to the value of 275 cm^{-1} found from the spectra of $Re_2Cl_4(PPr_3)_4{}^+$.[17] A Re–Re stretching frequency of 248 cm^{-1} was observed in the $\delta \rightarrow \delta^*$ excited state of $[Re_2Cl_8]^{2-}$.[20] This finding implies a stronger excited state for $[Re_2Cl_8]^{3-}$ compared to the excited state of $[Re_2Cl_8]^{2-}$ and therefore, by analogy, a stronger ground state, even though the bond order for $[Re_2Cl_8]^{2-}$ is higher than for $[Re_2Cl_8]^{3-}$, 4.0 and 3.5, respectively. These results are consistent with the experimental and theoretical results for $Re_2Cl_4(PPr_3)_4{}^+$.[17] The correlation between bond order and bond strengths has been discussed.[2-4]

The X-band ESR spectrum of $[Re_2Cl_8]^{3-}$ at 77 K is shown in Figure 3. Data from the spectrum as well as for other $Re_2{}^{5+}$ complexes appear in Table II. A broad, complex signal centered around 2400 G is observed. Cotton and Pedersen have presented a detailed analysis of ESR spectra of species with the $\sigma^2\pi^4\delta^2\delta^*$ configuration, such as $Re_2{}^{5+}$[16] and $Tc_2{}^{5+}$.[21] Their results indicate that the spectra of these species arise from a single unpaired electron residing in a δ^* orbital coupled to two Re atoms, each with nuclear spin $^5/_2$, or two Tc atoms, each with spin $^9/_2$. Spectra of the rhenium chlorophosphine complexes are further complicated by coupling of the electron to phosphorus. Our results are consistent with those found for other $Re_2{}^{5+}$ species (Table II) and confirm the $\sigma^2\pi^4\delta^2\delta^*$ configuration. Because of the lack of sufficient resolution and its expected complexity,[8-10,16,18] we make no attempt to interpret the spectrum in any detail.

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Registry No. $[Re_2Cl_8]^{3-}$, 53260-18-7.

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Structural Analysis of $[Et_3NH][Cu(1\text{-}B_{10}H_9N_2)_2]$ and $[Et_3NH][1\text{-}B_{10}H_9N_2]$

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We have previously reported the synthesis and spectroscopic characterization of $[1\text{-}B_{10}H_9N_2]^-$ (**1**).[1-4] We now report the utilization of this monoanion as a ligand and the synthesis and structural characterization of a new metallaborane derivative, $[Cu(1\text{-}B_{10}H_9N_2)_2]^-$ (**2**). The structure of the monoanion **1** was previously assigned on the basis of spectroscopic data, and we have now confirmed the initial structural assignment by a single-crystal X-ray diffraction study.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification unless otherwise stated. Triethylamine (MCB), 2,4,6-tribromoaniline (Eastman), sodium propionate (Aldrich), sodium nitrite (Mallinckrodt), fluoroboric acid (Aldrich), sodium tetrafluoroborate (Aldrich), and copper(I) chloride (Aldrich) were used without further purification. Acetonitrile was dried over CaH_2 and refluxed under nitrogen prior to use. Other solvents were used as received. ^{11}B NMR spectra were recorded on a Bruker AM500 (160.463 MHz) NMR spectrometer. The ^{11}B chemical shifts are referenced to external $BF_3 \cdot OEt_2$; peaks upfield of the reference are designated as negative, and areas are given in parentheses. Infrared spectra were obtained as KBr pellets by using a Beckman Model FT 1100 FT-IR spectrometer.

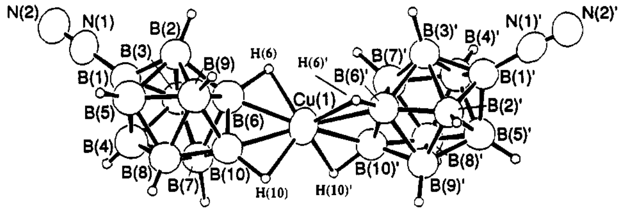

Figure 1. Structure of $[Et_3NH]\cdot\mathbf{2}$ with thermal ellipsoids for non-hydrogen atoms drawn at 50% probability and for hydrogen drawn artificially small.

