

## Coordination of Zn(II), Cd(II), Hg(II), and Ag(I) by Bis(benzimidazole) Ligands

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The coordinating environments provided by the 1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-thiopropane (**1**), 1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-oxapropane (**2**), 1-(*N*-methyl)benzimidazolyl-3-benzimidazolyl-2-oxapropane (**3**), and 1,7-bis(benzimidazol-2-yl)-2,6-dithiaheptane (**4**) ligands for a series of soft-to-borderline metal ions have been demonstrated by crystallographic structure determination in the solid state, supplemented by multinuclear NMR studies in solution. Structures of [Zn(**3**)(H<sub>2</sub>O)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> ([C<sub>19</sub>H<sub>21</sub>N<sub>5</sub>O<sub>2</sub>-Zn](ClO<sub>4</sub>)<sub>2</sub>, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 10.3247(11) Å, *b* = 11.0320(12) Å, *c* = 20.761(2) Å, β = 96.465(3)°, *V* = 2349.7(4) Å<sup>3</sup>, *Z* = 4), [Zn(**1**)Cl<sub>2</sub>]·CH<sub>3</sub>OH ([C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>4</sub>SZn]·CH<sub>4</sub>O, triclinic, space group *P*1̄, *a* = 9.0917(9) Å, *b* = 9.9186(10) Å, *c* = 12.2079(12) Å, α = 99.710(3)°, β = 94.252(2)°, γ = 95.598(3)°, *V* = 1075.3(2) Å<sup>3</sup>, *Z* = 2), [Hg(**1**)Br<sub>2</sub>]·CH<sub>3</sub>OH ([C<sub>18</sub>H<sub>18</sub>Br<sub>2</sub>HgN<sub>4</sub>S]·CH<sub>4</sub>O, triclinic, space group *P*1̄, *a* = 9.1956(12) Å, *b* = 9.9775(13) Å, *c* = 12.462(2) Å, α = 99.239(3)°, β = 97.676(3)°, γ = 94.036(3)°, *V* = 1113.4(3) Å<sup>3</sup>, *Z* = 2), [Cd(**1**)Cl<sub>2</sub>] ([C<sub>18</sub>H<sub>18</sub>CdCl<sub>2</sub>N<sub>4</sub>S], monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 14.5219(11) Å, *b* = 8.5315(7) Å, *c* = 15.6182(12) Å, β = 92.063(2)°, *V* = 1933.7(3) Å<sup>3</sup>, *Z* = 4), and [Ag(**4**)](NO<sub>3</sub>) ([C<sub>19</sub>H<sub>20</sub>AgN<sub>4</sub>S](NO<sub>3</sub>), monoclinic, space group *C*2/*c*, *a* = 13.7339(3) Å, *b* = 17.2710(1) Å, *c* = 9.8866(2) Å, β = 115.399(1)°, *V* = 2118.4(1) Å<sup>3</sup>, *Z* = 4) have been determined. Ligand **3** provided the expected N<sub>2</sub>O donor set to Zn(II) forming part of a pseudo-trigonal bipyramidal coordinating environment, tentatively extrapolated to the Zn(II), Cd(II), and Hg(II) complexes of ligand **2** from <sup>1</sup>H NMR studies. The thioether-bridged ligands (**1** and **4**) displayed a strikingly different coordination mode; in none of these structures was the thioether found to be coordinated to the central metal ion, resulting in pseudotetrahedral structures for the Zn(II) and Hg(II) complexes of ligand **1**, a bis(chloro)-bridged dimeric five-coordinate complex of Cd(II) with ligand **1**, and a near-linear coordination mode for the Ag(I) complex of ligand **4**. No significant distinction in geometric parameters around the metal ions could be observed resulting from the introduction of asymmetry and a change of p*K*<sub>a</sub> within the bis(benzimidazole) ligands. Using <sup>199</sup>Hg NMR spectroscopy, it was demonstrated that the thioether of ligand **1** did not coordinate in solutions of the 1:1 HgBr<sub>2</sub> complex; negligible shifts of the signals corresponding to the aliphatic bridging protons in the <sup>1</sup>H NMR spectra of ligand **1** when coordinated to Zn(II), Cd(II), and Hg(II) also suggested a noncoordinating behavior. Exchanges occurring in mixtures of HgBr<sub>2</sub> and ligand **1** were examined using <sup>199</sup>Hg, <sup>13</sup>C, and <sup>1</sup>H NMR. It is considered that there is little or no exchange occurring in a region of excess mercury on the <sup>199</sup>Hg NMR time scale, and in a region of excess ligand **1** the 1/1 complex predominates.

### Introduction

The proteins so far discovered which contain most of the *ca.* 2 g of Zn(II) found in the human body indicate Zn(II) to be unique in its variety of roles;<sup>1–6</sup> it operates in enzyme function (as a catalyst and as a structure former),<sup>1,4</sup> in gene expression (as a structure former for the Zn(II) fingers and related motifs),<sup>3,5</sup> in glucocorticoid and hormone receptors, and in storage proteins such as thioneins.<sup>4,6</sup> The coordination of Zn(II) is usually tetrahedral including HIS, CYS, ASP, GLU, or H<sub>2</sub>O donors.<sup>1</sup> In many catalytic sites histidines are found, apparently arranged to have different basicities,<sup>7</sup> which can coordinate metal ions (perhaps differentially) and can accept or donate protons under

relevant pH regimes.<sup>8</sup> Kinetic information indicates that Zn(II) release rates are markedly affected by the different environments.<sup>2,9</sup> Although Zn(II) is borderline hard/soft, its coordination to the thioether of MET is not established in biology; however, Hg(II) substituted into the Cu site of plastocyanin is believed to interact weakly with MET.<sup>10</sup> The highly toxic metal ions Cd(II) and Hg(II) are believed to operate in the Zn(II) biological pathways, where their different coordination, kinetics, and equilibria may be considered possible causes of their toxicity.<sup>9</sup> A major challenge for coordination chemistry is to develop good working models for the role of metal ions in biological systems. Many bis- and poly-(benzimidazoles) have been synthesized to this end. In our recent work we have tried to develop new and existing ligands (e.g. **1–4**) for coordination of M(II) which may be useful in designing future biomimetic model complexes.

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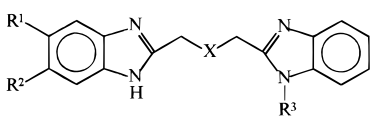
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**Table 1.** Bis(benzimidazole) Ligands 1–5


ligand	X	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
<b>1</b>	S	CH <sub>3</sub>	CH <sub>3</sub>	H
<b>1a</b>	S	H	H	H
<b>2</b>	O	CH <sub>3</sub>	CH <sub>3</sub>	H
<b>3</b>	O	H	H	CH <sub>3</sub>
<b>4</b>	S(CH <sub>2</sub> ) <sub>3</sub> S	H	H	H
<b>5</b>	S(CH <sub>2</sub> ) <sub>2</sub> S	H	H	H

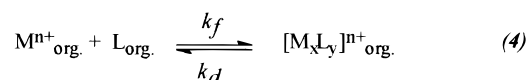
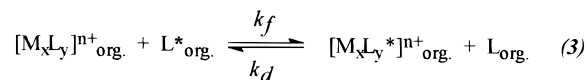
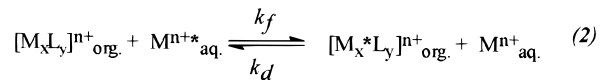
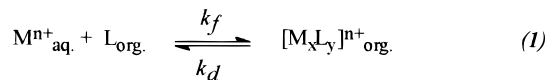
Methods we and others have used to introduce individual donor groups<sup>11</sup> such as imidazole, benzimidazole, pyrazole<sup>12</sup> (which might emulate the histidine side chain), and thioethers (emulating the methionine side chain)<sup>13</sup> are widely available (only token references are given). This study considers the coordination chemistry of the recently introduced asymmetric bis(benzimidazole) ligands **1–3**, (Table 1), each of which contains two different benzimidazole residues, a novel feature suitable to mimic different histidines in a metal binding site of a protein.<sup>11</sup> For example, the pK<sub>a</sub> of dimethylbenzimidazole (6.5) is approximately one pK unit higher than for unsubstituted benzimidazole, so that there are two benzimidazoles of different basicity in **1** and **2**. We wanted to explore features of their coordination, both structural and kinetic where feasible. We sought comparisons with Cu(II) systems examined recently<sup>11</sup> and looked for similarities and distinctions along the series Zn, Cd, and Hg where size and softness change. Within group 12, Cd is often anomalous, having a tendency to higher coordination numbers and weaker bonding. Ligand–ligand repulsions may promote tetrahedral geometry for Zn, enhanced for softer sulfide donors, whereas the larger Cd adopts six-coordination. The soft Hg is found in tetrahedral coordination with strongly coordinating softer donors, e.g. HgBr<sub>4</sub><sup>2-</sup>.

