

Structural Comparison of a Redox Pair of Copper(I/II) Complexes Having Benzimidazole Thioether Ligands

JEFFREY V. DAGDIGIAN, VICKIE McKEE, and CHRISTOPHER A. REED*

Received July 30, 1981

Differences in the intrinsic structural preferences of copper(I) and copper(II) have been investigated within the constraints of a tridentate benzimidazole thioether chelating ligand. A three-coordinate T-shaped copper(I) cation is formed with the 2N,S donor ligand 2,2'-bis(2-(*N*-propylbenzimidazolyl))diethyl sulfide (L_1 -Pr) while a five-coordinate distorted tetragonal-pyramidal stereochemistry is found for copper(II) with the closely related ligand 2,2'-bis(2-(5,6-dimethylbenzimidazolyl))diethyl sulfide (L_3). The fourth and fifth ligands to copper(II) are an equatorial water and an axial monodentate perchlorate. $[Cu^I(L_1-Pr)][BF_4]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.865$ (3) Å, $b = 17.614$ (5) Å, $c = 15.242$ (3) Å, $\beta = 109.93$ (2)°, and $Z = 4$; Cu-S = 2.469 (9) Å and N-Cu-S = 98.3 (2), 99.4 (2)°. $[Cu^{II}(L_3)(H_2O)(OCIO_3)][ClO_4]$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.909$ (4) Å, $b = 10.972$ (7) Å, $c = 16.65$ (1) Å, $\alpha = 103.10$ (6)°, $\beta = 96.56$ (6)°, $\gamma = 103.98$ (5)°, and $Z = 2$; Cu-S = 2.322 (2) Å, Cu-OH₂ = 2.045 (5) Å, and Cu-OCIO₃ = 2.346 (6) Å. The long Cu(I)-S distance appears to arise from a marked misalignment of the bonding sp³ lone pair on sulfur with the Cu-S vector. These structures allow estimates to be made for the intrinsic Cu-N and Cu-S bond distances for histidine and methionine ligated copper proteins, thereby focusing attention on the peculiarity of the very long copper-methionine bond reported for plastocyanin. Several new benzimidazole chelating ligands have been synthesized with use of the versatile carboxylic acid/*o*-phenylenediamine condensation method, and their copper(I) and copper(II) complexes are reported. UV-vis spectral assignments of $\pi(N)$ and $\sigma(S)$ to Cu(II) charge-transfer transitions have been made, and axial ESR spectra are found ($g_{\parallel} > g_{\perp}$).

Introduction

It is well-known that copper(I) and copper(II) complexes have quite different intrinsic stereochemical preferences.^{1,2} For example, tetrahedral and trigonal coordination is common for copper(I) while tetragonal geometries prevail in copper(II) complexes. The rationale for this appears to lie mainly in the electronic stabilization of the copper(II) ion in specific stereochemistries. While copper(I) is d¹⁰ and will therefore have ligand stereochemistries dictated essentially by steric and charge effects alone, copper(II) is d⁹ and will prefer stereochemistries that derive some ligand field stabilization from energetically favorable d-orbital splittings. Such stereochemical preferences have two interesting consequences for copper in biological redox chemistry. First, if a simple rapid valency change of copper is required such as in an electron carrier, then the protein is obliged to restrict structural rearrangement upon redox in order that Franck-Condon barriers are not too large. Blue (or type I) copper proteins appear to do just this by dictating a donor ligand set and stereochemistry that are a compromise between intrinsic preferences of copper(I) and copper(II).³ Second, one can ask whether biological systems actually exploit redox-induced stereochemical changes at copper to drive chemical reactions or stabilize particular states. There is speculation that they do.⁴⁻⁷ For example, it seems possible that cooperativity in oxygen binding to hemocyanin might arise from structural changes propagated from the copper stereochemical change that must accompany the redox reaction of dioxygen binding as peroxide. In this paper a structural comparison of a redox pair of copper complexes is made in order to gain more understanding of this interplay of stereochemistry and oxidation state with biologically relevant benzimidazole thioether coordination.

Structural comparisons of copper(I) and copper(II) redox pairs have recently been reported with imidazole,⁵ thioether,^{6,8,9} and mixed pyridine thioether¹⁰⁻¹³ donors, but none have been reported with mixed imidazole thioether ligation. Since protein constraints can impose unusual geometries upon copper, it is of interest to investigate model compound structures where the donor atoms are restrained from orienting independently of each other. The chelating nature of the present ligands introduces some degree of stereochemical constraint and makes thioether ligation obligatory as well.¹⁴

It has been known for some time that copper(II) methionine complexes do not involve thioether ligation,¹⁵ and it was only with the X-ray structure of plastocyanin that thioether ligation was proven in a copper protein.³ The reluctance of copper(II) complexes to bind thioethers has frequently been noted.^{16,17} However, it was not anticipated that the refined X-ray crystal structure of plastocyanin would reveal an unusually long (2.9 Å)⁷ copper-thioether bond. Model compound studies can be useful in deriving expectations for intrinsic copper-thioether (and copper-imidazole) bond distances as a reference point for discussing such unusual protein structure. Thioether ligation is also of interest in regard to its effect on the intensities of visible spectral maxima,¹⁸ the assignment of S→Cu charge-transfer transitions,¹⁹⁻²¹ its effect on Cu(II) EPR

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Table I. Analytical Data for New Ligands

ligand	formula	anal. calcd (found)				¹ H NMR data, δ [solvent]
		% C	% H	% N	% S	
L ₄	C ₂₆ H ₃₄ N ₄ S·C ₂ H ₅ OH·H ₂ O	65.09 (64.97)	8.58 (8.15)	10.84 (11.05)	6.20 (6.26)	1.95 (1, 3 H), 2.20 (1, 3 H), 2.8 (m, 2 H) [Me ₂ SO]
L ₄ -Pr	C ₃₂ H ₄₆ N ₄ S·0.17CHCl ₃	71.67 (71.77)	8.63 (8.43)	10.39 (10.74)	5.94 (5.90)	1.1 (3, 3 H), 1.85 (6, 2 H), 2.4 (1, 6 H), 2.66 (1, 3 H), 2.73 (1, 3 H), 3.5 (m, 4 H), 4.2 (3, 2 H) [CDCl ₃]
L ₅	C ₁₆ H ₁₄ SO·H ₂ O	61.51 (61.56)	5.16 (5.22)	17.94 (17.83)	10.26 (10.06)	4.1 (1, 2 H), 7.3 (m, 4 H) [Me ₂ SO]
L ₅ -Pr	C ₂₂ H ₂₆ N ₄ S	69.80 (69.92)	6.92 (6.91)	14.80 (14.65)	8.47 (8.39)	0.75 (3, 3 H), 2.62 (6, 2 H), 2.55 (3, 2 H), 4.0 (1, 2 H), 7.35 (m, 4 H) [CDCl ₃]
L ₆	C ₂₀ H ₂₂ N ₄ S	68.54 (68.29)	6.33 (6.32)	15.99 (15.90)	9.15 (9.04)	
L ₇	C ₂₀ H ₂₂ N ₄ S	68.54 (68.35)	6.33 (6.44)	15.99 (15.83)	9.15 (8.99)	1.9 (5, 2 H), 2.38 (3, 2 H), 2.8 (3, 2 H), 7.15 (m, 4 H) [Me ₂ SO]
L ₇ -Et	C ₂₄ H ₃₀ N ₄ S·0.06CHCl ₃ ^a	69.80 (69.98)	7.32 (7.28)	13.53 (13.52)	7.74 (7.50)	1.2 (3, 3 H), 2.15 (5, 2 H), 2.6 (3, 2 H), 2.9 (3, 2 H), 4.0 (4, 2 H), 7.35 (m, 4 H) [CDCl ₃]
L ₇ -Pr	C ₂₆ H ₃₄ N ₄ S	71.85 (71.57)	7.88 (7.81)	12.89 (12.72)	7.38 (7.32)	1.0 (3, 3 H), 1.9 (6, 2 H), 2.3 (5, 2 H), 2.75 (3, 2 H), 3.05 (3, 2 H), 4.1 (3, 2 H), 7.5 (m, 4 H) [CDCl ₃]
T ₁	C ₂₅ H ₂₂ N ₆ ·1.75H ₂ O	68.55 (68.68)	5.87 (5.41)	19.19 (19.10)		1.05 (1, 3 H), 3.05 (1, 4 H), 7.07 (m, 12 H) [Me ₂ SO]
T ₂	C ₃₁ H ₃₄ N ₆ ·2H ₂ O	70.69 (70.90)	7.27 (7.17)	15.96 (15.80)		1.0 (1, 3 H), 2.3 (1, 6 H), 3.0 (1, 4 H), 7.1 (1, 6 H) [Me ₂ SO]

^a Chlorine analysis: calcd, 1.60; found, 1.58.

Table II. Analytical Data and Properties of Copper(II) Complexes

complex (solvates)	anal. calcd (found)					$\mu_{\text{eff}}, \mu_{\text{B}}$ (25 °C)	UV-vis (acetonitrile), nm (ϵ , M ⁻¹ cm ⁻¹) ^b
	% C	% H	% N	% Cu	% Cl ^a		
[Cu(L ₅ -Pr)(H ₂ O)(OCIO ₃)] [ClO ₄]·H ₂ O·0.5(C ₂ H ₅) ₂ O	40.37 (40.55)	4.94 (4.55)	7.85 (7.78)	8.90 (8.90)	9.93 (9.77)	1.85	775 (130), 630 (220), 395 (430), 327 (1020)
[Cu(L ₅ -Pr)(H ₂ O)(F ₃ BF ₃)] [BF ₄]·0.5H ₂ O	41.11 (41.43)	4.55 (4.65)	8.72 (8.58)	9.89 (9.97)	4.99 ^a (4.68)	1.70	775 (40), 622 (72), 375-425 (-), 325 (880)
[Cu(L ₅ -Pr)Cl ₂] [Cl] ₂ ·2(CH ₃) ₂ CO	52.58 (52.60)	5.65 (5.61)	9.81 (10.80)	11.13 (11.10)	12.42 (12.50)	1.85	<i>b</i>
[Cu(L ₆ -Pr)(H ₂ O)(F ₃ BF ₃)] [BF ₄]·0.5C ₂ H ₅ OH	45.49 (45.61)	5.51 (5.75)	7.86 (8.00)	8.91 (9.11)	4.50 ^a (4.48)	1.75	775 (69), 630 (167), 415 (235), 325 (825)
[Cu(L ₆ -Pr)Cl ₂] [Cl] ₂	54.87 (54.59)	6.02 (6.04)	9.85 (9.64)	11.17 (10.90)	12.46 (12.35)		<i>b</i>
[Cu(L ₆ -Pr)(H ₂ O)(OCIO ₃)] [ClO ₄]·C ₂ H ₅ OH	44.18 (44.15)	5.56 (5.38)	7.36 (7.20)	8.35 (8.45)	9.32 (9.20)		775 (150), 630 (240), 415 (330), 325 (880)
[Cu(L ₇ -Et)(H ₂ O)(OCIO ₃)] [ClO ₄]							800 (-), 690 (117), 410 (735), 365 (1145)
[Cu(T ₁)(H ₂ O)(OCIO ₃)] [ClO ₄]							800 (-), 690 (157), 373 (416)
[Cu(T ₁ -Pr)(H ₂ O)(OCIO ₃)] [ClO ₄]							800 (-), 690 (195), 400 (482)