Preparation of $[Et_3NH][1\text{-}B_{10}H_9N_2]$ ($[Et_3NH]\cdot\mathbf{1}$). A 11.1-g (26-mmol) sample of 2,4,6-tribromobenzenediazonium tetrafluoroborate was dissolved in 200 mL of CH_3CN, and the resulting solution was added slowly to a solution of $[(Et_3NH)_2][B_{10}H_{10}]$[1-4] (8.4 g, 26.0 mmol) in 400 mL of CH_3CN maintained at 0 °C. After being stirred for 30 min, the solution was warmed to room temperature and 1 g of sodium propionate was added. After the reaction mixture was stirred overnight, CH_3CN was removed by rotary evaporation and the resulting solid was taken up in 200 mL of H_2O and extracted three times with ether. The ether fractions were combined, dried over $MgSO_4$, and evaporated to give 650 mg (10% yield) of solid residue of $[Et_3NH]\cdot\mathbf{1}$. Additional product was recovered by washing the $MgSO_4$ with acetone (three times) to give a dark green solution. Evaporation of the solvent gave a dark solid, which was recrystallized in hot 95% ethanol to afford an additional 1.84 g of the product for a total yield of 39%. IR spectrum (KBr): 3124 (s), 2510 (s), 2230 (s), 1450 (m), 1400 (m), and 1135 cm^{-1} (m). ^{11}B NMR (Et_2O): 23.23 (d, 1 B), −14.70 (s, 1 B), −16.48 (d, 4 B), and −24.86 ppm (d, 4 B).

Preparation of $[(Et_3)NH][Cu(1\text{-}B_{10}H_9N_2)_2]$ ($[Et_3NH]\cdot\mathbf{2}$). Into a 100-mL round-bottom flask equipped with a magnetic stirring bar and a reflux condenser was added CuCl (1.46 g, 14.8 mmol), 1.23 mL of 12 N HCl (14.8 mmol), and 200 mL of H_2O. To this was added $[Et_3NH]\cdot\mathbf{1}$ (1.84 g, 7.4 mmol) in 150 mL of acetonitrile, and the solution was gently refluxed for 2 h. After cooling, the acetonitrile was removed by rotary evaporation, and the solution was neutralized by the addition of triethylamine. The crude product mixture was extracted with ether (3 × 50 mL). The combined organic layers were then dried with brine and over $MgSO_4$, and the solvent was removed to dryness to obtain $[Et_3NH]\cdot\mathbf{2}$ as a light brown powder, which was then recrystallized from CH_2Cl_2/Et_2O. Clear plates having a pink coloration were obtained in 14% yield (227 mg, 0.5 mmol) after further recrystallizations. Anal. Calcd (found): C, 15.81 (15.78); H, 7.46 (6.99); B, 47.42 (46.75); N, 15.37 (15.29); Cu, 13.94 (14.11). IR spectrum (KBr): 2552 (s), 2457 (s), 2258 (s), 2218 (s), 1467 (m), 1395 (m), 1166 (m), 1134 (s), 1014 (s), and 685 cm^{-1} (m). ^{11}B NMR (Et_2O): 7.44 (d, 1 B), −7.90 (s, 1 B), −16.90 (d, 4 B), and −25.48 ppm (d, 4 B).

Solid-State Structures of $[Et_3NH]\cdot\mathbf{1}$ and $[Et_3NH]\cdot\mathbf{2}$. Crystallographic data, atomic coordinates, and selected bond distances and angles are reported in Tables I–V.

Results and Discussion

Milder reaction conditions for the preparation of $[Et_3NH]\cdot\mathbf{2}$ were investigated. The reaction of $[Et_3NH]\cdot\mathbf{1}$ with CuCl in the absence of added HCl did not result in the desired product. When HCl was added without bringing the solution to reflux, $[Et_3NH]\cdot\mathbf{2}$ formation was not observed. However, in the presence of HCl at the reflux temperature, the ^{11}B NMR spectrum of an aliquot of the reaction mixture taken after 2 h of reaction indicated an essentially quantitative conversion of $[Et_3NH]\cdot\mathbf{1}$ to $[Et_3NH]\cdot\mathbf{2}$. The $[Et_3NH]\cdot\mathbf{2}$ complex is soluble in common organic solvents such as MeCN, Et_2O, and CH_2Cl_2. After 3 weeks, no degradation of the complex was observed in the presence of air and moisture.

