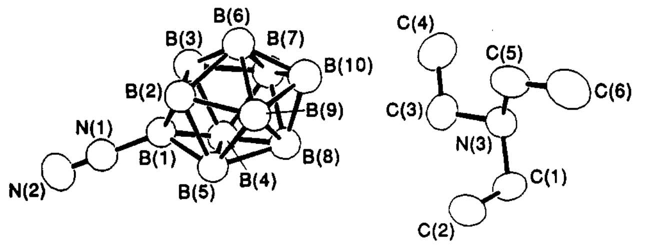

Figure 2. Structure of [Et$_3$NH]·**1** with thermal ellipsoids for non-hydrogen atoms drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

to these hydrogens is nearly tetrahedral, and the H-Cu-H angles are 108 ± 12°. Since the positions of these hydrogen atoms were not allowed to vary, this range of values is probably not significant. The Cu-H distances range from 1.96 to 2.01 Å. The planes defined by Cu-B(6)-B(10) and Cu-B(6')-B(10') are nearly perpendicular to each other (86°). Copper is at the center of a distorted tetrahedron formed by B(6), B(10), B(6'), and B(10'). The Cu-B(apical) distances are 2.168 (8) and 2.169 (9) Å and the Cu-B(equatorial) distances are 2.184 (9) and 2.186 (8) Å. In a carborane complex containing a single Cu-H-B bridge[7,8] the Cu-B distance is 2.120 (8) Å. In $Cu_2B_{10}H_{10}$ the hydrogen atoms were not located[5] and the Cu-B distances range from 2.14 to 2.33 Å.

A single-crystal X-ray diffraction study of the free ligand **1** reveals that the N-N distance is somewhat longer, the B-N distance is shorter, and the N(1)-B(1)···B(10) is more nearly linear than the corresponding features in [Et$_3$NH]·**2**. Figure 2 illustrates the molecular structure of [Et$_3$NH]·**1**. Selected interatomic distances and angles for the complex are shown in Table IV. For the free ligand the N-N and the B-N distances are 1.097 (6) and 1.489 (6) Å, respectively. In the complex, the two N-N distances are 1.073 (10) and 1.082 (10) Å and the two B-N distances are 1.509 (11) and 1.506 (11) Å. The shortening of the N-N and the lengthening of the B-N distances in the complex relative to the free ligand can be accounted for in terms of decreased back-bonding, since the copper center in anion **2** serves to withdraw electron density from the apical vertex that bears the dinitrogen ligand. The N(2)-N(1)-B(1)···B(10) angles for [Et$_3$NH]·**2** are 177.3 (5) and 176.9 (5)°, and for [Et$_3$NH]·**1** the angle is 179.4°. Observed B-B distances fall within the expected ranges; namely, distances from apical boron atoms B(1), B(1'), B(10), and B(10') range from 1.653 (12) to 1.732 (12) Å for anion **2** and 1.661 (7) to 1.698 (7) Å for anion **1**. In each case, the shorter distances involve the boron bound to nitrogen. For anion **2**, other B-B distances range from 1.778 (12) to 1.910 (12) Å, and for anion **1**, they range from 1.794 (7) to 1.870 (7) Å. The interatomic distances and angles for [Et$_3$NH]·**1**, shown in Table IV, do not deviate substantially from those observed for the bis(diazonium) species[9,10] 1,10-$B_{10}H_8(N_2)_2$, which suggests that the BH-bridge-bonded copper center is a superior electron-withdrawing appendage when compared with a η^1-dinitrogen substituent.

The ^{11}B NMR spectrum of [Et$_3$NH]·**2** proves that the complex is fluxional in solution, giving equivalence to each boron atom of the two sets of equatorial boron present in each ligand. The spectrum therefore consists of four resonances in the ratio of 1:4:4:1 corresponding to the axial, equatorial, equatorial, and axial boron atoms, respectively. A reasonable explanation for these observations is the migration of the copper center around the longitudinal B(1)···B(10) axis of each ligand, which is sufficiently rapid at room temperature to give time-averaged NMR resonances.

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Registry No. [Et$_3$NH]·**1**, 136460-25-8; [Et$_3$NH]·**2**, 136460-27-0; $[(Et_3NH)_2][B_{10}H_{10}]$, 55371-37-4; 2,4,6-tribromobenzenediazonium tetrafluoroborate, 4639-13-8.