^a Sulfur analysis (not chlorine) when superscript appears. ^b Missing data due to shoulders or unreliability arising from low solubility.

spectra,²² and its ability to raise Cu(I/II) redox potentials.²³ The present study allows comment on all but the last of these properties. The early synthetic aspects of this work have been communicated.¹⁴

Experimental Section

Synthesis. Conditions and reagents were as previously described.¹⁴ Shock sensitivity of perchlorate salts has not been observed, but caution against explosion is warranted. Except for those syntheses described in detail below, methods and procedures were as previously described.¹⁴ Elemental analyses and ¹H NMR data for new ligands are listed in Table I. Identifying data for new copper(II) complexes are listed in Table II. The appearance of a lattice solvate indicates the identity of the solvent used for recrystallization if other than ethanol. Where elemental analyses are not reported, the complex was prepared in

solution for spectroscopic study only. Analytical data for new copper(I) complexes are given below.

Dinitro-3,4,5,6-tetramethylbenzene (L₄). To a solution of fuming nitric acid (30 g) was slowly added concentrated sulfuric acid (130 g). An equal volume of CHCl₃ was then added and the mixture cooled to 5 °C. Pentamethylbenzene (10 g) was gradually added to the cooled HNO₃/H₂SO₄ mixture such that the temperature never rose above 10 °C. After each addition of a small amount of pentamethylbenzene the resulting red color was given time to dissipate before more was added. After all the pentamethylbenzene had been added and the reaction ceased, the CHCl₃ layer was isolated and washed first with water and then with dilute sodium carbonate solution. The resulting solution was stripped at low pressure, and as this process occurred, colorless crystals appeared. When all the CHCl₃ was removed, addition of H₂O and cooling to 0 °C crystallized the remaining product. This was collected, dried in a vacuum desiccator, and identified as dinitro-3,4,5,6-tetramethylbenzene. Anal. Calcd for C₁₀H₁₂N₂O₄: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.42; H, 5.41; N, 12.38. NMR (CDCl₃): δ 2.18 (1, 6 H), 2.22 (1, 6 H). A mixture of dinitro-3,4,5,6-tetramethylbenzene (8.0 g, 0.0363 mol), SnCl₂ (80 g, 0.422 mol), concentrated HCl (72 mL), and thiodipropionic acid (6.4 g, 0.0355 mol) was heated under reflux for 24 h. The solution was neutralized with NH₄OH, and the resulting precipitate was filtered off with the aid of Celite. The filtrate was collected and water added until a slight turbidity was induced. Colorless crystals were deposited

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Table III. Crystal Data for $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$

space group: $P\bar{1}$ (triclinic)	$\lambda(\text{Mo K}\alpha_1) = 0.70926 \text{ \AA}$
$a = 7.909(4) \text{ \AA}$	$\lambda(\text{Mo K}\alpha_2) = 0.71354 \text{ \AA}$
$b = 10.972(7) \text{ \AA}$	mol wt = 602.85
$c = 16.646(14) \text{ \AA}$	$\rho_{\text{calcd}} = 1.631 \text{ g/cm}^3$
$\alpha = 103.099(61)^\circ$	$\rho_{\text{obsd}} = 1.64 \text{ g/cm}^3$
$\beta = 96.563(56)^\circ$	2646 reflections with $I \geq 3[\sigma(I)]$
$\gamma = 103.979(45)^\circ$	data/parameter = 7.54
$V = 1342(1) \text{ \AA}^3$	$R_F = 0.065$
$Z = 2$	$R_{wF} = 0.085$

when the solution was left standing. These were collected, dried in a vacuum desiccator, and identified as $\text{L}_4 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ (see Table I). The EtOH and H_2O solvates were confirmed by NMR.

T₁. To finely ground phenylenediamine (3.52 g, 0.0326 mol) was added 2-methylpropanetricarboxylic acid (2.0 g, 0.0105 mol). The compounds were mixed until intimately associated and heated to 180 °C. At this temperature the reactants slowly melted and began to effervesce mildly. Heating was continued for 10 min after the effervescence ceased to ensure complete reaction. The mixture was cooled, dissolved in a minimum amount of a slightly acidic aqueous solution, and decolorized with charcoal at reflux for 10 min. Neutralization with NH_4OH yielded an off-white precipitate. Repetition of this purification procedure eventually yielded a colorless precipitate, which was collected, dried in a vacuum desiccator, and identified as **T₁** (see Table I). NMR confirmed the presence of approximately 1.75 H_2O of solvation. Copper complexes were prepared with use of methods described earlier.¹⁴

$\text{Cu}^1(\text{L}_5\text{-Pr})\text{Cl}$. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4\text{CuClS}$: C, 55.33; H, 5.49; N, 11.73; Cu, 13.31; Cl, 7.42; S, 6.71. Found: C, 55.21; H, 5.57; N, 11.80; Cu, 13.20; Cl, 7.40; S, 6.52.

$[\text{Cu}^1(\text{L}_5\text{-Pr})\text{BF}_4]$. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_4\text{CuBF}_4\text{S}$: C, 49.96; H, 4.95; N, 10.59; Cu, 12.01; S, 6.06. Found: C, 49.92; H, 4.97; N, 10.54; Cu, 12.0; S, 5.89.

$[\text{Cu}^1(\text{L}_6\text{-Pr})\text{BF}_4]$. Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{N}_4\text{CuBF}_4\text{S}$: C, 53.38; H, 5.86; N, 9.58; Cu, 10.86; S, 5.48. Found: C, 53.36; H, 6.01; N, 9.29; Cu, 10.40; S, 5.36.

X-ray Structure of the Copper(II) Complex $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$. A single crystal of $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$, grown from acetone/heptane, with approximate dimensions $0.19 \times 0.26 \times 0.30 \text{ mm}$ was used. From preliminary precession photographs the triclinic space group $P\bar{1}$ was assigned. A Syntex P2₁ computer-controlled diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) was employed in determining cell parameters and collecting data. The cell parameters were $a = 7.909(4) \text{ \AA}$, $b = 10.972(7) \text{ \AA}$, $c = 16.65(1) \text{ \AA}$, $\alpha = 103.10(6)^\circ$, $\beta = 96.56(6)^\circ$, $\gamma = 103.98(5)^\circ$, and $V = 1342(2) \text{ \AA}^3$. Crystal data for $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$ are summarized in Table III.

An ω scan over the range $4^\circ < 2\theta < 45^\circ$ at a scan rate of $2.44^\circ \text{ min}^{-1}$ was used. The intensities of 3 check reflections were recorded every 50 reflections to monitor long-term crystal stability. No decay was observed. Data processing²⁴ and merging yielded 3446 unique reflections. Of these, the 2646 reflections that had $I \geq 3[\sigma(I)]$ were retained for the subsequent structure analysis. The absorption coefficients ranged from 0.8–1.0 normalized to a maximum value of unity, and an absorption correction²⁵ was employed.

The structure was solved by direct methods with the program MULTAN²⁶ followed by two difference Fourier syntheses. Several cycles of least-squares refinement using isotropic temperature factors followed by several cycles using anisotropic temperature factors resulted in the final values of $R_F = 0.065$ and $R_{wR} = 0.085$. The goodness of fit value was 1.12, and the data to parameter ratio was 7.54. A final difference Fourier synthesis had no peaks greater than 0.80 e/\AA^3 . No attempt was made to locate any of the hydrogen atoms. Final atomic parameters are listed in Table IV. Anisotropic thermal parameters (Table V) and final observed and calculated structure factors (Table VI) are available in the supplementary material.

X-ray Structure of the Copper(I) Complex $[\text{Cu}(\text{L}_1\text{-Pr})\text{BF}_4]$. Colorless crystals were grown anaerobically from acetone/diethyl ether.

