.* **1992**, *24*, 267.

(46) Borzo, M.; Maciel, G. E. *J. Magn. Reson., Ser. A* **1975**, *19*, 279.

(47) Harris, R. K.; Becker, E. D.; Cabral De Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

(48) Sheldrick, G. M. *SHELXS 97 ed.*; University of Göttingen: Göttingen, Germany, 1997.

(49) Sheldrick, G. M. *SHELXL 97 ed.*; University of Göttingen: Göttingen, Germany, 1997.

**Table 1.** Selected Crystallographic Data for the Hg(II) Complexes of **1**

param	Hg(1)Cl <sub>2</sub>	Hg <sub>2</sub> (1)Cl <sub>4</sub>	Hg(1) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>
empirical formula	HgCl <sub>2</sub> C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> S	Hg <sub>2</sub> Cl <sub>4</sub> C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> S	HgCl <sub>2</sub> O <sub>8</sub> C <sub>24</sub> H <sub>24</sub> N <sub>4</sub> S <sub>2</sub>
fw	487.79	759.28	832.08
cryst size/mm <sup>3</sup>	0.4 × 0.5 × 0.60	0.66 × 0.35 × 0.20	0.20 × 0.45 × 0.68
cryst system	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 4)	<i>P</i> 2 <sub>1</sub> <i>cn</i> (No. 4)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> /Å	11.7382(5)	8.9643(8)	11.0894(7)
<i>b</i> /Å	8.5553(4)	12.3703(10)	11.9455(7)
<i>c</i> /Å	15.1543(6)	15.6460(14)	22.2423(14)
$\alpha$ /deg	90	90	94.2970(10)
$\beta$ /deg	111.9310(10)	90	95.4130(10)
$\gamma$ /deg	90	90	93.7370(10)
<i>V</i> /Å <sup>3</sup>	1411.72(11)	1735.0(3)	2917.3(3)
<i>Z</i>	4	4	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	2.295	2.907	1.895
$\mu$ /mm <sup>-1</sup>	11.411	18.404	5.656
temp/°C	-170(2)	-170(2)	-170(2)
indpdt reflcns ( <i>R</i> <sub>int</sub> )	3392 (0.0377)	3934 (0.0504)	13 591 (0.0209)
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0225, 0.0553	0.0316, 0.0798	0.0327, 0.0715
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> (all data)	0.0236, 0.0558	0.0334, 0.0806	0.0370, 0.0756

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

**Table 2.** Selected Crystallographic Data for the Cd(II) and Zn(II) Complexes of **1**

param	Cd(1)Cl <sub>2</sub>	Cd(1) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Zn(1)Cl <sub>2</sub>	Zn(1) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·CH <sub>3</sub> CN
empirical formula	CdCl <sub>2</sub> C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> S	CdCl <sub>2</sub> O <sub>8</sub> C <sub>24</sub> H <sub>24</sub> N <sub>4</sub> S <sub>2</sub>	ZnCl <sub>2</sub> C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> S	ZnCl <sub>2</sub> O <sub>8</sub> C <sub>26</sub> H <sub>27</sub> N <sub>5</sub> S <sub>2</sub>
fw	399.62	743.92	352.56	736.91
cryst size/mm <sup>3</sup>	0.4 × 0.45 × 0.85	0.55 × 0.7 × 0.7	0.45 × 0.50 × 0.55	0.35 × 0.40 × 0.55
cryst system	triclinic	monoclinic	tetragonal	orthorhombic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 4)	<i>P</i> 4 <sub>1</sub> 2 <sub>1</sub> 2 (No. 92)	<i>Cmcm</i> (No. 63)
<i>a</i> /Å	9.5155(9)	11.9256(11)	8.8379(6)	15.1477(9)
<i>b</i> /Å	10.2269(10)	14.7933(15)	8.8379(6)	11.9972(7)
<i>c</i> /Å	15.3232(15)	16.0047(16)	18.423(2)	17.1143(11)
$\alpha$ /deg	81.278(2)	90	90	90
$\beta$ /deg	88.263(2)	95.129(2)	90	90
$\gamma$ /deg	77.873(2)	90	90	90
<i>V</i> /Å <sup>3</sup>	1441.0(2)	2812.2(5)	1439.0(2)	3110.2(3)
<i>Z</i>	2	4	4	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.842	1.757	1.627	1.574
$\mu$ /mm <sup>-1</sup>	2.013	1.171	2.205	1.151
temp/°C	-125(2)	-125(2)	-180(2)	-180(2)
indpdt reflcns ( <i>R</i> <sub>int</sub> )	6859 (0.0406)	6770 (0.0809)	1784 (0.0366)	2035 (0.0335)
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0349, 0.0919	0.0353, 0.0884	0.0185, 0.0463	0.0226, 0.0618
<i>R</i> 1, <sup>a</sup> <i>wR</i> 2 <sup>b</sup> (all data)	0.0386, 0.0954	0.0384, 0.0922	0.0190, 0.0466	0.0249, 0.0627

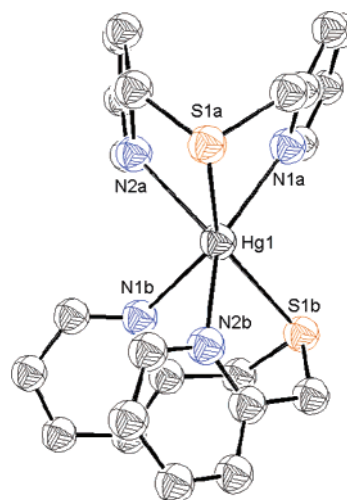
$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

## Results and Discussion

The mixed N,S-heteroatom-containing ligand **1** (Figure 1, left) mimics a potential collection of ligating moieties in biological systems. The synthesis of **1** followed slightly modified literature procedures.<sup>19,22</sup> The identity and purity of **1** were confirmed by elemental analysis, GC-MS (data not shown), and <sup>1</sup>H NMR spectroscopy. The crystal structures of seven Hg(II), Cd(II), and Zn(II) complexes of **1** (discussed below) are shown in Figures 2–8, and selected bond distances and angles are summarized in Tables 3–5, respectively. The structures of the perchlorate salts are discussed individually and then compared before discussing the chloride salt structures and finally the solution-state NMR data.

**Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> Structure.** The high-resolution X-ray structure of Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (Figure 2) reveals two similar but crystallographically independent Hg complexes. Two ligands bind the Hg(II) ion to form a six-coordinate, distorted trigonal prismatic geometry. Each triangular face is formed by a tridentate ligand **1** folded about the thioether in a V shape.

The resulting N–S–N angles of the two triangular faces (for Hg(1)) are 56.1° (ligand a) and 57.5° (ligand b), and the



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

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

Hg(1)Cl <sub>2</sub> <sup>a</sup>		Hg <sub>2</sub> (1)Cl <sub>4</sub> <sup>b</sup>		Hg(1) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	
Hg–N(1A)	2.452(3)	Hg(1)–Hg(2)	6.041(8)	Hg(1)–S(1A)	2.6539(12)
Hg–N(1B)	2.357(3)	Hg(1)–Hg(2)′	3.851(8)	Hg(1)–S(1B)	2.6707(11)
Hg–Cl(1)	2.4099(8)	Hg(1)–S	3.035(4)	Hg(1)–N(1A)	2.409(4)
Hg–Cl(2)	2.4049(8)	Hg(2)–S	3.048(4)	Hg(1)–N(2A)	2.511(4)
Hg–Cl(1)′	3.258(8)	Hg(1)–N(1A)	2.259(8)	Hg(1)–N(1B)	2.501(4)
Hg–S	4.362(6)	Hg(2)–N(1B)	2.175(7)	Hg(1)–N(2B)	2.382(4)
		Hg(1)–Cl(11)	2.555(2)	Hg(2)–S(1C)	2.5926(11)
		Hg(2)–Cl(21)	2.756(2)	Hg(2)–S(1D)	2.6604(10)
		Hg(1)–Cl(12)	2.395(2)	Hg(2)–N(1C)	2.496(4)
		Hg(2)–Cl(22)	2.336(2)	Hg(2)–N(2C)	2.447(4)
		Hg(1)–Cl(21)′	2.615(2)	Hg(2)–N(1D)	2.441(4)
		Hg(2)–Cl(11)′	2.765(2)	Hg(2)–N(2D)	2.467(4)
N(1A)–Hg–N(1B)	106.88(10)	Hg(1)–S–Hg(2)	166.51(8)	S(1A)–Hg(1)–S(1B)	143.23(3)
N(1A)–Hg–Cl(1)	91.67(7)	Hg(1)–Cl(11)–Hg(2)′	92.65(7)	S(1A)–Hg(1)–N(1B)	137.03(9)
N(1A)–Hg–Cl(2)	98.57(7)	Hg(1)–Cl(12)′–Hg(2)	91.57(7)	S(1A)–Hg(1)–N(2B)	93.94(10)
N(1A)–Hg–Cl(1)′	168.16(8)	S–Hg(1)–Cl(21)′	168.34(8)	S(1A)–Hg(1)–N(1A)	77.01(9)
N(1B)–Hg–Cl(1)	111.59(7)	S–Hg(2)–Cl(11)′	163.91(8)	S(1A)–Hg(1)–N(2A)	76.10(10)
N(1B)–Hg–Cl(2)	96.87(7)	S–Hg(1)–Cl(11)	84.66(7)	S(1B)–Hg(1)–N(1A)	92.39(9)
N(1B)–Hg–Cl(1)′	83.30(8)	S–Hg(1)–Cl(12)	88.80(7)	S(1B)–Hg(1)–N(2A)	135.38(10)
Cl(1)–Hg–Cl(2)	145.46(3)	S–Hg(1)–N(1A)	72.43(7)	S(1B)–Hg(1)–N(1B)	76.20(9)
Cl(1)–Hg–Cl(1)′	78.72(7)	S–Hg(2)–Cl(21)	83.45(8)	S(1B)–Hg(1)–N(2B)	76.74(10)
Cl(2)–Hg–Cl(1)′	85.89(7)	S–Hg(2)–Cl(12)	95.58(8)	N(1A)–Hg(1)–N(2B)	148.35(13)
		S–Hg(2)–N(1B)	73.66(7)	N(1A)–Hg(1)–N(1B)	129.54(12)
		N(1A)–Hg(1)–Cl(12)	129.6(2)	N(1A)–Hg(1)–N(2A)	74.61(12)
		N(1A)–Hg(1)–Cl(21)′	98.1(2)	N(2A)–Hg(1)–N(1B)	80.06(12)
		N(1A)–Hg(1)–Cl(11)	101.9(2)	N(2A)–Hg(1)–N(2B)	133.21(13)
		N(1B)–Hg(2)–Cl(22)	156.4(2)	N(1B)–Hg(1)–N(2B)	77.19(12)
		N(1B)–Hg(2)–Cl(11)′	96.8(2)	S(1C)–Hg(2)–S(1D)	141.04(4)
		N(1B)–Hg(2)–Cl(21)	90.04(19)	S(1C)–Hg(2)–N(1D)	95.23(9)
		Cl(11)–Hg(1)–Cl(12)	122.96(7)	S(1C)–Hg(2)–N(2D)	138.52(9)
		Cl(11)–Hg(1)–Cl(21)′	90.78(7)	S(1C)–Hg(2)–N(1C)	75.85(10)
		Cl(21)–Hg(2)–Cl(22)	109.95(7)	S(1C)–Hg(2)–N(2C)	78.03(9)
		Cl(21)–Hg(2)–Cl(11)′	83.63(7)	S(1D)–Hg(2)–N(1C)	138.60(10)
		Cl(12)–Hg(1)–Cl(21)′	102.65(8)	S(1D)–Hg(2)–N(2C)	91.81(9)
		Cl(22)–Hg(2)–Cl(11)′	97.83(7)	S(1D)–Hg(2)–N(1D)	75.46(9)
				S(1D)–Hg(2)–N(2D)	76.73(9)
				N(1C)–Hg(2)–N(2D)	79.48(13)
				N(1C)–Hg(2)–N(1D)	130.02(13)
				N(1C)–Hg(2)–N(2C)	76.52(13)
				N(2C)–Hg(2)–N(1D)	150.65(13)
				N(2C)–Hg(2)–N(2D)	127.39(13)
				N(1D)–Hg(2)–N(2D)	75.98(12)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $-x + 5/2, y - 1/2, -z + 3/2$ . <sup>b</sup> Symmetry transformations used to generate equivalent atoms:  $x + 1, y, z; x - 1, y, z$ .