Supplementary Material Available: Tables of crystallographic data collection details, atom coordinates, bond distances and angles, and anisotropic thermal parameters (11 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Effect of N-H···S Hydrogen Bonding in $[(C_6H_{11})_2NH_2]_2[Zn_2(SC_6H_5)_6]$: A Model for Metallothionein

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Introduction

Metallothionein (MT) is a Zn- and Cd-containing protein which has been implicated in a variety of biological functions ranging from protection from heavy-metal toxicity to the regulation of cellular metabolism, control of differentiation, and free-radical scavenging.[1] Several years ago it was noted in the primary structure of the protein that six of a total of seven lysines were located adjacent to at least one of the twenty cysteines of MT. On this basis it was speculated that lysine and cysteine side chains were linked by N-H···S hydrogen bonds which served to disperse the charges on the two metal clusters of the protein, $M_4(Cys)_{11}{}^{3-}$ and $M_3(Cys)_9{}^{3-}$ (M = Cd, Zn).[2] Recent X-ray crystallographic data show however that while N-H···S hydrogen bonding is extensive in MT, it occurs predominantly between the N-H groups of the amide backbone and the S atoms of cysteine. Two lysine side chain ammonium groups were noted to also participate in the N-H···S interactions.[3]

In recent work we have shown that N-H···S hydrogen bonds with *either* amide or ammonium N-H donors have quite similar effects on the metal-ligand bonds in monomeric $[Co(SC_6H_5)_4]^{2-}$ complexes.[4] The work reported here is a study of N-H···S interactions in the dimeric Zn thiolate complex $[(C_6H_{11})_2NH_2]_2[Zn_2(SC_6H_5)_6]$ (**1**) and related complexes which serve as models of the polynuclear metal thiolate sites of MT. We find that N-H···S hydrogen bonding in **1** results in a stabilization of the metal-bridging-ligand framework and may have an analogous effect in MT.

Experimental Section

All operations were performed under a nitrogen atmosphere in a glovebox or by employing Schlenk line techniques. All solvents were distilled before use, except for CH_3OD, which was used as received.

Dicyclohexylammonium chloride was prepared by bubbling hydrogen chloride gas into dicyclohexylamine dissolved in ether. The product formed as a white powder and was isolated by solvent evaporation.

Synthesis of $[(C_6H_{11})_2NH_2]_2[Zn_2(SC_6H_5)_6]$ (1). Sodium benzenethiolate (2.07 g, 15.6 mmol) was prepared by the reaction of sodium methoxide with benzenethiol in methanol. The resulting solution was added to a methanol solution of $ZnCl_2$ (0.71 g, 5.22 mmol) to form $Na_2[Zn_2(SC_6H_5)_6]$. The reaction mixture was stirred for 1 h, after which the solvent was removed by evaporation under vacuum, leaving a white powder. Acetonitrile (80 mL) was added, followed by dicyclohexyl-

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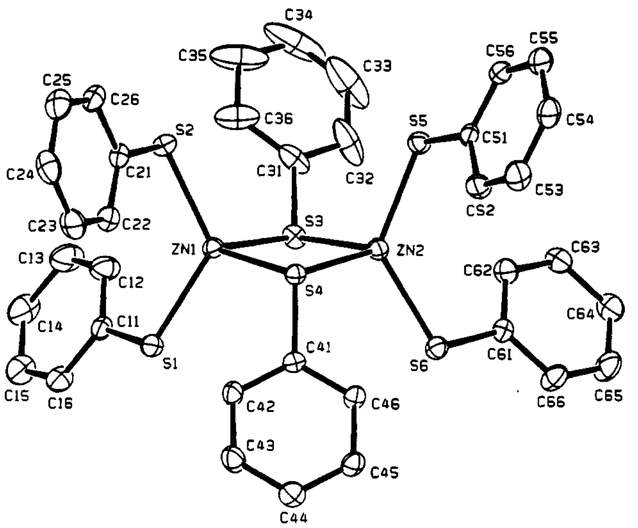

Figure 1. ORTEP diagram of the $[Zn_2(SC_6H_5)_6]^{2-}$ anion in **1** showing the atom-labeling scheme and 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Crystallographic data: space group $P2_1/c$ with $a = 19.627$ (8) Å, $b = 15.055$ (8) Å, $c = 21.163$ (6) Å, $\beta = 108.80$ (3)°, $V = 5920$ (8) Å^3, $Z = 4$, $R = 0.057$, and $R_w = 0.079$. Data were collected at −70 °C on a Rigaku AFC-6S diffractometer by using Mo Kα radiation.