Table IV. Final Atomic Parameters for $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$

atom	x	y	z
Cu	0.0084 (1)	0.5132 (1)	0.2623 (1)
N(1)	0.1341 (8)	0.5672 (6)	0.3804 (4)
N(2)	0.2733 (9)	0.5770 (7)	0.5054 (4)
N(3)	0.8981 (8)	0.4610 (6)	0.1436 (4)
N(4)	0.8210 (8)	0.3466 (6)	0.0110 (4)
O(1)	0.7886 (8)	0.6084 (6)	0.3078 (4)
O(2)	0.4932 (10)	0.5937 (8)	0.2699 (4)
O(3)	0.5728 (10)	0.4273 (6)	0.3128 (5)
O(4)	0.6093 (12)	0.6204 (8)	0.4065 (4)
O(5)	0.7439 (11)	0.1601 (6)	0.8518 (4)
O(6)	0.8756 (15)	0.0361 (10)	0.7702 (6)
O(7)	0.8501 (12)	1.0077 (8)	0.9008 (6)
O(8)	0.6003 (13)	0.9420 (8)	0.7956 (6)
O(9)	0.1892 (7)	0.6657 (5)	0.2413 (3)
Cl(1)	0.6146 (3)	0.5650 (2)	0.3242 (1)
Cl(2)	0.7598 (3)	0.0295 (2)	0.8307 (1)
S	0.9012 (3)	0.3051 (2)	0.2784 (1)
C(1)	0.1904 (11)	0.4999 (8)	0.4274 (5)
C(2)	0.1790 (10)	0.6983 (8)	0.4314 (4)
C(3)	0.2681 (10)	0.7012 (8)	0.5097 (5)
C(4)	0.6660 (12)	0.1804 (8)	0.4256 (5)
C(5)	0.6906 (12)	0.0697 (9)	0.4434 (5)
C(6)	0.6233 (14)	0.9375 (9)	0.3742 (6)
C(7)	0.1976 (13)	0.0549 (8)	0.4569 (6)
C(8)	0.2207 (11)	0.9289 (8)	0.4761 (5)
C(9)	0.1503 (11)	0.8125 (7)	0.4134 (5)
C(10)	0.8299 (9)	0.5369 (7)	0.0988 (4)
C(11)	0.8054 (10)	0.6612 (7)	0.1230 (5)
C(12)	0.7288 (10)	0.7094 (7)	0.0634 (5)
C(13)	0.6975 (13)	0.8448 (8)	0.0897 (6)
C(14)	0.4094 (11)	0.3088 (8)	0.0881 (5)
C(15)	0.3203 (10)	0.3661 (7)	0.0221 (5)
C(16)	0.2960 (10)	0.4858 (8)	0.0478 (5)
C(17)	0.7818 (10)	0.4663 (7)	0.0146 (4)
C(18)	0.8899 (10)	0.3492 (7)	0.0884 (4)
C(19)	0.9410 (12)	0.2372 (8)	0.1104 (5)
C(20)	0.8408 (12)	0.1935 (7)	0.1755 (5)
C(21)	0.8799 (12)	0.7127 (8)	0.6842 (6)
C(22)	0.1777 (13)	0.3564 (8)	0.4061 (5)

Table VII. Crystal Data for $[\text{Cu}(\text{L}_1\text{-Pr})\text{BF}_4]$

space group: $P2_1/c$	$\lambda(\text{Cu K}\alpha_1) = 1.5405 \text{ \AA}$
(monoclinic)	$\lambda(\text{Cu K}\alpha_2) = 1.5443 \text{ \AA}$
$a = 9.865(3) \text{ \AA}$	mol wt = 556.92
$b = 17.614(5) \text{ \AA}$	$\rho_{\text{calcd}} = 1.49 \text{ g/cm}^3$
$c = 15.242(3) \text{ \AA}$	3017 reflections with $I \geq 3[\sigma(I)]$
$\beta = 109.93(2)^\circ$	$R_F = 0.082$
$V = 2490(1) \text{ \AA}^3$	$R_{wF} = 0.109$
$Z = 4$	

Because of slow aerobic decomposition a suitable crystal of dimensions $0.27 \times 0.33 \times 0.53 \text{ mm}$ was sealed in a 0.33 mm diameter capillary tube. Precession photographs of the crystal revealed a monoclinic diffraction pattern and allowed formulation of the space group as $P2_1/c$.

Cell parameters and intensity data were obtained with a Syntex P2₁ computer-controlled diffractometer with graphite-monochromated Cu K α radiation. The cell parameters are listed in Table VII.

A θ - 2θ scan over the range $3.0^\circ < 2\theta < 113.0^\circ$ and a variable scan rate (2.55 – $14.65^\circ \text{ min}^{-1}$) were used. The long-term stability was monitored by recording 3 standard reflections at intervals of 50 reflections. No significant variation in the intensities of these reflections was detected. Data reduction²⁴ gave 3510 unique reflections. Of these 3017 had $I \geq 3[\sigma(I)]$ and were used for subsequent structural analysis. Absorption coefficients were in the range 0.8–1.0 normalized to a maximum value of unity, and the linear absorption coefficient was 22.1 cm^{-1} . No absorption correction was applied.

The structure was solved with use of conventional Patterson and difference Fourier heavy-atom methods. The uncoordinated tetrafluoroborate was disordered by 3-fold rotation about the B–F(1) bond. Refinement of the atom coordinates and anisotropic temperature factors of the three orientations, each with one-third occupancy, gave values of $R_F = 0.082$ and $R_{wF} = 0.109$. A final difference Fourier map revealed no other nonhydrogen atoms were present. No attempt

(24) Reflections were judged unsymmetrical if the ratio of the left and right backgrounds did not fall in the bounds 0.2–5.0.

(25) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

(26) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

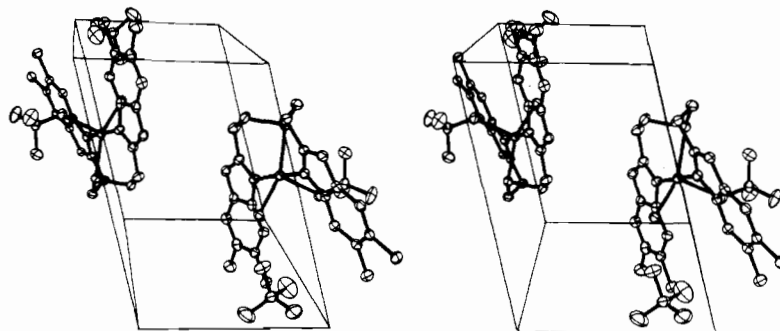


Figure 1. Unit cell drawing of $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)][\text{ClO}_4]$.

Table VIII. Final Atomic Parameters for $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$

atom	x	y	z
Cu	-0.1500 (1)	0.0209 (1)	0.0668 (1)
S	-0.1359 (2)	0.1477 (1)	0.1383 (1)
N(1)	0.0196 (6)	-0.0222 (3)	0.1552 (4)
N(2)	0.2014 (6)	-0.4495 (32)	0.2858 (37)
N(3)	-0.3297 (5)	-0.0312 (3)	-0.0329 (3)
N4	-0.5019 (5)	-0.0926 (3)	-0.1433 (4)
C(1)	0.0799 (6)	-0.0936 (4)	0.1480 (4)
C(2)	0.0382 (7)	-0.1458 (4)	0.0751 (5)
C(3)	0.1182 (8)	-0.2121 (4)	0.0876 (5)
C(4)	0.2350 (8)	-0.2254 (4)	0.1690 (6)
C(5)	0.2763 (8)	-0.1729 (4)	0.2427 (5)
C(6)	0.1914 (6)	-0.1076 (4)	0.2858 (4)
C(7)	0.3023 (9)	-0.0402 (5)	0.3823 (5)
C(8)	0.1202 (18)	-0.0660 (9)	0.4642 (10)
C(9)	0.2490 (12)	-0.0940 (9)	0.4482 (6)
C(10)	0.0954 (7)	0.0039 (4)	0.2392 (4)
C(11)	0.0816 (8)	0.0794 (4)	0.2794 (5)
C(12)	-0.0751 (8)	0.1078 (4)	0.2560 (5)
C(13)	-0.3324 (7)	0.1463 (4)	0.1117 (5)
C(14)	-0.4064 (8)	0.1617 (4)	0.0063 (5)
C(15)	-0.4100 (6)	0.0948 (4)	-0.0559 (4)
C(16)	-0.3777 (6)	-0.0144 (3)	-0.1112 (4)
C(17)	-0.3362 (7)	-0.0876 (4)	-0.1260 (5)
C(18)	-0.4029 (8)	-0.1199 (4)	-0.2145 (5)
C(19)	-0.5077 (8)	-0.0819 (5)	-0.2828 (5)
C(20)	-0.5511 (8)	-0.0070 (4)	-0.2694 (5)
C(21)	-0.4849 (7)	0.0233 (3)	-0.1825 (4)
C(22)	-0.6016 (7)	0.1531 (4)	-0.1947 (5)
C(23)	-0.7572 (7)	0.1356 (4)	-0.2010 (6)
C(24)	-0.8561 (8)	0.2003 (5)	0.2539 (6)
B	0.3218 (11)	0.3215 (6)	0.0132 (6)
F(1)	0.3746 (11)	0.1767 (5)	0.4396 (6)
F(2)	0.4289 (43)	0.2880 (23)	0.0893 (23)
F(3)	0.3124 (75)	0.3874 (23)	0.0486 (44)
F(4)	0.2215 (47)	0.2196 (35)	0.4802 (33)
F(5)	0.2699 (54)	0.2494 (14)	0.0201 (38)
F(6)	0.4406 (53)	0.3233 (34)	0.0904 (29)
F(7)	0.2335 (58)	0.3731 (24)	0.0172 (31)
F(8)	0.3627 (60)	0.2688 (26)	0.0785 (27)
F(9)	0.3690 (66)	0.3923 (31)	0.0516 (49)
F(10)	0.1675 (27)	0.1711 (40)	0.4718 (26)

was made to locate hydrogen atom positions. Final atomic parameters are listed in Table VIII. Anisotropic thermal parameters (Table IX) and final observed and calculated structure factors (Table X) are listed in the supplementary material.

Description of the Copper(II) Structure

Molecules of $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)][\text{ClO}_4]$ crystallize in the triclinic unit cell shown in Figure 1.²⁷ The overall structure of $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)][\text{ClO}_4]$ consists of two units: a $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)]^+$ cation and an uncoordinated perchlorate anion that is hydrogen bonded to the coordinated water molecule. The atom numbering scheme is shown in

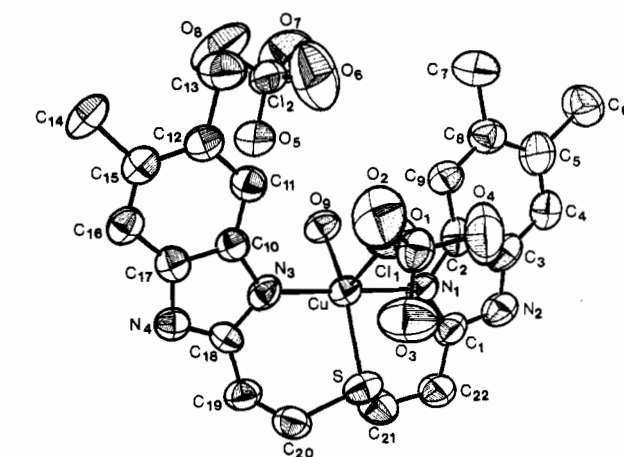


Figure 2. Atom numbering scheme for $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)][\text{ClO}_4]$.