pyridyl groups are roughly parallel, with the N atoms separated by 2.98 (a) and 3.05 (b) Å and the 4-position by 4.46 (a) and 4.80 (b) Å. The thioether group of **1** is rotated ~120° relative to the bottom thioether ligand. The [Hg(1)<sub>2</sub>]<sup>2+</sup> ion contains an approximate C<sub>2</sub> axis normal to the N–S–N–S rectangular face of the trigonal prism. A very similar trigonal prismatic coordination geometry was observed in [Hg([9]aneN<sub>2</sub>S)<sub>2</sub>]<sup>2+</sup><sup>50</sup> and Hg(BMPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub><sup>51</sup> (BMPA = bis(2-methylpyridyl)amine, Figure 1, right). Other six-coordinate bis(tridentate) HgL<sub>2</sub> complexes with tridentate thioether-containing donors were closer to octahedral in geometry.<sup>34,52,53</sup>

The Hg(II)–ligand bond distances (Table 3) are similar to those observed in other six-coordinate complexes. The Hg(II)–N(pyridyl) bonds consist of two shorter (2.382(4)

and 2.409(4) Å) and two longer (2.501(4) and 2.511(4) Å) distances. These are consistent with the range of bond lengths (2.352–2.557 Å) found in other pyridyl-containing six-coordinate Hg(II) complexes,<sup>51,54–56</sup> and they are similar to those found in Hg(BMPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (2.352, 2.414, 2.417, and 2.557 Å).<sup>51</sup> The Hg–S(thioether) distances of 2.6539(12) and 2.6707(11) Å are in the range observed in other six-coordinate Hg(II) complexes with crown-thioether type ligands, which have distances ranging from 2.458 to 2.751 Å.<sup>34,52,57–60</sup> The perchlorate counterions in the crystal lattice are located between the [Hg(1)<sub>2</sub>]<sup>2+</sup> ions and point at the

(50) Heinzel, U.; Mattes, R. *Polyhedron* **1992**, *11*, 597.

(51) Bebout, D. C.; DeLanoy, A. E.; Ehmman, D. E.; Kastner, M. E.; Parrish, D. A.; Butcher, R. J. *Inorg. Chem.* **1998**, *37*, 2952.

(52) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schroder, M. *Polyhedron* **1989**, *8*, 2041.

(53) Helm, M. L.; VanDerveer, D. G.; Grant, G. J. *J. Chem. Crystallogr.* **2003**, *33*, 625.

(54) Batten, S. R.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 820.

(55) Deacon, G. B.; Raston, C. L.; Tunaley, D.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 2195.

(56) Aakesson, R.; Sandstroem, M.; Staalhandske, C.; Persson, I. *Acta Chem. Scand.* **1991**, *45*, 165.

(57) Marcus, S. T.; Bernhardt, P. V.; Grondahl, L.; Gahan, L. R. *Polyhedron* **1999**, *18*, 3451.

(58) Setzer, W. N.; Tang, Y.; Grant, G. J.; VanDerveer, D. G. *Inorg. Chem.* **1991**, *30*, 3652.

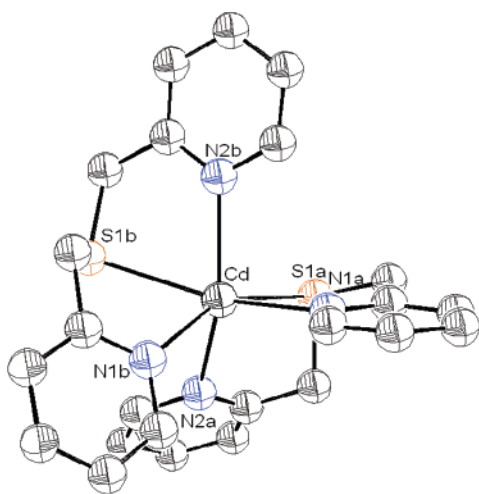
(59) Blake, A. J.; Reid, G.; Schroeder, M. *Polyhedron* **1990**, *9*, 2931.

(60) Herceg, M.; Matkovic, B.; Sevdic, D.; Matkovic-Calogovic, D.; Nagl, A. *Croat. Chem. Acta* **1984**, *57*, 609.

**Table 4.** Selected Bond Distances (Å) and Bond Angles (deg) for Cd(II) Complexes of **1**

	[Cd(1)Cl <sub>2</sub> ] <sub>2</sub> <sup>a</sup>		Cd(1) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	
	Cd <sub>2</sub> (1)	[Cd <sub>2</sub> (2)]		
Cd–S	2.7566(8)	[2.7956(10)]	Cd–S(A)	2.6889(6)
Cd–Cl(1)	2.4863(7)	[2.4670(10)]	Cd–S(B)	2.7206(6)
Cd–Cl(2)	2.5831(7)	[2.5716(9)]	Cd–N(1A)	2.371(2)
Cd–Cl(2)′	2.7036(8)	[2.6766(9)]	Cd–N(1B)	2.363(2)
Cd–N(1)	2.411(3)	[2.399(3)]	Cd–N(2A)	2.377(2)
Cd–N(2)	2.360(2)	[2.391(3)]	Cd–N(2B)	2.3800(19)
Cd–Cd	3.812(4)	[3.820(4)]	Cd–O(23)	3.919(4)
			Cd–O(22)	3.510(3)
S–Cd–Cl(1)	165.02(3)	[159.10(3)]	S(A)–Cd–N(1A)	74.65(5)
S–Cd–Cl(2)	83.88(3)	[93.62(3)]	S(A)–Cd–N(2A)	74.90(5)
S–Cd–Cl(2)′	90.08(2)	[93.20(3)]	S(A)–Cd–N(1B)	152.99(5)
S–Cd–N(1)	73.07(6)	[70.87(7)]	S(A)–Cd–N(2B)	93.01(5)
S–Cd–N(2)	74.61(7)	[71.84(7)]	S(A)–Cd–S(B)	126.264(19)
Cl(2)–Cd–Cl(2)′	87.75(2)	[86.60(3)]	S(B)–Cd–N(1B)	71.84(5)
Cl(2)–Cd–Cl(1)	104.34(3)	[100.54(4)]	S(B)–Cd–N(2B)	73.23(5)
Cl(2)–Cd–N(1)	96.10(6)	[93.25(7)]	S(B)–Cd–N(1A)	153.88(5)
Cl(2)–Cd–N(2)	156.58(6)	[159.36(7)]	S(B)–Cd–N(2A)	89.83(5)
Cl(2)′–Cd–Cl(1)	102.58(2)	[102.85(4)]	N(1A)–Cd–N(2A)	112.66(7)
Cl(2)′–Cd–N(1)	162.13(6)	[164.04(7)]	N(1A)–Cd–N(1B)	95.57(7)
Cl(2)′–Cd–N(2)	83.20(6)	[79.88(7)]	N(1A)–Cd–N(2B)	91.85(7)
Cl(1)–Cd–N(1)	93.38(6)	[92.88(7)]	N(2A)–Cd–N(1B)	86.38(7)
Cl(1)–Cd–N(2)	98.70(7)	[97.64(7)]	N(2A)–Cd–N(2B)	147.80(7)
N(1)–Cd–N(2)	86.54(9)	[95.52(9)]	N(1B)–Cd–N(2B)	112.71(7)

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



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

rectangular faces of the trigonal prism. The shortest Hg(1)–oxygen distances are 3.252(4) and 4.345(4) Å in the bidentate approach of one perchlorate and 4.594(4) Å for a second perchlorate. The closest Hg–O bond distance permits overlap of their van der Waals radii (1.70–2.00 Å for Hg(II)<sup>61</sup> and 1.54 Å for O<sup>62</sup>).

