

to be short and indicative of covalent bonding ($d(\text{T}-\text{D}) = 1.7 \text{ \AA}$ (Ir, Ru), $\sim 1.5 \text{ \AA}$ (Ni, Fe)), whereas the M-D distances were rather large and more typical for those in the ionic binary deuteride MD_2 . Thus, from a bonding point of view, one is led to consider the members of the M_2TH_n series as coordination compounds rather than as interstitial metal hydrides and to describe their structures as an array of divalent metal cations M^{2+} and complex anions TH_4^{4-} (T = Ni), TH_5^{4-} (T = Rh, Ir), or TH_6^{4-} (T = Fe, Ru). As pointed out previously¹ these complex anions appear to obey the 18-electron rule found for organometallic compounds, suggesting that the stability and maximal hydrogen content of this class of compounds are governed mainly by electronic factors. The discovery and properties of the new Fe-based representative Mg_2FeH_6 support this view. Its anion FeH_6^{4-} may be considered as a complex of low-spin t_{2g}^6 Fe(II) with six hydrido ligands and would be expected to have octahedral symmetry and a diamagnetic ground state, in agreement with the experimental data.

The Mg-D distances in Mg_2FeD_6 ($d(\text{Mg}-\text{D}) = 2.27 \text{ \AA}$) are close to those in β' - $\text{Mg}_2\text{NiD}_{3,9}$ (2.31 \AA at 280°C),¹ and they are both considerably greater than those in MgD_2 (1.95 \AA).²² These findings are consistent with the assumption of a more ionic character of the Mg-D bonds in the former compounds, as compared to that in MgD_2 . A Mg-H-Fe bridge bonding system similar to that found in BeH_2 or $\text{Al}(\text{BH}_4)_3$ can be excluded.

Octahedral coordination of Fe by hydrogen was also reported recently in $\text{FeH}_6\text{Mg}_4\text{X}_4(\text{THF})_8$ (X = halogen).¹⁸ The hydrido anion FeH_6^{4-} in this compound is surrounded by four Mg atoms which cap the faces of the H atom octahedron in a tetrahedral configuration. In Mg_2FeH_6 , by comparison, all octahedral faces are capped by Mg atoms which form a cubic configuration (Figure 3). The metal-hydrogen distances are

similar in both compounds ($\text{FeH}_6\text{Mg}_4\text{X}_4(\text{THF})_8$): $\bar{d}(\text{Fe}-\text{H}) = 1.69 \text{ \AA}$, $\bar{d}(\text{Mg}-\text{H}) = 2.06 \text{ \AA}$.

Finally we note that the hydrogen-to-metal weight ratio of Mg_2FeH_6 (5.4 wt %) is about 50% higher than that of Mg_2NiH_4 (3.6 wt %) and approaches that of MgH_2 (7.6 wt %). Moreover, its hydrogen content per unit volume (9.1×10^{22} atoms/cm³) exceeds by far those of Mg_2NiH_4 (5.4×10^{22}) and MgH_2 (6.5×10^{22}) and also those of the other known hydrogen storage media. With respect to thermal stability, Mg_2FeH_6 appears to be less promising for energy storage applications, mainly because of its high enthalpy of dissociation ($\Delta H_{\text{dis}} = 98 \text{ kJ/mol}$ of H_2), which exceeds those of Mg_2NiH_4 (64 kJ/mol of H_2)²³ and MgH_2 (74 kJ/mol of H_2).²²

In conclusion, we have prepared and characterized a new Fe-based ternary metal hydride having a favorable hydrogen-to-metal weight ratio and an exceptionally high density of hydrogen per unit volume. Structural analysis (X-ray and neutron powder diffraction) and spectroscopic measurements unambiguously indicate an octahedral H atom configuration for the Fe atoms in the crystal. The Mössbauer and infrared spectra of the compound are consistent with the presence of low-spin iron(II). No indication for a significant H deficiency or a homogeneity range could be detected within experimental error.

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Contribution from the Departments of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, and University of Virginia, Charlottesville, Virginia 22901

Spectroscopy and Structure of Thiolate and Thioether Complexes of Copper(II) and the Relationship of Their Redox Chemistry to That of Certain Copper Proteins

ANTHONY W. ADDISON,*^{1a} T. NAGESWARA RAO,^{1a} and EKKEHARD SINN^{1b}

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Several complexes of copper and zinc(II) have been synthesized, with use of multidentate ligands entailing thiolate, phenolate, imine, and thioether donor atoms. The thioethers include tridentate and linear and macrocyclic tetra- and pentadentate ligands. The copper(II) complex of L-2, a potential N_2S (pyridyl, imine, thioether) donor, crystallizes in the space group $P2_1/c$, with cell constants $Z = 4$, $a = 9.212(7) \text{ \AA}$, $b = 14.439(6) \text{ \AA}$, $c = 15.117(9) \text{ \AA}$, $\beta = 95.60(6)^\circ$, $V = 2001 \text{ \AA}^3$, and $\rho_{\text{calcd}} = 1.748 \text{ g}\cdot\text{cm}^{-3}$. The structure, refined to $R_w = 7.4\%$, contains elongated pseudooctahedral Cu(II) ions, with the slightly distorted equator occupied by an H_2O and the nitrogen and sulfur atoms of the tridentate ligand. Perchlorates are weakly bound on the axial positions. Electron spin resonance, optical absorption, and UV difference spectroscopy have been used to delineate the coordination of the thiolate and thioether complexes in the solid state and in nonaqueous solution. Binding of the terminal thioether donors in these oligodentate ligands is solvent dependent. Coordination is optimized in MeNO_2 , but in certain of the complexes, the thioether sulfur is noncoordinated in dimethylformamide, where coordinative disproportionation occurs, as for $\text{Cu}(\text{L}-2)^{2+}$, which yields $\text{Cu}(\text{L}-2)_2^{2+}$. Monomeric thiolates have been prepared and characterized as having "normal" ESR parameters. The redox thermodynamics of the complexes has been examined by dc polarography and cyclic voltammetry. Most of the compounds generate stable Cu(I) states, the macrocyclic $\text{Cu}^1\text{N}_2\text{S}_2$ systems being notably so. The consequence of transforming a thiolato-copper complex to its thioether analogue is that the $E_{1/2}$ is elevated by about 0.5 V. This information is used to deduce the E° of a tetragonal $[\text{Cu}^1\text{N}_2\text{S}_2]^+$ moiety and thus comment on the possible roles of structural distortion and ligand transmutation at the type-1 active sites of copper proteins.

Introduction

Copper-sulfur interactions have attracted attention for some time, originally because of the intense colors associated with such systems^{2,3} and, more recently, because of the chain of

logic⁴⁻⁷ leading to the confirmation of cysteine thiolate and methionine thioether sulfur as active-site ligands to pseudo-

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tetrahedral copper in three copper proteins.⁸⁻¹⁰ This last factor has greatly stimulated research activity in the areas of copper-thiolate¹¹⁻²² and copper-thioether^{16,23-33} coordination chemistry.

Although small-molecule (thiolato)copper(II) compounds (particularly those with alkanethiolates) tend to exhibit redox instability with respect to copper(I) and disulfide or higher oxidation products,²² there are stable copper(II) thiolate systems known. Some of these have apparently fortuitous stability, but various tactics have been adopted for the synthesis of redox-stable systems. These stratagems include (a) delocalization of cationic charge over polynuclear mixed-valence clusters,²¹ (b) introduction of multiple-bond character at the donor sulfur,^{14,18,34-37} (c) imposition at the metal of stereo-

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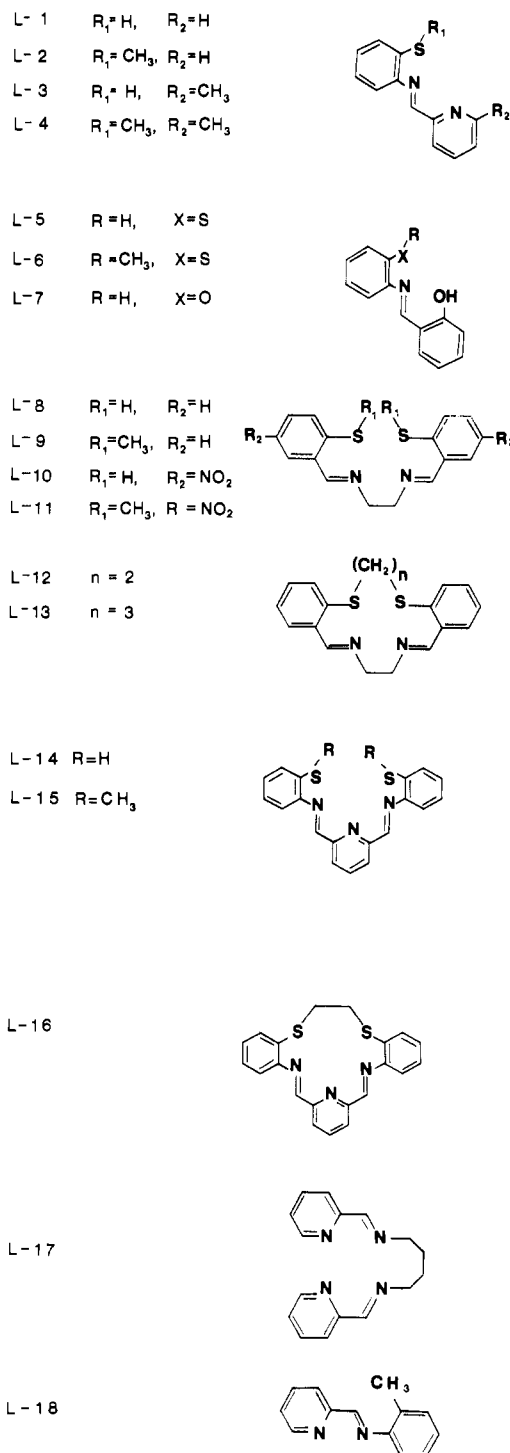


Figure 1. Ligands involved in this study. The thiolate and phenolate units are coordinated in the deprotonated form.

chemistry that favors the +2 oxidation state,^{16,38} and (d) the use of appropriate substituents on the thiol ligand.^{19,20,37,38} Kinetic barriers against the redox process have been erected by (e) performing experiments under cryogenic conditions^{14,19} and (f) sterically hindering the thiol, or otherwise hindering formation of the dimeric cis-bridged redox-complementary Cu^{II}₂(SR)₂ kinetic intermediate.^{16,19,38,39}

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We report here on part of a systematic study of the properties of various copper-thioether interactions and, by direct comparisons between the chemistry of thiolate complexes and that of their thioether analogues, draw conclusions regarding the properties of copper(II) thiolates in general. The copper complexes described herein have been constructed with use of the chelating ligands depicted in Figure 1.

