Volume 29
Number 12
June 13, 1990

Inorganic Chemistry

Communications

Models for Reduced Blue Copper Sites: Nearly Tetrahedral Complexes of Copper(I) and Silver(I) with a Novel N_2(imidazole)S^*_2(thioether) Ligand[1]

We report here the characterization of a novel, nearly tetrahedral $Cu^IN_2S^*_2$ complex with imidazole (N) and thioether (S^*) ligation. Such Cu(II) models can be used to identify the differential contributions of ligand types on the electronic structure[2] and electron-transfer reactivity[3,4] of *reduced* blue copper protein active sites. For example, we recently synthesized a nearly isostructural, pseudotetrahedral (D_{2d}) pair of $Cu^I/Cu^{II}N_4$ complexes using the geometrically constraining ligand **1** (see Scheme I);[5] electron self-exchange in this pair is remarkably slow.[6] We have now elaborated **1** into the linear, tetradentate $N_2S^*_2$ donor **4**, and have characterized its complexes with Cu(I), Cu(II), and Ag(I), including crystal structures of the Cu(I) and Ag(I) species. While other Cu(I) systems with $N_2S^*_2$ ligation have been structurally characterized,[7] the N donors had different hybridization and/or basicities than imidazole and presumably are less relevant as biological models.

Protection of 1 as its N,N′-(SEM)$_2$ derivative[8,9] [SEM = (2-(trimethylsilyl)ethoxy)methyl] allowed double ortho-metalation,[8-12] leading to a dilithio species formulated as **2**. Double sulfenylation[8-10] of **2** with the disulfide **3**, followed by deprotection,[8,9] led to **4** in 73% overall yield from **1**. The disulfide **3** was prepared from 2-(*tert*-butylthio)ethanol[13] by a short sequence in 66% overall yield: (a) CH_3SO_2Cl, Et_3N, CH_2Cl_2; (b) KSAc, EtOH; (c) NaOMe, MeOH, I_2. In the same fashion, reaction of **2** with dimethyl disulfide, followed by deprotection, gave the reference N_2 ligand 2,2′-bis(4-(methylthio)-2-imidazolyl)biphenyl (**5**). Complexes of **4** were prepared by treatment with 1.0 equiv of the M(I) salts in deoxygenated acetonitrile [Cu(I)] or methanol [Ag(I)]. Following evaporation, the colorless copper(I) tetrafluoroborate and silver(I) trifluoroacetate complexes were crystallized from acetone by slow vapor diffusion of ether. Full experimental details are given as supplementary material.

Table I. Structural Parameters[a]

	$Cu^I(4)^+$ cation 1	$Cu^I(4)^+$ cation 2	$Ag^I(4)^+$
Distances			
M–S(1)	2.376 (2)	2.409 (2)	2.586 (2)
M–S(1′)			2.586 (2)
M–N(1)	2.064 (5)	2.046 (6)	2.292 (4)
M–N(1′)			2.301 (5)
M···S	3.660 (2)	3.614 (3)	3.702 (2) 3.746 (2)
Angles			
S(1)–M–S(1′)	110.27 (9)	101.21 (9)	110.98 (7)
S(1)–M–N(1)	103.2 (2)	106.9 (2)	98.4 (1)
S(1)–M–N(1′)	109.3 (2)	109.9 (2)	116.8 (1)
S(1′)–M–N(1)			115.6 (1)
S(1′)–M–N(1′)			102.7 (1)
N(1)–M–N(1′)	121.6 (2)	120.4 (2)	113.3 (2)
Dihedral and Torsion Angles			
N(1)–M–S(1)/N(1′)–M–S(1′)	94.4 (1)	88.9 (1)	86.9 (1)
N(1)–M–S(1′)/N(1′)–M–S(1)	98.4 (1)	90.9 (1)	82.1 (1)
S(1)–C–C–S	−44.7 (8)	0 (2)	51.7 (7)
S(1′)–C–C–S			23 (1)

[a] Distances are in angstroms; angles are in degrees.