**Cd(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> Structure.** The X-ray structure of Cd(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (Figure 3) is similar to that of Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (Figure 2) in that two ligands coordinate the Cd(II) ion to form a six-coordinate complex. However, the geometry around the Cd(II) ion is a distorted octahedron. The ligand **1** binds in a tridentate fashion, but it is highly distorted with a zigzagged backbone. The S atoms bind the Cd(II) in a cis manner with

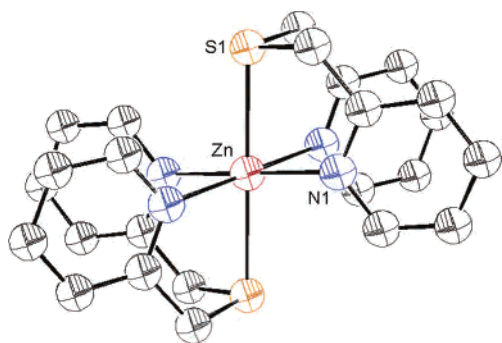
a S–Cd–S angle of 126.264(19)°. Despite ligand distortion, there is an approximate C<sub>2</sub> axis bisecting the S(A)–Cd–S(B) angle. The structure is different from that of the trigonal prismatic Cd(BMPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub><sup>51,63</sup> which more closely resembles the structure of Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and Hg(BMPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>.

The Cd(II)–ligand bond distances (Table 4) are similar to those observed in other six-coordinate Cd(II) complexes. The four Cd(II)–N(pyridyl) distances (2.371(2), 2.363(2), 2.377(2), and 2.3800(19) Å) resemble those (2.266–2.442 Å) found in most pyridyl-containing six-coordinate Cd(II) complexes.<sup>28,63–78</sup> The Cd(II)–S(thioether) bonds of 2.6889(6) and 2.7206(6) Å are in the range of 2.579–2.976 Å

- (63) Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K.; Nielsen, K. M.; Weihe, H. *Inorg. Chem.* **1992**, *31*, 4611.
- (64) March, R.; Pons, J.; Ros, J.; Clegg, W.; Alvarez-Larena, A.; Piniella, J. F.; Sanz, J. *Inorg. Chem.* **2003**, *42*, 7403.
- (65) Allred, R. A.; Arif, A. M.; Berreau, L. M. *J. Chem. Soc., Dalton Trans.* **2002**, 300.
- (66) Allred, R. A.; McAlexander, L. H.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2002**, *41*, 6790.
- (67) Tarulli, S. H.; Quinzani, O. V.; Baran, E. J.; Piro, O. E. *Z. Anorg. Allg. Chem.* **2002**, *628*, 751.
- (68) Berreau, L. M.; Makowska-Grzyska, M. M.; Arif, A. M. *Inorg. Chem.* **2000**, *39*, 4390.
- (69) Harvey, M.; Baggio, S.; Suescun, L.; Baggio, R. F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *C56*, 811.
- (70) Tong, M. L.; Zheng, S. L.; Chen, X. M. *Polyhedron* **2000**, *19*, 1809.
- (71) Kondo, M.; Shimamura, M.; Noro, S.-I.; Kimura, Y.; Uemura, K.; Kitagawa, S. *J. Solid State Chem.* **2000**, *152*, 113.
- (72) Harvey, M.; Baggio, S.; Baggio, R.; Momburu, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *C55*, 1457.
- (73) Harvey, M.; Baggio, S.; Baggio, R.; Pardo, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *C55*, 1278.
- (74) Xiong, R.-G.; Liu, C.-M.; Zuo, J.-L.; You, X.-Z. *Inorg. Chem. Commun.* **1999**, *2*, 292.
- (75) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.
- (76) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem.* **1990**, *102*, 703.
- (77) Teixidor, F.; Escriche, L.; Rodriguez, I.; Casabo, J.; Rius, J.; Molins, E.; Martinez, B.; Miravittles, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1381.

(61) Canty, A. J.; Deacon, G. B. *Inorg. Chim. Acta* **1980**, *45*, L225.

(62) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *B41*, 274.



**Figure 4.** Structure of the  $\text{Zn}(\mathbf{1})(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$  cation. Thermal ellipsoids are shown at the 50% level. Anions and solvent are omitted for clarity.

observed for six-coordinate  $\text{Cd}(\text{II})$  complexes with macrocyclic thioether ligands.<sup>34,58,65,66,68,77,79–86</sup> The longer  $\text{Cd}(\text{II})$ –thioether bond distances tend to be found in complexes that also have short  $\text{Cd}$ – $\text{S}$ (thiolate) bonds. The perchlorate counterions are noncoordinating with nearest  $\text{Cd}$ – $\text{O}$  distances of 3.510(3) and 3.919(4) Å. These distances are too far to result in overlap of their van der Waals radii (1.58 Å for  $\text{Cd}(\text{II})$ <sup>87</sup> and 1.54 Å for  $\text{O}^{62}$ ).

**$\text{Zn}(\mathbf{1})_2(\text{ClO}_4)_2$  Structure.** The  $\text{Zn}(\text{II})$  analogue of the above  $\text{Hg}(\text{II})$  and  $\text{Cd}(\text{II})$  complexes was synthesized for comparison. As with  $\text{Hg}(\text{II})$  and  $\text{Cd}(\text{II})$  perchlorate, the 1:2 complex of  $\text{Zn}(\text{ClO}_4)_2$  readily crystallizes (Figure 4).  $\text{Zn}(\mathbf{1})_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$  is also six coordinate with a distorted octahedral coordination geometry. The ligand is folded in a V shape, similar to **1** in  $\text{Hg}(\mathbf{1})_2(\text{ClO}_4)_2$ , with two  $\text{N}$ – $\text{S}$ – $\text{N}$  angles of 55.6°. The two  $\text{S}$  atoms bind the  $\text{Zn}(\text{II})$  in trans fashion with a  $\text{S}$ – $\text{Zn}$ – $\text{S}$  angle of 180.00(5)°. The two tridentate ligands of  $\text{Zn}(\mathbf{1})_2(\text{ClO}_4)_2$  are staggered about a pseudo- $\text{C}_3$  axis of the octahedron, with the thioether group of one pointing between the pyridyl groups of the other. The molecule belongs to the  $\text{C}_{2h}$  point group with an inversion center at the metal ion. The four  $\text{Zn}(\text{II})$ – $\text{N}$ (pyridyl) distances (Table 5) are all equivalent (2.1892(10) Å), and both  $\text{N}$ – $\text{Zn}$ – $\text{N}$  bond angles are 180.00(5)°. The  $\text{Zn}$ – $\text{N}$ (pyridyl) distance is on the long end of normal for six-coordinate  $\text{Zn}(\text{II})$  complexes (2.111 ± 0.058 Å<sup>88</sup>). The two  $\text{Zn}(\text{II})$ –

**Table 5.** Selected Bond Distances (Å) and Bond Angles (deg) for  $\text{Zn}(\text{II})$  Complexes of **1**

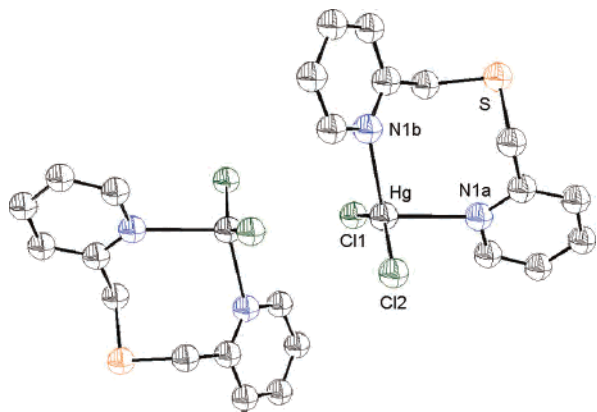
	$\text{Zn}(\mathbf{1})\text{Cl}_2^a$	$\text{Zn}(\mathbf{1})_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}^b$	
$\text{Zn}$ – $\text{Cl}$	2.2306(4)	$\text{Zn}$ – $\text{S}(1)$	2.4997(4)
$\text{Zn}$ – $\text{Cl}'$	2.2306(4)	$\text{Zn}$ – $\text{S}(2)$	2.4997(4)
$\text{Zn}$ – $\text{N}$	2.0509(13)	$\text{Zn}$ – $\text{N}(1)$	2.1892(10)
$\text{Zn}$ – $\text{N}'$	2.0509(13)	$\text{Zn}$ – $\text{N}(2)$	2.1892(10)
$\text{Zn}$ – $\text{S}$	4.063(4)	$\text{Zn}$ – $\text{N}(1)'$	2.1892(10)
		$\text{Zn}$ – $\text{N}(2)'$	2.1892(10)
$\text{N}$ – $\text{Zn}$ – $\text{N}'$	116.61(8)	$\text{S}(1)$ – $\text{Zn}$ – $\text{N}(1)$	82.18(3)
$\text{Cl}$ – $\text{Zn}$ – $\text{Cl}'$	119.21(3)	$\text{S}(1)$ – $\text{Zn}$ – $\text{N}(1)'$	82.18(3)
$\text{N}$ – $\text{Zn}$ – $\text{Cl}$	105.45(4)	$\text{S}(1)$ – $\text{Zn}$ – $\text{N}(2)$	97.82(3)
$\text{N}$ – $\text{Zn}$ – $\text{Cl}'$	105.38(4)	$\text{S}(1)$ – $\text{Zn}$ – $\text{N}(2)'$	97.82(3)
$\text{Cl}$ – $\text{Zn}$ – $\text{N}'$	105.38(4)	$\text{S}(1)$ – $\text{Zn}$ – $\text{S}(2)$	180.00(5)
$\text{Cl}'$ – $\text{Zn}$ – $\text{N}'$	105.45(4)	$\text{S}(2)$ – $\text{Zn}$ – $\text{N}(2)'$	82.18(3)
		$\text{S}(2)$ – $\text{Zn}$ – $\text{N}(2)$	82.18(3)
		$\text{S}(2)$ – $\text{Zn}$ – $\text{N}(1)$	97.82(3)
		$\text{S}(2)$ – $\text{Zn}$ – $\text{N}(1)'$	97.82(3)
		$\text{N}(1)$ – $\text{Zn}$ – $\text{N}(1)'$	82.38(5)
		$\text{N}(1)$ – $\text{Zn}$ – $\text{N}(2)$	180.00(5)
		$\text{N}(1)$ – $\text{Zn}$ – $\text{N}(2)'$	97.62(5)
		$\text{N}(1)'$ – $\text{Zn}$ – $\text{N}(2)$	97.62(5)
		$\text{N}(1)'$ – $\text{Zn}$ – $\text{N}(2)'$	180.00(5)
		$\text{N}(2)$ – $\text{Zn}$ – $\text{N}(2)'$	82.38(5)

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

$\text{S}$ (thioether) bond lengths are each 2.4997(4) Å with a 180.00(5)°  $\text{S}$ – $\text{Zn}$ – $\text{S}$  angle. This  $\text{Zn}$ –thioether bond distance is on the short end of normal for six-coordinate  $\text{Zn}(\text{II})$  complexes, reported to vary from 2.486 to 2.720 Å.<sup>34,37,38,41,42,44</sup> The  $\text{N}$ (pyridyl) atoms form a plane around the  $\text{Zn}(\text{II})$  with the thioether groups approximately normal to the plane. However, the ligand constraints held on the thioether sulfur atom result in angles less than 90° for  $\text{S}(1)$ – $\text{Zn}$ – $\text{N}(1)$  and  $\text{S}(1)$ – $\text{Zn}$ – $\text{N}(1)'$  angles (82.18(3)°), with  $\text{S}(1)$ – $\text{Zn}$ – $\text{N}(2)$  angles of 97.82(3)°. The perchlorate counterions and an acetonitrile solvent molecule are located between complexes in the crystal lattice and do not coordinate  $\text{Zn}(\text{II})$ . The shortest  $\text{Zn}$ – $\text{O}$ (perchlorate) distance is 4.954(4) Å.