Experimental Section

(1) Syntheses. (a) Reagents. All reagents were used as supplied by Aldrich, Fisher, and Eastman Kodak. The ligands L-1,^{12,40} L-3,⁴¹ L-4,⁴² L-5,⁴³ L-8,^{18,44} and L-10⁴⁵ were prepared according to procedures described in the literature. L-6, L-12, L-13, L-16, L-17,⁴⁶ and L-18 were not isolated as pure compounds but prepared and used in situ for the synthesis of their copper complexes. Analytical data for the ligands are given in Table VIII (supplementary material).

(b) Ligands. The ligands L-2, L-9, L-11, and L-15 were prepared by condensation of the appropriate aldehyde and primary amine and isolated as crystalline solids. For L-9, *o*-(methylthio)benzaldehyde was synthesized by the method of Eistert et al.,⁴⁷ while for L-11 and L-15, 5-nitro-2-(methylthio)benzaldehyde⁴⁸ and pyridine-2,6-dialdehyde,⁴⁹ respectively, were prepared as starting materials.

(c) Metal(II) Complexes. Cu(L-5),⁴³ Cu(L-7),⁵⁰ Cu(L-8),¹⁸ and Cu(L-1)Cl⁵¹ were prepared as described in the literature. Analytical data for the complexes are in Table IX (supplementary material).

The complexes Cu(L-1)(ClO₄)₂·¹/₂H₂O, Cu(L-2)(ClO₄)₂·2H₂O, Cu(L-2)₂(ClO₄)₂, Cu(L-4)(ClO₄)₂·³/₂H₂O, Cu(L-4)₂(ClO₄)₂, Cu(L-15)(ClO₄)₂, and Zn(L-2)(ClO₄)₂ were prepared by combining appropriate (though not necessarily stoichiometric) amounts of ligand with the metal perchlorate in an appropriate solvent (usually methanol) and were isolated as pure solids and dried in vacuo over phosphorus(V) oxide.

Zn(L-1)(ClO₄) was prepared by a procedure similar to that described for the preparation of Zn(L-1)(CH₃COO).⁴²

Other complexes were synthesized by a template procedure, which involved refluxing the appropriate aldehyde and amine in an alcohol, followed by addition of hydrated copper(II) perchlorate and further refluxing. Cu(L-6)(ClO₄)₂ was prepared thusly, as were Cu(L-9)(ClO₄)₂ and Cu(L-13)(ClO₄)₂·¹/₂C₂H₅OH, the latter from 1,5-bis(2-formylphenyl)-1,5-dithiapentane, which was synthesized by a procedure analogous to that used for the synthesis of 1,4-bis(2-formylphenyl)-1,4-dithiabutane⁵² used for the preparation of Cu(L-12)(ClO₄)₂. For Cu(L-16)(ClO₄)₂, pyridine-2,6-dialdehyde⁴⁹ and 1,4-bis(2-aminophenyl)-1,4-dithiabutane⁵³ were used, while Cu(L-17)(ClO₄)₂ and Cu(L-18)(ClO₄)₂ were prepared with use of pyridine-2-aldehyde in combination with 1,4-diaminobutane and *o*-toluidine, respectively.

(d) Bipyridyl Adducts. The bipyridyl adducts of the 1:1 complexes of copper(II) with L-1, L-2, and L-4 through L-7 inclusive were prepared by refluxing the complexes in an appropriate solvent with the stoichiometric amount of 2,2'-bipyridyl (bpy). Most crystallized when the solvent was evaporated to a small volume and were washed with methanol and dried over P₄O₁₀ in vacuo.

For [Cu(L-7)(bpy)], warm pyridine was used as solvent and was (rotary) evaporated off to give a slurry of brown crystals, which

Table I. Crystal and Unit Cell Data for [Cu(L-2)(OH₂)](ClO₄)₂·H₂O

space group: $P2_1/c$ (monoclinic)
$Z = 4$
$a = 9.212$ (7) Å
$b = 14.439$ (6) Å
$c = 15.117$ (9) Å
$\beta = 95.60$ (6) ^o
$V = 2001$ Å ³
$\mu(\text{Mo K}\alpha) = 15.6$ cm ⁻¹
CuCl ₂ SO ₁₀ N ₂ C ₁₃ H ₁₆ mol wt = 526.8
$\rho_{\text{calcd}} = 1.748$ g/cm ³
cryst dimens (centroid to named face, mm): (100) 0.37,
(010) 0.33, (001) 0.09, (100) 0.37, (010) 0.33, (001) 0.09
max, min transmission coeffs: 0.77, 0.52
$R = 6.3\%$
$R_w = 7.4\%$

dissolved on addition of methanol, the resulting solution then yielding green crystals, which were filtered off and dried in vacuo over phosphorus(V) oxide.

(e) Copper(II) Complex. For Cu^I(L-2)(bpy)(ClO₄) L-2 (0.22 g, 1 mmol), Cu^{II}(L-2)(bpy)(ClO₄)₂ (0.64 g, 1 mmol), and 2,2'-bipyridyl (0.15 g, 1 mmol) were dissolved in 50 mL of acetonitrile. An excess of copper powder was added, and after 18 h of refluxing under dinitrogen the copper powder was filtered off rapidly under dinitrogen and the deep brown solution was evaporated under dinitrogen to give reddish brown crystals, which were not of suitable habit for X-ray diffraction.

Attempts to prepare thioether-ligated copper(II) complexes with the ligands *N*-(*o*-(methylthio)phenyl)pyrrole-2-carboxaldimine or (methylthio)dibenzoylmethane were not successful. Neither the last compound nor *o*-tolualdehyde could be induced to form a stable Schiff base with ethylenediamine (with Cu²⁺ present). Attempts to isolate pure copper(II) complexes of L-3, L-10, and L-14 were also unsuccessful. More complete synthetic details are given in the appendix in the supplementary material.

(2) Physical Measurements. Electronic spectra were recorded on Cary-14 and Perkin-Elmer 320 spectrophotometers. Electron spin resonance (ESR) spectra were recorded on a Varian E-12 X-band spectrometer with diphenylpicrylhydrazyl as standard. g_0 and A_0 were measured at ambient temperature and g_{\parallel} , A_{\parallel} , and g_{\perp} (estimated from the center of the N shf) at 77 K. Second-order corrections⁵⁴ were applied to the resonance fields of the transitions used to compute g_0 and to all parameters in the ESR spectra simulated with use of the SIM-14 program.⁵⁵ Magnetic susceptibility was performed by Dr. A. B. P. Lever, at York University.

Proton NMR spectra were obtained at ambient temperatures with a JEOL FX-90Q instrument, chemical shifts being quoted as δ values with respect to tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan 4000 GC-MS. Elemental microanalyses were performed by Canadian Microanalytical Service Ltd. (Vancouver, Canada) and Galbraith Laboratories. Electrochemistry was performed at 25 ± 0.5 °C in solutions deoxygenated by bubbling argon, with a PAR-173 potentiostat incorporating a PAR-176 i/E converter. Voltammetric data were recorded on a Nicolet digital oscilloscope or an X-Y recorder. Rotating-disk electrodes (RDE's) for dc polarography were of platinum (RPE, 0.300 cm²), or mercury-coated gold amalgam (0.289 cm²), while for cyclic voltammetry, platinum sphere and horizontal disk electrodes were used. Tetraethylammonium perchlorate (G. F. Smith polarographic grade) was recrystallized from water and dried over P₄O₁₀ in vacuo before being used as the supporting electrolyte. The solvents DMF (dimethylformamide), MeCN, and MeNO₂ were purified by electrochemistry by distillation under dinitrogen (MeNO₂), off P₄O₁₀ under dinitrogen (MeCN), or under vacuum off calcium(II) hydride (DMF).

Kinematic viscosities were determined at 25 °C by Ubbelohde viscometry. The viscosities and densities measured for 0.1 M NET₄ClO₄ solutions in the three electrochemistry solvents were [solvent (η , in g/(cm s); ρ , in g/mL)]: MeCN (0.0038, 0.785), MeNO₂ (0.0065, 1.13), DMF (0.00865, 0.950). The 2 σ limits on the η values are ±0.0002 g/(cm s).

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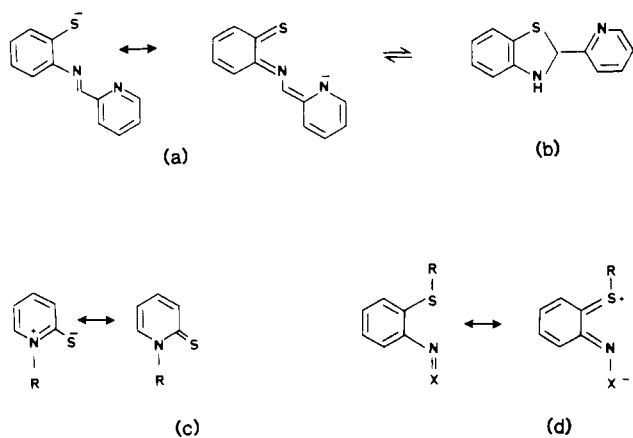


Figure 2. Tautomerism (b) and resonance (a, c, d) in N/S ligands.

