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Synthesis and Magnetic Properties of Binuclear Copper(II) Complexes of 2,6-bis-(N-2-pyridylformidolyl)-4-methylphenol

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The synthesis and magnetic characterization of two binuclear copper(II) complexes bridged by the binucleating ligand 2,6-bis-(N-2-pyridylformidoyl)-4-methylphenol (HL) and an additional ionic exogenous ligand is reported. The complexes are $[Cu_2LOH](ClO_4)_2$ *and* $[Cu_2LCl]Cl_2 \cdot 2H_2O$*. The magnetic susceptibility of these complexes was measured over the 6–300 K temperature region and each of the complexes exhibits antiferromagnetic intradimer coupling. The hydrated chloride bridged complex shows additional weak interdimer magnetic interaction resulting from hydrogen bonding in the crystal lattice. The magnetic parameters are:* $[Cu_2LOH](ClO_4)_2$ *- -* $g = 2.16$, $J = -160$ cm^{-1}; $[Cu_2LCl]Cl_2 \cdot 2H_2O$ *- -* $g = 2.09$, $J = -42$ cm^{-1}, $zJ' = -1.1$ cm^{-1}.

Introduction

The synthesis and investigation of structural and magnetic properties of metal complexes derived from macrocyclic binucleating ligands has attracted a great deal of attention [1–6]. Metal complexes prepared from binucleating ligands allow the experimentalist more control over structural factors that dominate the exchange process. The investigation of binuclear centers that result from the coordination of copper(II) ions to these types of ligands has focused primarily on the magnetic coupling between the two paramagnetic ($S = 1/2$) cupric ions as determined by variable temperature magnetic susceptibility or electron spin resonance measurements. The interest in binuclear complexes is generated in several widely divergent areas of inorganic chemistry. For example, the role of the magnetically coupled copper(II) ions in the binuclear blue copper proteins is the subject of much speculation and chemical interest [7–10]. Several copper(II) complexes of binucleating ligands have been proposed as structural and chemical models of these proteins.

The synthesis of large macrocyclic ligands permits molecular engineering of binuclear bridging systems and affords a more detailed and controled probe of the bridging geometry. Robson [3], Okawa [4], Urbach [5], and Vigee [6] have introduced 2,6-diformyl-4-methylphenol (dfmp) as an important building block for macrocyclic and non-macrocylic binucleating ligands and have reported extensively on the spectral and magnetic properties of transition metal complexes with these types of ligands. The non-macrocyclic binucleating ligands first reported by Urbach [5] are especially interesting because they permit bridging by an exogenous ligand that may be systematically varied. In this paper we report the synthesis of the binucleating ligand obtained from 2,6-diformyl-4-methylphenol and aminomethylpyridine and the variable temperature magnetic susceptibility from 6 to 300 K for two dicopper(II) complexes of this ligand with bridging hydroxide or chloride ligands.

Complexes with two metal ions (like or unlike) in close proximity can result from the association of two monomeric units *via* an appropriate bridging group or from the incorporation of two metal ions into a single binucleating ligand. Structural correlations of symmetrically bridged dimeric binuclear complexes have been extensively studied by Hatfield, Hodgson and others [11–14], and several empirical observations have been noted, especially for oxygen chlorine bridges. This study is undertaken to further investigate the magnetic structural effects that occur in asymmetric mixed ligand bridging of binuclear copper(II) complexes.

We report here on the variable temperature magnetic susceptibility measured over the 6–300 K temperature region for the two complexes $[Cu_2LOH](ClO_4)_2$ and $[Cu_2LCl]Cl_2 \cdot 2H_2O$, where HL = 2,6-Bis(N-2-pyridylformidoyl)-4-methylphenol.

Experimental

Synthesis

2,6-diformyl-4-methylphenol: The dialdehyde 2,6-diformyl-4-methylphenol (hereafter referred to as dfmp) was prepared by the method of Ullman and Brittener [15].