Complexes $[Et_3NH]\cdot\mathbf{1}$ and $[Et_3NH]\cdot\mathbf{2}$ have been obtained as a brownish yellow and as a pale pink crystalline solid, respectively. In order to establish the molecular geometry of the complexes, suitable single crystals of $[Et_3NH[\cdot\mathbf{1}$ were grown from H_2O and

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Table I. Crystallographic Data Collection for [Et$_3$NH]·**1** and [Et$_3$NH]·**2**[a]

	[Et$_3$NH]·**1**	[Et$_3$NH]·**2**
formula	$C_6H_{25}B_{10}N_3$	$CuC_6H_{34}B_{20}N_5$
fw	247.3	456.1
temp/K	298	298
wavelength/Å	0.7107	0.7107
space group	$P2_1/n$	$P2_1/a$
a/Å	7.483 (1)	10.363 (1)
b/Å	10.652 (2)	24.133 (3)
c/Å	20.521 (4)	11.115 (1)
β/deg	95.690 (4)	107.670 (2)
V/Å	1641	2649
Z	4	4
ρ(calcd)/g cm^{-3}	0.93	1.14
μ/cm^{-1}	0.46	8.4
R, R_w, GOF	0.055, 0.066, 1.94	0.077, 0.094, 2.53

[a] Crystal data for [Et$_3$NH]·**2** are as follows. A pale pink crystal was mounted on a fiber on a Huber diffractometer with graphite monochromator. Data were collected in the θ–2θ scan mode to a maximum 2θ of 50°. Of the 4669 unique reflections measured ($+h,+k,\pm l$), 2097 were considered observed [$I > 3\sigma(I)$] and were used in the subsequent structure analysis. No equivalent reflections were merged. Reflections were corrected for Lorentz and polarization effects but not for absorption or extinction, using locally written programs (UCLA package) and a local modification of SHELX76 (G. Sheldrick, University of Cambridge, 1976). Scattering factors for H atoms were obtained from Stewart et al. (Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175) and for other atoms were taken from the following: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. Anomalous dispersion terms were applied to the scattering of Cu. The larger peaks on a final difference electron density map were of density 0.5 e Å^{-3}. Crystal data for [Et$_3$NH]·**1** are as follows. An orange crystal was mounted on a fiber on a modified Picker FACS-1 diffractometer with graphite monochromator. Data were collected in the θ–2θ scan mode to a maximum 2θ = 45°. Of the 2122 unique reflections measured ($+h$, $+k,\pm l$), 1105 were considered observed [$I > 3\sigma(I)$] and were used in the subsequent structure analysis. No equivalent reflections were merged. Reflections were corrected for Lorentz and polarization effects but not for absorption or extinction. Scattering factors were obtained from the references mentioned above for [Et$_3$NH]·**2**. The larger peaks on a final difference electron density map were of density 0.2 e Å^{-3}.

Table II. Positional and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms for [Et$_3$NH]·**1**

atom	x	y	z	U_{equiv},[a] Å^2
C(01)	1.22004 (56)	0.03747 (44)	0.88316 (19)	0.0579
C(02)	1.07567 (59)	0.13582 (47)	0.87688 (24)	0.0708
C(03)	1.22105 (59)	−0.00283 (43)	0.76321 (21)	0.0601
C(04)	1.33198 (68)	−0.03521 (47)	0.70930 (22)	0.0706
C(05)	1.43596 (60)	0.15089 (44)	0.81681 (23)	0.0668
C(06)	1.55091 (67)	0.19243 (55)	0.87726 (25)	0.0902
N(01)	0.37358 (54)	0.16579 (34)	0.52741 (18)	0.0551
N(03)	1.33369 (44)	0.03425 (32)	0.82625 (17)	0.0509
N(02)	0.24094 (55)	0.14817 (41)	0.50117 (19)	0.0749
B(01)	0.5535 (6)	0.1899 (5)	0.5631 (2)	0.047 (1)*
B(02)	0.6694 (6)	0.3228 (5)	0.5678 (2)	0.052 (1)*
B(03)	0.7528 (6)	0.1741 (5)	0.5346 (2)	0.054 (1)*
B(04)	0.6829 (6)	0.0869 (5)	0.6069 (2)	0.049 (1)*
B(05)	0.5999 (6)	0.2373 (5)	0.6399 (2)	0.050 (1)*
B(06)	0.9059 (7)	0.2881 (5)	0.5736 (2)	0.055 (1)*
B(07)	0.9165 (6)	0.1236 (5)	0.6003 (2)	0.054 (1)*
B(08)	0.8073 (6)	0.1688 (5)	0.6743 (2)	0.051 (1)*
B(09)	0.7987 (6)	0.3337 (5)	0.6467 (2)	0.053 (1)*
B(10)	0.9872 (7)	0.2444 (5)	0.6492 (3)	0.060 (2)*