(3) **Crystallographic Data Collection and Structure Analysis.** Cell dimensions and space group data (Table I) for a single deep green crystal of $\text{Cu(L-2)(ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ were obtained by standard methods on an Enraf-Nonius CAD-4 four-circle diffractometer. The θ - 2θ scan technique was used, as previously described,⁵⁶ to record the intensities for all nonequivalent reflections for which $1^\circ < 2\theta < 54^\circ$. Scan widths were calculated as $A + B \tan \theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to $K\alpha_1$ - $K\alpha_2$ splitting. The values of A and B were 0.6 and 0.35, respectively.

The intensities of three standard reflections showed fluctuations during the data collection no greater than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 4595 independent intensities, there were 3195 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.⁵⁷ These data were used in the final calculation of the structural parameters.

A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.⁵⁶ Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for four least-squares cycles and then held fixed.

The model converged to yield a featureless final Fourier difference map. Listings of the observed and calculated structure factors and calculated anisotropic thermal parameters and least-squares planes are available as supplementary material. The principal programs used are those described previously.⁵⁶

Table II contains the final positional parameters for the refined atoms of $\text{Cu(L-2)(ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. Standard deviations in the least significant figures in the tabulated parameters were derived from the inverse matrix in the course of least-squares refinement calculations.

Results and Discussion

Synthetical Aspects. Certain of the ligands have been used previously for the formation of isolable copper(II) complexes.^{12,18,37,42,46,50,51} However, the results for the thiolates have often been complicated by the formation of polynuclear or nonstoichiometric compounds.^{12,13,21} In addition, ligands of the L-1 type (Figure 1) equilibrate between the imino-thiol and benzothiazoline tautomers (Figure 2a,b). For the majority of metals, the ring-opened imino-thiolate form is stabilized by coordination.^{40,58,59} In contrast to that of alkanethiolates, arenethiolate anionic charge can presumably be effectively delocalized by conjugation, particularly in systems like L-1. This corresponds to the introduction of double-bond character into the C-S linkage (Figure 2a), a situation of

Table II. Fractional Positional Parameters (and Their Standard Deviations) for the Atoms of $[\text{Cu(L-2)(OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

atom	x/a	y/b	z/c
Cu	0.18074 (9)	0.25775 (5)	0.15143 (5)
Cl(1)	-0.1531 (2)	0.2225 (1)	0.2564 (1)
Cl(2)	0.4141 (2)	0.2948 (1)	-0.0382 (1)
S	0.2752 (2)	0.1121 (1)	0.1874 (1)
O(W1)	0.2824 (5)	0.3235 (3)	0.2500 (3)
O(W2)	0.5452 (7)	0.3892 (5)	0.2167 (5)
O(1)	0.0021 (6)	0.2238 (6)	0.2605 (5)
O(2)	-0.2126 (6)	0.2338 (4)	0.1671 (3)
O(3)	-0.1999 (7)	0.1383 (4)	0.2906 (4)
O(4)	-0.2015 (7)	0.2939 (5)	0.3089 (4)
O(5)	0.3778 (6)	0.2967 (6)	0.0491 (4)
O(6)	0.5002 (9)	0.2191 (5)	-0.0523 (6)
O(7)	0.2812 (6)	0.2904 (4)	-0.0967 (3)
O(8)	0.4859 (7)	0.3768 (5)	-0.0552 (5)
N(1)	0.0466 (5)	0.3612 (3)	0.1098 (3)
N(8)	0.0883 (5)	0.1971 (3)	0.0459 (3)
C(2)	-0.0456 (6)	0.3343 (4)	0.0388 (4)
C(3)	-0.1614 (7)	0.3887 (5)	0.0061 (4)
C(4)	-0.1825 (7)	0.4733 (5)	0.0462 (5)
C(5)	-0.0869 (8)	0.5006 (5)	0.1164 (5)
C(6)	0.0275 (8)	0.4425 (5)	0.1460 (5)
C(7)	-0.0157 (7)	0.2426 (4)	0.0032 (4)
C(9)	0.1397 (6)	0.1106 (4)	0.0177 (4)
C(10)	0.2366 (6)	0.0641 (4)	0.0808 (4)
C(11)	0.2961 (7)	-0.0199 (5)	0.0575 (5)
C(12)	0.2621 (8)	-0.0552 (5)	-0.0273 (5)
C(13)	0.1690 (8)	-0.0094 (5)	-0.0869 (5)
C(14)	0.1052 (7)	0.0742 (5)	-0.0658 (4)
C(15)	0.4719 (8)	0.1225 (6)	0.1987 (6)
H(3)	-0.218 (7)	0.366 (5)	-0.054 (4)
H(4)	-0.248 (10)	0.514 (7)	0.015 (6)
H(5)	-0.104 (10)	0.557 (6)	0.144 (6)
H(6)	0.082 (8)	0.456 (5)	0.195 (5)
H(7)	-0.070 (7)	0.225 (4)	-0.060 (4)
H(11)	0.345 (7)	-0.050 (5)	0.099 (4)
H(12)	0.286 (9)	-0.111 (6)	-0.042 (6)
H(13)	0.135 (9)	-0.034 (6)	-0.146 (6)
H(14)	0.051 (8)	0.108 (5)	-0.115 (5)
H(15 1)	0.501 (10)	0.058 (7)	0.223 (6)
H(15 2)	0.505 (11)	0.176 (7)	0.259 (7)
H(15 3)	0.509 (10)	0.128 (6)	0.159 (6)
H(W11)	0.329 (8)	0.344 (5)	0.257 (5)
H(W12)	0.276 (9)	0.297 (6)	0.311 (5)
H(W21)	0.522 (5)	0.395 (4)	0.253 (3)
H(W22)	0.537 (8)	0.444 (5)	0.163 (5)

which the *N*-alkylpyridine-2-thiones (Figure 2c) are more extreme examples.³⁷ A study of the electronic consequences of such effects has been made.³⁵ The response of thioether sulfur to such conjugative influences (Figure 2d) is qualitatively similar,⁶⁰ though perhaps less in intensity. Nonetheless, the electronic consequences of S methylation of arenethiolates presumably parallel those in alkanethiolate chemistry.

Several of the ligands reported here are novel; their characteristic properties and those of the new complexes that were prepared are listed, along with their elemental analyses, in the supplementary material. The complexes' syntheses are not without some complications, associated with coordinative disproportionation of certain of the thioether complexes and autoredox reactions involving the thiols. The former situation could to some extent be controlled by appropriate choice of solvent, while this and also the latter problem was most often overcome by the simple expedient of maintaining a large excess of copper(II) over the ligand present during the synthesis.

The constitutions of the coordination spheres are to a large extent revealed by consideration of the spectroscopic data and its relationship to the structures of $\text{Cu(L-2)(ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and similarly N,S-ligated complexes.⁶¹⁻⁶³

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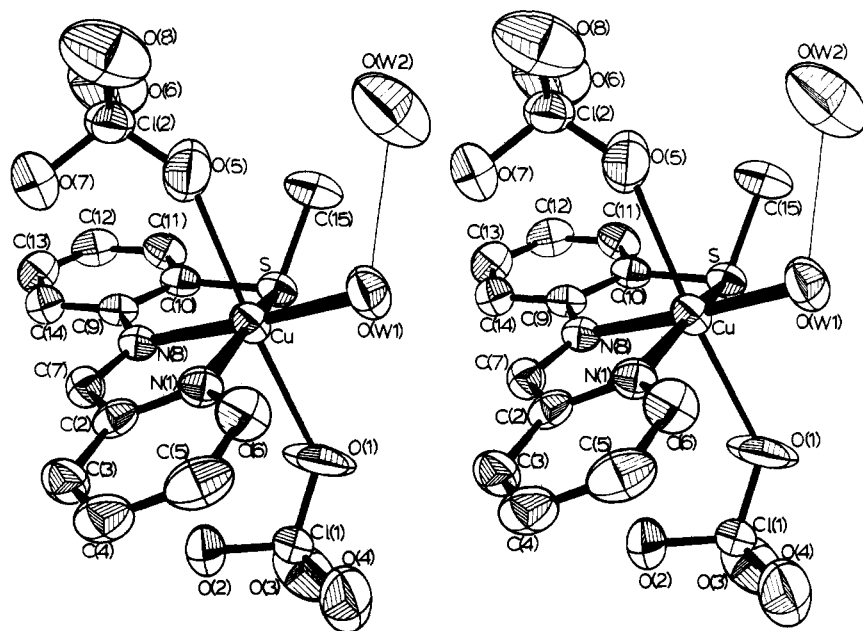


Figure 3. ORTEP stereoview of the complex coordination in $\text{Cu}(\text{L-2})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, with H atoms omitted for clarity of presentation.