Interesting differences exist between the group 12 complexes  $\text{Zn}(\mathbf{1})_2(\text{ClO}_4)_2$ ,  $\text{Cd}(\mathbf{1})_2(\text{ClO}_4)_2$ , and  $\text{Hg}(\mathbf{1})_2(\text{ClO}_4)_2$ . The average  $\text{M}(\text{II})$ – $\text{N}$ (pyridyl) bond distances follow a trend (2.1892 Å for  $\text{Zn}$ – $\text{N}$  < 2.373 Å for  $\text{Cd}$ – $\text{N}$  < 2.457 Å for  $\text{Hg}$ – $\text{N}$ ) that is consistent with ionic radii. Although all the  $\text{M}(\text{II})$ –thioether bond distances of these complexes are within normal ranges, the average  $\text{M}(\text{II})$ – $\text{S}$  distance (2.4997 Å for  $\text{Zn}$ , 2.707 Å for  $\text{Cd}$ , and 2.637 Å for  $\text{Hg}$ ) does not follow the trend in ionic radii. This highlights a pattern of shorter  $\text{Hg}(\text{II})$ –thioether bond lengths compared to similar  $\text{Cd}(\text{II})$ –thioether distances. Another difference between the structures of these two complexes is the conformation of ligand **1** around the metal ion. In the  $\text{Hg}(\text{II})$  and  $\text{Zn}(\text{II})$  complexes the ligand is neatly folded with the thioether at the apex (Figures 2 and 4). The  $\text{N}$ – $\text{S}$ – $\text{N}$  angles are similar at 56.1 and 57.5° for  $\text{Hg}(\text{II})$  and 55.6 and 55.6° for  $\text{Zn}(\text{II})$ . The  $\text{Cd}(\text{II})$  complex displays a disordered ligand with a zigzagged backbone and twisted pyridyl groups (Figure 3). The smaller ionic radius of  $\text{Zn}(\text{II})$  versus  $\text{Hg}(\text{II})$  permitted a  $\text{Zn}(\text{II})$  complex with tightly packed tridentate **1** coordinated at opposite triangular faces of an octahedron, in a staggered fashion. The geometry of the analogous  $\text{Hg}(\text{II})$  complex, with

- (78) Gagnon, C.; Beauchamp, A. L.; Tranqui, D. *Can. J. Chem.* **1979**, *57*, 1372.  
 (79) Helm, M. L.; Loveday, K. D.; Combs, C. M.; Bentzen, E. L.; VanDerveer, D. G.; Rogers, R. D.; Grant, G. J. *J. Chem. Crystallogr.* **2003**, *33*, 447.  
 (80) Loi, M.; Graf, E.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Chem. Commun.* **1999**, 603.  
 (81) Glass, R. S.; Steffen, L. K.; Swanson, D. D.; Wilson, G. S.; de Gelder, R.; de Graaff, R. A. G.; Reedijk, J. *Inorg. Chim. Acta* **1993**, *207*, 241.  
 (82) Reddy, H. K.; Zhang, C.; Schlemper, E. O.; Schrauzer, G. N. *Inorg. Chem.* **1992**, *31*, 1673.  
 (83) Chan, W. H.; Mak, T. C. W.; Yip, W. H.; Smith, G.; O'Reilly, E. J.; Kennard, C. H. L. *Polyhedron* **1987**, *6*, 881.  
 (84) Herbstein, F. H.; Ashkenazi, P.; Kaftory, M.; Kapon, M.; Reisner, G. M.; Ginsburg, D. *Acta Crystallogr., Sect. B: Struct. Sci* **1986**, *B42*, 575.  
 (85) Mak, T. C. W.; Yip, W. H.; Smith, G.; O'Reilly, E. J.; Kennard, C. H. L. *Inorg. Chim. Acta* **1984**, *84*, 57.  
 (86) Whitlow, S. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1975**, *B31*, 2531.  
 (87) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.  
 (88) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.



**Figure 5.** Structure of one pair of loosely associated  $\text{Hg}(\mathbf{1})\text{Cl}_2$  monomers. Thermal ellipsoids are shown at the 50% level.

a larger metal ion and thus relieved steric constraints, was closer to trigonal prismatic with the ligands on triangular faces of the prism and nearly eclipsed. It also appears that intermolecular  $\pi$ -stacking of the pyridyl groups for the Zn(II) and Hg(II) complexes exists in the crystal lattice. The pyridyl groups in the Cd(II) complexes have no such interaction. Previous studies of bis-tridentate chelates<sup>51</sup> indicate that the interconversion of octahedral and trigonal prismatic complexes is very facile when metal–ligand bond distances are comparable and the structure differences may primarily reflect differences in crystal packing.

**$\text{Hg}(\mathbf{1})\text{Cl}_2$  and  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  Solid-State Structures.** Slow evaporation of a 1:1 mixture of  $\text{HgCl}_2$  and  $\mathbf{1}$  in acetonitrile/methanol provided two different crystalline complexes. The transparent yellow crystal form appearing first was  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$ . The clear and colorless crystals forming later were the mononuclear complex  $\text{Hg}(\mathbf{1})\text{Cl}_2$ . The order of formation of these complexes suggests that  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  formation is kinetically more favorable.

Key differences between the mercuric chloride complexes of  $\mathbf{1}$  included their nuclearity and the binding mode of the ligand. The  $\text{Hg}(\mathbf{1})\text{Cl}_2$  complex (Figure 5) consisted of discrete monomeric Hg(II) ions arranged such that a dimeric structure is suggested. A bonding interaction between the thioether and metal center was notably absent in this complex. In contrast, the  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  complex (Figure 6) was polymeric and the thioether functionality bridged two metal centers.

The  $\text{Hg}(\mathbf{1})\text{Cl}_2$  complex (Figure 5) had a distorted tetrahedral geometry with  $\text{N}(1\text{A})\text{—Hg—N}(1\text{B})$  and  $\text{Cl}(1)\text{—Hg—Cl}(2)$  angles of  $106.88(10)$  and  $145.46(3)^\circ$ , respectively (Table 3). The  $\text{Hg—N}(\text{pyridyl})$  bonds were  $2.357(3)$  and  $2.452(3)$  Å, consistent with pyridyl coordination in other four coordinate Hg(II) complexes ( $2.36\text{—}2.49$  Å<sup>89–91</sup>) and similar to the distances in the six-coordinate Hg(II) complexes mentioned above.<sup>51,54–56</sup> The complex contained chloride ligands with  $\text{Hg—Cl}$  bond distances of  $2.4049(8)$  and  $2.4099(8)$  Å. The latter distance is associated with a very asym-

metric  $\text{Hg}_2\text{Cl}_2$  diamond core with a second  $\text{Hg—Cl}$  distance of  $3.258(8)$  Å. A similar arrangement with one short  $\text{Hg—Cl}$  bond ( $2.358$  Å) and one long  $\text{Hg—Cl}$  distance ( $3.51$  Å) was found in  $[\text{Hg}(\text{TLA})\text{Cl}]_2^{2+}$ .<sup>92</sup> Four-coordinate Hg(II) complexes with two symmetrically bridging chloride ions typically have  $\text{Hg—Cl}$  distances ranging from  $2.564$  to  $2.976$  Å. Representative pairs of  $\text{Hg—Cl}(\text{bridging})$  distances in symmetrically bridged four-coordinate complexes include  $2.720$  and  $2.976$ ,<sup>93</sup>  $2.713$  and  $2.714$ ,<sup>94</sup>  $2.564$  and  $2.791$ ,<sup>95</sup>  $2.659$  and  $2.789$ ,<sup>84</sup> and  $2.729$  and  $2.764$  Å.<sup>84</sup> While the discrepancies between the two  $\text{Hg—Cl}(\text{bridging})$  distances of these pairs are small relative to those in the core of  $[\text{Hg}(\mathbf{1})\text{Cl}_2]_2$ , the very same complexes have  $\text{Hg—Cl}(\text{terminal})$  distances of  $2.386$ ,<sup>93</sup>  $2.391$ ,<sup>94</sup>  $2.381$ ,<sup>95</sup>  $2.326$ ,<sup>84</sup> and  $2.332$  Å.<sup>84</sup> These distances are similar to the  $\text{Hg—Cl}(\text{terminal})$  distances in  $\text{Hg}(\mathbf{1})\text{Cl}_2$  and also similar to the short  $\text{Hg—Cl}$  bond distance in the  $[\text{Hg}(\mathbf{1})\text{Cl}_2]_2$  core. This analysis indicates that the complex is more correctly described as two monomers that are loosely associated than a dimer. Furthermore, the  $\text{Hg—Hg}$  separation is  $4.415(6)$  Å, longer than the sum of their van der Waals radii ( $1.70\text{—}2.00$  Å for  $\text{Hg}(\text{II})$ <sup>61</sup>). This is intermediate in the  $\text{Hg—Hg}$  distances ( $5.196$ ,<sup>93</sup>  $3.842$ ,<sup>94</sup>  $3.936$ ,<sup>95</sup>  $3.956$ ,<sup>84</sup> and  $4.001$  Å.<sup>84</sup>) found in the above-mentioned Hg complexes that have bridging chloride ligands.