ammonium chloride (1.42 g, 6.52 mmol), and the reaction mixture was stirred overnight. The resulting solution was filtered to remove sodium chloride and the filtrate concentrated to a volume of approximately 5 mL, resulting in a viscous liquid. After the addition of ether (50 mL) at 0 °C, compound **1** separated as a white solid, which was collected by filtration, washed with ether, and vacuum-dried (yield 2.1 g, 70%). Recrystallization was carried out by dissolution of **1** in a minimum of CH_3CN at 40 °C, followed by filtration and slow cooling to 0 °C. Crystals suitable for X-ray crystallographic characterization were obtained by the diffusion of ether vapor into a saturated CH_3CN solution of **1**. Elemental analysis was carried out by Galbraith Laboratories. Anal. Calcd for $C_{60}H_{78}N_2S_6Zn_2$: C, 62.64; H, 6.83; N, 2.44; S, 16.72; Zn, 11.37. Found: C, 62.50; H, 6.88; N, 2.42; S, 16.26; Zn, 11.01. ^1H NMR data obtained in CH_3CN-d_3 at room temperature (GE QE-300) revealed resonances at 6.88, 7.01, and 7.74 ppm, in agreement with previously reported spectra.[5]

Synthesis of $[(C_6H_{11})_2ND_2]_2[Zn_2(SC_6H_5)_6]$. Crystals of **1** (0.1 g) were dissolved in a mixture of CH_3OD (1 mL) and CH_3CN (5 mL). After 15 min of stirring, the solvents were removed by evaporation under vacuum, and the process repeated.

Far-IR data were acquired on a Nicolet 20F FTIR spectrometer. Samples were prepared as mineral oil mulls held between polyethylene windows in a demountable cell.

Results and Discussion

Crystal Structure. $[(C_6H_{11})_2NH_2]_2[Zn_2(SC_6H_5)_6]$ (**1**) crystallizes in the space group $P2_1/c$. The asymmetric unit consists of cations and dimeric anions in a 2:1 ratio. The structure of the dicyclohexylammonium cation is unexceptional. The anionic complex (Figure 1) is a dimer of Zn(II) ions with two bridging and four terminal benzenethiolate ligands which provide approximate tetrahedral coordination of the metal. It belongs to the C_{2h} point group. The two dicyclohexylammonium cations sit above and below the plane of the anionic complex (Figure 2). The nitrogen atom of each cation symmetrically bridges the sulfur atoms of the two neighboring terminal ligands of the $[Zn_2(SC_6H_5)_6]^{2-}$ anion employing its protons to form N–H⋯S hydrogen bonds to the ligands. The effects of hydrogen bonding on the structure of the anionic complex in **1** are readily observed. The average Zn–S_t (t = terminal) and Zn–S_b (b = bridging) bond lengths are 2.292 (2) and 2.412 (2) Å, respectively. By comparison, the structurally similar non-hydrogen-bonding complex $[(C_6H_5)_4P]_2[Zn_2(SC_6H_5)_6]$[5] (**2**) has average Zn–S_t and Zn–S_b bond lengths of 2.298 (1) and 2.428 (1) Å, respectively. Only the *bridging* metal–ligand bond lengths are significantly different for complexes **1** and **2**. In both complexes the phenyl rings of the bridging ligands assume an anti conformation. The ethanethiolate complex $[(C_2H_5)_4N]_2[Zn_2(SC_2H_5)_6]$[8] (**3**) has bond distances and bridging-ligand geometry similar to those of **1** and **2**. The average S_t–Zn–S_t angles in **1**–**3** are 126.59 (6), 111.2 (1), and 113.9 (1)°, respectively. The large bond angle of **1** is attributable to the hydrogen-bonding interactions between the ammonium cations and the sulfur atoms of the terminal ligands. The average N⋯S_t distance of 3.399 (5) Å is in the middle of the range of distances, 3.3–3.5 Å, typical of N–H⋯S hydrogen bonds,[9] observed earlier in the monomeric complex $[(C_6H_{11})_2NH_2]_2[Co(SC_6H_5)_4]$.[4] It appears that the cations, by virtue of their flanking positions on opposite sides of the anionic complex (Figure 2), act in concert through their hydrogen bonds to pry open the S_t–Zn–S_t angle. The terminal phenyl rings are turned away from the center of inversion of the Zn dimer, oriented in such a way as to make the sulfur sp^3-hybridized valence orbitals available for hydrogen bonding to the bridging counterions. The terminal phenyl groups approach the plane of the Zn_2S_2 ring more closely than do those of the non-hydrogen-bonding complex **2**. In the non-hydrogen-bonding Zn thiolate dimers, two of the terminal phenyl rings of **2** and ethane groups of **3** are turned toward the center of inversion, resulting in approximate C_i symmetry for the two anionic complexes. In this conformation, the lone pairs for two of the ligands related by an approximate center of inversion would be unable to participate in a hydrogen-bonding bridge.