Structure of the Copper Complex of L-2. The tridentate nature of the thioether L-2 in the solid state is indicated by Figure 3. The complex coordination consists of an N_2OS donor set in the equatorial plane of the copper(II), with the four positions occupied by the pyridyl nitrogen, the imine nitrogen, the thioether sulfur, and a water molecule's oxygen. The coordination is of the "4+2" type and thus belongs with the myriad of such Jahn-Teller-elongated pseudooctahedral examples. The axial donors are the two perchlorate oxygens, at an average of 2.535 Å (Table III). The equatorial water oxygen is bound 0.60 Å closer, and the nitrogens are similarly strongly bonded, the distances being close to those in $\text{Cu}(\text{cyclam})^{2+}$ complexes,³⁸ with the tridentate ligand's imino nitrogen slightly closer (by 0.06 Å) than the terminal pyridyl one. The Cu-S(thioether) bond length is typical of equatorially bound examples, lying in the lower third of the observed range of data.²⁷ The CuN_2OS core is not precisely planar, although the metal atom is in fact closer to the mean plane (0.06 Å displaced) than any of the remaining atoms (0.12–0.15 Å displaced). It may be more illuminating to characterize the CuN_2OS core as being very slightly tetrahedrally distorted. The least dihedral angle, ω , in this CuN_2OS core is 11.6°, between the $\text{SCuN}(8)$ and $\text{OCuN}(1)$ planes. This represents a 13% distortion of the N_2OS coordination plane toward the tetrahedral, which probably carries no great impact for the spectroscopic or redox properties of the complex. Along with this slight irregularity of the N_2OS plane, there is a twist in the ligand itself, the pyridine ring being rotated by 20.0° with respect to the benzene ring, of which twist 16° is localized about the aniline $\text{N}(8)\text{--C}(9)$ bond. As the five-membered chelate rings are fairly planar, we perceive the twisting distortions to arise from a ligand "bite" that is a little smaller than is ideal for the metal, so that the pyridyl $\text{N}(1)$ and the thioether S are forced apart on coordination.

The second water molecule (W2) in $\text{Cu}(\text{L-2})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ is not coordinated but is hydrogen bonded to the coordinated water (W1, Table III) and to perchlorate O(4) of an adjacent molecule. A less indirect intermolecular linkage is provided

Table III. Selected Distances (Å) and Angles (deg) in $[\text{Cu}(\text{L-2})(\text{OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and Their Standard Deviations (in Parentheses)

Cu-S	2.320 (1)	N(8)-C(7)	1.283 (4)
Cu-O(W1)	1.931 (2)	N(8)-C(9)	1.415 (4)
Cu-O(1)	2.490 (3)	C(9)-C(10)	1.410 (4)
Cu-O(5)	2.560 (4)	C(2)-C(7)	1.466 (4)
Cu-N(1)	2.000 (3)	O(W1)-O(W2)	2.693 (5) ^a
Cu-N(8)	1.943 (2)	O(W1)-O(7)	2.843 (5) ^b
S-C(10)	1.758 (3)	O(W2)-O(4)	2.940 (5) ^c
S-C(15)	1.810 (4)	C-H	0.96
N(1)-C(2)	1.358 (4)		
S-Cu-O(W1)	97.05 (8)	O(1)-Cu-N(1)	85.82 (10)
S-Cu-O(1)	85.62 (7)	O(1)-Cu-N(8)	100.96 (9)
S-Cu-O(5)	93.94 (8)	O(5)-Cu-N(1)	95.67 (11)
S-Cu-N(1)	163.01 (8)	O(5)-Cu-N(8)	83.27 (11)
S-Cu-N(8)	84.70 (8)	N(1)-Cu-N(8)	82.56 (10)
O(W1)-Cu-O(1)	83.56 (10)	Cu-S-C(10)	96.0 (1)
O(W1)-Cu-O(5)	92.23 (12)	Cu-S-C(15)	107.2 (2)
O(W1)-Cu-N(1)	96.54 (10)	C(10)-S-C(15)	103.4 (2)
O(W1)-Cu-N(8)	175.29 (11)	O-CI-O	109.5
O(1)-Cu-O(5)	175.68 (11)		

^a Symmetry transformation: x, y, z . ^b Symmetry transformation: $x, 1/2 - y, 1/2 + z$. ^c Symmetry transformation: $1 + x, y, z$.

by another H bond from the coordinated water (W1) to the perchlorate O(7) of an adjacent molecule.

On the basis of the structural results, we shall identify the complex as $[\text{Cu}(\text{L-2})(\text{OH}_2)](\text{ClO}_4)_2$ for succeeding discussion and draw analogies between it and the coordination spheres of other complexes. We now consider those aspects of the spectroscopy that are most germane to defining the solution coordination, to which the redox results in turn relate.

Coordination Constitution. (1) Thioether Complexes. Nitrogen donors generally tend to displace the weaker thioether from the equatorial plane.⁶³ We have therefore attempted to limit this study to 1:1 complexes of mostly planar tridentate and tetradentate ligands. Strong donor solvents may likewise be suspected of displacing the thioether, but other limitations placed on the solvent properties (e.g. UV transparency, electrochemical stability) have compelled us to use more than one solvent here. The various coordination equilibria in solution are exemplified well by $\text{Cu}(\text{L-2})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. In MeCN, there are two reduction processes, with $E_{1/2}$ values of +0.24 and 0.0 V at the RPE, for which the limiting currents (i_L) indicate division of the total copper into two species. If S

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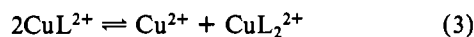
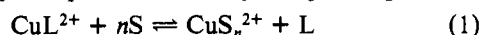
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Table IV. Electron Spin Resonance Data^a

compd	no.	medium ^b	g_{\parallel}	$-10^4 A_{\parallel}$	g_0	$-10^4 A_0$	g_{\perp}^c	$-10^4 A_{\perp}$
Cu(L-1)ClO ₄ ·0.5H ₂ O	1	DMF	2.186	172	2.096	70	2.05	20
		neat powder	2.148				2.03	
Cu(L-2)(ClO ₄) ₂ ·2H ₂ O	2	acetone/toluene	2.240	175	2.119	74	2.06	23
		MeNO ₂	2.188	179	2.105	76	2.06	24
		MeOH	2.246	173	2.121	68	2.06	16
		DMF ^{d,e} A	2.39	140				
		B	2.305	155				
		C	2.283	150				
Cu(L-2) ₂ (ClO ₄) ₂ ^d	3	MeNO ₂	2.202	190	2.110	62	2.06	-2
Cu(L-1)(bpy)ClO ₄	4	DMF	2.178	180	2.091	76	2.05	24
		neat powder	2.140				2.07	
Cu(L-2)(bpy)(ClO ₄) ₂	5	DMF	2.278	170	2.150	65	2.09	13
Cu(L-4)(ClO ₄) ₂ ·H ₂ O	6	acetone/toluene	2.267	159	2.133	65	2.07	18
Cu(L-4)(bpy)(ClO ₄) ₂ ·0.5H ₂ O	8	MeNO ₂	2.232	182	2.097	44	2.03	-25
Cu(L-5)	9	DMF	2.211	180	2.093	63	2.03	5
		pyridine	2.204	178	2.097	69	2.04	15
Cu(L-6)ClO ₄	10	MeNO ₂	2.236	187	2.097	81	2.03	28
Cu(L-5)(bpy)·H ₂ O	11	DMF	2.195	179	2.093	68	2.04	12
Cu(L-6)(bpy)ClO ₄ ·H ₂ O	12	DMF	2.278	170	2.122	64	2.04	12
Cu(L-9)(ClO ₄) ₂ ^d	15	MeNO ₂	2.161	180	2.083	80	2.04	30
		MeCN/DMF	2.39	140				
		MeCN/MeNO ₂	2.150	183				
		MeNO ₂ /MeOH ^f	2.168	183	2.084	77	2.04	24
		neat powder	2.160				2.07, 2.04	
Cu(L-11)(ClO ₄) ₂	16	MeNO ₂	2.204	192	2.087	78	2.03	21
		neat powder	2.160				2.05	
Cu(L-12)(ClO ₄) ₂	17	DMF	2.143	175	2.077	77	2.04	29
		neat powder	2.121				2.04	
Cu(L-13)(ClO ₄) ₂ ·0.5EtOH	18	DMF	2.159	188	2.088	75	2.05	18
		neat powder	2.111				2.06	
Cu(L-15)(ClO ₄) ₂ ·1.5H ₂ O	19	MeNO ₂	2.204	180	2.107	72	2.06	18
Cu(L-16)(ClO ₄) ₂	20	MeNO ₂	2.177	190	2.107	71	2.07	11
Cu(L-7)	24	pyridine	2.239	188	2.120	70	2.06	11
		neat powder	2.227	198			2.05	
Cu(L-1)Cl	25	DMF	2.172	174	2.084	80	2.04	33
Cu(L-17)(ClO ₄) ₂	26	DMF	2.246	182	2.135	60	2.08	-1
Cu(L-18) ₂ (ClO ₄) ₂	27	DMF	2.284	161	2.16 ^g	60 ^g		

^a Values determined as described in Experimental Section: $g_0, g_{\parallel}, \pm 0.003; g_{\perp}, \pm 0.01; A$ in $\text{cm}^{-1}, \pm 0.0003 \text{ cm}^{-1}$. ^b Neat powder spectra recorded at 77 K. ^c $g_{\perp} = (3g_0 - g_{\parallel})/2, A_{\perp} = (3A_0 - A_{\parallel})/2$. ^d Compound yields three species in DMF. ^e Lower precision than above, because of overlap of different species' resonances. ^f MeOH in excess. ^g Approximate values; poorly resolved spectrum.

represents a solvent molecule, and L represents the chelating agent, then any of equilibria 1–3 may be operating.⁶⁴



L' represents a ligand with "dangling" sulfur.⁶⁵ In MeCN, the $E_{1/2}$'s correspond to those for $\text{Cu}(\text{MeCN})_n^{2+}$ and $\text{Cu}(\text{L}-2)_2^{2+}$ and the two i_L values are the same, so that the coordinative disproportionation process (3) is inevitably indicated.