[a] U values with asterisks indicate atoms isotropically refined.

Table III. Positional and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms for [Et$_3$NH]·**2**

atom	x	y	z	U_{equiv},[a] Å^2
Cu(1)	0.3236 (1)	0.14191 (5)	0.0706 (1)	0.095
C(11)	0.2787 (16)	0.9260 (6)	0.0408 (13)	0.170
C(12)	0.2686 (13)	0.9441 (5)	0.1589 (11)	0.144
C(13)	0.2259 (14)	0.8269 (5)	0.0535 (14)	0.171
C(14)	0.3585 (11)	0.8017 (4)	0.0658 (9)	0.119
C(15)	0.0808 (21)	0.9096 (10)	−0.1000 (20)	0.107
C(16)	0.0903 (26)	0.8572 (13)	−0.1260 (23)	0.135
C(17)	0.0130 (13)	0.8846 (8)	−0.2152 (12)	0.174
N(1)	0.2319 (7)	0.0387 (3)	−0.4787 (6)	0.076
N(1′)	0.8018 (7)	0.2270 (3)	0.5454 (6)	0.070
N(1A)	0.2054 (14)	0.8798 (5)	−0.0213 (12)	0.227
N(2)	0.2500 (8)	0.0193 (3)	−0.5589 (7)	0.098
N(2′)	0.8843 (7)	0.2489 (3)	0.6118 (7)	0.083
B(01)	0.2050 (9)	0.0671 (4)	−0.3681 (8)	0.067 (2)*
B(02)	0.3027 (9)	0.1159 (4)	−0.2801 (8)	0.070 (2)*
B(03)	0.2573 (9)	0.0480 (4)	−0.2172 (8)	0.071 (2)*
B(04)	0.0766 (10)	0.0602 (4)	−0.3086 (9)	0.081 (3)*
B(05)	0.1215 (10)	0.1271 (4)	−0.3707 (9)	0.082 (3)*
B(06)	0.2950 (9)	0.1095 (4)	−0.1192 (8)	0.074 (3)*
B(07)	0.1383 (9)	0.0706 (4)	−0.1381 (8)	0.069 (2)*
B(08)	0.0428 (9)	0.1269 (4)	−0.2423 (8)	0.072 (3)*
B(09)	0.2012 (9)	0.1650 (4)	−0.2268 (9)	0.077 (3)*
B(10)	0.1536 (8)	0.1395 (4)	−0.1009 (8)	0.068 (2)*
B(1′)	0.6869 (8)	0.1946 (4)	0.4576 (8)	0.066 (2)*
B(2′)	0.5298 (8)	0.2152 (3)	0.3876 (7)	0.063 (2)*
B(3′)	0.6474 (9)	0.1845 (4)	0.3018 (8)	0.067 (2)*
B(4′)	0.6926 (9)	0.1276 (4)	0.4193 (8)	0.076 (3)*
B(5′)	0.5736 (9)	0.1571 (4)	0.5023 (8)	0.073 (3)*
B(6′)	0.4646 (8)	0.1776 (4)	0.2408 (8)	0.067 (2)*
B(7′)	0.5788 (10)	0.1159 (4)	0.2639 (9)	0.078 (3)*
B(8′)	0.5243 (9)	0.0968 (4)	0.4016 (8)	0.075 (3)*
B(9′)	0.4153 (9)	0.1576 (4)	0.3812 (8)	0.068 (2)*
B(10′)	0.4126 (9)	0.1120 (4)	0.2619 (8)	0.070 (2)*