A previous study of the coordination of asymmetric bis(benzimidazole) ligands to Cu(II) showed that the two distinct benzimidazole residues coordinated with almost identical bond length, suggesting that the effect of having two different histidine residues of distinct basicity (lightly constrained) in a binding site was not likely to give structural differences but to provide pH switchable coordination in two different pH regimes.<sup>11</sup> Interaction of representative examples of these ligands with Zn(II), Cd(II), and Hg(II) has now been studied crystallographically with the aims of discovering the coordination to Zn(II), how it compares to that found earlier for Cu(II), distinctive features of coordination to Cd(II) and Hg(II) which might shed light on the way in which Cd and Hg compete with Zn, and any perturbation of geometry consequent on the asymmetry of the ligands and the different pK<sub>a</sub> values available within one ligand. Solution NMR studies were also employed for this work, since the metal ions of concern were all diamagnetic. Studies for the relatively soft monovalent Ag(I) have been made to establish if thioether is coordinated here (as expected) or if there is linear N–Ag–N coordination. The work also helps to define the soft/hard donor power of thioether with the range of metal ions considered. Crystallographic studies are presented for five of the complexes prepared.

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**Scheme 1.** Equations 1–4 Showing Possible Exchange Processes in a Region of Excess Metal (Eqs 1 and 2) and Ligand (Eqs 3 and 4)

An exploration of the exchange processes occurring in mixtures of HgBr<sub>2</sub> with the asymmetric bis(benzimidazole) ligand **1** was conducted which complemented the work previously reported by our group on similar Cd(II) systems.<sup>14</sup> Some structural information on coordination of the ligand in solution to Zn(II), Cd(II), and Hg(II) (in competition with the donor solvent DMSO) was adduced. The exchange processes were monitored using multinuclear NMR (<sup>199</sup>Hg, <sup>13</sup>C, and <sup>1</sup>H) techniques. The <sup>199</sup>Hg NMR active nucleus (*I* = 1/2, natural abundance 16.8%) was used as a probe to monitor possible exchange processes in a region of excess metal (eqs 1 and 2 of Scheme 1), whereas <sup>1</sup>H and <sup>13</sup>C were used to give information on the exchange rates occurring in a region of excess ligand (eqs 3 and 4 of Scheme 1). The sensitivity of the <sup>199</sup>Hg chemical shifts to donor atoms of the primary coordination sphere of the mercury complexes makes it a powerful tool for the elucidation of the coordinating environment in mercuric complexes and mercury substituted metalloproteins.<sup>15,16</sup> Typically, the <sup>199</sup>Hg chemical shifts span a range<sup>17</sup> of ca. 5000 ppm, the most common shifts falling into a range<sup>18</sup> from +400 to –1600 ppm (commonly referenced to dimethylmercury) dependent on the number and type of ligand atoms as well as coordination geometry. For example, <sup>199</sup>Hg shifts for Hg(II) substituted in type I copper sites of known proteins are believed to show Hg(II) fits into the Cu(II) binding site.<sup>15,16</sup> Thus, a 135 ppm difference in shift of Hg(II) in the plastocyanin binding site relative to the azurin binding site is interpreted as showing N<sub>2</sub>S (HIS, HIS, CYS) coordination in each site,<sup>15</sup> with additional deshielding in the plastocyanin site from the proximity of the MET sulfur (known in the crystal structure<sup>10</sup> of Hg(II)-substituted plastocyanin to be 3.02 Å away).

## Experimental Section

Reagents and solvents used were of commercially available reagent grade quality. **Caution!** Shock sensitivity of the perchlorate complex synthesized has not been observed, but care should be taken to prevent

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**Table 2.** Elemental Analyses (Calculated Values in Parentheses), Melting Points, and FAB Mass Spectrometry Data (Assignments in parentheses) for the Complexed Ligands 1–3

reagents	product	mp (°C)	anal. (%)			FAB-MS ( <i>m/z</i> )
			C	H	N	
1 + ZnCl <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> S·ZnCl <sub>2</sub>	310	(47.1) 47.2	(4.0) 3.7	(12.2) 12.1	421 ([Zn(1)(Cl)] <sup>+</sup> )
1 + CdCl <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> S·CdCl <sub>2</sub>	287	(42.8) 42.7	(3.6) 3.3	(11.1) 10.9	471 ([Cd(1)(Cl)] <sup>+</sup> )
1 + HgBr <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> S·HgBr <sub>2</sub> ·CH <sub>3</sub> OH	204	(31.9) 32.0	(3.1) 2.9	(7.8) 7.8	603 ([Hg(1)(Br)] <sup>+</sup> )
2 + ZnCl <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O·ZnCl <sub>2</sub>	296	(48.8) 49.1	(4.1) 3.8	(12.7) 12.4	405 ([Zn(2)(Cl)] <sup>+</sup> )
2 + CdCl <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O·CdCl <sub>2</sub>	275	(44.2) 44.1	(3.7) 3.6	(11.4) 11.3	455 ([Cd(2)(Cl)] <sup>+</sup> )
2 + HgBr <sub>2</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O·HgBr <sub>2</sub>	269	(32.4) 32.2	(2.7) 2.7	(8.4) 8.4	587 ([Hg(2)(Br)] <sup>+</sup> )
3 + Zn(ClO <sub>4</sub> ) <sub>2</sub>	C <sub>17</sub> H <sub>16</sub> N <sub>4</sub> O·Zn(ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	228	(34.5) 34.7	(3.4) 3.3	(9.5) 9.3	455 ([Zn(3)(ClO <sub>4</sub> )] <sup>+</sup> )

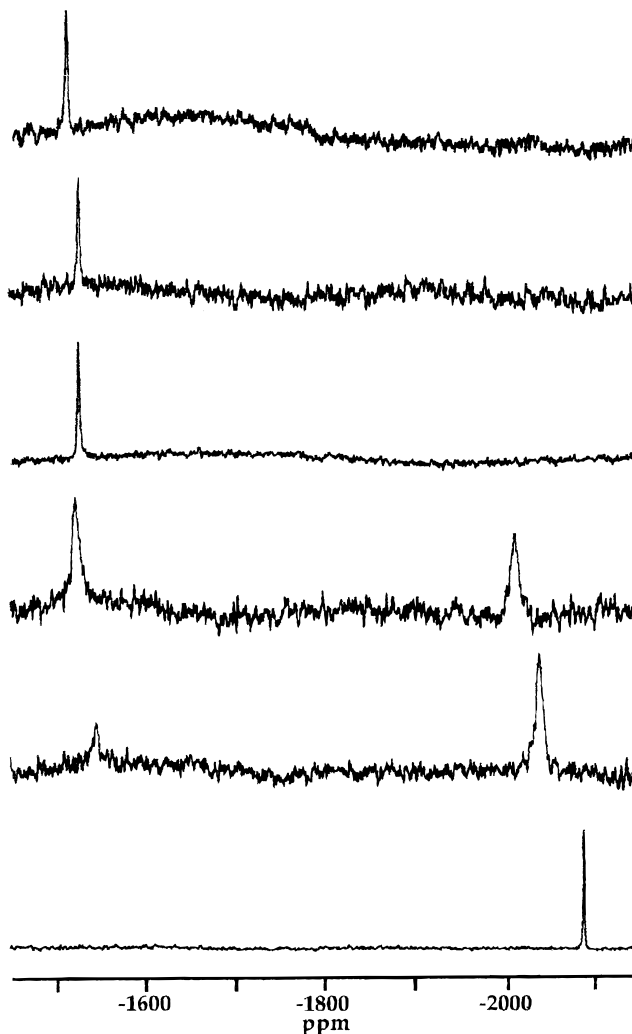
**explosion.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker WP200 (<sup>1</sup>H at 200.13 MHz, <sup>13</sup>C at 50.32 MHz) and WM300-WB spectrometers (<sup>1</sup>H at 300.132 MHz, <sup>13</sup>C at 75.457 MHz, and <sup>199</sup>Hg at 53.760 MHz). Chemical shifts ( $\delta$ ) for <sup>1</sup>H and <sup>13</sup>C spectra are reported in parts per million (ppm) relative to deuteriated solvents as internal standards, and <sup>199</sup>Hg chemical shifts ( $\delta$ ) are referenced to dimethylmercury. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer; fast atom bombardment and electron impact mass spectra were obtained on a Kratos MS80 RF instrument.