Table XI. Selected Bond Distances (Å) for $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)][\text{ClO}_4]$

Cu-S	2.322 (2)	C(1)-C(22)	1.51 (1)
Cu-N(1)	1.985 (6)	C(2)-C(3)	1.40 (1)
Cu-N(3)	1.960 (6)	C(2)-C(9)	1.41 (1)
Cu-O(1)	2.346 (6)	C(3)-C(4)	1.42 (1)
Cu-O(9)	2.045 (5)	C(4)-C(5)	1.36 (1)
N(1)-C(1)	1.30 (1)	C(5)-C(6)	1.56 (1)
N(1)-C(2)	1.43 (1)	C(5)-C(8)	1.43 (1)
N(2)-C(1)	1.37 (1)	C(7)-C(8)	1.53 (1)
N(2)-C(3)	1.36 (1)	C(18)-C(19)	1.49 (1)
N(3)-C(10)	1.39 (1)	C(19)-C(20)	1.51 (1)
N(3)-C(18)	1.34 (1)	C(20)-S	1.80 (1)
N(4)-C(17)	1.41 (1)	C(21)-S	1.84 (1)
N(4)-C(18)	1.33 (1)	C(21)-C(22)	1.48 (1)
		C(8)-C(9)	1.40 (1)

Figure 2. The stereoscopic drawing of $[\text{Cu}^{\text{II}}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)]^+$ (Figure 3) shows the coordination around Cu^{II} to be distorted square pyramidal where the donor atoms are the 2N,S chelate, a water molecule, and a monodentate perchlorate anion.

Selected bond distances and angles are summarized in Tables XI and XII, respectively. The O(1)-Cu-O(9) and O(1)-Cu-S bond angles are 102.8 (3) and 100.5 (2)°, respectively, demonstrating that it is better to consider the structure a distorted square pyramid with two equatorial angles increased from 90° than a trigonal bipyramid with equatorial bond angles decreased from 120°. Figure 3 demonstrates that thioether-copper coordination has occurred, producing two six-membered rings, which are in differing conformations. One exists in a twist conformation while the other is in a pseudoboat conformation. The 2N,S chelate coordinates to copper in a stereochemistry very close to T-shaped. The N(1)-Cu-S and N(2)-Cu-S bond angles are 88.3 (2) and 92.9 (2)°, and the N(1)-Cu-N(3) angle is 176.6 (3)°. Also, the coordinated nitrogen atoms N(1) and N(3), the sulfur atom, and the copper

(27) Drawings were made with use of the program ORTEP II: Johnson, C. K. Report No. ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

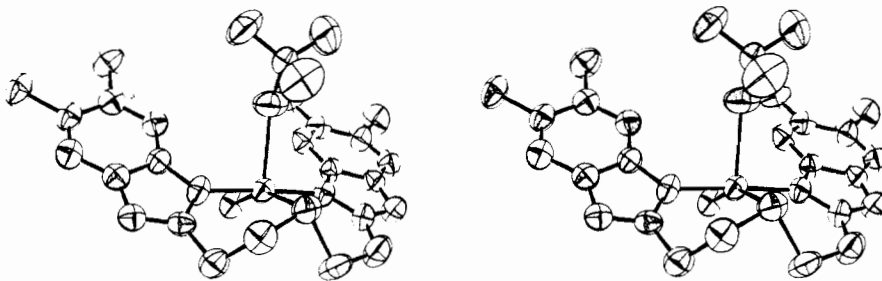


Figure 3. Stereoscopic drawing of the copper(II) cation $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)]^+$.

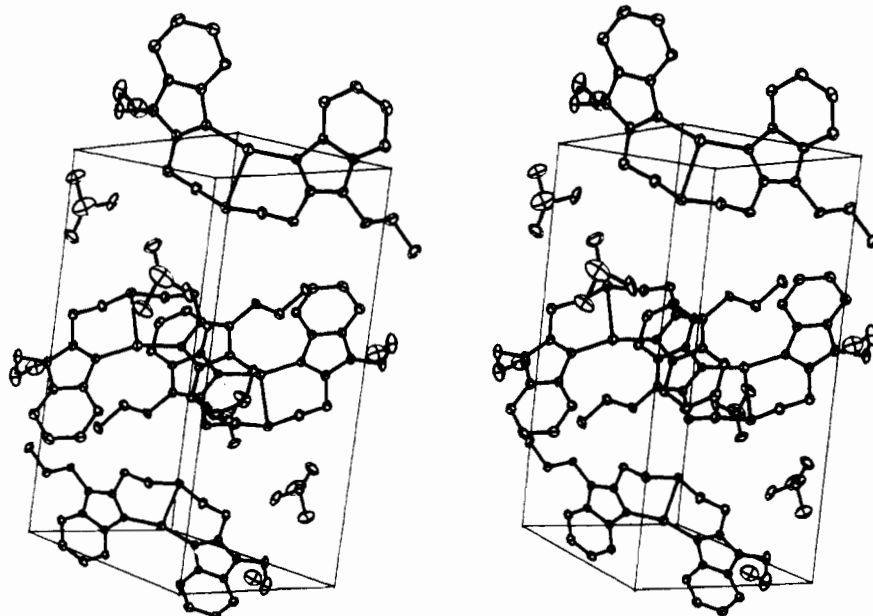


Figure 4. Unit cell drawing of $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$.

Table XII. Selected Bond Angles (Deg) for $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OCIO}_3)]^+[\text{ClO}_4]^-$

N(1)-Cu-N(3)	176.6 (3)	Cu-S-C(20)	107.6 (3)
N(1)-Cu-S	88.3 (2)	Cu-S-C(21)	95.4 (3)
N(1)-Cu-O(1)	88.5 (3)	C(20)-S-C(21)	102.1 (4)
N(1)-Cu-O(9)	88.0 (2)	N(1)-C(1)-N(2)	111.4 (8)
N(3)-Cu-S	92.9 (2)	N(1)-C(1)-C(22)	129.2 (7)
N(3)-Cu-O(1)	94.3 (3)	N(2)-Cu-C(22)	119.4 (7)
N(3)-Cu-O(9)	89.6 (2)	N(2)-C(18)-N(4)	111.8 (7)
O(1)-Cu-S	100.5 (2)	N(39)-C(18)-C(19)	124.7 (7)
O(1)-Cu-O(9)	102.8 (3)	N(4)-C(18)-C(19)	123.4 (7)
O(9)-Cu-S	156.3 (2)	C(18)-C(19)-C(20)	110.8 (7)
Cu-N(1)-C(1)	130.6 (6)	C(19)-C(20)-S	115.3 (6)
Cu-N(1)-C(2)	123.1 (5)	C(22)-C(21)-S	109.5 (7)
Cu-N(1)-C(2)	106.2 (6)	C(1)-C(22)-C(21)	115.0 (8)
Cu-N(3)-C(10)	127.0 (5)		
Cu-N(3)-C(18)	125.7 (5)		
C(10)-N(3)-C(18)	106.9 (6)		
O(5)-Cl(2)-O(6)	101.5 (6)	O(1)-Cl(1)-O(2)	110.5 (5)
O(5)-Cl(2)-O(7)	108.9 (5)	O(1)-Cl(1)-O(3)	108.2 (5)
O(5)-Cl(2)-O(8)	111.2 (6)	O(1)-Cl(1)-O(4)	109.9 (5)
O(6)-Cl(2)-O(7)	107.7 (6)	O(2)-Cl(1)-O(3)	109.5 (5)
O(6)-Cl(2)-O(8)	110.8 (6)	O(2)-Cl(1)-O(4)	111.2 (5)
O(7)-Cl(2)-O(8)	115.7 (6)	O(3)-Cl(1)-O(4)	107.3 (5)

atom are essentially planar. That the S-Cu-O(9) angle is $156.3(2)^\circ$ means that the water molecule subtends an angle of approximately 24° below this plane. Thus, the intentional design of the 2N,S chelate to prevent square-planar coordination has been achieved. The moderately strongly coordinated water molecule has a relatively short Cu-O distance, $2.045(5) \text{ \AA}$, consistent with its site as a pseudoequatorial ligand. The apical monodentate perchlorate has a Cu-O

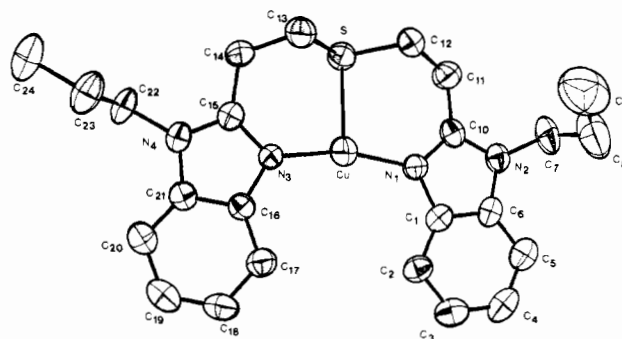


Figure 5. Atom numbering scheme for the cation $[\text{Cu}(\text{L}_1\text{-Pr})]^+$.

distance of $2.346(6) \text{ \AA}$, which is at the short end of the range ($2.26\text{--}2.88 \text{ \AA}$) for copper(II) complexes. This can be rationalized by the five-coordination (as opposed to six) and the driving force of charge neutralization on the otherwise dipositive cation. No distinguishable differences were detected in the Cl-O distances. The uncoordinated perchlorate is hydrogen bonded to the coordinated water molecule, and this probably prevents disorder.

Description of the Copper(I) Structure

The monoclinic unit cell and the four equivalent orientations in which $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$ was found to crystallize are illustrated in Figure 4. $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$ consists of discrete monomeric units composed of a cationic copper complex and a tetrafluoroborate anion. The atom numbering scheme for the copper complex is shown in Figure 5, and a stereoscopic drawing is displayed in Figure 6. Selected bond distances and bond angles are listed in Tables XIII and XIV, respectively.