X-ray analysis revealed[14] that the Cu(I) complex is an acetone solvate with two structurally similar, crystallographically distinct Cu^I(**4**) cations, each with point symmetry 2. The Ag^I(**4**) cations show no crystallographic symmetry. Each cation has a distorted

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(14) Crystallography for $Cu(4)BF_4\cdot(CH_3)_2CO$, $CuS_4F_4ON_4C_{33}BH_{44}$: orthorhombic, *Pbcn*, $a = 20.400$ (2) Å, $b = 18.360$ (2) Å, $c = 20.395$ (3) Å, $Z = 8$; $d_{obsd} = 1.37$ (1) g/cm^3, $d_{calcd} = 1.376$ g/cm^3. The structure was solved (2845 reflections ($F_o^2 > 3\sigma(F_o^2)$), Mo Kα radiation, $\lambda = 0.71073$ Å, empirical absorption corrections) by using the Enraf-Nonius SDP program package and refined to give $R_{F(wF)} = 0.057$ (0.073) and a goodness of fit of 2.30. Despite the near equivalence of the *a* and *c* cell edges, the Laue group clearly indicated an orthorhombic space group, and solution of the structure revealed no evidence of twinning. Crystallography for $Ag(4)O_2CCF_3$, $AgS_4F_3O_2N_4C_{32}H_{38}$: monoclinic, $P2_1/n$, $a = 10.428$ (1) Å, $b = 23.145$ (5) Å, $c = 15.517$ (3) Å, $\beta = 99.71$ (1)°, $Z = 4$; $d_{obsd} = 1.44$ (1) g/cm^3, $d_{calcd} = 1.446$ g/cm^3, 3482 reflections ($F_o^2 > 3\sigma(F_o^2)$), $R_{F(wF)} = 0.052$ (0.070), and GOF = 2.32. The tetrafluoroborate anion in the Cu system showed high thermal parameters, and the trifluoroacetate anion in the Ag complex exhibited positional disorder, resulting in higher than normal *R* factors.

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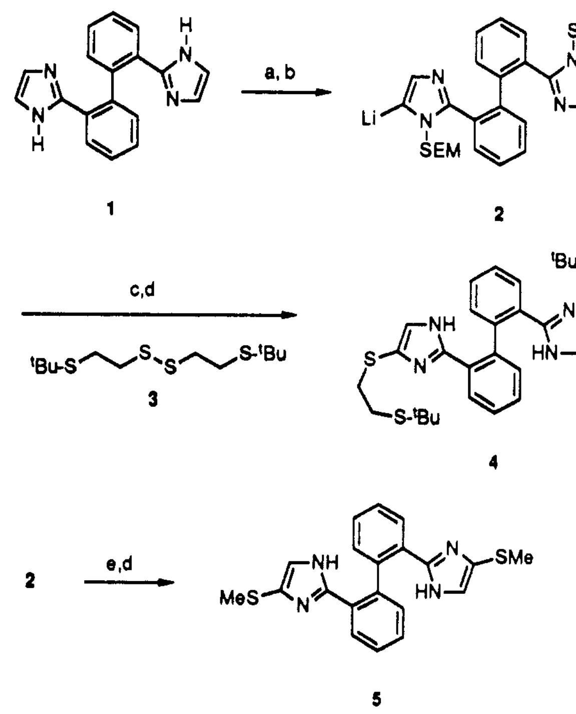
Scheme I[a]



[a] (a) SEM-Cl, KH, THF, HMPA, 0°C, 85%; (b) LDA, THF, -78°C; (c) disulfide 3, THF, 88%; (d) aq HF, MeOH, reflux, 98%; (e) MeSSMe, THF, 88%.