**Synthesis.** The ligands (1–4) and 1/1 ligand–metal complexes were prepared as previously described.<sup>11</sup> Analytical data for the new complexes are shown in Table 2. FAB mass spectra contained peaks corresponding to [ML(X)]<sup>+</sup> (L = 1–3, X = Cl, Br, and ClO<sub>4</sub>) for the 1/1 complexes.

**NMR Studies.** The <sup>199</sup>Hg NMR spectra recorded at 260 K (the optimum temperature for the range of systems studied) for a series of mixtures of ligand 1 with HgBr<sub>2</sub>, of composition ranging from excess ligand to excess metal salt in a 1/1 mixture of DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>, are shown in Figure 1. In each sample the mercuric concentration was maintained at 0.04 mol dm<sup>-3</sup> and the amount of ligand 1 varied. The samples typically had a liquid range down to *ca.* 230 K and permitted observations of NMR spectra at low temperatures for these solutes. Variable-temperature <sup>13</sup>C and <sup>1</sup>H NMR spectra were also recorded using the same series of samples. A <sup>199</sup>Hg shift correlation for benzimidazole N–Hg coordination in the absence of potential thioether coordination was recorded under comparable conditions. A sample containing free benzimidazole and HgBr<sub>2</sub> at a L:M composition of 2:1 was required to maintain the correct imidazole Hg–N stoichiometry since ligand 1 provides an N<sub>2</sub> donor set.

**X-ray Crystallography.** Crystals of [Zn(1)Cl<sub>2</sub>]·CH<sub>3</sub>OH, [Hg(1)Br<sub>2</sub>]·CH<sub>3</sub>OH, [Cd(1)Cl<sub>2</sub>], and [Ag(4)](NO<sub>3</sub>) suitable for X-ray diffraction were grown by slow evaporation of methanolic solutions. Crystals of the complex [Zn(3)(H<sub>2</sub>O)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> were produced by vapor diffusion of diethyl ether into a saturated solution of Zn(3)(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O in acetonitrile. Crystal data are given in Table 3, and further details of the experiment and calculations are in the Supporting Information. All measurements were made at 160 K on a Siemens SMART CCD area-detector diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were refined from the observed rotation angles for all strong reflections in the complete data set in each case, and intensities were integrated from more than a hemisphere of data recorded on 0.3° frames by  $\omega$  rotation, with unique data essentially complete to more than 50° in 2 $\theta$ . No significant intensity decay was observed. Semi-empirical absorption corrections were applied, based on symmetry-equivalent and repeated reflections.

The structures were solved variously by heavy-atom and direct methods and were refined by full-matrix least-squares on *F*<sup>2</sup> for all data. Anisotropic displacement parameters were refined for all non-H atoms, and isotropic H atoms were included with appropriate riding model constraints. Programs used were standard Siemens control (SMART) and integration (SAINT) software, SHELXTL,<sup>19</sup> and local programs. Selected bond lengths and angles are listed in Table 4. Complete tables of coordinates, geometry, and displacement parameters can be found in the Supporting Information.



**Figure 1.** <sup>199</sup>Hg NMR spectra at 260 K in (CD<sub>3</sub>)<sub>2</sub>SO/CDCl<sub>3</sub> of 0.04 mol dm<sup>-3</sup> solutions of HgBr<sub>2</sub> (lowest trace) and its mixtures with ligand 1, in ascending order of ratio of [HgBr<sub>2</sub>]/[ligand 1] of 4, 2, 1, 0.5, and 0.33. The signal for Hg(1)Br<sub>2</sub> is on the left, and that for HgBr<sub>2</sub>, on the right.

## Results and Discussion

The solid-state structures of the complexes of [Zn(1)Cl<sub>2</sub>]·CH<sub>3</sub>OH, [Hg(1)Br<sub>2</sub>]·CH<sub>3</sub>OH, [Cd(1)Cl<sub>2</sub>], and [Ag(4)](NO<sub>3</sub>) were determined *via* X-ray crystallography. Despite considerable effort, no suitable crystals were obtained of complexes of the ether ligand 2 with these four salts. However, the [Zn(3)(H<sub>2</sub>O)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> structure of an analogous ligand (3), also having ether (O) instead of thioether (S) in the linking bridge, was examined for comparison. These were the crystals found suitable for X-ray analysis after many attempts; the direct comparisons which the resultant data afford are governed by the different anions present.

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**Table 3.** Crystallographic Data

	complex				
	[Zn(3)(H <sub>2</sub> O)(MeCN)](ClO <sub>4</sub> ) <sub>2</sub>	[Zn(1)Cl <sub>2</sub> ]·CH <sub>3</sub> OH	[Hg(1)Br <sub>2</sub> ]·CH <sub>3</sub> OH	[Cd(1)Cl <sub>2</sub> ]	[Ag(4)](NO <sub>3</sub> )
chem formula	[C <sub>19</sub> H <sub>21</sub> N <sub>5</sub> O <sub>2</sub> Zn](ClO <sub>4</sub> ) <sub>2</sub>	[C <sub>18</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>4</sub> SZn]·CH <sub>4</sub> O	[C <sub>18</sub> H <sub>18</sub> Br <sub>2</sub> HgN <sub>4</sub> S]·CH <sub>4</sub> O	[C <sub>18</sub> H <sub>18</sub> CdCl <sub>2</sub> N <sub>4</sub> S]	[C <sub>19</sub> H <sub>20</sub> AgN <sub>4</sub> S <sub>2</sub> ](NO <sub>3</sub> )
fw	615.7	490.7	714.9	505.7	538.4
space group	<i>P2<sub>1</sub>/c</i>	<i>P1</i>	<i>P1</i>	<i>P2<sub>1</sub>/n</i>	<i>C2/c</i>
<i>a</i> , Å	10.3247(11)	9.0917(9)	9.1956(12)	14.5219(11)	13.7339(3)
<i>b</i> , Å	11.0320(12)	9.9186(10)	9.9775(13)	8.5315(7)	17.2710(1)
<i>c</i> , Å	20.761(2)	12.2079(12)	12.462(2)	15.6182(12)	9.8866(2)
$\alpha$ , deg		99.710(3)	99.239(3)		
$\beta$ , deg	96.465(3)	94.252(2)	97.676(3)	92.063(2)	115.399(1)
$\gamma$ , deg		95.598(3)	94.036(3)		
<i>V</i> , Å <sup>3</sup>	2349.7(4)	1075.3(2)	1113.4(3)	1933.7(3)	2118.4(1)
<i>Z</i>	4	2	2	4	4
$\rho_{\text{obsd}}$ , g cm <sup>-3</sup>	1.740	1.516	2.132	1.737	1.688
$\mu$ , cm <sup>-1</sup>	13.4	15.1	106.1	15.2	11.8
<i>R</i> <sup>a</sup>	0.0554	0.0371	0.0404	0.0311	0.0449
<i>R</i> <sub>w</sub> <sup>b</sup>	0.1407	0.0902	0.1122	0.0704	0.1268

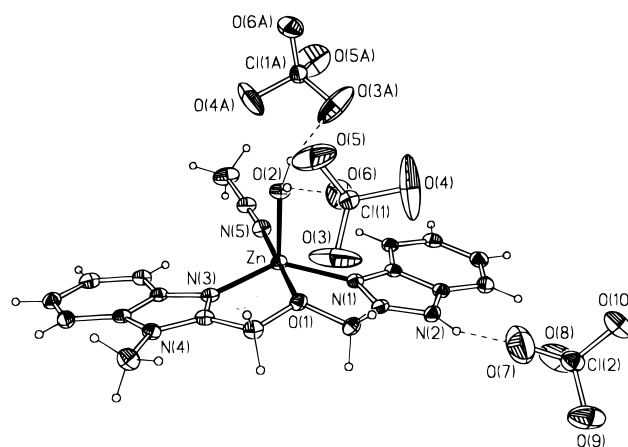
<sup>a</sup> Conventional  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  for "observed" reflections having  $F_o^2 > 2\sigma(F_o^2)$ . <sup>b</sup>  $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$  for all data.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg)