This disproportionation also occurs for the DMF solution, wherein both $[\text{Cu}(\text{L}-2)(\text{OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{L}-2)_2(\text{ClO}_4)_2$ give rise to three species, detected in the cryogenic ESR. One of these (A, Table IV) is DMF-solvated Cu^{2+} , while the other major species (C) has g_{\parallel} and A_{\parallel} values akin to the CuN_4 equatorial core of $\text{Cu}(\text{L}-17)_2^{2+}$ and can be assigned to a like $\text{Cu}(\text{L}-2)_2^{2+}$ species, with pyridyl nitrogens presumably mutually trans and the L-2 ligands thus folded by rotation about the N–C(phenyl) bond. The minor species (B) may be its isomer, in which the four nitrogen donor atoms are all mutually cis. A recent report⁶⁶ assigns $g_{\parallel} = 2.28$ and 2.31 resonances, respectively, to *trans*- and *cis*- CuN_2S_2 cores, but we have here no evidence for thioether rather than pyridyl equatorial coordination in DMF. Nor does pyridyl *cis*–*trans*

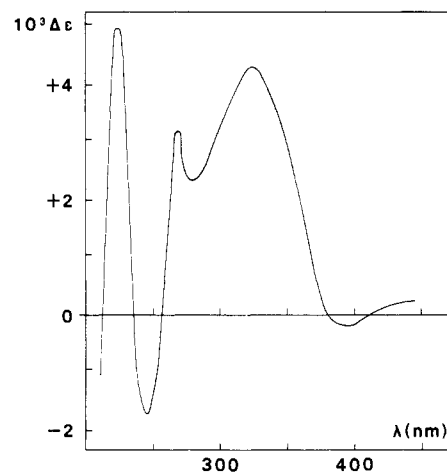


Figure 4. UV difference spectrum for $\text{Cu}(\text{L}-2)(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in methanol, with $\text{Zn}(\text{II})$ complex as reference.

isomerism seem appropriate to the data (cf. $\text{Cu}(\text{L}-17)_2^{2+}$ vs. $\text{Cu}(\text{L}-18)_2^{2+}$). $\text{Cu}(\text{L}-4)_2^{2+}$ also disproportionates in MeCN.

The optical spectra of various of the complexes have been recorded by difference spectrophotometry, with the analogous zinc(II) or non-sulfur copper analogue as reference, so that intraligand transitions may be canceled and those due to copper(II) coordination resolved (Table V). For $\text{Cu}(\text{L}-2)(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ in MeCN solution, the $\text{Cu}(\text{L}-2)_2^{2+}$ cation formed likely retains its thioether coordination, as evidenced by the intense near-UV absorption at 335 nm attributable to

(64) Only the additional necessary S molecules are shown. $\text{Cu}(\text{II}) E_{1/2}$ values refer to the corresponding $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ couple.

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Table V. UV-Visible Spectra λ (nm) (ϵ ($M^{-1} \text{ cm}^{-1}$))

complex	no.						
Cu(L-1)ClO ₄ ·0.5H ₂ O	1	535 ^a (2500)	340 ^b (8600)	300 ^b (8600)	260 ^b (8600)		
Cu(L-2)(ClO ₄) ₂ ·2H ₂ O	2	625 ^c	610 ^d (235)	335 ^e (5500)	325 ^b (4500)	270 ^b (3400)	245 ^b (5600)
Cu(L-2) ₂ (ClO ₄) ₂	3	640 ^c	635 ^d (235)				
Cu(L-1)(bpy)ClO ₄	4	535 ^a (2400)	340 ^f (8000)	300 ^f (7600)	255 ^f (7900)		
Cu(L-2)(bpy)(ClO ₄) ₂	5	660 ^d (240)	610 ^c	460 ^c sh	330 ^f (7100)	315 ^f (5900)	220 ^f (6100)
Cu(L-4)(ClO ₄) ₂ ·1.5H ₂ O	6	650 ^d (200)					
Cu(L-4)(bpy)(ClO ₄) ₂ ·0.5H ₂ O	8	685 ^d (250)					
Cu(L-5)	9	580 ^a (600)	410 ^a (10 700)				
Cu(L-6)ClO ₄	10	650 (170)	420 (8700)				
Cu(L-5)(bpy)·1.5H ₂ O	11	600 ^a sh (250)	410 ^a (9700)				
Cu(L-6)(bpy)(ClO ₄)·H ₂ O	12	625 ^g (200)	390 ^g (6300)				
Cu(L-9)(ClO ₄) ₂	15	620 ^c	545 ^d (600)	440 ^c	345 ^f (3800)		
Cu(L-11)(ClO ₄) ₂	16	620 ^c sh	565 ^d (300)	490 ^c sh	420 ^c		
Cu(L-12)(ClO ₄) ₂	17	550 ^c sh	525 ^a (500)	390 ^c			
Cu(L-13)(ClO ₄) ₂ ·0.5EtOH	18	565 ^a (500)	550 ^c sh	400 ^c			
Cu(L-15)(ClO ₄) ₂ ·1.5H ₂ O	19	700 ^d (470)	390 ^d (6100)	370 ^c sh			
Cu(L-16)(ClO ₄) ₂	20	890 ^{c,d} (450)	610 ^c	600 ^d (250)	390 ^c		
Cu(L-17)(ClO ₄) ₂	26	660 ^d (135)					
Cu(L-18) ₂ (ClO ₄) ₂	27	715 ^d (240)					

^a DMF solution. ^b Cu(II) complex vs. Zn(II) complex in MeOH. ^c Solid, milled in Nujol. ^d MeNO₂ solution. ^e Cu(II) complex vs. Cu(L-18)₂(ClO₄)₂ in MeCN. ^f Cu(II) complex vs. Zn(II) complex in MeCN. ^g MeOH solution.

the consequent S → Cu LMCT transition.^{25-27,62,63} The difference spectrum (Figure 4) in MeOH also provides strong evidence for thioether coordination in this solvent, where a single species is observed in the cryogenic ESR. In solvents that (by the donor number criterion⁶⁷) are considered less strongly Lewis basic, such as MeNO₂, Cu(L-2)²⁺ does not disproportionate, so that the ESR spectra show single species. The value of g_{\parallel} is reduced by S donors, in comparison with N or O donors,⁶⁸ and the values for Cu(L-2)²⁺ and Cu(L-2)₂²⁺, particularly in MeNO₂, are considered a clear indication of sulfur coordination. The similar visible absorption spectra for [Cu(L-2)(OH₂)](ClO₄)₂·H₂O in the solid state and in MeNO₂, both consisting of a single band at 16 200 ± 200 cm⁻¹, also evidence that the coordination sphere is essentially conserved on dissolution in MeNO₂. The same is true of Cu(L-2)₂(ClO₄)₂.

For the linear tetradentate dithioether complex Cu(L-9)(ClO₄)₂, the ESR again reveals three species and coordinative disproportionation in DMF, which implies the occurrence of at least two "dangling" thioethers in the bis complex. In DMF/MeCN, extensive dissociation (equilibrium 1) occurs. For MeOH solution, the ESR and near-UV spectra clearly show retention of the sulfur donors and the absence of disproportionation. The wavelength of the maximum in the optical absorption spectrum of Cu(L-9)(ClO₄)₂ in MeNO₂ corresponds to the average of the wavelengths observed for the two corresponding planar N₂S₂ macrocyclic complexes, [Cu(L-12)]²⁺ and [Cu(L-13)]²⁺, in the same solvent, and the band intensities are similarly enhanced in all three, presumably by the sulfur coordination.⁶³ The additional similarity in g_{\parallel} values among these compounds reinforces the conclusion that L-9 endows equatorial N₂S₂ coordination in MeNO₂ solution. The optical spectra imply that its nitrated analogue Cu(L-11)(ClO₄)₂ is also similarly ligated.

There are no remarkable spectroscopic consequences of the bipyridyl adduction of the thiolate Cu(L-1)⁺ or the thioether Cu(L-2)²⁺. For these, and for the phenolic thiolate and thioether, [Cu(L-5)(bpy)] and [Cu(L-6)(bpy)]⁺, the relatively smaller values computed for A_{\perp} are consistent with a strong z component of the donor set, associable with a roughly axial 2,2'-bipyridyl nitrogen, in an essentially square-pyramidal CuN₄S structure. Difference spectroscopy again provides

evidence that the thioether S is coordinated in [Cu(L-2)-(bpy)]²⁺. The solution spectra of the linear and macrocyclic N₃S₂ ligand complexes [Cu(L-15)]²⁺ and [Cu(L-16)]²⁺ are appreciably different (2400 cm⁻¹ shift). The single, longer wavelength absorption band of [Cu(L-15)]²⁺ is suggestive of a coordination geometry more irregular than that of [Cu(L-16)]²⁺.⁶² The copper(II) complex of a macrocycle similar to L-16 has roughly rectangular-pyramidal N₃S₂ coordination (one sulfur axial) and spectroscopic properties⁶¹ (g_{\parallel} , A_{\parallel} values, two d-d bands near 600 and 900 nm) very similar to those of [Cu(L-16)]²⁺. Displacement of the axial sulfur of such ligands tetragonalizes the complex,^{61,69} so the apparently irregular geometry for Cu(L-15)(ClO₄)₂ leads us to infer that the ligand actually is pentadentate.