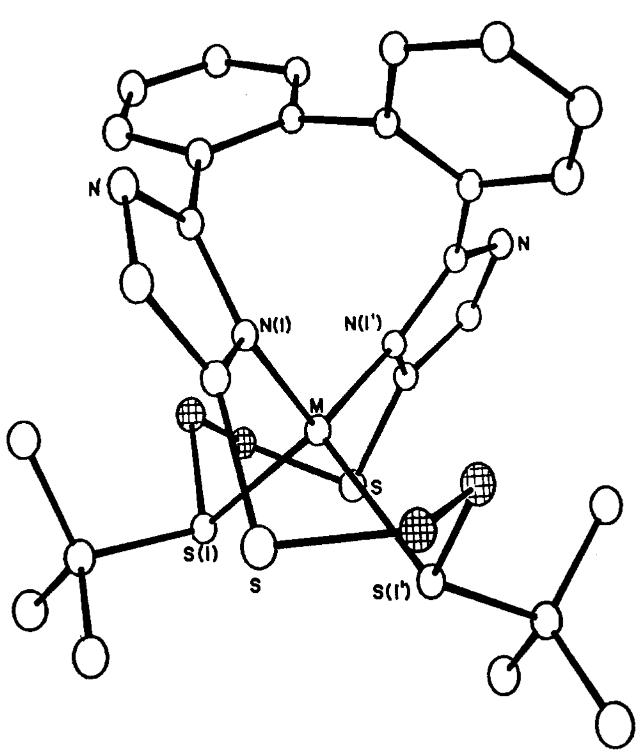


Figure 1. View of one of the two similar cations in $Cu^I(4)BF_4{\cdot}(CH_3)_2CO$. Ethano bridge C atoms are indicated by crosshatching. H atoms have been omitted for clarity.

tetrahedral coordination geometry as judged by the simple (A–M–B) and dihedral (A–M–B/C–M–D) angles (Table I), which show relatively modest deviations (ca. ±10°) from the tetrahedral values (109.5 and 90°, respectively). For the Cu(I) cations, deviations of the A–Cu–B angles from 109.5° are substantially smaller than those reported for the related $Cu^IN_2S^*_2$ complexes.[7] The Cu–S(thioether) bond lengths are relatively long; they lie outside the range [2.211 (1)–2.345 (1) Å] determined[7] for the related complexes, yet are substantially shorter than those observed[4] (2.51–2.90 Å) for reduced plastocyanin over the 3.8–7.8 pH range. Metal–ligand bond lengths in the Ag complex are ca. 0.24 Å longer than those in the Cu complex, while the N–Ag–N′ angle is smaller, consistent with the larger size of the Ag ion.[15] The seven-membered chelate rings adopt a variety of conformations in the solid state as judged by the SCCS torsion angles, which vary from 0 (2) (eclipsed) to 51.7 (7)° (gauche) (Table I). Thermal parameters of the carbon atoms of the ethano bridges (cross-hatched atoms in Figure 1) are relatively large compared with those of the remaining ligand atoms, consistent with some conformational flexibility and/or disorder in the solid state. Proton NMR spectra at 400 MHz[16] show broadened, overlapping four-spin patterns for the ethano bridge protons in the seven-membered chelate rings. These shift and sharpen at higher temperatures, implying analogous conformational flexibility in solution.