Zn Complex of <b>3</b>			
Zn–N(1)	2.002(3)	Zn–N(3)	2.005(3)
Zn–O(1)	2.278(3)	Zn–O(2)	2.044(3)
Zn–N(5)	2.059(4)		
N(1)–Zn–N(3)	138.49(14)	N(1)–Zn–O(1)	74.76(12)
N(3)–Zn–O(1)	74.92(12)	N(1)–Zn–O(2)	102.72(13)
N(3)–Zn–O(2)	103.07(13)	O(1)–Zn–O(2)	86.58(11)
N(1)–Zn–N(5)	106.39(14)	N(3)–Zn–N(5)	104.45(14)
O(1)–Zn–N(5)	178.60(13)	O(2)–Zn–N(5)	92.37(14)
Zn Complex of <b>1</b>			
Zn–N(1)	2.045(2)	Zn–N(3)	2.008(2)
Zn–Cl(1)	2.2487(7)	Zn–Cl(2)	2.2621(8)
N(1)–Zn–N(3)	107.76(9)	Cl(1)–Zn–Cl(2)	112.26(3)
N(1)–Zn–Cl(1)	109.42(6)	N(3)–Zn–Cl(1)	113.60(7)
N(1)–Zn–Cl(2)	103.41(7)	N(3)–Zn–Cl(2)	109.81(7)
Hg complex of <b>1</b>			
Hg–N(1)	2.333(5)	Hg–N(3)	2.234(5)
Hg–Br(1)	2.5357(7)	Hg–Br(2)	2.5832(7)
N(1)–Hg–N(3)	100.1(2)	Br(1)–Hg–Br(2)	113.47(2)
N(1)–Hg–Br(1)	113.59(12)	N(3)–Hg–Br(1)	117.74(12)
N(1)–Hg–Br(2)	96.91(12)	N(3)–Hg–Br(2)	112.30(12)
Cd Complex of <b>1</b> <sup>a</sup>			
Cd–N(1)	2.230(2)	Cd–N(3)	2.248(2)
Cd–Cl(1)	2.5618(8)	Cd–Cl(2)	2.4869(8)
Cd–Cl(2A)	2.8211(8)		
N(1)–Cd–N(3)	106.47(9)	N(1)–Cd–Cl(2)	121.33(6)
N(1)–Cd–Cl(1)	97.74(6)	N(3)–Cd–Cl(1)	98.87(7)
N(3)–Cd–Cl(2)	129.91(7)	Cl(1)–Cd–Cl(2)	89.32(3)
N(1)–Cd–Cl(2A)	83.41(6)	N(3)–Cd–Cl(2A)	92.38(7)
Cl(1)–Cd–Cl(2A)	167.82(2)	Cl(2)–Cd–Cl(2A)	79.84(3)
Cd–Cl(2)–Cd(A)	100.16(3)		
Ag Complex of <b>4</b> <sup>b</sup>			
Ag–N(1)	2.137(4)	Ag···S(1)	3.0047(11)
N(1)–Ag–N(1A)	172.3(2)	S(1)···Ag···S(1A)	80.01(4)
N(1)–Ag···S(1)	75.28(9)	N(1)–Ag···S(1A)	110.96(9)

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

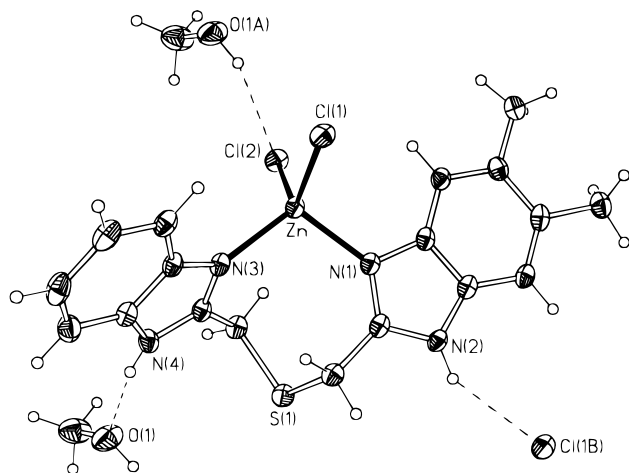
**Crystal Structure of [Zn(3)(H<sub>2</sub>O)(MeCN)](ClO<sub>4</sub>)<sub>2</sub>.** The structure is shown in Figure 2. The complex consists of a [Zn(3)(H<sub>2</sub>O)(MeCN)]<sup>2+</sup> cation and two perchlorate anions, and the crystal structure is held together by hydrogen bonding as well as by ionic interactions. The coordinated water molecule hydrogen bonds to two symmetry-related anions [O(2)···O(6) 2.898 Å, O(2)···O(3A) 3.022 Å], and the other crystallographi-

**Figure 2.** Structure of [Zn(3)(H<sub>2</sub>O)(MeCN)](ClO<sub>4</sub>)<sub>2</sub>, showing hydrogen-bonding interactions of the cation to neighboring anions.

cally independent anion is hydrogen bonded to the secondary nitrogen (NH) of the asymmetric benzimidazole ligand (**3**) [N(2)···O(7) 3.056 Å]; the opposing nitrogen, N(4), is blocked by a methyl substituent. The hydrogen bonding forms chains along the *b* axis.

The zinc atom is five-coordinate, with the expected N<sub>2</sub>O donor set from the ether oxygen atom of the linking bridge and the two benzimidazole tertiary nitrogen atoms. The remaining coordination sites are occupied by a molecule of water and a molecule of acetonitrile, the solvent from which the complex was crystallized. The structure can be best described as pseudo-trigonal bipyramidal with N(5) and O(1) axial and N(1), N(3), and O(2) in the equatorial plane. The interaxial N(5)–Zn–O(1) angle of 178.60(13)<sup>o</sup> is very nearly linear. The zinc atom deviates from the plane of N(3), N(1), and O(2) by 0.442 Å, toward the N(5) atom of the axially coordinated acetonitrile molecule. The distortion in the coordination polyhedron ( $\tau$ ) from a perfect trigonal bipyramidal geometry ( $\tau = 1$ ) toward a regular tetragonal pyramid ( $\tau = 0$ ) has been calculated according to the method of Addison and Reedijk described previously.<sup>20</sup> For this treatment, O(2) is regarded as apical, and  $\tau = 0.67$ . Ligand **2** which possesses the same linking bridge (CH<sub>2</sub>OCH<sub>2</sub>) also adopts a very similar coordination mode toward Cu(II) described previously,<sup>11</sup> which is evident in the structure of [Cu(2)(H<sub>2</sub>O)(MeCN)](ClO<sub>4</sub>)<sub>2</sub>. Both central metal atoms are

(20) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. *C. J. Chem. Soc., Dalton Trans.* **1984**, 1349.



**Figure 3.** Structure of  $[\text{Zn}(\mathbf{1})\text{Cl}_2]$ , with hydrogen-bonding interactions to solvent molecules and one neighboring Cl ligand.

surrounded by an identical donor atom set, including two solute molecules, and the Cu(II) complex is approximately square-based pyramidal ( $\tau = 0.146$ ). A reviewer has suggested that since this structure lacks a coordinating anion, it may be more likely to bind a fifth ligand such as ether.

Coordination from the ether-donating atom of the linking bridge results in two five-membered chelate rings which are similar in conformation; these Zn–O and Zn–N bond lengths are in the expected range and are similar to those found in related complexes.<sup>21</sup> The familiar “T-shape” or meridional arrangement in which the nitrogen donors of the bis(benzimidazole) ligands are trans to each other which is often found with bis(benzimidazole)s of a slightly longer bridge length<sup>14b,22</sup> ( $\text{CH}_2\text{CH}_2\text{XCH}_2\text{CH}_2$ , X = S or O) is here highly distorted by the small chelate bite angles of 74.92(12) and 74.76(12)° for N–Zn–O. The arrangement of the coordinating bis(benzimidazole) could be considered more facial and thus have implications in the modeling<sup>23</sup> of enzymes such as thermolysin, which protein typically binds Zn(II) in a facial manner (pseudotetrahedral).