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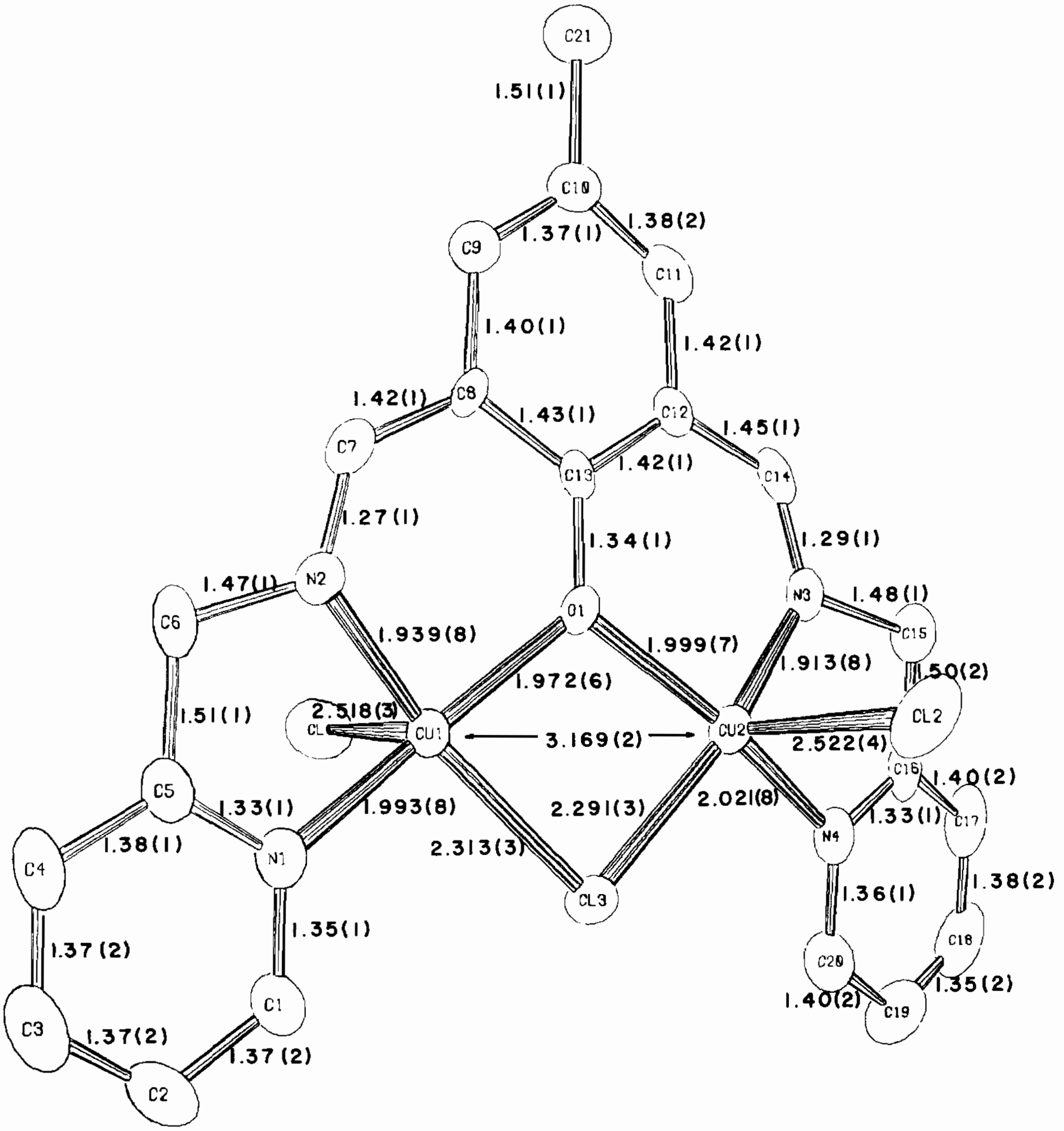

Fig. 1. ORTEP diagram of the binuclear coordination sphere for [Cu$_2$LCl]Cl$_2$·2H$_2$O.

[Cu$_2$LCl]Cl$_2$·2H$_2$O

2.68 g of anhydrous copper chloride was dissolved in 50 ml of absolute ethanol. A solution of dfmp dissolved in about 20 ml of absolute ethanol was added to the copper chloride solution and the resultant solution was heated to about 70 °C in the presence of small amount of triethylorthoformate (TEOF). A solution of 0.54 g of aminomethylpyridine (AMP) in 20 ml of absolute ethanol also warmed to 70 °C was added to the CuCl$_2$/dfmp solution and allowed to stir at this temperature for about 20 minutes. A dark green powder precipitated when the solution was allowed to cool. The powder was dissolved in a mixture of hot ethanol and water and the solution was allowed to stand in a covered beaker. Well developed emerald green crystals were obtained after two days, and these crystals were used for susceptibility measurement.

Anal. Calcd. for C$_{21}$H$_{19}$N$_4$O$_1$Cu$_2$Cl$_3$·2H$_2$O: C, 41.14; H, 3.10; N, 9.14; O, 2.61; Cu, 20.75; Cl, 17.36%. Found: C, 41.42; H, 3.79; N, 8.95; Cu, 20.14%.