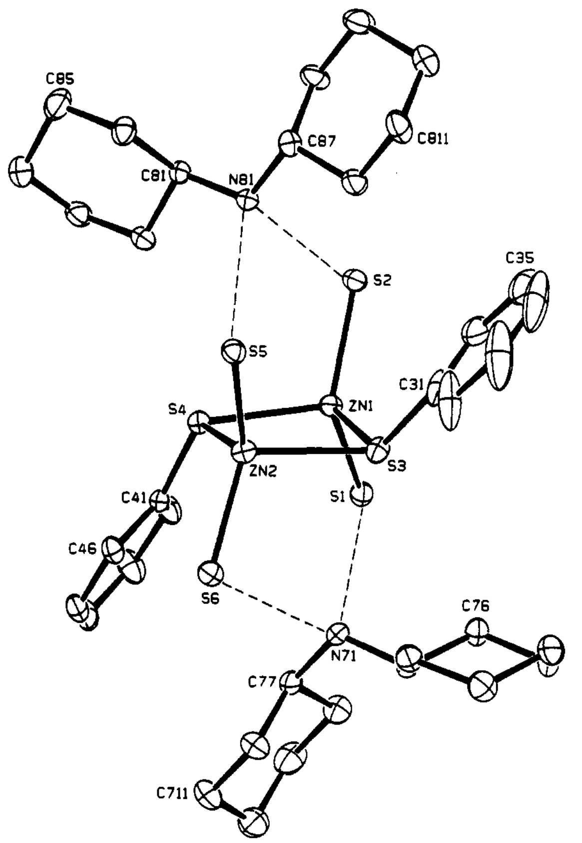

Figure 2. ORTEP diagram of **1** showing the nature of the cation–anion hydrogen-bonding interactions, together with the atom-labeling scheme and 30% probability thermal ellipsoids. Phenyl rings of the terminal ligands and all hydrogen atoms are omitted for clarity.

In the bridging framework of **1**, structural perturbation due to hydrogen bonding is evident in the size of the average Zn–S_b–Zn

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Table I. Bond lengths (Å) and angles (deg) for $[(C_6H_{11})_2NH_2]_2[Zn_2(SC_6H_5)_6]$ (**1**), $[(C_6H_5)_4P]_2[Zn_2(SC_6H_5)_6]$ (**2**), and $[(C_2H_5)_4N]_2[Zn_2(SC_2H_5)_6]$ (**3**)

atoms	**1**[a]	**2**[b–d]	**3**[c–e]
Zn···Zn	3.220 (1)	3.421 (1)	3.179 (1)
Zn(1)–S_t(1)	2.298 (2)	2.293 (1)	2.296 (1)
Zn(1)–S_t(2)	2.299 (2)	2.302 (1)	2.304 (1)
Zn(2)–S_t(5)	2.280 (2)		
Zn(2)–S_t(6)	2.292 (2)		
Zn(1)–S_b(4)	2.411 (2)	2.424 (1)	2.394 (1)
Zn(2)–S_b(3)	2.452 (2)	2.431 (1)	2.456 (1)
Zn(1)–S_b(3)	2.399 (2)		
Zn(2)–S_b(4)	2.386 (2)		
S_b(3)–Zn(1)–S_b(4)	96.22 (5)	90.7 (1)	98.1 (1)
S_b(3)–Zn(2)–S_b(4)	95.48 (5)		
S_t(1)–Zn(1)–S_t(2)	124.51 (6)		
S_t(5)–Zn(2)–S_t(6)	128.66 (6)	111.2 (1)	113.9 (1)
Zn(1)–S_b(3)–Zn(2)	83.16 (5)		
Zn(1)–S_b(4)–Zn(2)	84.33 (5)	89.3 (1)	81.9 (1)

[a] This work. [b] Reference 5. [c] This molecule has a center of inversion. [d] Atom numbering for this complex has been reassigned in this table. [e] Reference 8.