**Crystal Structure of  $[\text{Zn}(\mathbf{1})\text{Cl}_2]\cdot\text{CH}_3\text{OH}$ .** The structure is shown in Figure 3. An analogous  $\text{ZnBr}_2$  structure  $\text{Zn}(\mathbf{1a})\text{Br}_2$ , in which the coordinating bis(benzimidazole) ligand ( $\mathbf{1a}$ , in Table 1) is symmetrical in nature,<sup>24</sup> is almost identical to the  $\text{ZnCl}_2$  structure presented here. The zinc atom is four-coordinate with a slightly distorted tetrahedral geometry. The bond angles at Zn range between 103.4(7) and 113.60(7)°. Here, the N–Zn–N and Cl–Zn–Cl angles are 107.76(9) and 112.26(3)°, respectively; for the bromide derivative<sup>24</sup> the analogous angles are essentially equal, 109.6(2) and 109.3(1)°.

The asymmetric bis(benzimidazole) ligand  $\mathbf{1}$  acts as a bidentate donor and provides an  $\text{N}_2$  donor set to the central zinc atom with Zn–N bond lengths of 2.045(2) and 2.008(2) Å. The Zn–N bond lengths are about equal to those observed [2.037(6) and 2.034(6) Å]<sup>24</sup> in the analogous  $\text{Zn}(\mathbf{1a})\text{Br}_2$  structure. The thioether S atom of the linking bridge of the bis(benzimidazole)

ligand  $\mathbf{1}$  is remote from the zinc (4.296 Å) and is, in fact, pointing away in an *exogenous* manner. The typical Zn–S bond length is *ca.* 2.35 Å, for  $\text{ZnS}_4$  units in proteins and bridged and nonbridged compounds.<sup>25</sup> The eight-membered chelate ring adopts a distorted irregular boat-chair conformation. The remaining coordination sites are occupied by the coordinating chloride anions with Zn–Cl bond lengths of 2.2487(7) and 2.2621(8) Å [cf. bromide derivative, 2.394(1) and 2.385(1) Å for Zn–Br]; these compare well with previously reported Zn–Cl bond distances.<sup>26</sup> The Zn–N and Zn–X bond distances and the N–Zn–N and X–Zn–X (where X = Br, Cl) bond angles decrease on going from the bromo derivative to the chloro derivative. This observation can be explained by the larger atomic radius of bromine, which in turn forces the ligand to adopt a slightly larger bite angle around the central zinc to accommodate the steric requirements. The twisted orientation of the two benzimidazole moieties which arises through the tetrahedral coordination preferred by zinc is reflected by the angle of 55.7° between the imidazole planes.

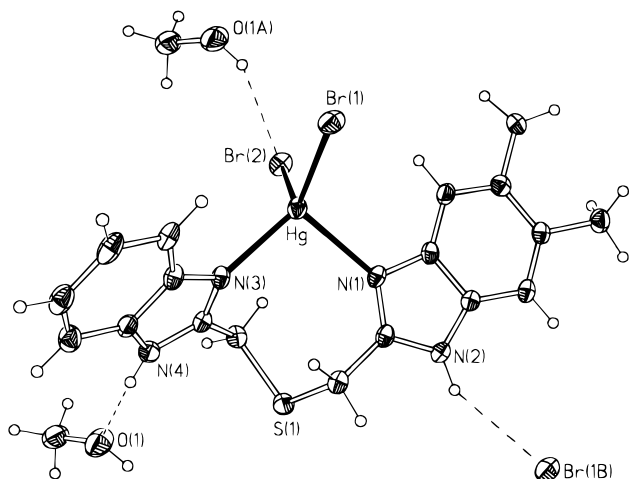
The complex crystallizes with a molecule of methanol, and the crystal structure is stabilized by hydrogen bonding. Centrosymmetric pairs of complex molecules are formed by  $\text{NH}\cdots\text{Cl}$  hydrogen bonding [ $\text{N}(2)\cdots\text{Cl}(1\text{B}) = \text{N}(2\text{B})\cdots\text{Cl}(1) = 3.205$  Å], and these loose dimers are linked into chains along the *a* axis by  $\text{OH}\cdots\text{Cl}$  and  $\text{NH}\cdots\text{O}$  hydrogen bonding involving methanol molecules [ $\text{N}(4)\cdots\text{O}(1)$  2.746 Å,  $\text{Cl}(2)\cdots\text{O}(1\text{A})$  3.157 Å].

The  $\text{N}_2\text{S}$  donor arrangement for ligands of this nature is frequently observed in coordination to Cu(II).<sup>14b,22</sup> The copper complex of ligand  $\mathbf{1}$  did not give crystals suitable for X-ray diffraction; however the coordination mode is believed to be very similar to that observed in the crystal structure of  $[\text{Cu}(\mathbf{2})\text{Br}_2]\cdot\text{CH}_3\text{OH}$  which was described previously,<sup>11</sup> and the ether-bridged ligand  $\mathbf{2}$  provides the expected  $\text{N}_2\text{O}$  donor set toward the central Cu(II). Evidence of  $\text{N}_2\text{S}$  thioether–copper coordination by ligand  $\mathbf{1}$  is taken from solid-state and solution-state UV/vis data<sup>11,14b,22</sup> and from comparing the related  $\text{CuBr}_2$  complex of a bis(benzimidazole) ligand possessing a  $\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2$  linking bridge which is known from X-ray crystallography to involve thioether–copper coordination.<sup>14b</sup> A pseudo-trigonal bipyramidal structure around the central copper is acquired with  $\text{N}_2\text{S}$  coordination from the ligand; the remaining sites are occupied by the coordinated bromide anions. Zn(II) complexes with the bis(benzimidazole) ligand  $\mathbf{1a}$  of a 2:1 L:Zn stoichiometry have also been structurally characterized in the distorted tetrahedral structure<sup>27</sup> of  $[\text{Zn}(\mathbf{1a})_2](\text{SiF}_6)$  in which each ligand retains its  $\text{N}_2$  coordinating geometry around the central zinc atom (the thioether does not coordinate).

**Crystal Structure of  $[\text{Hg}(\mathbf{1})\text{Br}_2]\cdot\text{CH}_3\text{OH}$ .** This complex (Figure 4) is isostructural with the analogous complex of  $\text{ZnCl}_2$  just described. The distortion from tetrahedral geometry is more pronounced than in the  $[\text{Zn}(\mathbf{1})\text{Cl}_2]\text{CH}_3\text{OH}$  structure, with bond angles centered on Hg ranging from 96.91(12) to 117.74(12)°. The isostructural relationship is quite surprising considering the highly thiophilic nature of mercury. The thioether atom from

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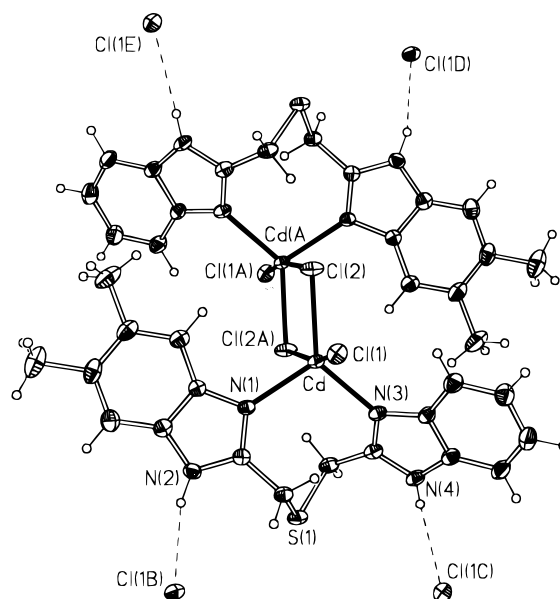
**Figure 4.** Structure of  $[\text{Hg}(\mathbf{1})\text{Br}_2]$ , with hydrogen-bonding interactions to solvent molecules and one neighboring Br ligand.