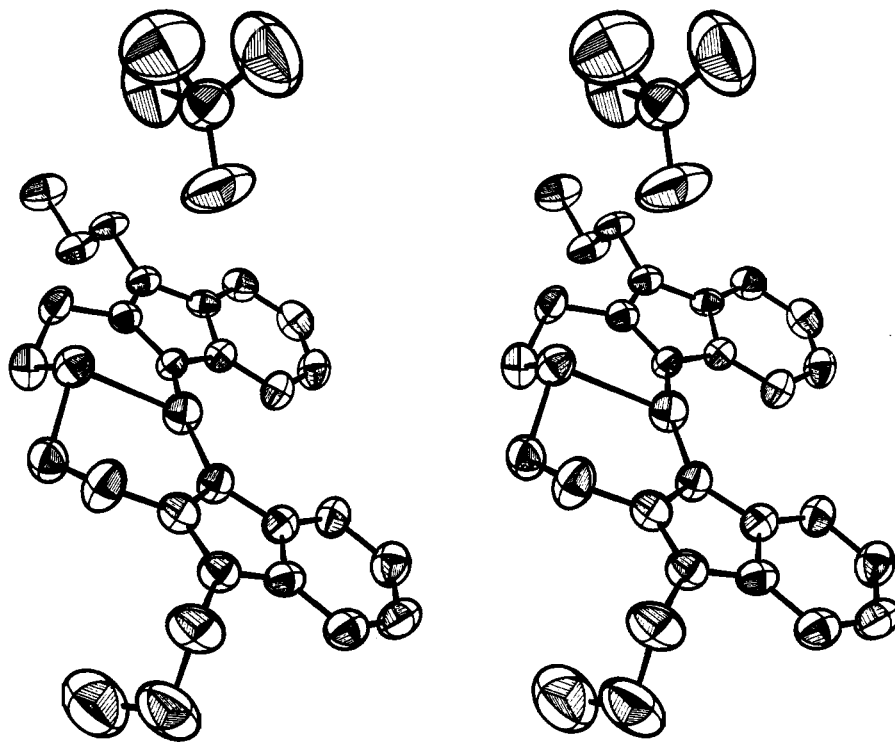


Figure 6. Stereoscopic drawing of the copper(I) complex $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$.

Table XIII. Selected Interatomic Distances (Å) for $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$

Cu-N(1)	1.912 (5)	C(1)-C(2)	1.392 (9)
Cu-N(3)	1.910 (5)	C(1)-C(6)	1.365 (9)
Cu-S	2.469 (9)	C(2)-C(3)	1.39 (9)
N(1)-C(1)	1.411 (8)	C(3)-C(4)	1.40 (1)
N(1)-C(10)	1.327 (8)	C(4)-C(5)	1.40 (1)
N(2)-C(6)	1.389 (8)	C(5)-C(6)	1.395 (9)
N(2)-C(7)	1.471 (9)	C(10)-C(11)	1.49 (1)
N(2)-C(10)	1.354 (9)	C(11)-C(12)	1.55 (1)
N(3)-C(15)	1.348 (8)	C(12)-S	1.828 (7)
N(3)-C(16)	1.381 (8)	C(13)-S	1.841 (8)
N(4)-C(15)	1.333 (8)	C(13)-C(14)	1.55 (1)
N(4)-C(22)	1.481 (8)	C(14)-C(15)	1.505 (9)
N(4)-C(24)	1.394 (8)		

Figure 6 shows that the copper(I) complex is three-coordinate and has adopted an approximately T-shaped planar geometry. The angles around copper sum to 360° within experimental error. The bond lengths are discussed in a subsequent section. Two six-membered rings are formed as a result of thioether-copper ligation, both in a twist conformation, which is far removed from the ideality of a chair conformation. This presumably arises from the constraints of the ligand, which can only provide T-shaped coordination to a metal that would prefer trigonal coordination. The noncoordinated tetrafluoroborate ion fits a disorder model having three equal populations arising from rotation about the B-F(1) bond.

Results and Discussion

Synthesis. The benzimidazole synthetic method is turning out to be a very versatile route to new chelating ligands. Almost any carboxylic acid can be condensed with *o*-phenylenediamine in a one-step reaction, frequently giving good purity and high yields of the corresponding benzimidazole. The varied ring substitution patterns (X, Y, and Z in Figure 7) and varied N-alkylation products (R) create a family of ligands within each type having a convenient gradation of solubilities and crystallizing abilities. Figure 7 summarizes the ligands reported herein as well as those re-

Table XIV. Selected Bond Angles (Deg) for $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$

N(1)-Cu-N(3)	161.8 (2)	N(1)-C(10)-N(2)	111.5 (6)
N(1)-Cu-S	98.3 (2)	N(1)-C(10)-C(11)	127.4 (6)
N(3)-Cu-S	99.4 (2)	N(2)-C(10)-C(11)	120.9 (6)
Cu-N(1)-C(1)	126.2 (4)	C(10)-C(11)-C(12)	114.7 (6)
Cu-N(1)-C(10)	127.7 (5)	C(11)-C(12)-S	108.6 (5)
C(1)-N(1)-C(10)	105.7 (5)	C(14)-C(13)-S	108.3 (5)
Cu-N(3)-C(15)	126.1 (4)	C(13)-C(14)-C(15)	114.7 (5)
Cu-N(3)-C(16)	125.8 (4)	N(3)-C(15)-N(14)	112.0 (5)
C(15)-N(3)-C(16)	105.1 (5)	N(3)-C(15)-N(14)	127.0 (6)
Cu-S-C(12)	89.6 (2)	N(4)-C(15)-C(14)	121.0 (6)
Cu-S-C(13)	92.0 (2)		
C(12)-S-C(13)	100.3 (3)		

ported in our prior note.¹⁴ Our ligand nomenclature adds R to the L designation if N-alkylation with R is present. For example, N-methylated L_1 is written $\text{L}_1\text{-Me}$. Related "tripod" ligands,²⁸⁻³⁰ as well as the tetrabenzimidazole derived from EDTA,^{31,32} are currently receiving attention as their copper chelates. We have prepared two new unsymmetrical tripod ligands having three benzimidazoles. These are designated T_1 and T_2 in Figure 7. Other advantages of benzimidazoles include chemical inertness (more than imidazoles) and convenient ^1H NMR identification. This latter property is illustrated in Figure 8, where the splitting patterns of both the aromatic groups and the 5,6-dimethyl substituents X, Y (when present) are usefully diagnostic. Also, the steric bulk of the benzimidazole ring can be exploited to control stereochemistry. For example, as the X-ray structural studies show, the $n = 2$ ligands $\text{L}_1\text{-L}_4$ provide T-shaped ligation and discourage square-planar coordination by virtue of steric interference at the 4-position. This effect should be more pronounced in the permethylated ligand L_4 . The ligands L_5 and L_6 , having $n =$

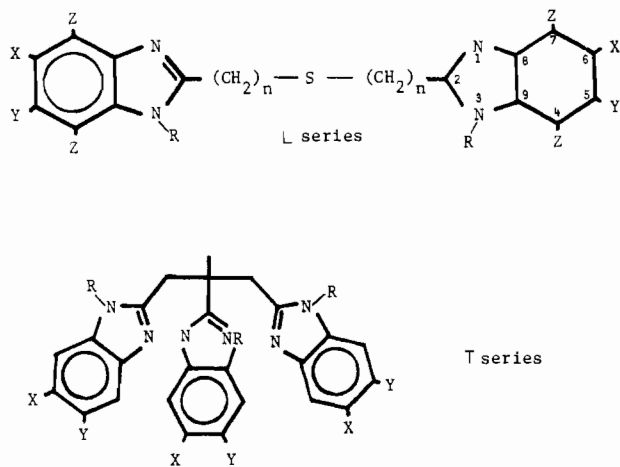
(28) Thompson, L. K.; Ramaswamy, B. S.; Dawe, R. D. *Can. J. Chem.* **1978**, *56*, 1311-1318.

(29) Hendriks, H. M. J.; Reedijk, J. *Inorg. Chim. Acta* **1979**, *37*, L507-508.

(30) Addison, A. W.; Hendriks, H. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *20*, 103-110.

(31) Birker, P. J. M. W. L.; Gorter, S.; Hendriks, H. M. J.; Reedijk, J. *Inorg. Chim. Acta* **1980**, *45*, L63-64.

(32) Birker, P. J. M. W. L.; Hendriks, H. M. J.; Reedijk, J. *Inorg. Chim. Acta* **1981**, *55*, L17.



Ligand	n	X	Y	Z	R
L ₁	2	H	H	H	H, Me, Et, Pr, Bzl
L ₂	2	Me	H	H	H
L ₃	2	Me	Me	H	H, Me, Et, Pr
L ₄	2	Me	Me	Me	H, Pr
L ₅	1	H	H	H	H, Pr
L ₆	1	Me	Me	H	H
L ₇	3	H	H	H	H, Et, Pr
T ₁	-	H	H	H	H, Et, Pr
T ₂	-	Me	Me	H	H, Et

Figure 7. Scheme for identification of the ligands.

1, should provide a trigonal-pyramidal donor set while the L₇ ligands, having $n = 3$, should allow square-planar coordination. Finally, the coordination of the thioether is intentionally enhanced in the L series of ligands by a chelate effect.

The synthetic methods for preparing the copper(II) chelates are unexceptional. Conditions were adopted that optimized the ease of isolation and purity. In a number of cases non-integral solvation was found. The new compounds are listed in Table II. On the basis of the present X-ray structure all these copper(II) complexes are considered to be five-coordinate. EPR data discussed below corroborate this. With respect to an ultimate goal of synthesis of a blue copper model, such five-coordination is notable. The preference of copper(II) for five-coordination seems to be very strong, and this underscores the difficulty of trying to force copper(II) into distorted four-coordinate geometries without having a rigid, sterically encumbered chelate and one that compensates at least partially the dipositive charge.³³ The presence of coordinated perchlorate (and presumably tetrafluoroborate in some derivatives) is ascribed to the driving force for charge compensation in complexes having electrically neutral chelating ligands.

Similarly, the synthesis of copper(I) complexes with the present ligands is not particularly problematical. While difficulties such as disproportionation and lability have been identified in the preparation of copper(I) complexes,³⁴ it is clear

(33) For definitive examples of markedly nonplanar four-coordinate copper(II) see: Elder, R. C.; Hill, M. C. *Inorg. Chem.* **1979**, *18*, 729-732. Bereman, R. D.; Shields, G. D.; Bordner, J.; Dorfman, J. R. *Ibid.* **1981**, *20*, 2165-2169.