Equimolar solutions of Cu(II) salts with **4** or **5** afforded crystals that analyzed as $Cu(\mathbf{4})_2$ or $Cu(\mathbf{5})_2$ complexes.[17] $Cu(\mathbf{4})_2(CF_3SO_3)_2$ exhibits axial EPR spectra at 80 K both as a neat solid ($g_\parallel = 2.23$, $g_\perp = 2.02$, $A_\parallel^{Cu} = 142 \times 10^{-4}$ cm^{-1}) and glassed in acetone (3.5 mM, $g_\parallel = 2.26$, $g_\perp = 2.03$, $A_\parallel^{Cu} = 142 \times 10^{-4}$) that closely resemble those reported for the CuN_4 imidazole complex $Cu^{II}(\mathbf{1})_2(ClO_4)_2$ (5.0 mM, CH_3CN, 80 K, $g_\parallel = 2.25$, $g_\perp = 2.02$, $A_\parallel^{Cu} = 147 \times 10^{-4}$ cm^{-1}),[5,6] and the N_4 model complex $Cu^{II}(\mathbf{5})_2(ClO_4)_2$ (6.4 mM, 80K, CH_3CN, $g_\parallel = 2.25$, $g_\perp = 2.03$, $A_\parallel^{Cu} = 137 \times 10^{-4}$), suggesting that *Cu(II) preferentially forms an N_4 complex (one Cu to two ligands) and that the thioether arms of **4** do not ligate Cu(II) strongly*. This is also supported by the electronic spectrum of $Cu^{II}(\mathbf{4})_2(CF_3SO_3)_2$ (1.7 mM, ethanol) which includes LF absorptions at 820 (ϵ ca. 80) and 665 nm (155), and a band at 475 nm (195) which we assign as π(imH) → Cu(II) LMCT. Similarly, $Cu(\mathbf{1})_2(ClO_4)_2$ shows bands at 800 (120), 650 (260), and 440 (260)[5,6] while $Cu^{II}(\mathbf{5})_2(ClO_4)_2$ shows absorptions at 660 (225) and 480 (245) nm. Imidazole ring sulfenylation in **4** and **5** may account for the LMCT band red-shift of 35–40 nm relative to the copper(II) complex of **1**.[18] In the copper complexes, the ultraviolet spectral region is obscured by strong absorptions of the ligand **4**, the longest wavelength of which is approximately 275 nm (ϵ = 19 800). Consequently, the higher energy LMCT of the $Cu^{II}(\mathbf{4})_2$ complex and the MLCT of the $Cu^I(\mathbf{4})$ complex could not be located.

In summary, **4** provides a distorted tetrahedral $N_2S_2^*$ coordination sphere for Cu(I) and Ag(I); its complex with Cu(I) is a useful model for pseudotetrahedral binding sites. Efforts to prepare copper complexes of the monomercaptan corresponding to **4** are currently underway.

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(16) The 400-MHz ^1H NMR spectra of **4** and its complexes with AgO_2CCF_3 and $CuBF_4$ were examined in CD_3OD from −80 to +50 °C. Upon complexation at 50 °C, the imH ring proton (H-4) moves downfield by 0.27 and 0.21 ppm, respectively, and the *tert*-butyl singlet moves upfield by 0.08 and 0.09 ppm, respectively, compared with free **4**. At −80 °C, the *tert*-butyl peak of the Ag (Cu) complex moves another 0.06 (0.06) ppm upfield and the imidazole singlet another 0.21 (0.16) ppm downfield, suggesting tighter complexation at the lower temperature. Neither complex shows any free **4** by ^1H NMR. In the presence of excess **4**, the Ag and Cu complexes each show two distinct species at −60 °C (free and bound **4**), the *tert*-butyl singlets of which coalesce at about +20 °C, indicating rapid ligand exchange at the higher temperature. Whereas the phenylene protons of **4** and its complexes are well resolved and relatively unchanging, the protons of the ethano bridges broaden and shift over the temperature range studied. Best resolved is the spectrum for the Ag complex at 50 °C, whose four signals show J_{gem} = 12.5 and 13.4 Hz, and J_{vic} = 3.8, 4.6, 5.7, and 9.5 Hz.

(17) Anal. Calcd for $Cu^{II}(\mathbf{4})_2{\cdot}2OTf$, $C_{62}H_{76}CuF_6N_8O_6S_{10}$: C, 48.75; H, 5.02; Cu, 4.16; N, 7.34; S, 20.99. Found: C, 48.49; H, 4.95; Cu, 3.98; N, 7.23; S, 21.16. Anal. Calcd for $Cu^{II}(\mathbf{5})_2(ClO_4)_2$, $C_{40}H_{36}Cl_2CuN_8O_8S_4$: C, 47.13; H, 3.56; Cu, 6.23; N, 10.99; S, 12.58. Found: C, 47.35; H, 3.80; Cu, 6.10; N, 10.49; S, 12.34.