(2) Thiolate Complexes. The occurrence of antiferromagnetic coupling is an indicator for phenolate and thiolate bridging,^{21,32,70} as in the phenolic thiolate Cu(L-5)⁴³ and the dimeric bis(phenolate)[Cu₂(L-7)₂].⁷¹ By contrast, the dithiolate [Cu(L-8)] is monomeric.¹⁸ With the other systems reported here, thiolate-bridged self-association is not strong, as there is no evidence for strong antiferromagnetism in the solid state and the ESR data reveal no triplet-state species in solution in coordinating solvents. Nonetheless, in weakly coordinating MeNO₂, Cu(L-1)ClO₄ has a considerably broadened ESR spectrum, suggesting an exchange interaction. Adduction with 2,2'-bipyridyl leads to an ESR spectrum normal for a mononuclear complex, the added N donors coordinatively saturating the metal cation and inhibiting the bridging thiolate coordination. Even in the solid state, the ESR of Cu(L-1)ClO₄ is not diminished in intensity when the temperature is reduced from 300 to 77 K. The same is true for Cu(L-1)Cl. Moreover, the bulk susceptibility of the latter as a function of temperature (80–300 K) is consistent with Curie-Weiss behavior ($C = 0.481 \pm 0.010$, $|\Theta| = 15.0 \pm 4.3$ K (2σ limits)). The cryogenic solution ESR is thus also that of a monomeric copper(II) complex.

That the ligand in Cu(L-1)ClO₄ is coordinated in the imino-thiolate (Figure 2a) rather than the benzothiazoline form (Figure 2b) is borne out by (i) the presence of normal copper(II) ESR spectra (Table IV), (ii) the absence of a ν_{N-H} absorption in the infrared spectra of the complexes, (iii) the

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normal magnetic moment of the complex Cu(L-1)Cl , and (iv) the intense absorption in the visible region of the optical spectrum of Cu(L-1)ClO_4 . The presence of the last has been considered to indicate the imino-thiolate tautomer.^{40,58,59}

In the spectrum of Cu(L-1)ClO_4 in DMF, no absorptions attributable to d-d transitions are discernible, as the appropriate region is obscured by the tail of the intense band at 535 nm. A similar band is also observed (at lesser intensity) in the zinc(II) complex in DMF (and in the Cd(II) chelate⁴⁰) and is there likely due to a ligand $\pi-\pi^*$ or $n-\pi^*$ transition.⁵¹ The provenance of its intensity enhancement in the copper(II) complex is unclear, but the occurrence of intense $S \rightarrow \text{Cu}$ charge-transfer (LMCT) absorptions near this wavelength (e.g. 532 nm) in some copper(II) thiolate complexes^{15,20} leads us to suspect that a portion of the intensity may be attributable to $S \rightarrow \text{Cu}$ LMCT. It has been proposed^{26,51} that there are LMCT transitions to be expected from both σ and π ground states of coordinated sulfur, with the former at higher energy. Indeed, the near-UV difference spectrum includes a band at 340 nm, which in the thioether complexes is assigned to $\sigma(S) \rightarrow d(\text{Cu})$ LMCT.^{26,27,62,63} The enhancement could also be d-d in origin, but most of the complexes here have their d-d transitions at wavelengths longer than 535 nm.

Other Spectroscopic Aspects. The ESR spin Hamiltonian parameters of the neat powders are reported only for those complexes that gave some resolution of the g anisotropy. The remainder gave broad, featureless resonances in the $g = 2$ region.

The solution spectra ($g_{\parallel} > g_{\perp}$) all indicate $d_{x^2-y^2}$ ground states. The increases in g_{\parallel} expected when nitrogen or oxygen replaces sulfur donors⁶⁸ are indeed observed (e.g. Figure 5), and in an $A_{\parallel}:g_{\parallel}$ plot, the N_2SO equatorial donor sets lie at somewhat higher g_{\parallel} than the N_2S_2 and N_3S sets. Conversion of the thiolato complex to its methyl thioether raises g_{\parallel} significantly, by ca. 0.04 in most cases. This shift is partially redressed when the thioether is macrocyclic, with smaller ring size, as in dithiolate $[\text{Cu(L-8)}]$ ($g_{\parallel} = 2.12^{18}$) vs. dithioether $[\text{Cu(L-9)}]^{2+}$ (2.16) vs. macrocycle $[\text{Cu(L-12)}]^{2+}$ (2.13).

Comparison of the dithioether complex $[\text{Cu(L-9)}]^{2+}$ with its nitro-substituted analogue $[\text{Cu(L-11)}]^{2+}$ shows that g_{\parallel} is quite sensitive to nitration, increasing by 0.04 in both the solid and solution states. A similar increase in g_{\parallel} is also often observed (e.g. for the macrocycle $[\text{Cu(L-13)}]^{2+}$) on dissolution of the solid, in both donor (DMF) and poorly donating (MeNO_2) solvents, but similarity of solution g_0 and solid (g) suggests similar coordination environments.

The optical spectrum of the dithioether complex $\text{Cu(L-9)(ClO}_4)_2$ in the solid state is appreciably different from its solution spectrum and those of its macrocyclic analogues $[\text{Cu(L-12)}]^{2+}$ and $[\text{Cu(L-13)}]^{2+}$. The 2200-cm^{-1} red shift for this solution-to-solid conversion implies to us a less regular solid-state coordination,⁶² and indeed the solid-state ESR of $\text{Cu(L-9)(ClO}_4)_2$ is the only spectrum in which g_x is resolved from g_y . This rhombic spectrum resembles those observed for some pentacoordinate CuN_3O_2 and CuN_3Cl_2 donor-set complexes^{72,73} with geometries intermediate between square pyramidal and trigonal bipyramidal. A perchlorate anion of $\text{Cu(L-9)(ClO}_4)_2$ must therefore be coordinated in the solid state. Such irregular coordination polyhedra are often readily tetragonalized in solution.⁶²

The tetragonal-equatorial planar nature of the solution coordination in most of the complexes is also indicated by the normal values of A_{\parallel} ($(170\text{--}200) \times 10^{-4} \text{ cm}^{-1}$). A significant departure therefrom is indicated for $\text{Cu(L-4)(ClO}_4)_2$ in so-

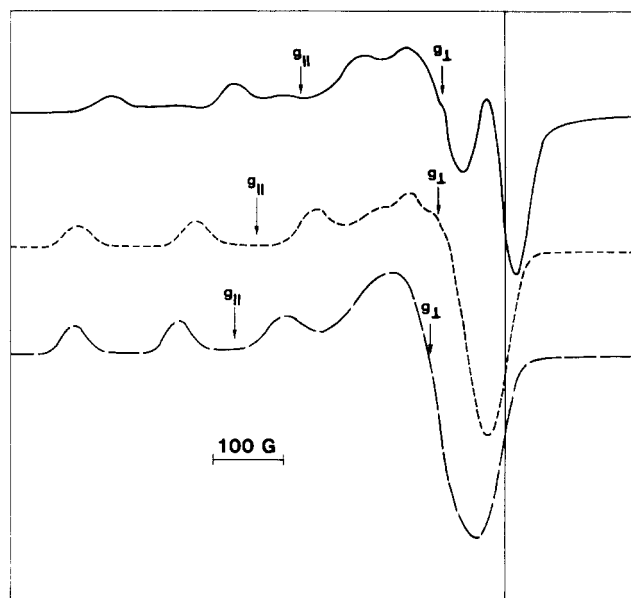


Figure 5. X-band ESR spectra at 77 K of (top) $\text{Cu(L-1)(ClO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}$ in DMF, (center) $[\text{Cu(L-2)(OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ in acetone/toluene, and (bottom) $\text{Cu(L-4)(ClO}_4)_2 \cdot \frac{3}{2}\text{H}_2\text{O}$ in acetone/toluene. The arrows mark the g values and the vertical bar the position of $g = 2$.

lution (Figure 5). Its thioether ligand differs from L-2 only by the remaining α position of the pyridine ring bearing a methyl substituent, which is expected to cause steric interference with the adjacent equatorial donor. The relationship between the g_{\parallel} value of this L-4 complex and that of the L-2 complex of known structure allows application of a simple ESR model for tetrahedral distortion of the equatorial donor set⁶⁸ and estimation of the dihedral angle between the NCuO and NCuS planes to be $\omega = 33^\circ$. The reduced value of A_{\perp} is also in qualitative agreement with the presence of such a distortion.⁷⁴

The complexes with the thiols L-1 and L-5 and the 2,2'-bipyridyl adducts of them provide further evidence that thiolato complexes of copper(II) do not have intrinsically low values of A_{\parallel} . Recent work has shown that small hyperfine splittings in the low-field region of some sulfur-donor complexes are the consequence of a triplet state resulting from weak dimerization interactions between copper(II) centers.⁶³ Certain (thiolato)copper(II) complexes with small hyperfine splittings in the g_{\parallel} region have been proposed as models for protein type-1 copper, on the basis of assignment¹⁵ as monomeric species with $A_{\parallel} < 90 \times 10^{-4} \text{ cm}^{-1}$. However, the general appearance of their spectra in comparison with those of the coupled systems leads us to the conclusion that they are most probably of dimeric species, whose A_{\parallel} values are actually double the observed splittings.