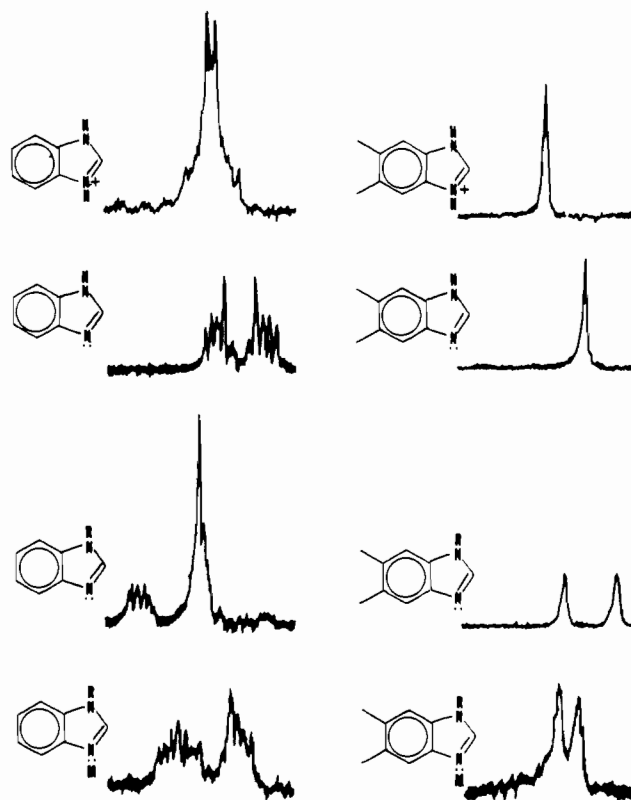


Figure 8. Partial ¹H NMR spectra of benzimidazole ligands. On the left is the aromatic region while the right shows the aliphatic ring methyl region.

that chelating ligands whose donor atoms are not too "hard" can readily overcome the inherent instability of uncomplexed copper(I). Three-coordination presumably obtains in all derivatives. This in itself should not be considered unusual since a number of examples now exist.³⁵ In fact, the lack of particular electronic effects in a d¹⁰ ion means that copper coordination numbers can vary from 2^{6,32} to 5,³⁴ depending mainly on the steric constraints of the ligands.

Stereochemical Comparison of Copper(I) and Copper(II). The benzimidazole thioether ligands in the copper(II) complex [CuL₃(H₂O)(OCIO₃)] [ClO₄] and the copper(I) complex [Cu(L₁-Pr)] [BF₄] have identical bond connectivity (see Figures 2 and 5). Since the differing peripheral substitution is unlikely to influence the coordination parameters, these two complexes make a good comparison pair. The increase in coordination number from 3 in copper(I) to 5 in copper(II) is the most obvious gross structural change and seems to reflect intrinsic properties of copper. It is interesting to note that recent spectroscopic analyses of the structure of hemocyanin are consistent with an increase of coordination number by 2 upon valency change.³⁶⁻³⁹ The bond angles at copper(II) in

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Table XV. Correlation of Cu-S Distance with Angular Deviation from Tetrahedrality

complex	Cu ^I -S, Å	Cu-S-C, deg	Cu-S-C, deg	C-S-C, deg	$\Sigma \Delta_{109,6}^{\text{Cu-S-C}}$, deg	ref
[Cu(dto) ₂][BF ₄]	2.280	103.0	96.1	106.5	20.1	8
	2.303	101.1	97.1	105.7	21.0	
	2.310	102.6	97.0	104.2	19.6	
	2.318	93.3	102.1	106.9	23.8	
Cu(tbmp) ₂ Br	2.304	100.3	111.2	105.4	5.8	12
	2.358	104.7	113.7	93.9	19.8	
[Cu(L ₁ -Pr)][BF ₄]	2.469	89.6	92.0	100.3	37.6	this work

[CuL₃(H₂O)(OCIO₃)⁺ are closer to an idealized tetragonal pyramid than a trigonal bipyramid. This falls in line with what must be considered a general preference of copper(II) for tetragonal stereochemistries and also illustrates how the designed bulk of the benzimidazoles prevents strict tetragonal coordination. The T-shaped coordination provided by the *n* = 2 ligands is found in both the copper(II) and the copper(I) complexes, albeit with some opening up of the chelate N-Cu-N angle in copper(I), viz., 177° for Cu(II) and 198° for Cu(I). Such a stereochemistry is unusual for copper(I) since trigonal planar is the preferred geometry of three-coordinate d¹⁰ complexes³⁵ and must represent a compromise between ideality and the limits of stretching of the bond connectivity between the donor atoms. Both six-membered N-S chelate rings in the copper(I) complex display a twist conformation, which is far removed from the ideal chair conformation. A T-shaped copper(I) stereochemistry has also been seen in a structurally related phenoxide-bis(imine) chelate.⁴⁰

Cu-N Bond Length Comparison. There is now a modest number of reported imidazole-copper(II) bond lengths. Distances in the range 1.94–2.06 Å are known, typically with imidazole as an equatorial ligand in an axially elongated octahedral stereochemistry.^{6,20,41} Thus the short distances in the present copper(II) complex, 1.985 (6) and 1.960 (6) Å, probably reflect the lower coordination number. The overall positive charge on the complex is also expected to result in shorter bond lengths compared to those of complexes with good coordinating anions, which fully compensate the charge on copper. Four-coordinate copper(II) proteins such as plastocyanin are therefore expected to have Cu-N distances near the shorter end of the present model compound range provided protein constraints are minimal. The current estimate from single-crystal X-ray studies on oxidized plastocyanin⁷ is 2.01 (5) Å while an EXAFS study on oxidized azurin⁴² gives 1.97 (2) Å. Since plastocyanin is believed to have a very long Cu-S bond to methionine and therefore approaches three-coordination, particularly short bonds to the other ligands might be expected. Indeed, a short Cu-S cysteine bond, 2.10 (2) Å, has been noted in azurin.⁴² We consider that Cu-N distances in the range 1.95–1.99 Å are consistent with expectations derived from model complexes, and the congruence (within experimental error) implies that protein constraints are controlling the histidine stereochemistry in blue copper proteins but not its coordinate bond length. The question of how much the stereochemistry influences the bond length in four-coordinate copper(II) complexes cannot be answered rigorously at present. A decrease of 0.05 Å in Cu-Cl distances has been observed in [CuCl₄]²⁻ on changing from a planar to distorted

tetrahedral stereochemistry.⁴³ This is expected on steric grounds. However, smaller effects are seen with Schiff base complexes³³ and in pyridine complexes there is little evidence for sensitivity of Cu-N to stereochemistry.^{11–13} Of course, these comments do not apply to ligands that are axially coordinated in five- or six-coordinate tetragonal systems; such Cu-L distances are frequently long and can be readily rationalized in terms of a Jahn-Teller distortion.

To our knowledge there is only one report of an imidazole Cu-N distance for the copper(I) oxidation state. A distance of 1.87 Å is found in a two-coordinate bis(benzimidazole) chelate.³² The present complex also has very short bonds close to 1.91 Å. These can be compared with the range 2.00–2.11 Å for copper(I) pyridine complexes¹³ and the range 1.93–2.05 Å for copper(I) pyrazolylborate derivatives.⁴⁴ All other factors being equal, one might expect bond lengths to increase from copper(II) to copper(I). So the decrease observed here must arise from the concomitant decrease in coordination number from 5 to 3. Also, the positive charge on the copper(I) ion is uncompensated by a coordinating anion; this factor probably also contributes to the strong coordination of imidazole. It is also possible that the expected σ -bond length increase on going from a d⁹ to a d¹⁰ complex is offset by some π back-bonding from Cu(I) to imidazole. Expectations for unconstrained Cu(I)-N distances to histidine in copper(I) proteins are therefore longer than those for the present complex except perhaps for deoxyhemocyanin, whose coordination number may be as low as 2. The most recent estimate from EXAFS studies³⁸ on deoxyhemocyanin is 1.95 (2) Å while with plastocyanin⁷ a distance of 2.02 (5) Å is reported for the four-coordinate form at pH 7 and 2.00 (5) Å for the three-coordinate form at pH 4.

Cu-S Bond Length Comparison. The Cu(II)-S distance of 2.322 (2) Å in [Cu(L₃)(H₂O)(ClO₃)⁺ lies at the short end of the range of those reported for equatorial copper(II)-thioether bonds (2.31–2.48 Å).^{6,8–11,13,45} Whereas all reported comparative studies of copper-thioether bond lengths show insignificant differences between copper(II) and copper(I) (<0.04 Å),^{6,8–12} or a decrease,^{9,13} the present comparison shows a significant increase in the reduced state. The Cu(I)-S distance increases by 0.15 Å to 2.469 (9) Å. This is particularly unexpected because of the concomitant decrease in coordination number. The rationale for the long Cu(I)-S distance in [Cu(L₁-Pr)]⁺ appears to lie, at least in part, in the less than ideal alignment of an sp³ hybridized lone pair on sulfur with the Cu-S vector. Table XV lists the Cu(I)-S distances together with the three angles about sulfur for the copper(I) thioether structures that have been fully reported

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Table XVI. EPR Parameters for Various Copper(II) Complexes

complex ^a	g_{\perp}	g_{\parallel}	A_{\parallel} , cm ⁻¹
[Cu(T ₁)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.10	2.348, 2.403	0.0167, 0.0140
[Cu(T ₁ -Pr)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.10	2.348, 2.410	0.0197, 0.0141
[Cu(L ₁)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.11	2.34	0.0153
[Cu(L ₃)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.11	2.34	0.0142
[Cu(L ₁ -Me)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.11	2.36	0.0143
[Cu(L ₁ -Me)(H ₂ O)(OCIO ₃)] [ClO ₃]	2.13	2.35	0.0148
[Cu(L ₃ -Me)(H ₂ O)(ClO ₄)] [ClO ₄] ^b	2.08	2.33	0.0210
[Cu(L ₅ -Pr)(OCIO ₃)] [ClO ₄] ^c	2.08	2.28	0.0186
[Cu(L ₅ -Pr)(H ₂ O)(F ₃ BF ₃)] [BF ₄]	2.08	2.30	0.0195
[Cu(L ₆ -Pr)(H ₂ O)(OCIO ₃)] [ClO ₄] ^c	2.08	2.21	0.0196
[Cu(L ₆ -Pr)(H ₂ O)(F ₃ BF ₃)] [BF ₄] ^c	2.08	2.28	0.0203
[Cu(L ₅ -Pr)Cl] ₂ [Cl] ₂ ^b	2.09	2.39	
[Cu(L ₆ -Pr)Cl] ₂ [Cl] ₂ ^b	2.10	2.40	
[Cu(L ₇ -Et)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.09	2.34	0.0164
[Cu(L ₇ -Pr)(H ₂ O)(OCIO ₃)] [ClO ₄]	2.08	2.33	0.0163