(18) Alkylation of the imH C atoms is known to red-shift imH → Cu(II) LMCT absorptions: Bernarducci, E.; Bharadwaj, P. K.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1983**, *105*, 3860.

Acknowledgment. This research was supported by the NSF (Grant CHE-8417548), the David and Johanna Busch Foundation, and the NIH (Instrumentation Grant 1510 RRO 1486 01A).

Supplementary Material Available: Full details for the synthesis of **4**, **5**, and their complexes, tables of crystal and refinement data, positional and thermal parameters, and bond distances and angles, and figures depicting the structures and numbering schemes of $Ag(\mathbf{4})^+$ and the two cations of $Cu(\mathbf{4})^+$ (27 pages); tables of observed and calculated structure factors for $Cu(\mathbf{4})BF_4{\cdot}(CH_3)_2CO$ and $Ag(\mathbf{4})O_2CCF_3$ (33 pages). Ordering information is given on any current masthead page.

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Received December 11, 1989

Preparation and Characterization of [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$: The First Structural Characterization of a Polymeric Self-Assembling Metallacarborane

There has been considerable current research interest in the organometallic chemistry of alkaline-earth metals.[1-11] In particular, the beautiful cyclopentadienyl chemistry of these metals has shown novel structural arrangements.[1-7] We have recently reported the solid state structure of the first calcium carborane,[12] *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$, in which the $Ca(MeCN)_4^{2+}$ unit caps the open hexagonal face of the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand. In this communication, we report the synthesis and characterization of a strontium carborane, [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$, which has been shown by X-ray diffraction to possess a novel polymeric structure. To our knowledge, it represents the first structurally characterized example of a polymeric metallacarborane.

The reaction of SrI_2 with Na_2[*nido*-7,9-$C_2B_{10}H_{12}]$[13] in THF affords a colorless complex (**1**), which precipitates from THF. Complex **1** is soluble in other coordinating solvents such as MeCN or DMF. Recrystallization of complex **1** from $MeCN/Et_2O$ produces colorless needlelike crystals; the X-ray study showed it to have the composition $Sr(C_2B_{10}H_{12})(MeCN)_3$ (**2**).[14] Complex **2** reverts to **1** in the presence of THF. On the basis of these

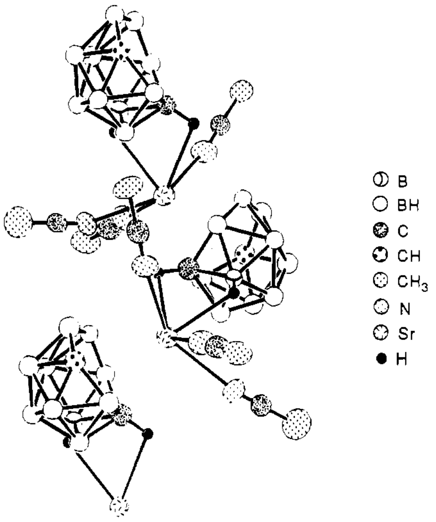

Figure 1. Three units of one of the spiral polymeric chains of [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ (**2**).