Both tridentate-<sup>20,22</sup> and bidentate-nitrogen<sup>20</sup> coordination modes of  $\mathbf{1}$  are preceded. Although coordination numbers greater than 4 are common for Hg(II) complexes and the thiophilicity of Hg(II) is well preceded, only the two flanking pyridyls of  $\mathbf{1}$  are bound to the metal in  $\text{Hg}(\mathbf{1})\text{Cl}_2$  (Figure 5). The  $\text{Hg—S}$  distance,  $4.362(6)$  Å, is much longer than the sum of the van der Waals radii of these atoms ( $1.70\text{—}2.00$  Å for  $\text{Hg}(\text{II})$ <sup>61</sup> and  $1.60\text{—}2.03$  Å for  $\text{S}^{62}$ ), and the S lone pairs point away from the Hg center. It is well established that Hg(II) prefers thiolate coordination, while thioethers may be among the weakest ligands.<sup>96</sup> Nonetheless, there are numerous examples of Hg(II) complexes containing thioether ligands, the most common of which are the macroheterocyclic ligands (see for recent examples<sup>34,53,58,97–100</sup> and references therein). However, Hg(II) complexes of benzothiazole<sup>101</sup> and thiadiazole<sup>102</sup> ligands have the aromatic nitrogen bound to the metal rather than the thioether sulfur.

(89) Canty, A. J.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 677.

(90) Arnold, A. P.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 607.

(91) Castineiras, A.; Diaz, G.; Florencio, F.; Garcia-Blanco, S.; Martinez-Carrera, S. *Z. Anorg. Allg. Chem.* **1988**, *567*, 101.

(92) Bebout, D. C.; Bush, J. F., II; Crahan, K. K.; Kastner, M. E.; Parrish, D. A. *Inorg. Chem.* **1998**, *37*, 4641.

(93) Davidovic, N.; Matkovic-Calogovic, D.; Popovic, Z.; Vedinara-Dragojevic, I. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *C54*, 574.

(94) Romero, I.; Sanchez-Castello, G.; Teixidor, F.; Whitaker, C. R.; Rius, J.; Miravittles, C.; Flor, T.; Escriche, L.; Casabo, J. *Polyhedron* **1996**, *15*, 2057.

(95) Wang, Q.-H.; Long, D.-L.; Huang, J.-S. *Polyhedron* **1998**, *17*, 3665.

(96) Fairhurst, M. T.; Rabenstein, D. L. *Inorg. Chem.* **1975**, *14*, 1413.

(97) Setzer, W. N.; Guo, Q.; Grant, G. J.; Hubbard, J. L.; Glass, R. S.; VanDerveer, D. G. *Heteroat. Chem.* **1990**, *1*, 317.

(98) Caltagirone, C.; Bencini, A.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Mariani, P.; Papke, U.; Tei, L.; Verani, G. *J. Chem. Soc., Dalton Trans.* **2003**, 901.

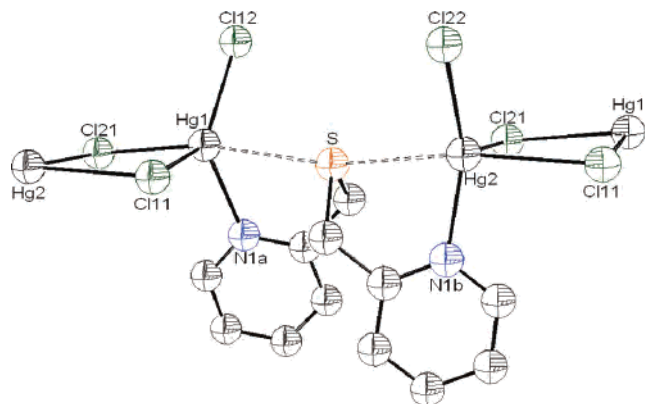
(99) Tsuchiya, T.; Shimizu, T.; Hirabayashi, K.; Kamigata, N. *J. Org. Chem.* **2003**, *68*, 3480.

(100) Marchand, A. P.; Cal, D.; Mlinaric-Majerski, K.; Ejsmont, K.; Watson, W. H. *J. Chem. Crystallogr.* **2002**, *32*, 447.

(101) Battaglia, L. P.; Bonamartini Corradi, A.; Cramarossa, M. R.; Vezzosi, I. M.; Gusti, J. G. *Polyhedron* **1993**, *12*, 2235.

(102) Fabretti, A. C.; Peyronel, G.; Franchini, G. C. *Spectrochim. Acta, Part A* **1979**, *35A*, 229.

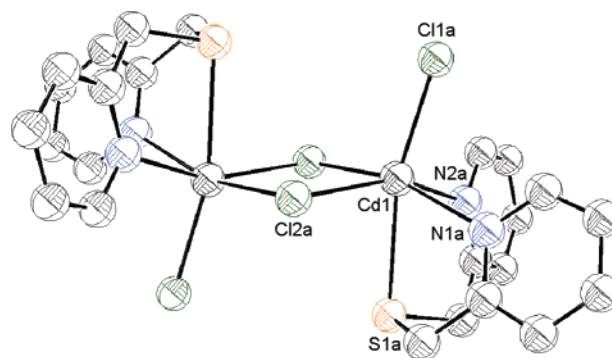




**Figure 6.** Structure of a segment of the  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  linear chain. Thermal ellipsoids are shown at the 50% level.

Furthermore, the central thioether of ligands structurally related to **1** is frequently uncoordinated in the structurally characterized halide complexes of Hg(II). For example, a four-coordinate  $\text{HgBr}_2$  complex was published by Lockhart et al. that contains a bis(benzimidazole)sulfide ligand with a noncoordinating central thioether.<sup>103</sup> Also, a four-coordinate  $\text{HgCl}_2$  complex with a similar bis(benzimidazole) linked by a dithiahexane bridge is bidentate.<sup>104</sup>

The  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  complex (Figure 6) forms parallel and linear chains. Each Hg(II) ion is found in a distorted square pyramidal geometry. The thioether atom of **1** forms a bridge between Hg(II) ions. The resulting linear Hg–S–Hg unit (angle of  $166.51(8)^\circ$ ) forms a chain to neighboring Hg–S–Hg units with two bridging chloride ligands. In addition to these bridging ligands, the Hg(II) ions have terminal ligands. There are two different Hg(II) sites, and one Hg(II) has shorter terminal ligand bonds (Table 3). This Hg(II) ion has a Hg–N(pyridyl) distance of  $2.175(7)$  Å and a Hg–Cl(terminal) distance of  $2.336(2)$  Å. The Hg(II) ion with longer terminal ligand distances has a Hg–N(pyridyl) distance of  $2.259(8)$  Å and a Hg–Cl length of  $2.395(2)$  Å. The terminal Hg–pyridyl and Hg–Cl bond distances are short for five-coordinate Hg complexes, possibly compensating for weak interactions between Hg and the bridging thioether linkage (see below). A five-coordinate  $\text{Hg}(2,2'\text{-bipyridine})_2(\text{NO}_3)_2$  complex displays a short Hg(II)–N(pyridyl) average bond distance of  $2.229$  Å<sup>105</sup> that is similar to those observed here. The Hg–Cl(terminal) bond distances fall within the observed range  $2.326$ – $2.391$  Å.<sup>84,93–95</sup> The bridging Hg(II)–S(thioether) bond distances are  $3.035(4)$  and  $3.048(4)$  Å. To our knowledge, only one other Hg(II) complex with a bridging thioether S atom has been reported.<sup>84</sup> This six-coordinate complex also forms a polymer but has two terminal Hg(II)–Cl bonds and four bridging thioether bonds ranging from  $2.978$  to  $3.212$  Å. The bridging chlorides of  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  result in a chain with a zigzagging backbone. The Hg(II) ion with the long Hg–terminal bond lengths is coordinated



**Figure 7.** Structure of dimeric  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$ . Thermal ellipsoids are shown at the 50% level.

more closely to two bridging chloride ligands ( $2.555(2)$  and  $2.615(2)$  Å), while the other Hg(II) ion forms longer Hg–Cl(bridging) bond distances ( $2.756(2)$  and  $2.765(2)$  Å). This type of asymmetry introduced into the  $\text{Hg}_2\text{Cl}_2$  core is unique among the complexes found in the literature with bridging chloride ligands. As discussed regarding  $\text{Hg}(\mathbf{1})\text{Cl}_2$ , these complexes usually have one short and one long Hg–Cl(bridging) bond on each metal center, giving a rhomboid core. Instead, this complex has two short Hg–Cl(bridging) bonds to one Hg(II) and two long bonds to the other Hg(II). The result is an asymmetric  $\text{Hg}_2\text{Cl}_2$  core with a kite shape. The Hg–Hg separation is  $3.851(8)$  Å which is on the shorter end of such distances in complexes with bridging chlorides ( $3.842$ – $5.196$  Å<sup>84,93–95</sup>).

Other Hg(II) complexes are known to form linear chains in the solid state.<sup>95,106,107</sup> The structure of  $\text{Hg}_2(\mathbf{1})\text{Cl}_4$  is unique because of the alternating chloride and thioether bridges (Figure 6). A similar binding mode for **1**, with the thioether bridging of two different metal ions, was observed in the nonpolymeric bis(6-methyl-2-methylpyridyl) sulfide (6-methylated analogue of **1**) complex of copper(I) iodide.<sup>19</sup>

**[Cd(1)Cl<sub>2</sub>]<sub>2</sub> Structure.** The  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$  complex exists in the solid state as dimers bridged by two chloride ligands (Figure 7). There are two similar but crystallographically independent dimers in the unit cell, and the cadmium ions of each dimer are related by an inversion center. The Cd–Cd distance is  $3.812(4)$  Å and precludes overlap of the van der Waals radii of the two ions.<sup>87</sup> The Cd–Cd distances in other Cd(II) complexes with two bridging chlorides range from  $3.76$  to  $4.077$  Å.<sup>39,66,80,103,108</sup> Each Cd(II) ion is six coordinate with a distorted octahedral coordination environment. Dinuclear cadmium complexes with bridging chlorides are known and have Cd–Cl(bridging) bond distances ranging from  $2.54$  to  $2.89$  Å.<sup>77,80,103,108</sup> The bridging chlorides of  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$  are asymmetric and fit within this range (Table 4), with Cd–Cl(bridging) bonds of  $2.5831(7)$  and  $2.7036(8)$  Å (for dimer 1). The terminal chloride ligand bond distances are typically shorter than the bridging bond distances (ranging

(103) Matthews, C. J.; Clegg, W.; Heath, S. L.; Martin, N. C.; Hill, M. N. S.; Lockhart, J. C. *Inorg. Chem.* **1998**, *37*, 199.