^a All spectra run at 77 K in frozen acetone solution except as noted below. ^b Spectrum run on crystalline material. ^c Spectrum run in frozen acetonitrile solution.

and have more than one Cu-S bond. The C-S-C angle is seen to be fairly constant (100–107°) while the Cu-S-C angles vary considerably. Also listed is the sum of the differences of the two Cu-S-C angles from the tetrahedrally ideal 109.6°. This sum is taken as a measure of how far the sulfur-bonding lone pair deviates from collinearity with the Cu-S vector. With only one minor exception the longest Cu-S distance in a particular compound correlates with the largest deviation. Between the different compounds the correlation is also quite good, but other factors contribute. The present complex, [Cu(L₁-Pr)]⁺, has the largest deviation yet reported. This arises from the very small Cu-S-C angles (89.6 (2) and 92.0 (2)°) and correlates with the twist conformation of the six-membered chelate rings. By contrast, the copper(II) complex has one twist conformation with a Cu-S-C angle of 95.4 (3)° and one pseudoboat configuration with a Cu-S-C angle of 107.6 (3)°. Such an orientation effect of a lone pair on sulfur with respect to the metal-sulfur vector suggests a subtle way that a protein might influence methionine ligation. Another factor that probably contributes to the long Cu(I)-S bond is the less than ideal stereochemistry at copper. Three-coordinate d¹⁰ systems prefer trigonal sp² hybridization. T-shaped coordination probably offers rather little stabilization of copper over the dominant sp linear hybridization. A long middle bond in a T-shaped Cu(I) structure has also been observed to an oxygen donor.⁴⁰

Since the Cu-S bond to methionine in plastocyanin at neutral pH is believed to be extremely long in both oxidation states (~2.9 Å),⁷ there appears to be a very large protein constraint upon bond length, increasing it above its intrinsic value by ~0.5 Å. It has been noted^{20,45} that long Cu(II)-S bonds (2.47–2.82 Å) are intrinsic to *apical* thioether ligation in tetragonal copper(II) complexes, but, presently, it seems rather artificial to consider methionine an apical ligand in plastocyanin. Only in the three-coordinate, low pH form of plastocyanin in the copper(I) oxidation state does the methionine Cu-S bond (2.5 Å)⁷ approach the range of normal complexes. A possible model for a large protein constraint is presented by the copper(I) complex of 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane, where ligand constraints seem to prevent a copper(I)-thioether approach of closer than 2.9 Å.⁴⁶ This situation for copper proteins is in marked contrast to that for the hemoproteins where there is still no definitive

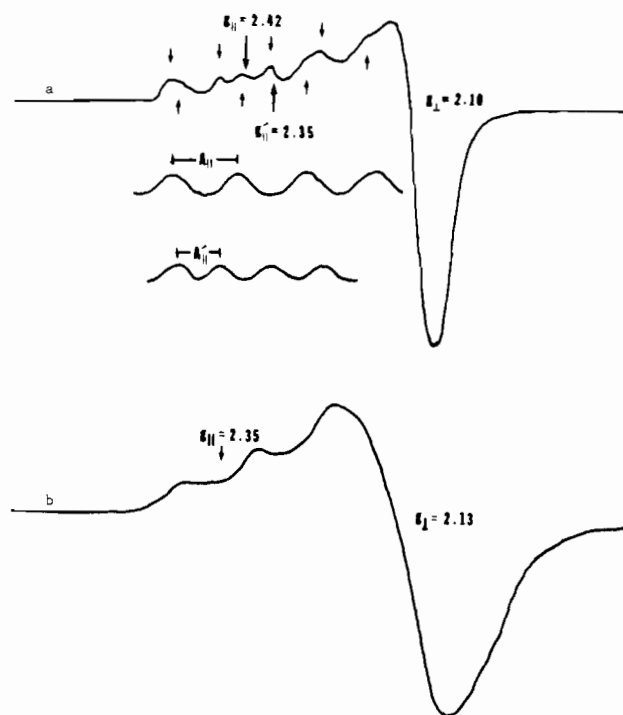


Figure 9. Representative EPR spectra of the copper(II) complexes (a) [Cu(T₁-Pr)(H₂O)(OCIO₃)] [ClO₄] (apparently having two distinct but similar structures) and (b) [Cu(L₄-Pr)(H₂O)(OCIO₃)] [ClO₄].

evidence for metrically significant protein constraints upon iron-ligand bond lengths.⁴⁷

EPR Spectra. Table XVI lists the EPR parameters for a representative group of copper(II) complexes. A typical axial spectrum ($g_{\parallel} > g_{\perp}$) is observed for all the benzimidazole thioether complexes L₁-L₇ indicative of approximate tetragonal stereochemistry (see Figure 9). The relatively large values of g_{\parallel} and A_{\parallel} are typical of tetragonal N- and O-donor complexes⁴⁸ so that any decrease that might be expected from the presence of an S donor²² is apparently too small to observe. Stereochemistry, rather than ligand type, is probably the major determinant of the EPR parameters in these complexes. The spectra of the tripod ligand complexes (T) are also of the axial type, but the appearance of two g values (see Figure 9) indicates that two different species are present in frozen solution. Since the A_{\parallel} values are in the range observed for the tetragonal L-type ligand systems, and since the spectra are quite unlike those of trigonal-bipyramidal complexes with related symmetrical tripod ligands where a "reverse axial" spectrum ($g_{\perp} > g_{\parallel}$) is observed,²⁸⁻³⁰ we tentatively assign five-coordinate distorted tetragonal-pyramidal structures to the T-type ligand complexes also. A mixture of four- and five-coordinate species is equally possible. Finally, the copper(II) chloro complexes with ligands L₅-Pr and L₆-Pr show simple axial spectra with no detectable hyperfine splitting. On this basis we tentatively assign them dichloro-bridged dimeric structures with five-coordinate pseudotetragonal stereochemistry about copper.

Copper(II) Electronic Spectra. Comparison of the UV-vis spectra of the copper(II) complexes of the all-benzimidazole T ligands with those of the mixed benzimidazole/thioether L ligands allows an empirical assignment of the major absorption maxima. Thus, from Figure 10 and the data in Table II it can be seen that all the thioether-ligated complexes (L₁-L₇) have an intense band (ϵ 760–2610) in the region 325–380 nm that is absent in the non-thioether-containing complexes. Its

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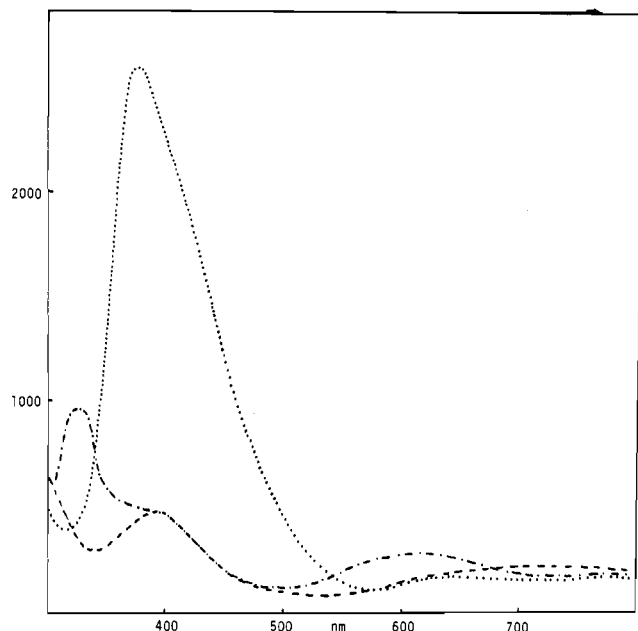


Figure 10. Representative UV-vis spectra of the copper(II) complexes (—) $[\text{Cu}(\text{L}_7\text{-Pr})(\text{H}_2\text{O})(\text{OClO}_3)]^+$, (---) $[\text{Cu}(\text{T}_1\text{-Pr})(\text{H}_2\text{O})(\text{OClO}_3)]^+$, and (-·-·) $[\text{Cu}(\text{L}_5\text{-Pr})(\text{H}_2\text{O})(\text{OClO}_3)]^+$.

assignment to $\sigma(\text{S}) \rightarrow d_\sigma$ charge transfer is consistent with similar empirical assignments (320–390 nm) for mixed-ligand N,S thioether complexes.^{19–21,49} The most flexible thioether ligand L_7 (having three methylene groups ($n = 3$) in Figure 7) has the most intense band consistent with the least constrained Cu–S σ overlap. In tetrakis(thioether)copper(II) complexes¹⁸ this band is somewhat red shifted in energy to ~ 400 nm, and its assignment is supported by a resonance Raman excitation profile.⁵⁰ The methionine $\sigma(\text{S}) \rightarrow \text{Cu}$ transition (written $\sigma(\text{S}^*) \rightarrow d_{x^2-y^2}$) in oxidized azurin and plastocyanin has been assigned near 560 nm (ϵ 500–1100) by analogy to the celebrated cysteine $\sigma(\text{S}) \rightarrow d_{x^2-y^2}$ transition.⁵¹ Although such a large red shift from the present range of complexes could possibly arise from the atypical stereochemistry of the blue copper site, it has not yet been modeled. Rather, the assignment itself has been questioned.^{20,52}

The all-benzimidazole T ligand complexes of copper(II) show a band of moderate intensity ($\epsilon \sim 400$) near 400 nm. The same band appears as a shoulder or a broadening on the low-energy side of the aforementioned $\sigma(\text{S}) \rightarrow d_\sigma$ LMCT transition in all of the mixed benzimidazole/thioether complexes. Figure 10 shows some representative spectra. Assignment of this ~ 400 -nm band is made to a benzimidazole $\pi(\text{N}) \rightarrow d_\sigma$ charge-transfer transition following recent detailed work where ~ 300 nm is considered one of the diagnostic regions for tetragonally coordinated imidazole-copper LMCT bands.⁵³ The lower energy of this transition in our complexes is consistent with an easier oxidation of benzimidazole compared to that of imidazole. Similarly, where comparisons are possible (e.g., L_5 and L_6), the ring-methylated benzimidazoles have lower energy bands (~ 425 nm) than unsubstituted benzimidazoles (~ 400 nm) consistent with electron-donating

methyl groups increasing the ease of formal oxidation.