[a] U values with asterisks indicate atoms isotropically refined.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for [Et$_3$NH]·**1**

N(1)–N(2)	1.097 (6)	N(1)–B(1)	1.489 (6)
B(1)–B(2)	1.658 (7)	B(1)–B(3)	1.663 (7)
B(1)–B(4)	1.666 (7)	B(1)–B(5)	1.661 (7)
N(1)–B(1)–B(2)	128.2 (4)	N(1)–B(1)–B(3)	127.5 (4)
N(1)–B(1)–B(4)	126.9 (4)	N(1)–B(1)–B(5)	128.2 (4)
N(2)–N(1)–B(1)	179.9 (4)		

Table V. Selected Interatomic Distances (Å) and Angles (deg) for [Et$_3$NH]·**2**

Cu–B(6)	2.184 (9)	Cu–B(6′)	2.186 (8)
Cu–B(10)	2.168 (8)	Cu–B(10′)	2.169 (9)
N(1)–N(2)	1.073 (10)	N(1′)–N(2′)	1.082 (10)
N(1′)–B(1′)	1.509 (11)	N(1)–B(1)	1.506 (11)
Cu–H(6)	1.96	Cu–H(10)	1.99
Cu–H(6′)	2.00	Cu–H(10′)	2.01
B(6)–Cu–B(10)	46.0 (3)	B(6)–Cu–B(6′)	146.7 (3)
B(6)–Cu–B(10′)	136.1 (3)	B(10)–Cu–B(6′)	157.3 (3)
B(10)–Cu–B(10′)	147.5 (3)	B(6′)–Cu–B(10′)	46.2 (3)
H(10)–Cu–H(6)	121	H(6′)–Cu–H(6)	112
H(10′)–Cu–H(6)	111	H(6′)–Cu–H(10)	105
H(10)′–Cu–H(10)	96	H(10′)–Cu–H(6′)	111

single crystals of [Et$_3$NH]·**2** were grown from CH_2Cl_2/Et_2O at room temperature.

The molecular structure of [Et$_3$NH]·**2** is illustrated in Figure 1, and selected interatomic distances and angles are tabulated in Table V. A similar complex, $Cu_2B_{10}H_{10}$, in which the copper and $B_{10}H_{10}{}^{2-}$ ligand form an alternating polymeric structure, has been previously reported by Lipscomb.[5] Later studies[6] proved the existence of strong B–H–Cu bridge interactions in this polymeric species and in the species [1,10-$(L_2Cu)_2B_{10}H_{10}$], where L = PPh_3. The anion **2**, on the other hand, has a discrete molecular structure. The complex [Et$_3$NH]·**2** is composed of a tetrahedral Cu(I) ion bound to each of two $[1\text{-}B_{10}H_9N_2]^-$ polyhedral units through an apical and an equatorial B–H vertex derived from each decaborate ligand. The Cu(I) thus forms two three-center Cu–H–B bridge bonds with each cage. The coordination about copper with respect

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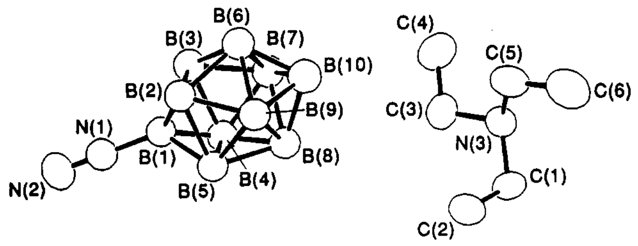

Figure 2. Structure of $[Et_3NH]\cdot\mathbf{1}$ with thermal ellipsoids for non-hydrogen atoms drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

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 $[Et_3NH]\cdot\mathbf{2}$. Figure 2 illustrates the molecular structure of $[Et_3NH]\cdot\mathbf{1}$. 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 $[Et_3NH]\cdot\mathbf{2}$ are 177.3 (5) and 176.9 (5)°, and for $[Et_3NH]\cdot\mathbf{1}$ 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 $[Et_3NH]\cdot\mathbf{1}$, 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 $[Et_3NH]\cdot\mathbf{2}$ 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. $[Et_3NH]\cdot\mathbf{1}$, 136460-25-8; $[Et_3NH]\cdot\mathbf{2}$, 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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