angle, 83.75 (5)°. An ideal edge-shared tetrahedral dimer possesses bridging angles of 70.5°.[10] Departures from this value are common for the hexakis(thiolato)dizincates[5,8] and hexachlorodizincates,[11–17] which feature Zn–L–Zn angles in the vicinity of 87°. In **2**, the Zn–S_b–Zn angle is 89.3 (1)° (Table I).[5] The larger angle in **2** correlates with a longer Zn–Zn distance, 3.421 (1) Å, as compared with that of **1**, 3.220 (1) Å (Table I). Hydrogen bonding to the terminal sulfur atoms is accompanied by a corresponding reduction in the Zn–S_b distance. This may be due to the removal of electron density on the metal through the hydrogen-bonded terminal sulfur ligands.[18] The ethanethiolate Zn dimer[8] is unusual with its small Zn–S_b–Zn angle and Zn···Zn separation relative to those of **1** and **2**. The large bridging angle in **1** gives rise to an average S_b–Zn–S_b angle of 95.85 (5)°, well below the ideal tetrahedral value. The reduced average Zn–S_b bond distance is indicative of a stabilizing influence of hydrogen bonding.[4]

A combination of reduced steric interactions and the availability of two lone electron pairs probably favors hydrogen bonding to the terminal sulfur ligands. Similar results are reported for the crystal structure of rat liver MT, where N–H···S hydrogen bonds with distances less than 3.5 Å occur only to cysteine residues which occupy terminal positions in the metal–cysteine binding arrangement of the protein.[3]

Far-IR Metal–Ligand Frequencies. Assuming local D_{2h} symmetry for the Zn_2S_6 framework of **1**, eight IR-active metal–ligand modes are expected, five of which correspond to terminal metal–ligand vibrations, which would be sensitive to hydrogen bonding. In keeping with assignments suggested for monomeric anionic complexes $[M(SC_6H_5)_4]^{2-}$, bands above 280 cm^{-1} are assigned to counterion and ligand internal vibrational modes.[4] Bands observed at 246, 232, 196, and 178 cm^{-1} in the IR spectrum of **1** can therefore reasonably be ascribed to metal–ligand modes. The two highest bands are assigned to terminal metal–ligand modes and the two lowest to bridging metal–ligand modes. These assignments are based on a comparison with the spectrum of the complex Fe_2Cl_6,[19] which has D_{2h} symmetry.[20] For this simple structure, the four highest far-IR peaks, at 468, 406, 328, and 280 cm^{-1}, are assigned to the ν_8 (t), ν_{16} (t), ν_{13} (b), and ν_{17} (b) stretching vibrations, respectively[19] (t = terminal modes; b = bridging modes). In **1** the bands corresponding to ν_8 and ν_{16} are expected to shift upon deuteration. However, the spectrum of $[(C_6H_{11})_2ND_2]_2[Zn_2(SC_6H_5)_6]$, recorded at 4-cm^{-1} resolution, reveals frequency shifts no greater than ±1 cm^{-1}, with bands now observed at 246, 233, 195, and 179 cm^{-1}. Only one of the three frequency shifts occurs in a band assignable to a terminal metal–ligand mode which should be affected by H/D exchange to an extent greater than the bridging metal–ligand modes. We therefore do not consider the frequency shifts to arise from *local* effects of H/D exchange on metal–ligand bond strengths or normal modes. They likely result from overall changes in anion–cation distances and effects on crystal packing.

Conclusion. The shortened bond lengths of the Zn–S_b bonds suggest that the bridging framework of **1** is stabilized by hydrogen bonding. Similar N–H···S hydrogen bonding occurs in MT, albeit with amide N–H as the predominant hydrogen-bond donor.[3] The results obtained herein suggest that the hydrogen bonds in the protein may exert a similar stabilizing influence on the metal centers of the protein.

Supplementary Material Available: General structure report for compound **1** including a textual presentation of the details of the structure determination, listings of experimental details, positional and thermal parameters, inter- and intramolecular bond distances and bond angles involving non-hydrogen atoms, and intermolecular distances involving hydrogen atoms, and an ORTEP diagram of the structure, a table of selected far-IR bands for **1** and its deuterated ammonium derivative, and a figure showing the vibrational spectrum of **1** (60 pages); a listing of final observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Stereoselectivity in the Oxidation of Horse Cytochrome *c* by $[Co(ox)_3]^{3-}$

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Over the past decade, significant advances have been made in the detection and interpretation of chiral induction in outer-sphere electron-transfer reactions involving metal ion complexes.[3–5] Electron-transfer metalloproteins are chiral reagents that might be expected to show considerable enantioselectivity, but few investigations of chiral induction in their reactions with metal ion complexes have been reported. Early studies failed to detect rate differences for Δ- and Λ-$[Co(en)_3]^{3+}$ with parsley ferredoxin[6] and for Δ- and Λ-$[Co(sep)]^{2+}$ with horse cytochrome *c*.[7] However,

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