Finally, all complexes have two bands (or one broad asymmetric band) in the 610–800-nm visible region of weak intensity (ϵ 40–300) assignable to d–d transitions.^{1,49} As expected for ligand field bands, there is negligible effect on the energies of these bands as the degree of alkyl substitution on the benzimidazole changes. One of the assignments is, however, tentative because of the possibility¹⁹ that a weak thioether $\pi(\text{S}) \rightarrow d_\sigma$ LMCT transition could also appear in this region. Unusually intense $\pi(\text{S}) \rightarrow d_\sigma$ transitions are evident at ~ 560 nm in polythioether complexes.⁵⁰ Resolution of this problem awaits the synthesis of a series of ligands that are isostructural to the L_1 – L_7 ligands but that replace the sulfur with oxygen- and nitrogen-donor atoms.

Conclusion

The structural comparison of a redox pair of copper complexes reveals how the intrinsic structural preferences of copper(I) and copper(II) are manifest within the constraints of a chelating bis(benzimidazole) ligand. The three-coordinate copper(I) species suggests that with biologically relevant ligands, focus should be placed on low rather than high coordination numbers for copper(I). The present structure determinations also help to establish the range of bond lengths expected for copper proteins if such bonds are unconstrained. Comparison with currently available imidazole Cu–N and thioether Cu–S distances in copper proteins highlights the long copper to methionine distance reported for plastocyanin. As with methionine binding to iron(III) in cytochrome c^{54} there does not appear to be any intrinsic reason why good thioether binding should not be observed in copper proteins. We have found evidence that the orientation of the bonding lone pair on sulfur can significantly affect the Cu–S distance, but it is most unlikely that this alone can explain the very long distance (2.9 Å) in neutral pH plastocyanin. The possibility that it may arise from its pseudoaxial position with respect to the $d_{x^2-y^2}$ ground state^{20,52} has yet to be tested in model compounds. Intrinsic differences in bond lengths between copper(I) and copper(II) are relatively small (≤ 0.2 Å), and although these are greater than those for iron in cytochromes,⁵⁴ they do not particularly support the case for significant intrinsic Franck-Condon barriers to electron transfer. Moreover, there is little support for the expectation⁵⁵ that Cu–S bond lengths will be predictably sensitive to the oxidation state of copper. Finally, some of the synthetic advantages of benzimidazole ligation may be helpful in attaining the elusive⁵⁶ but desirable⁵⁷ goal of synthesizing a true synthetic analogue of a blue copper protein. Related ligands have already provided useful models for deoxyhemocyanin³² and oxidized hemocyanin.⁵⁸

Acknowledgment. We are indebted to Professor Robert Bau and his students for sharing their expertise and facilities to enable us to carry out the X-ray structure determinations. Professors Keith Hodgson, Jan Reedyk, Hans Freeman, and Dr. Nigel Larsen very kindly supplied preprints of their work, and financial support was provided by the National Science Foundation (Grant CHE 78-09813). J.V.D. was the recipient of a Sigma Xi Research Award.

Registry No. $[\text{Cu}(\text{L}_1\text{-Pr})][\text{BF}_4]$, 70814-12-9; $[\text{Cu}(\text{L}_3)(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$, 80583-94-4; $[\text{Cu}(\text{L}_5\text{-Pr})(\text{H}_2\text{O})(\text{OClO}_3)][\text{ClO}_4]$, 80583-96-6; $[\text{Cu}(\text{L}_5\text{-Pr})(\text{H}_2\text{O})(\text{FBF}_3)][\text{BF}_4]$, 80584-47-0; $[\text{Cu}(\text{L}_5$

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Pr)Cl]₂[Cl]₂, 80583-97-7; [Cu(L₆-Pr)(H₂O)(FBF₃)] [BF₄], 80584-45-8; [Cu(L₆-Pr)Cl]₂[Cl]₂, 80593-39-1; [Co(L₆-Pr)(H₂O)(OCIO₃)] [ClO₄], 80584-02-7; [Cu(L₇-Et)(H₂O)(OCIO₃)] [ClO₄], 80584-04-9; [Cu(T₁)(H₂O)(OCIO₃)] [ClO₄], 80584-43-6; [Cu(T₁-Pr)(H₂O)(OCIO₃)] [ClO₄], 80593-67-5; Cu^I(L₅-Pr)Cl, 80583-98-8; [Cu^I(L₅-Pr)] [BF₄], 80584-00-5; [Cu^I(L₆-Pr)] [BF₄], 80584-06-1; L₄, 80583-50-2; L₄-Pr, 80572-94-7; L₅, 33007-61-3; L₅-Pr, 80572-95-8; L₆, 80572-96-9; L₇, 80572-97-0; L₇-Et, 80572-98-1; L₇-Pr, 80572-99-2; T₁, 80573-00-8; T₂, 80573-01-9; dinitro-3,4,5,6-tetramethylbenzene,

18801-63-3; pentamethylbenzene, 700-12-9; thiodipropionic acid, 111-17-1; phenylenediamine, 95-54-5; 2-methylpropanetricarboxylic acid, 1590-02-9.

Supplementary Material Available: Tables VI and X giving observed and calculated structure factor amplitudes (×10) and Tables V and IX giving anisotropic thermal parameters for the copper(II) and copper(I) structures, respectively (96 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Manchester University, Manchester M13 9PL, England, and the Inorganic Chemistry Institute, University of Göttingen, 3400 Göttingen, West Germany

Preparation and Crystal Structure of Tetracopper(I) Tetrakis(6-methyl-2-oxypyridine), [Cu₄(mhp)₄]

MADELEINE BERRY,^{1a} WILLIAM CLEGG,^{*1b} C. DAVID GARNER,^{*1a} and IAN H. HILLIER^{1a}

Received July 22, 1981

Sodium 6-methyl-2-oxypyridine, Na(mhp), reacts with copper(I) trifluoroacetate in ethanol to produce the tetrameric complex [Cu₄(mhp)₄], the structure of which has been determined by X-ray diffraction. Crystals are monoclinic, of space group P2₁, with *a* = 7.499 (2) Å, *b* = 14.572 (3) Å, *c* = 12.210 (3) Å, β = 107.61 (2)°, and *Z* = 2. The final *R* is 0.0297 for 2199 unique diffractometer-measured reflections. The copper atoms in the molecule form a puckered square, each edge of which is bridged by a single mhp ligand. The Cu...Cu edges range from 2.656 (1) to 2.709 (1) Å.

Introduction

The mhp anion (Hmhp = 6-methyl-2-hydroxypyridine) has been introduced in recent years as a bridging ligand for metal-metal-bonded dimers of the type [M₂(mhp)₂]. It belongs to the class of ligands which, by virtue of their electronic and steric properties, promote extremely short quadruple bonds between metal atoms of the group 6 triad (Cr, Mo, W).² Very short separations between pairs of metal atoms are also observed in the corresponding complexes of ruthenium,³ rhodium,^{4,5} and palladium,⁶ in which the formal metal-metal bond orders are considered to be 2, 1, and 0, respectively. In all these complexes, the four bridging mhp ligands are arranged with M-N and M-O bonds each trans to their own kind, so that the overall molecular symmetry approximates closely to *D*_{2d}. In the case of rhodium, apart from this 2:2 ligand arrangement, a 3:1 arrangement is possible, such that the rhodium atom bonded to three mhp oxygen atoms also takes up an axial ligand approximately collinear with the Rh-Rh bond.^{5,7} Mixed-ligand complexes of rhodium have also been prepared, containing both mhp and acetate bridges, the total number of bridging ligands being always 4.⁵

The mhp anion can also act as a bidentate ligand to a single metal atom⁸ and, in a protonated form, as an unidentate ligand.⁷

We now report the preparation and crystal structure determination of the tetrameric copper(I) complex [Cu₄(mhp)₄], in which pairs of copper atoms are spanned by *single* mhp bridges.

Experimental Section

Preparation of [Cu₄(mhp)₄]. Sodium (0.219 g, 9.5 mmol) was dissolved in ethanol (AnalaR grade). Hmhp (1.039 g, 9.5 mmol) was added, followed by copper(I) trifluoroacetate (1.682 g, 9.5 mmol in terms of the monomeric formula). A white precipitate formed almost immediately. The reaction mixture was stirred at room temperature for 1 h and then evaporated to dryness. Extraction with CH₂Cl₂ (50 mL) gave a pale yellow solution, which was reduced to a small volume by pumping. Addition of pentane afforded pale yellow flat needles, suitable for X-ray crystallographic investigation; yield 1.40 g, 86%. Anal. Calcd for C₂₄H₂₄N₄O₄Cu₄: Cu, 42.0; H, 3.5; N, 8.2; Cu, 37.0. Found: C, 42.0; H, 3.5; N, 7.9; Cu, 37.5. The compound is somewhat air sensitive.

Spectra. Mass spectra were recorded on an AEI MS 30 instrument using a 70-eV electron beam to produce ionization and fragmentation. ¹H NMR spectra (90 MHz) were recorded, for CDCl₃ solutions at room temperature, with a Perkin-Elmer R32 spectrometer.

Crystal Structure Determination. A crystal of dimensions 0.27 × 0.33 × 0.15 mm³ (cut from a needle) was mounted in a glass capillary tube. All crystallographic measurements were made at room temperature, with a Stoe-Siemens AED diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Unit cell dimensions were obtained from 40 automatically centered strong reflections with 20 < 2θ < 25°. The cell is monoclinic, with *a* = 7.499 (2) Å, *b* = 14.572 (3) Å, *c* = 12.210 (3) Å, β = 107.61 (2)°, and *V* = 1271.7 Å³; *Z* = 2 for the formula Cu₄(mhp)₄, *D*_{calcd} = 1.688 g cm⁻³, and μ = 33.5 cm⁻¹. The compound's air sensitivity and ready solubility in a range of organic solvents precluded the accurate measurement of its density.

Intensities were measured in the θ/ω scan mode by a profile-fitting procedure.^{9,10} From 2532 reflections with 2θ_{max} = 50°, *h* ≥ 0 and *k* ≥ 0, 2199 unique data with *I* > 2σ(*I*) were obtained after *Lp* and absorption corrections were applied and were used for structure solution

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- (10) Computer programs used in this study were written by G. M. Sheldrick (SHELXTL system; Göttingen, F.R.G.) and W. Clegg (diffractometer control program) for the Data General Eclipse S250 computer.