$[\text{Cu(L-7)(bpy)}]$ is unstable (in DMF for example) toward dissociation of 2,2'-bipyridyl and subsequent precipitation of Cu(L-7) . This rather insoluble parent diphenolate is monomeric in pyridine solution, as is the thiolate-phenolate complex Cu(L-5) in DMF, despite the strong self-association present in the solid state.⁴³

Redox Chemistry. The redox behavior of the complexes was examined by cyclic voltammetry and rotating-disk dc polarography, mainly at platinum electrodes. The relatively positive $E_{1/2}$ values and/or presence of thiolate sulfur abrogated the use of mercury electrodes in most cases. Data are reported for those complexes in solvents for which there is evidence that the complex integrity is retained in solution

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Table VI. Electrochemical Data

compd	no.	solvent	$E_{1/2}$, V ^a	$E_{1/2}$, V (vs. SCE) ^b	type ^c	$10^6 D_2$, cm ² /s ^d	$10^8 D\eta_1$, g cm/s ²
Cu(L-1)ClO ₄ ·0.5H ₂ O	1	DMF	-0.56	-0.25	q	3.8	3.2
Cu(L-2)(ClO ₄) ₂ ·2H ₂ O	2	MeNO ₂	+0.12 ^e	+0.44	q	2.5	1.6
Cu(L-2) ₂ (ClO ₄) ₂	3	MeNO ₂	-0.045	+0.27	r	4.6	3.0
		MeCN	0.000	+0.30	r	8.8	3.3
Cu(L-1)(bpy)ClO ₄	4	DMF	-0.62	-0.30	q	3.1	2.7
		MeCN	-0.52	-0.22	r	6.2	2.3
Cu(L-2)(bpy)(ClO ₄) ₂	5	MeCN	-0.13	+0.17	i	6.0	2.3
		MeNO ₂	-0.08 ^e	+0.23	q	2.8	1.9
Cu(L-4)(ClO ₄) ₂ ·1.5H ₂ O	6	MeCN	+0.11	+0.41	r		
		MeNO ₂	+0.21	+0.53	i		
Cu(L-4)(bpy)(ClO ₄) ₂ ·0.5H ₂ O	8	MeNO ₂	-0.04	+0.28	i	2.9	1.9
Cu(L-8)·1.5H ₂ O		DMF		-0.83 ^{f,g}			
Cu(L-9)(ClO ₄) ₂	15	MeCN	+0.12	+0.42	r	8.5	3.2
			+0.10	+0.42	r		
Cu(L-12)(ClO ₄) ₂	17	DMF	-0.24	+0.08	r	3.1	2.7
		MeCN	-0.04	+0.26	r	7.8	2.9
Cu(L-13)(ClO ₄) ₂ ·0.5EtOH	18	MeCN	-0.01	+0.29	r	7.1	2.7
		DMF	-0.23	+0.08	q	2.0	1.6
Cu(L-15)(ClO ₄) ₂ ·1.5H ₂ O	19	MeCN	+0.17	+0.47	r		
Cu(L-16)(ClO ₄) ₂	20	MeCN	+0.18	+0.48	r		
Cu(L-17)(ClO ₄) ₂	26	DMF ^g	-0.46	-0.15	q	4.4	3.8
Cu(P2A ₂ -bun) ^h		DMF ^g	-1.22	-0.91	q	2.3	2.0
		MeCN ⁱ	-1.15	-1.12	r		

^a From RPE polarography and cyclic voltammetry, referred to nonaqueous Ag⁺/Ag⁰ electrode, as in ref 77. ^b Normalized to MeCN and referred to SCE via ferrocenium/ferrocene couple in MeCN, used as liquid-junction potential compensation standard, and for which $E_{1/2}$ is thus +0.374 V, which is depressed by 22 mV in MeNO₂ and 14 mV in DMF. ^c $n = 1$, r = Nernstian, q = quasi-reversible, i = irreversible. ^d Computed by application of the Levich equation to the RPE limiting current, with use of measured viscosities. ^e The irreversible RPE $E_{1/2}$ is somewhat different. ^f From ref 79. ^g At Hg electrode. ^h [Butylenediamine-*N,N'*-bis(pyrrole-2-carboxaliminato)]copper(II). ⁱ From ref 74.

without the occurrence of coordinative disproportionation. The second column of $E_{1/2}$ values in Table VI has been normalized to MeCN as solvent and referred to the saturated calomel electrode (SCE) by using the ferrocenium/ferrocene couple to correct for liquid-junction potential and then applying logic outlined previously.⁷⁵ Couples denoted as reversible have a Nernstian anodic-to-cathodic peak potential separation in the cyclic voltammogram. Others have kinetically limited voltammetry (the iR -corrected peak potential separations are greater than the Nernstian value, but the ratio of anodic to cathodic peak currents approaches unity), and the behavior is denoted as quasi-reversible. The current functions are comparable with those of other $n = 1$, Cu(II) → Cu(I) reduction processes.^{23,74,76,77} The values of $D\eta$, which should be solvent-independent for a given complex, average 2.6×10^{-8} g cm/s², a value similar to that observed previously.²³ All the complexes exhibited two RPE polarographic waves, the one at more negative potential being attributed to the Cu^I → Cu⁰ reduction. Some of the complexes (with L-5, L-6, L-7, L-11) are not amenable to straightforward electrochemical interpretation. For example, the nitrated thioether complex Cu(L-11)(ClO₄)₂ bleaches on dissolution in DMF. The thiolate Cu(L-1)ClO₄ has "clean" electrochemistry in DMF, but in MeNO₂, it is complicated, probably by the weak self-association. There is, however, a reduction wave at the same potential as in DMF. The picolyal-thioether complexes Cu(L-4)²⁺ and [Cu(L-4)(bpy)]²⁺ have $i_{p,a} = 0$ and are the only ones irreversibly reduced. The limiting-current normalized RPE polarogram slopes⁷⁷ for these last two compounds are 3–4 V⁻¹, while for the other complexes studied, the values range from 5 to 8 V⁻¹, suggesting varying degrees of electron transfer rate limitation in the time regime of the RPE, in accordance with the cyclic voltammetry results. It should be noted that, for copper complexes like these, observation of quasi-reversible

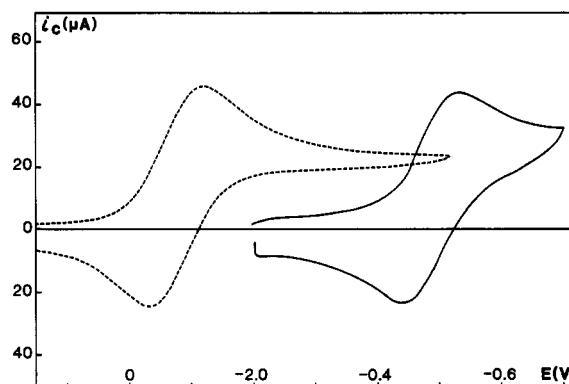


Figure 6. Cyclic voltammograms for (left) 1.8 mM [Cu(L-2)-(bpy)](ClO₄)₂ in MeNO₂/NEt₄ClO₄ and (right) 0.80 mM [Cu(L-1)(bpy)](ClO₄) in MeCN/NEt₄ClO₄.

redox chemistry may be a consequence of the use of Pt as the electrode material, rather than of intrinsically non-Nernstian behavior of the couple.⁷⁶

The data in Table VI show that the observed $E_{1/2}$ of a given thiolate is generally raised by S methylation. The result is exemplified by comparison of the data from the RPE polarograms of [Cu(L-1)(bpy)]⁺ and [Cu(L-2)(bpy)]²⁺, whereby one observes that replacement of thiolate by thioether raises the $E_{1/2}$ by 0.38 V. We and other workers⁷⁸ have had difficulty with the electrochemistry of the dithiolate [Cu(L-8)]. Addition by 2,2'-bipyridyl resolves such problems for the thiolate complex [Cu(L-1)]⁺, but this tactic is not applicable to [Cu(L-8)], which does not form a stable adduct. Comparison of the previously published⁷⁹ $E_{1/2}$ value for [Cu(L-8)] with that for our thioether analogue [Cu(L-9)]²⁺ suggests that, in this case, two substitutions of thiolate by thioether raise $E_{1/2}$ by about 1.2 V. Even the non-Nernstian results (0.7 V) for [Cu(L-1)]⁺ and [Cu(L-2)]²⁺ serve to illustrate the trend of

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marked elevation in $E_{1/2}$, which we propose holds universally when thioether replaces thiolate.

The cyclic voltammograms in Figure 6 show that the bpy adducts of the L-1 and L-2 complexes are quite reversible couples. The prevailing view would have it that the degree of structural reorganization between the two oxidation states is therefore minimal in these two compounds. There is ample precedent⁸⁰⁻⁸² for the possibility that the copper(I) species are pentacoordinate. It seems most unlikely to us that the thiolate would not remain coordinated to copper(I), while the preference displayed by copper(I) for the terminal donors of multidentate ligands³⁰ should promote S coordination in $[\text{Cu}(\text{L}-2)(\text{bpy})]^+$ as well.

The $E_{1/2}$ elevation associated with each S methylation thus averages about 450 mV for these aryl systems. Another recent paper³⁷ agrees qualitatively with this conclusion, although the principal thiolate therein (Figure 2c) entailed some uncompensated differences in structural features (other than just S demethylation of the thioether), and reduction potentials in chelates of this type are quite sensitive to remote substituents.⁷⁶ Overall, the results show that, on passing from thioether to thiolate, the increased anionic charge stabilizes Cu(II) relative to Cu(I), more than the Cu(I) is relatively stabilized by any increased "softness" of thiolate. That the charge effect is quite the dominant one is shown by the similar comparison made for two non-sulfur complexes, the dicationic pyridyl Schiff base complex $[\text{Cu}(\text{L}-17)]^{2+}$ and uncharged [butylenediamine-*N,N'*-bis(pyrrrole-2-carboxaldiminato)]copper(II), $[\text{Cu}(\text{P}2\text{A}_2\text{-bun})]$.⁷⁴ These are *cis*- $\text{CuN}_2\text{N}'_2$ chelates, whose tetramethylene linkages are flexible enough to allow (quasi) reversible reduction to pseudotetrahedral copper(I) states. Conversion of each uncharged pyridyl nitrogen to an anionic pyrrolide nitrogen depresses $E_{1/2}$ by 0.4 V. We infer that any difference between N and S in polarizability-attributable stabilization of the copper(I) state is probably modest (about 50 mV).

The elevation of $E_{1/2}$ as a consequence of S methylation is readily rationalizable in terms of the process being equivalent to the covalent addition of a methyl carbonium ion to the sulfur in the coordination sphere of the metal.