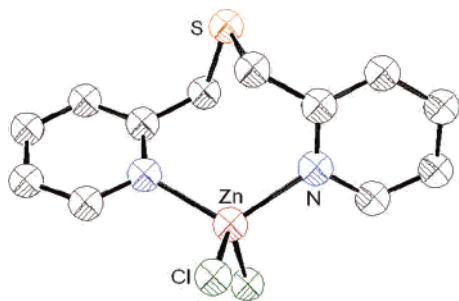
(104) Carballo, R.; Castineiras, A.; Conde, M. C. G.; Hiller, W. *Polyhedron* **1993**, *12*, 1655.

(105) Grdenic, D.; Kamenar, B.; Hergold-Brundic, A. *Croat. Chem. Acta* **1979**, *52*, 339.

(106) Zhang, X.; Yu, W.; Xie, Y.; Zhao, Q.; Tian, Y. *Inorg. Chem. Commun.* **2003**, *6*, 1338.

(107) Zhang, X.; Xie, Y.; Yu, W.; Zhao, Q.; Jiang, M.; Tian, Y. *Inorg. Chem.* **2003**, *42*, 3734.

(108) Cannas, M.; Marongiu, G.; Saba, G. *J. Chem. Soc., Dalton Trans.* **1980**, 2090.



**Figure 8.** Structure of  $\text{Zn}(\mathbf{1})\text{Cl}_2$ . Thermal ellipsoids are shown at the 50% level.

from 2.49 to 2.76 Å in the above complexes<sup>77,80,103,108</sup>). The terminal Cd–Cl bond length in  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$  (2.4863(7) Å) is consistent with this observation. The Cd–N(pyridyl) bond lengths are 2.411(3) and 2.360(2) Å, also similar to the other six-coordinate Cd(II) complexes mentioned above (2.266–2.442 Å).<sup>28,63–78</sup> Finally, the Cd–thioether distance is 2.7566(8) Å and is normal for six-coordinate Cd(II) complexes (range 2.579–2.976 Å).<sup>34,58,65,66,68,77,79–86</sup>

**$\text{Zn}(\mathbf{1})\text{Cl}_2$  Structure.** The  $\text{ZnCl}_2$  complex of **1** formed a 1:1 structure analogous to the other group 12 metal ions (Figure 8). However, the  $\text{Zn}(\mathbf{1})\text{Cl}_2$  complex was monomeric and not arranged for dimeric interactions such as the Cd(II) or Hg(II) analogues. The lack of bridging chloride ligands for the Zn(II) complex yielded a four-coordinate, approximately tetrahedral complex with equivalent Zn–Cl bonds (2.2306(4) Å) and Zn–N(pyridyl) bonds (2.0509(13) Å) (Table 5). The Zn–Cl bonds are slightly shorter than the reported average ( $2.253 \pm 0.033$  Å<sup>88</sup>) while the Zn–N(pyridyl) bonds are nearly average ( $2.064 \pm 0.057$  Å<sup>88</sup>) for four-coordinate Zn(II) complexes. Another feature of  $\text{Zn}(\mathbf{1})\text{Cl}_2$  is the bidentate binding of **1** as observed in  $\text{Hg}(\mathbf{1})\text{Cl}_2$  (Figure 5) and unlike  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$  (Figure 7). The Zn–S(thioether) separation of 4.063(4) Å is well beyond the sum of their covalent radii (1.39 Å for Zn(II)<sup>87</sup> and 1.60–2.03 Å for S<sup>62</sup>). Similar four-coordinate complexes of Zn(II) forego thioether coordination,<sup>37,109</sup> including some with potential tridentate ligands containing a central thioether.<sup>103,110,111</sup>

A comparison of the  $\text{Hg}(\mathbf{1})\text{Cl}_2$ ,  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$ , and  $\text{Zn}(\mathbf{1})\text{Cl}_2$  complexes reveals some key differences. The Hg(II) and Cd(II) complexes have a  $\text{M}_2\text{Cl}_2$  core in the solid state with chloride ligands between two metals. The Hg(II) complex is an asymmetric, loosely associated dimer better described as two monomers, while the Cd(II) complex is more accurately described as a dimer. The Hg–Hg separation is more distant at 4.415(6) Å while the Cd–Cd distance is 3.812(4) Å. Also, the Zn(II) and Hg(II) complexes are essentially four coordinate, lacking thioether coordination by **1**, while the Cd(II) complex forms a six-coordinate complex, including thioether coordination. It is unusual that the M(II)–thioether bonds in  $\text{Cd}(\mathbf{1})_2(\text{ClO}_4)_2$  are longer than the bonds in  $\text{Zn}(\mathbf{1})_2(\text{ClO}_4)_2$  and  $\text{Hg}(\mathbf{1})_2(\text{ClO}_4)_2$ , and yet a M(II)–

thioether bond is present in  $[\text{Cd}(\mathbf{1})\text{Cl}_2]_2$  but absent in the Zn(II) and Hg(II) analogues. The presence of the coordinated chloride ligands in the Zn(II) and Hg(II) complexes could counter the divalent charge, thus mitigating the need for additional electron density from the thioether. This does not explain why the Cd(II) complex coordinates the thioether. However, it is known that lower coordination numbers (<6) are less common for Cd(II) but quite common for Hg(II). As discussed above, there are examples of Zn(II) and Hg(II) complexes that forego thioether coordination even when the coordination number is 5 or less.<sup>37,103,104,109–111</sup> The absence of possible thioether coordination is also seen in some complexes of Cd(II),<sup>71,103,112–114</sup> particularly those with coordination numbers of 6 or more. Interestingly, the five-coordinate Cd(II) complex of bis(benzimidazole)sulfide lacks thioether coordination just like its Zn(II) and Hg(II) analog<sup>103</sup> but unlike the complexes of **1**. These data indicate that **1** and related ligands have potentially hemilabile<sup>115</sup> coordination behavior.

**Solution-State Behavior: <sup>1</sup>H NMR Spectroscopy.** Metal ion binding to **1** with the chloride and perchlorate salts of divalent zinc triad metals were studied in the solution state using <sup>1</sup>H NMR spectroscopy. The proton chemical shifts of the complexes were generally downfield of the free ligand, a common result of the deshielding influence of  $\sigma$  donation to a metal cation (Table S1). The only exceptions were the chemical shifts of  $\text{H}_a$  in the 1:2 M(II):**1** complexes. As explained previously for the equivalent complexes of BM-PA,<sup>51</sup> these upfield shifts are likely to stem from interactions with the ring current of the opposing ligand. The differences between the chemical shifts of comparable complexes were generally smaller than their differences with free ligand.

Since Hg(II) and Cd(II) are diamagnetic and have high natural abundance spin  $I = 1/2$  isotopes, the proton NMR spectra for their complexes were examined for evidence of slow exchange on the coupling constant time scale. Heteronuclear coupling of <sup>1</sup>H to <sup>199</sup>Hg or <sup>111/113</sup>Cd was not observed in the NMR spectra of mixtures of **1** with  $\text{HgCl}_2$  or  $\text{CdCl}_2$ . A titration study of  $\text{HgCl}_2$  (2 mM) and **1** in acetonitrile-*d*<sub>3</sub> showed a single set of sharp resonances with chemical shifts that drifted from M(II):**1** ratios of 0 to 1.0 and then remained constant at ratios above 1.0 (data not shown). The data suggested fast exchange between free ligand and a 1:1 complex. This is not surprising since d<sup>10</sup> complexes are known to commonly undergo rapid ligand exchange. As a coordinating anion, chloride competes with the ligand for the metal ion by reducing the available charge density. Precedent for detection of <sup>199</sup>Hg<sup>1</sup>H couplings in coordination compounds of  $\text{HgCl}_2$  has been limited to tetradentate chelating ligands.<sup>29,92,116</sup> Also, to the best of our knowledge

(109) Grapperhaus, C. A.; Tuntulani, T.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1998**, *37*, 4052.

(110) Ghosh, P.; Wood, M.; Bonanno, J. B.; Hascall, T.; Parkin, G. *Polyhedron* **1999**, *18*, 1107.

(111) Gregorzik, R.; Vahrenkamp, H. *Chem. Ber.* **1994**, *127*, 1857.

(112) Griffith, E. A. H.; Charles, N. G.; Rodesiler, P. F.; Amma, E. L. *Polyhedron* **1985**, *4*, 615.

(113) McCleverty, J. A.; Gill, S.; Kowalski, R. S. Z.; Bailey, N. A.; Adams, H.; Lumbard, K. W.; Murphy, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 493.

(114) De Meester, P.; Hodgson, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6884.

(115) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

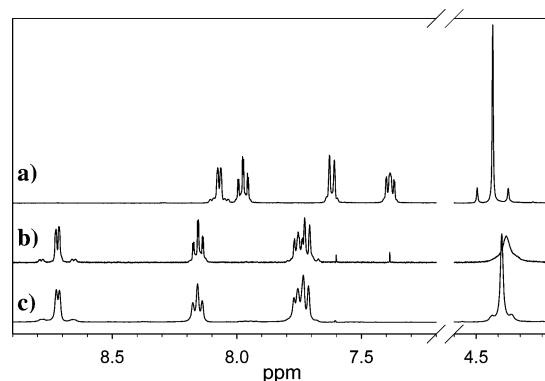
(116) Bebout, D. C.; Ehmann, D. E.; Trinidad, J. C.; Crahan, K. K.; Kastner, M. E.; Parrish, D. *Inorg. Chem.* **1997**, *36*, 4257.

couplings have never been reported for any Hg(II) complex with bidentate ligands and the solid-state structure of Hg(1)Cl<sub>2</sub>, as discussed above, displays a bidentate coordination mode for **1**.