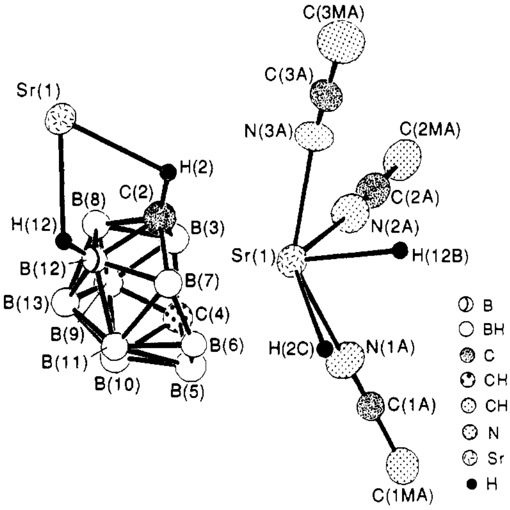

Figure 2. Closer view of the metal to carborane interactions in the polymeric complex [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ (**2**). All terminal hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Sr(1)–N(1A), 2.630 (9) [2.688 (9)]; Sr(1)–N(2A), 2.777 (10) [2.703 (9)]; Sr(1)–N(3A), 2.682 (8) [2.695 (9)]; Sr(1)–C(2)*, 2.997 (10) [3.064 (10)]; Sr(1)–B(3)*, 2.873 (10) [2.948 (13)]; Sr(1)–C(4)*, 3.176 (10) [3.142 (11)]; Sr(1)–B(5)*, 3.129 (10) [3.032 (13)]; Sr(1)–B(6)*, 2.909 (10) [2.826 (10)]; Sr(1)–B(7)*, 3.082 (10) [3.061 (13)]; C(2)–B(3), 1.716 (14) [1.731 (14)]; C(2)–B(7), 1.791 (14) [1.821 (14)]; C(4)–B(3), 1.695 (14) [1.604 (13)]; C(4)–B(5), 1.609 (14) [1.624 (15)]; B(5)–B(11), 2.003 (15) [1.99 (2)]; B(5)–B(10), 1.806 (16) [1.83 (2)]; C(2)–B(8), 1.732 (15) [1.730 (16)]; B(3)–B(8), 1.787 (15) [1.781 (16)]; C(2)–B(12), 1.731 (14) [1.719 (15)]; B(7)–B(12), 1.775 (15) [1.804 (16)]; Sr(1)–H(2), 2.62 (9) [2.70 (8)]; Sr(1)–H(12), 2.56 (9) [2.87 (9)]; C(2)–H(2), 1.12 (9) [1.43 (9)]; B(12)–H(12), 0.88 (9) [0.94 (9)]; Sr(1)–C(2), 3.153 (10) [3.166 (10)]. Asterisks denote atoms of the open hexagonal face of the carborane fragment that interacts directly with Sr(1). Distances in brackets are those of a second molecule. Note: Lines are for the purpose of orientation only and do not imply covalent bonding.

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(13) This dianion has been generated by the 2-electron reduction of 1,2-$C_2B_{10}H_{12}$ and has been formulated as Na_2[*nido*-7,9-$C_2B_{10}H_{12}]$ with carbon atoms occupying the 7- and 9-positions. This assignment is further supported by the fact that the [*nido*-$C_2B_{10}H_{13}]^-$ monoanion (kinetic isomer) and all of the metallacarboranes derived from this dianion contain carbon atoms in these positions.

(14) Data for **1**: IR (Nujol mull, NaCl) ν_{B-H} 2524 s, 2472 vs, br cm^{-1}, ν_{Sr-H-E} 2390 m cm^{-1} (E = B or C), ν_{THF} 1032 s, 884 m cm^{-1}. Data for **2**: IR (Nujol mull, NaCl) ν_{B-H} 2512 s, br, 2429 s, br cm^{-1}, ν_{MeCN} 2300 m, 2265 s cm^{-1}; ^1H NMR (CD_3CN, 20 °C, ppm) 3.99 (s, br, carboranyl C–H); ^{11}B NMR (in MeCN, 20 °C, chemical shifts referenced to external $BF_3{\cdot}OEt_2$, peaks upfield of the reference are designated as negative, areas given in parentheses) 2.6 (4), $^1J_{BH}$ = 111 Hz, −7.2 (3), $^1J_{BH}$ = 143 Hz, −18.1 (3), $^1J_{BH}$ = 129 Hz.

0020-1669/90/1329-2191$02.50/0