Substitution of a coordinated water by a thioether sulfur raises the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ reduction potential by an average of about 120 mV.²⁹ One can thus deduce that the corresponding contribution ΔE_L^{29} of a thiolate sulfur to the reduction potential is about -330 mV. Anderson et al. have quite recently published a very similar conclusion (350 mV)⁸³ regarding the relatively destabilizing effect of thiolate coordination on copper(I). Agreement between the two sets of data is remarkably good, considering the differences in structures and solvents. It is not clear, though, why a prior result for an alkanedithiolate²⁴ should be so different.

Other features of the redox chemistry are noteworthy. In comparison with the $[\text{Cu}(\text{L}-2)]^{2+}$ complex, the introduction of the distortion in $[\text{Cu}(\text{L}-4)]^{2+}$ somewhat elevates the $E_{1/2}$. In passing from the linear tetradentate dithioether L-9 to the electronically similar N_2S_2 macrocycles L-12 and L-13, one observes a depression of 150 mV in $E_{1/2}$. It is generally accepted^{25,28,29,79} that the Cu(I) state is increasingly stabilized by added flexibility. This criterion also fits the depression in the copper $E_{1/2}$ observed when the pentadentate N_3S_2 ligand L-15 is cyclized to L-16. Some sensitivity of the $E_{1/2}$ values to axial solvation is also revealed by the data for the N_2S_2

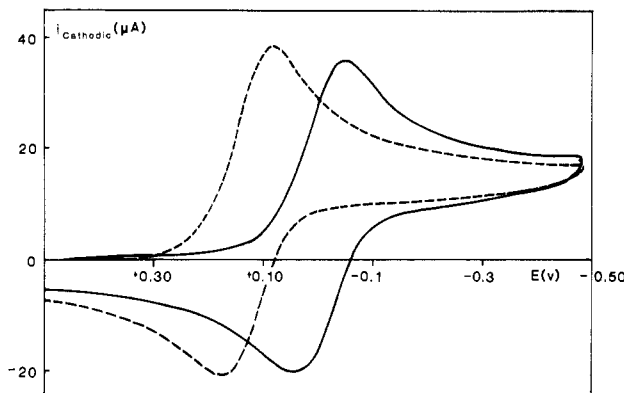


Figure 7. Cyclic voltammograms of (broken line) 0.75 mM $[\text{Cu}(\text{L}-9)](\text{ClO}_4)_2$ and (solid line) 0.77 mM $[\text{Cu}(\text{L}-12)](\text{ClO}_4)_2$ in $\text{MeCN}/\text{NEt}_4\text{ClO}_4$.

Table VII. Redox Potentials of Type-1 Copper Centers

system	E° , V	ref
Tetragonal $[\text{Cu}^{\text{II}}\text{N}_2\text{S}_2]^+$	+0.08	<i>a</i>
<i>R. vernicifera</i> stellacyanin	+0.18	85
<i>P. denitrificans</i> azurin	+0.23	86
<i>Alcaligenes</i> spp. azurin	+0.26	87
<i>A. faecalis</i> azurin	+0.27	87
<i>C. sativus</i> plantacyanin	+0.27	88
Mavicyanin	+0.29	89
<i>P. vulgaris</i> plastocyanin	+0.35	85
<i>Scenedesmus</i> plastocyanin	+0.35	87
<i>C. sativus</i> plastocyanin	+0.35	90
<i>S. oleracea</i> plastocyanin	+0.38	91
<i>P. aeruginosa</i> azurin	+0.38	85
<i>C. sativus</i> ascorbate oxidase	+0.42	88
<i>R. vernicifera</i> laccase	+0.43	92
Rusticyanin	+0.68	93
<i>P. versicolor</i> laccase	+0.78	94

^a This work.

macrocycles $[\text{Cu}(\text{L}-12)]^{2+}$ or $[\text{Cu}(\text{L}-13)]^{2+}$ in the two different solvents, MeCN and DMF. This would decrease the $E_{1/2}$ difference between the L-8 and L-9 complexes.

Of all the ligands used here, the 14-membered macrocycle L-12 is presumably the most rigid in imposing tetragonal stereochemistry at the metal, so it was unexpected that the reduction of $[\text{Cu}(\text{L}-12)]^{2+}$ is so reversible a process (Figure 7). This may be taken as further evidence that these thioether-imine systems tend to undergo minimal coordinative reorganization on reduction. In the case of the N_3S_2 macrocycle $[\text{Cu}(\text{L}-16)]^{2+}$, it seems very likely, on the basis of the work of Nelson et al.⁸⁰ on similar systems, that the reduced complex is pentacoordinate, and this may also be true for the linear pentadentate $[\text{Cu}(\text{L}-15)]^{2+}$.

All of the complexes in Table VI were examined electrochemically for ability to bind carbon monoxide in the reduced state. No significant activity was found.

Relationship to Thiolate-Coordinated Protein Copper. The ΔE_L values for the individual donors in variously ligated copper complexes can now be applied to sulfur-containing nonsynthetic systems. These are most notably represented by the type-1 cuproproteins, particularly the azurins and plastocyanins. Using +0.15 V as the E° of the aquo $\text{Cu}^{2+}/\text{Cu}^+$ couple,⁸⁴ and ΔE_L values²⁹ for the various donors of +0.08 V

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(His imidazole), +0.12 V (Met thioether), and -0.33 V (Cys thiolate), one can estimate the E° of a tetragonal $[\text{CuN}_2\text{S}_2]^+$ complex of this composition (Table VII). Reduction potentials of various azurins and plastocyanins (Table VII) lie in the range +0.23-0.38 V. The contribution of the marked departure from tetragonal geometry in most of these proteins' copper centers would thus appear to be about +0.25 V, which deduction involves the assumption that the axial -SCH₃ donor exerts its usual ΔE_L in that situation. Nonetheless, this contribution attributable to the geometric factor is similar to some of the values proposed previously from a ligand field computational model⁹⁵ and from model compound studies.⁶⁸ The combined redox and ESR^{96,97} data suggest that fungal laccase

and rusticyanin may have similarly unusual S-containing donor atom sets, though with slightly different geometries. At the opposite E° extreme, stellacyanin lacks methionine,⁹⁸ and cystine disulfide sulfur has been suggested as a donor in its stead.⁹⁵ The redox and ESR⁹⁹ data seem equally consistent with the presence of an N or O donor.

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Supplementary Material Available: Further synthetic details (Appendix), ORTEP stereoview of the $[\text{Cu}(\text{L}-2)(\text{OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ unit cell (Figure 8), susceptibility data for $\text{Cu}(\text{L}-1)\text{Cl}$ (Figure 9), RPE polarograms for $\text{Cu}(\text{L}-1)(\text{bpy})\text{ClO}_4$ and $\text{Cu}(\text{L}-2)(\text{bpy})(\text{ClO}_4)_2$ (Figure 10), analytical data for ligands and precursors (Table VIII), analytical data for complexes (Table IX), and positional and thermal parameters (Table X), bond lengths and distances (Table XI), bond angles (Table XII), least-squares planes (Table XIII), and observed and calculated structure factors (Table XIV) for $[\text{Cu}(\text{L}-2)(\text{OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (30 pages).

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Notes

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405

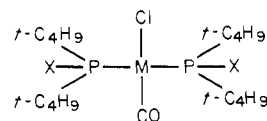
Evidence for a Strong Similarity in Conformational and Phosphorus-31 NMR Parameters between Two Series of *trans* - $[(t\text{-C}_4\text{H}_9)_2\text{PX}]_2\text{M}(\text{CO})\text{Cl}$ Complexes [M = Rh(I), Ir(I); X = H, CH₃, C₂H₅, *n*-C₄H₉, C₆H₅]

C. Hackett Bushweller,*¹ Christopher D. Rithner,* and David J. Butcher

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A variety of square-planar Rh(I) and Ir(I) complexes are important catalysts.² It is now apparent that catalysis in general and asymmetric induction in particular depend on the unique stereodynamics of a given achiral or chiral complex.³ In spite of this, there is a paucity of information concerning the dynamics of rotation about metal-ligand bonds and substituent effects on rotamer preferences.^{4,5} We report here a remarkable similarity in the conformational preferences and

³¹P NMR parameters between two series of Rh(I) and Ir(I) complexes (1-10).



- | | |
|---|---|
| 1: M = Rh(I), X = H | 6: M = Ir(I), X = H |
| 2: M = Rh(I), X = CH ₃ | 7: M = Ir(I), X = CH ₃ |
| 3: M = Rh(I), X = C ₂ H ₅ | 8: M = Ir(I), X = C ₂ H ₅ |
| 4: M = Rh(I), X = <i>n</i> -C ₄ H ₉ | 9: M = Ir(I), X = <i>n</i> -C ₄ H ₉ |
| 5: M = Rh(I), X = C ₆ H ₅ | 10: M = Ir(I), X = C ₆ H ₅ |

The ³¹P{¹H} NMR spectra (101.2 MHz) of 1-4 (0.05 M in toluene-*d*₈) below 200 K are consistent with slow rotation about the rhodium-phosphorus bonds on the ³¹P NMR time scale and reveal the presence of *three* subspectra. A complete set of spectra for all 10 complexes is available as supplemental Figure 1S. The three subspectra for each of the rhodium complexes 1-4 (Figure 1S) include the B₂ portion of a B₂X spectrum (X = ¹⁰³Rh; *I* = 1/2), the AC portion of an ACX spectrum, and a minor D₂X spectrum (e.g., see the spectrum of 4 in Figure 1).⁶ For the Ir(I) complexes 6-9, each spectrum at slow exchange shows a B₂ singlet, an AC spectrum, and a minor D₂ singlet (e.g., see the spectrum of 9 in Figure 1).

Tolman's cone angles for chlorine and carbon monoxide are 102 and 95°, respectively.⁷ Chlorine possesses slightly more

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