Analysis of the <sup>1</sup>H NMR data for Hg<sub>2</sub>(1)Cl<sub>4</sub> suggested the polymeric form (Figure 6) does not exist in acetonitrile solution. Dissolution of the polymeric Hg<sub>2</sub>(1)Cl<sub>4</sub> crystals in acetonitrile-*d*<sub>3</sub> yielded <sup>1</sup>H NMR chemical shifts similar to those for dissolved Hg(1)Cl<sub>2</sub> crystals. Significant differences in the chemical shifts of the ligand protons of these two complexes would be expected since **1** is bound to two metal ions through the bridging thioether in Hg<sub>2</sub>(1)Cl<sub>4</sub>, while **1** is bidentate or possibly weakly tridentate in the solution structure of Hg(1)Cl<sub>2</sub> (Figure 5). Furthermore, <sup>1</sup>H NMR data for 2 mM HgCl<sub>2</sub> with **1** in ratios above 1.0 showed nearly constant chemical shifts (data not shown) with no evidence for the formation of or equilibration with a second species at Hg(II):**1** ratios greater than one.

For the titrations of **1** with Cd(ClO<sub>4</sub>)<sub>2</sub>, broadened proton resonances were present for Cd(II):**1** ratios of less than 1.0 at -20 °C (data not shown). This broadening is presumably due to exchange on the NMR chemical shift time scale. H<sub>a</sub> and H<sub>f</sub> proton resonances were particularly broadened, and their chemical shifts were observed to change the most over the course of the titration. One set of broadened resonances with chemical shifts that varied approximately linearly for **1** was present for Cd(II):**1** ratios of 0 to 0.5. This is consistent with rapid exchange between the free ligand and a [Cd(1)<sub>2</sub>]<sup>2+</sup> complex, similar to the solid-state structure. Two sets of proton resonances with constant chemical shifts were distinguished for Cd(II):**1** ratios of 0.5 to 1.0, and above 1.0, one set of sharp resonances remained. Intermediate exchange on the chemical shift time scale between a [Cd(1)<sub>2</sub>]<sup>2+</sup> and a [Cd(1)(NCCH<sub>3</sub>)<sub>x</sub>]<sup>2+</sup> species likely gave rise to the two sets of broadened resonances observed. At Cd(II):**1** of 1.0 and higher, the [Cd(1)(NCCH<sub>3</sub>)<sub>x</sub>]<sup>2+</sup> species predominated and, due to slow exchange on the chemical shift time scale, sharpened resonances resulted.

The rare and typically weak heteronuclear <sup>111/113</sup>Cd<sup>1</sup>H couplings<sup>28</sup> were not observed for the Cd(ClO<sub>4</sub>)<sub>2</sub> complexes of **1** down to -20 °C. As noted above, the Cd-S bond distance is longer than the Hg-S distance in the solid-state structure of the perchlorate salts. Weaker coordination of the central thioether group of **1** in the Cd(II) complex could contribute to rapid ligand exchange on the coupling constant time scale, as well as weaker through bond interactions, and preclude <sup>111/113</sup>Cd<sup>1</sup>H couplings. Characterization of Cd(II) complexes by <sup>113</sup>Cd NMR is of limited value under conditions of exchange and was not attempted.



**Figure 9.** <sup>1</sup>H NMR spectra of 2 mM solutions of (a) [Hg(1)<sub>2</sub>]<sup>2+</sup> in CD<sub>3</sub>CN at -20 °C, (b) [Hg(1)(CD<sub>3</sub>CN)<sub>x</sub>]<sup>2+</sup> in CD<sub>3</sub>CN at -20 °C, and (c) [Hg(1)(CD<sub>3</sub>CN)<sub>x</sub>]<sup>2+</sup> in CD<sub>3</sub>CN at 0 °C.

Unlike the above solutions of the chloride salts, the <sup>1</sup>H NMR spectra of **1** in acetonitrile-*d*<sub>3</sub> solutions of Hg(ClO<sub>4</sub>)<sub>2</sub> displayed many notable features (Figure S1). From 0 to 0.5 Hg(II):**1**, the ligand resonances shifted linearly from the free ligand values to those observed for Hg(1)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (Figure 9a) indicating rapid exchange between these species. The chemical shifts of 2 mM [Hg(1)<sub>2</sub>]<sup>2+</sup> in acetonitrile-*d*<sub>3</sub> at -20 °C are compared to those observed for an equivalent solution of [Hg(BMPA)<sub>2</sub>]<sup>2+</sup> at -40 °C in Table 6. The proton NMR spectra of acetonitrile-*d*<sub>3</sub> solutions of [Hg(1)<sub>2</sub>]<sup>2+</sup> (Figure 9a) displayed <sup>3</sup>J, <sup>4</sup>J, and <sup>5</sup>J(<sup>199</sup>Hg<sup>1</sup>H) to the pyridyl protons, indicating that the ligand remained bound to the Hg(II) ion on the coupling constant time scale. The <sup>3</sup>J(<sup>199</sup>Hg<sup>1</sup>H) of 24 Hz for H<sub>a</sub> was similar to that observed in [Hg(BMPA)<sub>2</sub>]<sup>2+</sup>, with <sup>3</sup>J(<sup>199</sup>Hg<sup>1</sup>H<sub>a</sub>) of 20 Hz, and the <sup>3</sup>J was not as large as couplings observed in complexes with one polydentate ligand (see below). <sup>4</sup>J and <sup>5</sup>J(<sup>199</sup>Hg<sup>1</sup>H) were observed for [Hg(1)<sub>2</sub>]<sup>2+</sup> with values of ~10 and 8 Hz, respectively (Table 6). Interestingly, the <sup>3</sup>J-<sup>5</sup>J(<sup>199</sup>Hg<sup>1</sup>H) of the pyridyl groups for [Hg(BMPA)<sub>2</sub>]<sup>2+</sup> are either not resolved or less than in those in [Hg(1)<sub>2</sub>]<sup>2+</sup> and their solid-state Hg-N(pyridyl) bond distances (see above) are not appreciably different.<sup>51</sup>

The methylene (H<sub>f</sub>) protons of [Hg(1)<sub>2</sub>]<sup>2+</sup> appeared equivalent (Figure 9a) despite being in different environments in the solid state structure. Similar fast exchange (and equivalence of the H<sub>f</sub> protons) on the NMR chemical shift time scale has been observed with **1** before in Pd(II)<sup>25</sup> and Cu(I)<sup>19</sup> complexes. However, for [Hg(1)<sub>2</sub>]<sup>2+</sup>, two different resonances were expected, one signal for the H<sub>f</sub> protons in the acute angle of the coordinated V-shaped ligand (Figure 2) and one signal for the protons pointing out. Two H<sub>f</sub> signals were observed in Hg(BMPA)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (Table 6),<sup>51</sup> which has a similar structure and inequivalent protons. A possible

**Table 6.** Chemical Shifts and Coupling Constants for Hg(ClO<sub>4</sub>)<sub>2</sub> Complexes of **1** and BMPA under Slow Exchange Conditions (2 mM, CD<sub>3</sub>CN)

	[Hg(1)(NCCH <sub>3</sub> ) <sub>x</sub> ] <sup>2+</sup>		[Hg(BMPA)(NCCH <sub>3</sub> ) <sub>x</sub> ] <sup>2+</sup>		[Hg(1) <sub>2</sub> ] <sup>2+</sup>		[Hg(BMPA) <sub>2</sub> ] <sup>2+</sup>	
	ppm	<sup>199</sup> Hg <sup>1</sup> H (Hz)	ppm	<sup>199</sup> Hg <sup>1</sup> H (Hz)	ppm	<sup>199</sup> Hg <sup>1</sup> H (Hz)	ppm	<sup>199</sup> Hg <sup>1</sup> H (Hz)
H <sub>a</sub>	8.72	52	8.63	46	8.07	24	7.85	20
H <sub>c</sub>	8.16	10	8.13	10	7.98	8	7.99	
H <sub>b</sub>	7.75	22	7.71	20	7.38	8	7.38	
H <sub>d</sub>	7.72	28	7.61	24	7.62	10	7.55	
H <sub>f</sub>	4.36	36	4.48	79	4.42	56	4.35	72
H <sub>f</sub>			3.91	42			3.99	69

mechanism for exchange and equivalence of the methylene protons of a bis(tridentate) complexes is outlined in a previous publication.<sup>51</sup> The mechanism involves only rotations about the multiple pseudo- $C_3$  axes of pseudo trigonal prismatic and pseudooctahedral coordination spheres, which are similar in energy. The reason the  $H_f$  protons of  $[\text{Hg}(\mathbf{1})_2]^{2+}$  are equivalent while  $[\text{Hg}(\text{BMPA})_2]^{2+}$  displays inequivalent  $H_f$  protons is presumably due to a lower barrier for inversion of the central thioether compared to a central amine. No bond breaking is required for the exchange mechanism, important for maintaining the observed  $J(^{199}\text{Hg}^1\text{H})$ . The  $^3J(^{199}\text{Hg}^1\text{H})$  observed for  $[\text{Hg}(\mathbf{1})_2]^{2+}$  was 56 Hz (Table 6). This coupling is larger than the previously observed  $^4J(^{199}\text{Hg}^1\text{H})$  that range from 10 to 30 Hz.<sup>10,27,29,51,116,117</sup> The observation of a  $J$  greater than all previously reported  $^4J$  suggests at least some contribution from  $^3J$ , which requires that a thioether bonding interaction be maintained on the coupling constant time scale. Furthermore, no couplings have yet been observed between  $^{199}\text{Hg}$  and protons of bidentate ligands. In addition, the  $^3J$  of the methylene group in  $[\text{Hg}(\text{BMPA})_2]^{2+}$ , with inequivalent  $H_f$  protons, has larger  $^3J(^{199}\text{Hg}^1\text{H})$  values, likely reflecting the shorter Hg–amine bond length in  $[\text{Hg}(\text{BMPA})_2]^{2+}$  (2.350(4) and 2.404(4) Å) compared to the Hg–thioether bond in  $[\text{Hg}(\mathbf{1})_2]^{2+}$  (2.6539(12) and 2.6707(11) Å).