the linking bridge is best described as noncoordinating at a  $\text{Hg}\cdots\text{S}$  distance of 4.509 Å, on the basis of known bonding distances of 2.51–2.75 Å for Hg(II) coordination to thioether of thiomacrocycles,<sup>28</sup> and there are no apparent intermolecular  $\text{Hg}\cdots\text{S}$  contacts in the crystal structure which might have been expected. The mercury chloride complex of 1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane, hereinafter  $\text{Hg}(\text{BBDH})\text{Cl}_2$ , the only other known mercury bis(benzimidazole) complex,<sup>29</sup> displays a similar, distorted, four-coordinated tetrahedral geometry [bond angles ranging 101.0(2)–117.0(2)°] provided by the two tertiary nitrogens of the bis(benzimidazole) and two coordinated chloride anions; the two thioether atoms from the linking chain do not coordinate. Hg–N bond distances are similar in the two complexes [2.258(5) and 2.236(6) Å in  $\text{Hg}(\text{BBDH})\text{Cl}_2$ ] and are classed as intermediate between the two fairly well-defined Hg–N bond distances of 2.14 and 2.40 Å reported by Orpen *et al.*<sup>26</sup>

There is a slight change in the twisted orientation of the benzimidazole moieties when coordinated to mercury as opposed to zinc, seen in the angle of 54.2° between the imidazole planes, a decrease of *ca.* 1.3°, and a decrease in the N–Hg–N angle by *ca.* 7° compared with N–Zn–N. This probably reflects the greater steric hindrance imposed on the relatively small ligand while trying to satisfy the tetrahedral coordination preference of a large metal ion such as Hg(II) and results in a highly distorted tetrahedron. In comparison the ligand BBDH possesses a longer linking bridge and is more flexible in providing a closer tetrahedral coordinating environment to the large mercury atom which results in a larger N–Hg–N bite angle of 109.1(1)° for  $\text{Hg}(\text{BBDH})\text{Cl}_2$ . The X–Hg–X (X = Cl, Br) angles for the  $[\text{Zn}(\mathbf{1})\text{Cl}_2]\text{CH}_3\text{OH}$  and  $\text{Hg}(\text{BBDH})\text{Cl}_2$  complexes of 112.26(3) and 111.44°, respectively, are comparable with those in the present structure, 113.59(12)°.

The hydrogen bonding is as for the  $[\text{Zn}(\mathbf{1})\text{Cl}_2]\cdot\text{CH}_3\text{OH}$  structure, with  $\text{N}(2)\cdots\text{Br}(\mathbf{1B})$  3.399,  $\text{N}(4)\cdots\text{O}(\mathbf{1})$  2.754, and  $\text{Br}(\mathbf{2})\cdots\text{O}(\mathbf{1A})$  3.281 Å.

**Crystal Structure of  $\text{Cd}(\mathbf{1})\text{Cl}_2$ .** This complex crystallizes unsolvated. The molecular structure is shown in Figure 5. In marked contrast to the Zn(II) and Hg(II) complexes, this Cd(II) complex exists as centrosymmetric dimers with two highly asymmetric chloro bridges [Cd–Cl 2.4869(8) and 2.8211-



**Figure 5.** Structure of the dimer of  $[\text{Cd}(\mathbf{1})\text{Cl}_2]$ , with hydrogen bonding to neighboring Cl ligands.

(8) Å] and two terminal chloro ligands with intermediate Cd–Cl bond lengths [2.5618(8) Å]. A  $\text{N}_2$  donor set from the bis(benzimidazole) ligand (Cd–N distances within the expected<sup>26,30</sup> range) makes each Cd(II) five-coordinate, with a distorted trigonal bipyramidal geometry. Two Cl ligands (one terminal, one bridging) occupy the axial sites with an interaxial Cl–Cd–Cl angle of 167.82(2)°. The Cd atom is displaced 0.202 Å from the equatorial plane, toward the terminal Cl. The coordination polyhedron distortion parameter  $t = 0.63$  for this structure, N(1) being regarded as apical.<sup>20</sup> The thioether atom from the linking bridge of the bis(benzimidazole) remains noncoordinating and exogenous with a Cd–S separation of 4.498 Å, which is beyond any realistic Cd–S bond length<sup>25</sup> and essentially the same as the Hg–S separation in the preceding structure. The N–Cd–N angle is very similar to those in the preceding tetrahedral Zn and Hg complexes. The twisted orientation of the two benzimidazole moieties and the dimeric five-coordinate structure is reflected in the angle of 46.1° between the imidazole planes which is significantly less than the twist observed for the  $[\text{Zn}(\mathbf{1})\text{Cl}_2]\cdot\text{CH}_3\text{OH}$  and  $[\text{Hg}(\mathbf{1})\text{Cl}_2]\cdot\text{CH}_3\text{OH}$  structures by *ca.* 10°. Each of the N–H groups hydrogen bonds to a nonbridging chloro ligand in an adjacent complex, so that Cl(1) forms two  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds [ $\text{N}(2)\cdots\text{Cl}(\mathbf{1B})$  3.172,  $\text{N}(4)\cdots\text{Cl}(\mathbf{1C})$  3.366 Å]. These interactions link the dimeric molecules into bulky chains parallel to the *b* axis.

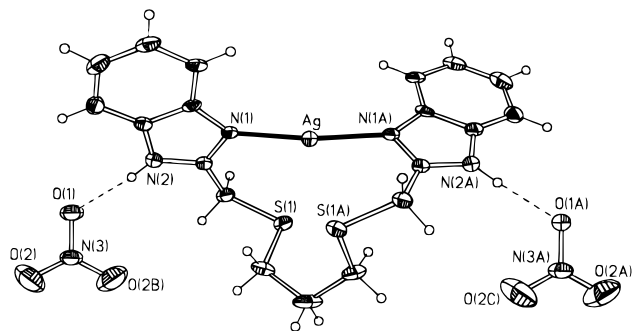
**Crystal Structure of  $[\text{Ag}(\mathbf{4})](\text{NO}_3)$ .** The structure is shown in Figure 6. It reveals a near-linear 2-fold coordination mode with the central Ag(I), on a crystallographic 2-fold rotation axis, exposed slightly toward the thioether atoms of the linking chain between the benzimidazole moieties. Recently the term hemicoordination has been suggested for  $\text{Ag}\cdots\text{S}(\text{thiophen})$  distances of ~3.2–3.3 Å.<sup>31</sup> The  $\text{Ag}\cdots\text{S}$  distance of 3.004 Å found in this structure probably represents a weak interaction forming what may be considered as a quasi-linear  $\text{N}_2\text{S}_2$  structure around the central Ag(I). In a range of N, S donor macrocycle complexes of silver, five coordination is usually favored.<sup>32</sup> The

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**Figure 6.** Structure of  $[Ag(4)](NO_3)$ , with hydrogen bonding to nitrate anions.

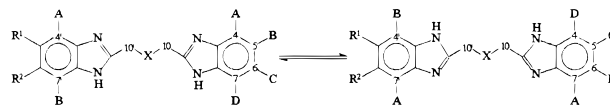
N–H groups are hydrogen bonded to nitrate anions, which also have crystallographic 2-fold rotation symmetry; just one oxygen atom of each nitrate anion acts as a bridge in N–H $\cdots$ O $\cdots$ H–N interactions [O(1) $\cdots$ N(2) 2.723 Å], giving chains of alternating cations and anions parallel to the *a* axis.

**NMR Studies.** The behavior of the ligands and complexes in solution was probed with NMR spectroscopy. A series of mixtures of  $HgBr_2$  with ligand **1** (ranging in composition from pure  $HgBr_2$  to its 1/4 mixture with ligand) was examined using  $^{199}Hg$  NMR, while  $^1H$  and  $^{13}C$  NMR were used for the comparisons of the interaction of ligand **1** with the Zn, Cd, and Hg series.

**$^{199}Hg$  NMR.** The series of spectra (Figure 1) indicated that there are only two mercuric species present in solution. In a region of excess metal ion ( $[Hg^{2+}]/[L] > 1$ ) two Hg signals were observed at *ca.*  $\delta$  –1500 and –2100 ppm (referenced to dimethylmercury). The shifts of these signals are associated with the  $Hg(1)Br_2$  and  $HgBr_2$  species, respectively, and the signals do not deviate significantly at different Hg/L compositions:  $\delta(HgBr_2)$  –2092 to –2013 ppm;  $\delta(Hg(1)Br_2)$  –1541 to –1490 ppm. The  $^{199}Hg$  shift for a 2/1 mixture of benzimidazole and  $HgBr_2$  was recorded at –1504 ppm which correlates well with the  $^{199}Hg$  chemical shift of –1490 ppm for the complex  $Hg(1)Br_2$ , indicating that the thioether-donating atom of the linking bridge probably does not coordinate. The thioether would be expected to have a considerable deshielding effect, whereas the benzimidazole nitrogen atoms are considered less deshielding. Since the complex has been structurally characterized in the solid state in this work, the NMR shift will be a useful marker for characterization of similar donor sets in solution.

As the amount of ligand was increased, the intensities of the  $HgBr_2$  and  $Hg(1)Br_2$  signals decreased and increased, respectively, the intensity of the signals being approximately proportional to the concentration of each species present in solution. At the composition of  $[M]/[L] = 1$  only one signal was observed, corresponding to the  $Hg(1)Br_2$  complex. In a region of excess ligand ( $[M]/[L] < 1$ ) only one  $^{199}Hg$  chemical shift, that of the  $Hg(1)Br_2$ , was observed. There was no evidence of 2/1  $[L]/[M]$  complex forming which suggests that the  $Hg(1)Br_2$  complex is the most thermodynamically and kinetically stable complex.

The  $^{199}Hg$  NMR signals of the  $Hg(1)Br_2$  and  $HgBr_2$  species were found to be temperature dependent and shift from –1490 to –1850 ppm and –2092 to –2431 ppm, respectively, upon increasing the temperature from 260 to 297 K. A change in the chemical shift was also accompanied by a line-broadening



**Figure 7.** Representation of the ABCD  $\leftrightarrow$  DCBA and AB  $\leftrightarrow$  BA exchanges.

effect with increasing temperature which was attributed to chemical shift anisotropy commonly associated with  $^{199}Hg$  NMR.<sup>33</sup> This phenomenon was evident in the excess metal region when the temperature was gradually increased from 260 to 297 K, and it is therefore considered that there is little or no exchange occurring in this region. The pre-exchange lifetime of a Hg nucleus in either site  $\gg 10^{-5}$  s at 260 K estimated from the shift separations of the two “potentially” exchanging sites [signals associated with  $HgBr_2$  and  $Hg(1)Br_2$  which have equal populations]. However, in the region of excess ligand there is only one single relatively sharp signal at  $\delta$  –1490 ppm in the  $^{199}Hg$  NMR, indicating only the  $Hg(1)Br_2$  complex is present, with no indication of other complexes of different  $[M]/[L]$ .

**$^1H$  and  $^{13}C$  NMR.** To avoid the problems of chemical shift anisotropy in the  $^{199}Hg$  NMR, 1/1 mixtures of ligand **1** and metal salt were examined using both  $^1H$  and  $^{13}C$  variable-temperature NMR, which methodology gave the opportunity of observing the exchange processes in a different time window. Unfortunately, the exchange processes generally remained in the relatively fast domain in the  $^{13}C$  and in  $^1H$  NMR spectra down to 238 K and it was not possible to analyze the kinetics in detail since the precise shift separations in the slow exchange region could not be determined. However, the shift differences between free ligand and its complexes gave structural information on coordination in solution.

The  $^1H$  NMR spectra of the ligands **1** and **2** exhibit three sets of aromatic resonances (two multiplets and one singlet) at ambient temperature because of the asymmetric nature of the ligands. These signals are time averaged due to the rapid movement of protons between the secondary and tertiary nitrogen atoms of the bis(benzimidazole) ligand, such that the ABCD aromatic protons of the unsubstituted half of the ligand appear as an AA'BB' system (two sets of multiplets) in the fast-exchange region arising from the process ABCD  $\leftrightarrow$  DCBA (Figure 7). Aromatic substitution of the opposite half of the ligand with methyl substituents at the 5 and 6 positions simplifies the spectrum, which is reduced to an AB system, the process AB  $\leftrightarrow$  BA (Figure 7) averaging the observed pattern to AA', an apparent singlet, in the fast-exchange region.<sup>14</sup> The fast exchange of protons between the secondary and tertiary nitrogens of the benzimidazole ligand is slowed by cooling or by the addition of a metal salt. The metal ion is considered to be coordinated to the tertiary nitrogen atom of the ligand (see Figures 2–6) and thus causes a greater shift for the aromatic protons (4, 4', 5, 6, 7, 7'), the protons closest to the tertiary nitrogen atom shifting most in the sequence 4, 4' > 7, 7' (Table 5; but note the different substitution pattern for the *N*-methyl ligand **3**). The metal halide interaction ( $M^{2+} = Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$ ) with ligands **1** and **2** gave considerable downfield shifts of the aromatic protons. In each case the downfield multiplet (protons 4 and 7) was poorly resolved, whereas the singlet observed for the protons 4' and 7' broadened considerably, indicating an averaging system not yet at the fast-exchange limit. The upfield multiplet (protons 5 and 6) usually remained well resolved beyond the fast-exchange limit.

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**Table 5.**  $^1\text{H}$  NMR Absorptions of the Free Ligands **1–3** and Their Diamagnetic Coordination Compounds<sup>a,b</sup>

	aromatics			X-CH <sub>2</sub> $\delta$ (H10/10')	R $\delta$ (CH) <sub>3</sub>
	$\delta$ (H4/7)	$\delta$ (H4'/7')	$\delta$ (H5/6)		
<b>1</b>	7.68–7.60 (m, 2H)	7.40 (s, 2H)	7.31–7.23 (m, 2H)	4.15 (s, 2H), 4.14 (s, 2H)	2.39 (s, 6H)
Zn( <b>1</b> )Cl <sub>2</sub>	$\delta$ (H4), 8.45 (br s, 1H); $\delta$ (H7), 8.20 (br s, 1H)	$\delta$ (H4'), 7.80 (br s, 1H)	$\delta$ (H7',H5,H6), 7.52–7.48 (br m, 3H)	4.15 (s, 4H)	2.45 (s, 6H)
Cd( <b>1</b> )Cl <sub>2</sub>	7.91 <sup>c</sup> (br m, 2H)	7.67 (s, 2H)	7.44–7.40 (m, 2H)	4.14 (s, 4H)	2.42 (s, 6H)
Hg( <b>1</b> )Br <sub>2</sub>	8.01 <sup>c</sup> (br m, 2H)	7.77 (br s, 2H)	7.48–7.44 (m, 2H)	4.14 (s, 4H)	2.45 (s, 6H)
<b>2</b>	7.70–7.65 (m, 2H)	7.46 (s, 2H)	7.33–7.28 (m, 2H)	4.98 (s, 2H) 4.97 (s, 2H)	2.42 (s, 6H)
Zn( <b>2</b> )Cl <sub>2</sub>	8.09 <sup>c</sup> (br m, 2H)	7.85 (br s, 2H)	7.47 <sup>e</sup> (br m, 2H)	5.06 (s, 4H)	2.45 (s, 6H)
Cd( <b>2</b> )Cl <sub>2</sub>	7.93 <sup>c</sup> (br m, 2H)	7.68 (s, 2H)	7.42–7.40 (m, 2H)	5.21 (s, 2H) 5.19 (s, 2H)	2.44 (s, 6H)
Hg( <b>2</b> )Br <sub>2</sub>	8.02 (br m, 2H)	7.76 (s, 2H)	7.48–7.44 (m, 2H)	5.10 (s, 2H) 5.08 (s, 2H)	2.44 (s, 6H)
<b>3</b>	7.77–7.62 <sup>c</sup> (m, 4H)		7.43–7.24 <sup>d</sup> (m, 4H)	5.02 (s, 2H) 4.92 (s, 2H)	
Zn( <b>3</b> )(ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	$\delta$ (H4/H7), 7.66 (br s, 1H)	$\delta$ (H7'), 7.90–7.86 (m, 1H)	$\delta$ (H5,H5',H6,H6',H4') 7.53–7.38 (br m, 5H)	5.51 (s, 2H) 5.46 (s, 2H)	2.17 (s, 3H)

<sup>a</sup> Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to DMSO-*d*<sub>6</sub> as an internal standard. The abbreviations b, m, s, and t indicate broad, multiplet, singlet, and triplet resonances, respectively. Relative intensities are also shown in parentheses. <sup>b</sup>  $\delta$ (NH): 1, 6.48 (br, s); 2, 5.93. The NH resonances are not detected for the 1:1 complexes, probably due to fast exchange with small amounts of H<sub>2</sub>O from the deuterated solvent. For proton nomenclature, see Figure 7. <sup>c</sup> H4/H7 + H 4'/7'. <sup>d</sup> H5/H6, H5'/H6'. <sup>e</sup>  $\delta$  quoted as the midpoint of the broad multiplet due to the presence of exchange.