For Hg:1 ratios from 0.5 to 1.0 the ligand resonances broadened and separate resonances appeared that eventually became a single species assigned to  $[\text{Hg}(\mathbf{1})(\text{NCCH}_3)_x]^{2+}$  (Figure 9b). The chemical shift of these ligand resonances remained unchanged with addition of excess  $\text{Hg}(\text{ClO}_4)_2$ . Importantly, this complex also displayed  $^3J$ ,  $^4J$ , and  $^5J(^{199}\text{Hg}^1\text{H})$  to the pyridyl protons, indicating that the ligand remained bound to the Hg(II) ion on the coupling constant time scale.  $^3J(^{199}\text{Hg}^1\text{H})$  was greatest for the pyridyl protons adjacent to the coordinating nitrogens, with a value of 52 Hz. This is among the largest pyridyl proton to  $^{199}\text{Hg}$  couplings observed, with  $^3J$  of 46 and 40 Hz observed for BMPA<sup>51</sup> and tris(2-methylpyridyl)amine<sup>116</sup> complexes, respectively.  $^4J(^{199}\text{Hg}^1\text{H})$  of 22 and 23 Hz were also observed for the pyridyl protons  $H_b$  and  $H_d$ , respectively. These values are at the high end of  $^4J(^{199}\text{Hg}^1\text{H})$  for coordination compounds, which have been reported to span from 15 to 24 Hz with pyridyl ligands<sup>27,51,116</sup> and 10 to 30 Hz with other coordinating ligands.<sup>10,29,117</sup> Finally, a rare  $^5J(^{199}\text{Hg}^1\text{H})$  of 10 Hz was observed that is comparable to those previously reported for Hg(II) coordination complexes.<sup>27,51</sup>

Similar to  $[\text{Hg}(\mathbf{1})_2]^{2+}$ , the methylene protons of  $[\text{Hg}(\mathbf{1})(\text{NCCH}_3)_x]^{2+}$  are equivalent on the chemical shift time scale at temperatures as low as  $-40^\circ\text{C}$ . A single broadened resonance is observed for all  $H_f$  protons that becomes sharp enough to detect a  $^3J(^{199}\text{Hg}^1\text{H})$  of 36 Hz around  $0^\circ\text{C}$  (Figure 9c). Presumably, intermediate exchange between methylene environments of the tridentate ligand on the chemical shift time scale at  $-20^\circ\text{C}$  caused broadening of the  $H_f$  resonances preventing detection of  $^{199}\text{Hg}$  satellites. At the higher temperature, rapid exchange on the chemical shift time scale

between methylene environments of the tridentate ligand and sharpening of the  $H_f$  peak allowed detection of the satellites.

The 36 Hz  $^3J$  value is lower than the 90 and 40 Hz  $^3J$  found to the methylene protons of an octahedral  $\text{N}_2\text{S}_2\text{Cl}_2$  thioether-containing mercury complex.<sup>118</sup> However, this coupling is larger than the previously observed  $^4J(^{199}\text{Hg}^1\text{H})$  mentioned above that ranges from 10 to 30 Hz.<sup>10,27,29,51,116,117</sup> Again, the thioether must be bonded on the coupling constant time scale for  $[\text{Hg}(\mathbf{1})(\text{NCCH}_3)_x]^{2+}$  to display a  $J$  greater than previously reported  $^4J$  which suggests at least some contribution from  $^3J$ . Also, since couplings have yet to be reported between  $^{199}\text{Hg}$  and the protons of bidentate ligands, minimally tridentate coordination appears to be a prerequisite for observation of couplings.

A comparison of the NMR data (Table 6) for  $\mathbf{1}$  and BMPA with  $\text{Hg}(\text{ClO}_4)_2$ <sup>51</sup> reveals some interesting differences. Both the 1:1 and 1:2 Hg:Lig complexes of BMPA have inequivalent  $H_f$  protons while they are equivalent in the complexes of  $\mathbf{1}$ . Also, the  $^3J(^{199}\text{Hg}^1\text{H})$  are larger for  $H_f$  of BMPA than for  $\mathbf{1}$ . This implies that the central amine in BMPA is a better ligand than the central thioether of  $\mathbf{1}$  and is better able to resist inversion in both the 1:1 and 1:2 Hg(II):Lig complexes. In contrast, the  $^3,^4J$  couplings to the pyridyl protons of BMPA are less than those for  $\mathbf{1}$  in complexes with both metal-to-ligand ratios. This suggests internuclear interactions are stronger in the complexes of  $\mathbf{1}$  than in the BMPA complexes, perhaps to compensate for the weaker Hg(II)–thioether interactions even though the solid-state structures have similar Hg–N(pyridyl) bond distances.

**$^{199}\text{Hg}$  NMR Data.** The  $^{199}\text{Hg}$  NMR data of the  $\text{Hg}(\text{ClO}_4)_2$  complexes of  $\mathbf{1}$  provided more support for thioether coordination in solution. A comparison of the  $^{199}\text{Hg}$  resonances of 20 mM acetonitrile- $d_3$  solutions showed the 1:2 complex shifted downfield from the 1:1 complex. The  $[\text{Hg}(\mathbf{1})_2]^{2+}$  complex displays a line ( $\sim 100$  Hz at half-height) at  $-1247$  ppm while the  $[\text{Hg}(\mathbf{1})(\text{NCCH}_3)_x]^{2+}$  complex displays a broad line ( $\sim 800$  Hz at half-height) at  $-1497$  ppm. The larger line width for  $[\text{Hg}(\mathbf{1})(\text{NCCH}_3)_x]^{2+}$  is consistent with a less spherical electron distribution around the metal ion. NMR studies report that coordination of sulfur groups results in deshielding of the Hg(II) ion compared to amine coordination.<sup>119</sup> The downfield chemical shift of the 1:2 complex from the 1:1 complex is consistent with coordination of another thioether group.

A comparison of the complexes of  $\mathbf{1}$  with the all nitrogen BMPA complexes also reveals that sulfur donation causes downfield shifts. A 20 mM sample of the  $[\text{Hg}(\text{BMPA})_2]^{2+}$  complex displays a  $^{199}\text{Hg}$  resonance at  $-1503$  ppm with  $\sim 150$  Hz line width, while the  $[\text{Hg}(\text{BMPA})(\text{NCCH}_3)_x]^{2+}$  complex has a resonance at  $-1604$  ppm ( $\sim 800$  Hz at half-height). As with the complexes of  $\mathbf{1}$ , the chemical shift of the 1:2 complex is downfield from the 1:1 complex. The deshielded Hg(II) nuclei of the thioether complexes relative

(117) McWhinnie, W. R.; Monsef-Mirzai, Z.; Perry, M. C.; Shaikh, N.; Hamor, T. A. *Polyhedron* **1993**, *12*, 1193.

(118) McCrindle, R.; Ferguson, G.; McAlees, A. J.; Parvez, M.; Ruhl, B. L.; Stephenson, D. K.; Wieckowski, T. J. *Chem. Soc., Dalton Trans.* **1986**, 2351.

(119) Utschig, L. M.; Wright, J. G.; Dieckmann, G.; Pecoraro, V.; O'Halloran, T. V. *Inorg. Chem.* **1995**, *34*, 2497.

to the amine complexes are consistent with chemical shift trends reported for S versus N coordination to Hg(II).<sup>119</sup> Alternately, it has been observed that mercury complexes with higher coordination numbers are known to display resonances with upfield shifts.<sup>45</sup> It is possible that the weaker donating ability of the thioether complex results in a complex with an effective lower coordination number.

### Conclusions

Complexes of the group 12 metal chlorides readily crystallized with 1 equiv of polydentate **1**, while conditions for isolating the metal chloride complexes with higher M(II):**1** ratios have not been found. Chloride effectively competes with a second 1 equiv of **1** for these d<sup>10</sup> transition metal ions, as evidenced by rapid exchange in the solution-state NMR data. In addition, the hemilability of **1** is indicated by the noncoordinated thioether in the chloride salts of Zn(II) and Hg(II). On the other hand, complexes of the metal perchlorates readily crystallized with two tridentate ligands. Obtaining crystals of these perchlorate salts with only one polydentate ligand is rare but has been accomplished in the presence of coordinating solvent molecules.<sup>28,29,51</sup>

The <sup>1</sup>H NMR data for **1** and Hg(ClO<sub>4</sub>)<sub>2</sub> reveal slow exchange complexes with coordinated thioether groups. The 1:1 and 1:2 Hg:**1** complexes display <sup>3-5</sup>J(<sup>199</sup>Hg<sup>1</sup>H) with some of the largest couplings observed to pyridyl protons. The <sup>3</sup>J(<sup>199</sup>Hg<sup>1</sup>H) to the methylene protons (H<sub>f</sub>) are not as large as the similar complexes of Hg(II) and BMPA. The methylene protons of Hg(II) and **1** are equivalent on the NMR chemical shift time scale. These data suggest that in ligands with comparable architecture, a thioether is prone to making weaker bonds to metals than an amine and to have less resistance to inversion. The <sup>199</sup>Hg NMR data reflect the deshielding effect of sulfur coordination to Hg(II).

These results suggest that polydentate chelating ligands can be designed to reflect the ability of thioethers to coordinate to divalent metal ions in biological systems such as proteins. However, the presence of strongly coordinating anions, such as chloride, can overcome the chelate effect advantage for thioether coordination to Hg(II) and Zn(II). Interestingly, several aspects of the coordination chemistry of Zn(II) to **1** were more similar to those for its softer and larger cogener Hg(II) than the typically more similar cogener Cd(II). This suggests that Hg(II) should not be overlooked as a potential metalloprobe of biological Zn(II) coordination environments and further substantiates the toxicological potential of Hg(II) substitution of Zn(II) proteins. Furthermore, additional studies of the zinc triad with biologically relevant multidentate ligands are warranted to elucidate changes in coordination behavior relative to simpler ligands.

**Acknowledgment.** Special thanks to Robert Pike for his review of a preliminary version of this manuscript. We thank both the National Science Foundation and the Petroleum Research Fund for their partial support of this research. We also thank the Camille and Henry Dreyfus Foundation for a Scholar Fellow award to D.C.B. for support of S.M.B. and the research. R.J.B. acknowledges the DoD-ONR instrumentation program for funds to upgrade the diffractometer and the NIH-MBRS program for funds to maintain the diffractometer.

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

IC048915S