The downfield shift of the signals on complexation and the progress of the ABCD  $\leftrightarrow$  DCBA exchange in the  $^1\text{H}$  NMR spectra at room temperature depended on the nature of the metal salt added for ligands **1** and **2**. The aliphatic bridging protons behaved differently for the ether and the thioether ligands; these were shifted in the order Cd > Hg > Zn for ligand **2** (ether bridge), but for ligand **1** (thioether bridge), the change in aliphatic shift upon coordination was negligible. This is consistent with the information from the crystal structures that thioether sulfur is not coordinated, so that little effect on the chemical shifts would be expected; in contrast, the shift for the ether ligands is detectable (ligand **2**) or pronounced (ligand **3** with the perchlorate salt of Zn).

The greater shift of bridging protons (ligand **2**) in the presence of Cd may be related to the greater tendency of Cd(II) for octahedral coordination relative to Zn(II) and Hg(II). The aromatic protons **3** (Table 5) were shifted in the order Zn > Hg > Cd. Earlier work has shown that ligand exchange in complexes of bis(benzimidazole) ligands with metal ions such as Cd(II) and Zn(II) is dependent upon the rate of separation of the L from ML<sub>x</sub> (*x* denotes the varying L/M stoichiometries that have been observed) complex. In this work, the  $^1\text{H}$  NMR spectra for the 1/1 M/L mixtures dissolved in DMSO-*d*<sub>6</sub> exhibited a broadening of peaks, especially the aromatic region, which reflects a decrease in the exchange rate of the processes ABCD  $\leftrightarrow$  DCBA and AB  $\leftrightarrow$  BA. The –NH and H<sub>2</sub>O signals could be seen separately in the spectra of the Zn mixture, but in the Cd and Hg spectra these were averaged, indicating a faster exchange process. The slowest exchange, that for Zn, should denote the most kinetically stable complex. It is, however, believed that the ML<sub>2</sub> complex is the main component of the Zn mixture, while the ML complex is the only one noted for the Hg mixture, so that a direct rate comparison is not feasible. The series of mixtures having [HgBr<sub>2</sub>]/[**1**] ratios of 1, 2, 3, and 4 in DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub> showed progressively slower exchange along the series: Indeed at 230 K in the 1/4 mixture, prototropy was completely slowed on the  $^1\text{H}$  NMR time scale. Since there was only one observable complex in these mixtures (as shown in the  $^{199}\text{Hg}$  NMR studies), this slowing of the exchange is qualitative verification of the hypothesis that exchange is dependent on a rate-determining separation of L from the ML complex (dissociative or solvent-assisted) prior to the prototropic exchange.

**Silver Complex.** Silver(I) ions also have an affinity for thioether and for aromatic nitrogen such as the tertiary nitrogen of

benzimidazoles, imidazoles, and pyrazoles.<sup>34</sup> There has been no published structure for a silver bis(benzimidazole) complex. In this work we have obtained a crystal structure of the silver complex of ligand **4** in which the two types of donor (thioether and aromatic nitrogen) are present and the competing tendency for each to coordinate to silver can be gauged. The Ag(I) complex of ligand **4** was isolated and characterized by Rushton,<sup>34</sup> who postulated that the thioethers of the bridge would coordinate to silver. Crystal structures for this ligand (**4**) complexed to Cu(I) (with perchlorate<sup>35</sup> or hexafluorophosphate<sup>36</sup> anions) were established some years ago in which one set of authors<sup>35</sup> argued that the thioether could not physically get closer to Cu(I) than the observed 2.9 Å separation although the second set of authors suggested that conceivably the structure is pseudotetrahedral.<sup>36</sup> The structure of the [Cu(**4**)ClO<sub>4</sub>] in each of these studies<sup>35,36</sup> is closely similar to that of the present [Ag(**4**)NO<sub>3</sub>] with the same space group and very similar unit cell; hydrogen-bonding of the perchlorate to the –NH is also similar to that which we describe here, although the relevant perchlorate oxygen is not in a special position.

In thiamacrocyclic complexes, Ag(I) bonds to thioether with bond lengths quoted averaging Ag···S 2.5–2.7 Å, while separations up to 3.995 Å have been quoted as proof for weak interactions.<sup>37</sup> A search of the Cambridge Data Base<sup>38</sup> for Ag coordinated to aliphatic sulfur produced 241 observations with distances between 2.399 and 3.995 Å with a mean of 2.658 and median 2.611 Å. All the distances beyond 3.1 Å noted were taken from structures of (pentathio-cyclopentadecane)silver complexes.<sup>39</sup> Tertiary nitrogens are found in the linear coordination of Ag(I) when the Ag–N values are generally very short, *ca.* 2.1 Å, but seldom perfectly linear—distortion toward some additional donor atom is common.<sup>40</sup> Where tetrahedral

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coordination of silver is found, the Ag–N distance is much greater, 2.264–2.455 Å in a recent pyrazolylborate chelate.<sup>41</sup> These factors led to our description of the silver chelate geometry of [Ag<sup>I</sup>(**4**)]NO<sub>3</sub> as quasi-linear, with Ag–N 2.137(4) Å, close to the “linear” value, and Ag⋯S(1) at 3.0047(11) Å, a weak perturbing interaction.

### Conclusions

Structural comparisons may be made between coordination for Cu(II) versus Zn(II), for Zn(II) versus Cd(II) and Hg(II), and for Hg(II) versus Ag(I). Structural effects of the different benzimidazole units in the asymmetric bis(benzimidazole) ligands may be considered, as well as the coordination or not of thioether versus ether links in the chain. The outcome of the structural studies is that thioether does not coordinate to Zn, Cd, or Hg in the crystalline complexes of **1**, nor by inference in solution in dimethyl sulfoxide, whereas the ether bridge of **3** was found to coordinate in the crystalline five-coordinate Zn complex, with a different donor set; perturbations of the bridging methylene proton signals in the NMR spectra also pointed to ether coordination in all of the Zn, Cd, and Hg complexes of **2** and the five-coordinate Zn complex of **3**. No structural effect (e.g. bond lengthening) could be observed for the asymmetric ligands **1–3** coordinated to Zn(II), Cd(II), and Hg(II). As with the previously studied Cu(II) complexes, much greater structural distortions arose from H-bonding than from the differentiated benzimidazoles. Zn(II) gave a five-coordinate TBP structure with **3**, compared with the SBP adopted by Cu(II) using an exact

match of donors. The ether bridge coordinated, there being no competing coordinating anion present. Where coordinating halides were present, N<sub>2</sub>X<sub>2</sub> and N<sub>2</sub>X<sub>2</sub>X' donor sets were found in the crystals. The Zn(II) and Hg(II) structures were tetrahedral, but the Cd(II) anomalously used one halide as bridge to give a halide-bridged five-coordinate dimer. The conformations adopted by ligand **1** are very similar in the complexes shown in Figures 3–5, with thioether over 4.2 Å distant from the metal ion in each case. Despite Hg(II) and Ag(I) being soft metal atoms, with a perceived high affinity for thioether where it is sole donor, only the silver ion showed slight affinity for thioether sulfur in these complexes, the competition between available donors resulting in N–Ag–N linear, or the N<sub>2</sub>–Hg–Br<sub>2</sub> tetrahedral, coordination virtually excluding thioether coordination, unlike the M(II) binding site of plastocyanin, where Hg(II) does bind to thioether. Neighboring ether oxygen was attractive to Hg(II) in the NMR study. A <sup>199</sup>Hg solution shift was characterized for the N<sub>2</sub>Br<sub>2</sub> donor set found in the crystal. Dynamic NMR studies for the HgBr<sub>2</sub> complex of **1** were consistent with the hypothesis that **1** must separate from Hg(II) before ligand exchange can occur in the system. It did not prove possible to examine kinetic distinctions between the differentiated benzimidazole units of **1–3** in their interaction with M(II). These ligands should prove useful in future biomimetic studies.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the five complexes are available on the Internet only. Access information is given on any current masthead page.

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