[Cu$_2$LOH](ClO$_4$)$_2$

A solution containing 0.54 g of copper perchlorate dissolved in 100 ml of ethanol was mixed with 0.41 g of dfmp dissolved in 20 ml of ethanol and the resulting solution was warmed to 70 °C in the presence of TEOF. To this solution 0.54 g of AMP in 20 ml of ethanol was added and allowed to stir for a few minutes. Greyish looking powder precipitated immediately. The powder was filtered off. Oxygen

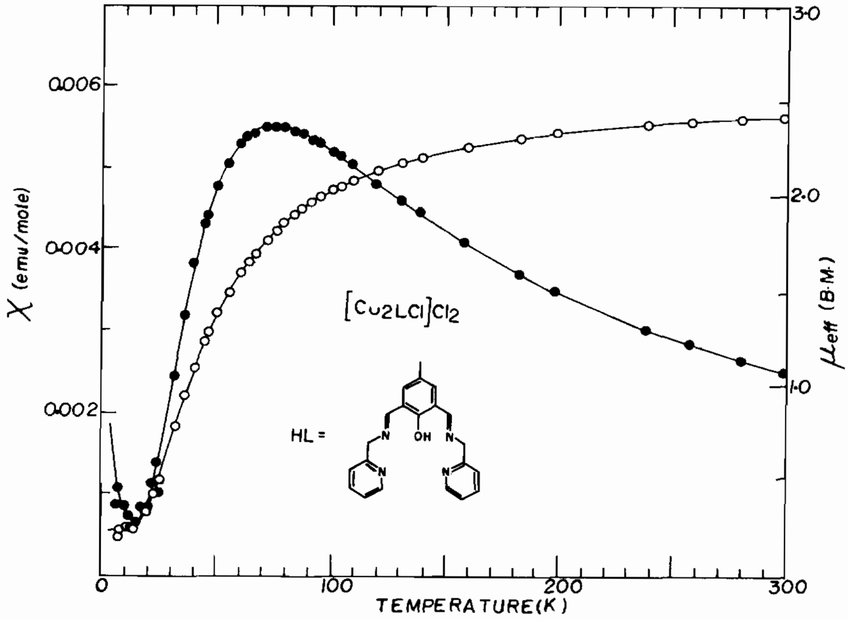

Fig. 2. Magnetic susceptibility (●) and effective magnetic moment (○) plotted as a function of temperature for $[Cu_2LCl]Cl_2 \cdot 2H_2O$.

was bubbled through the supernatant solution for about one hour. The solution was allowed to stand overnight whereby a green microcrystalline product was collected. *Anal.* Calcd. for $Cu_2C_{23}H_{28}N_4O_{12}Cl_2$: C, 36.80; H, 3.73; N, 7.47; Cl, 9.45; Cu, 16.94; O, 25.60%. Found: C, 36.31; H, 3.50; N, 9.08; Cl, 9.45; Cu, 15.91; O, 25.48%.

Magnetic Susceptibility

Magnetic susceptibility measurements were carried out on an alternating force magnetometer (AFM) [16]. The instrument was calibrated with Hg Co(NCS) [17] and data was recorded over the 6–300 K temperature range. Measurement techniques are described elsewhere [16, 18].

Results and Discussion

An ORTEP diagram of the molecular unit of $[Cu_2LCl]Cl_2 \cdot 2H_2O$ is illustrated in Fig. 1. A single-crystal X-ray diffraction study of $C_{21}H_{19}N_4O_1Cu_2Cl_3 2H_2O$ has been completed and reported elsewhere [19]. Each copper(II) ion is coordinated to two nitrogen atoms and both copper(II) ions are coordinated to the phenolic oxygen forming an oxygen atom bridge. The copper(II) ions are also bridged by a single chlorine atom. Both copper(II) ions are pentacoordinate resulting in coordination spheres with distorted square pyramid geometries with non-bridging chlorine atoms at the apex of the pyramid. Attempts to prepare single crystals of $[Cu_2LOH](ClO_4)_2$ suitable for crystal structure analysis have so far been fruitless.

The magnetic data for the two binuclear copper(II) complexes are listed in Table II (supplementary material) and are shown in Figs. 2 and 3 as magnetic susceptibility (χ = M/H) and effective magnetic moment ($\mu eff = \sqrt{7.997\chi T}$) plotted as a function of temperature over the 6–300 K region. Each of the plots exhibit a maximum in the variable temperature magnetic susceptibility. This behavior is indicative of antiferromagnetic coupling between two copper(II) ions of the binuclear unit. Both of the complexes showed an increase in the magnetic susceptibility at the lowest temperatures. This behavior is characteristic of a small amount of paramagnetic (monomeric) impurity. The data were corrected for this impurity before a theoretical analysis was attempted.

Magnetic exchange between two paramagnetic centers may be described by the Heisenberg-Dirac-Van Vlek spin Hamiltonian

$$\hat{H} = -2J\, S_1 \cdot S_2 \tag{1}$$

This spin Hamiltonian yields the Bleaney-Bowers equation [20] for the magnetic susceptibility of magnetically coupled spin S = ½ copper(II) dimers

$$\chi = \frac{2Ng^2\mu_B{}^2}{kT} \cdot \frac{e^{-x}}{1 + 3e^{-x}} \tag{2}$$

where x = 2J/kT and 2J is energy separation between the spin coupled singlet and triplet states.

The crystal structure of the chloride bridged complex $[Cu_2LCl]Cl_2 \cdot 2H_2O$ indicates extensive hydrogen bonding between the noncoordinated water molecules and the coordinate chloride ions that

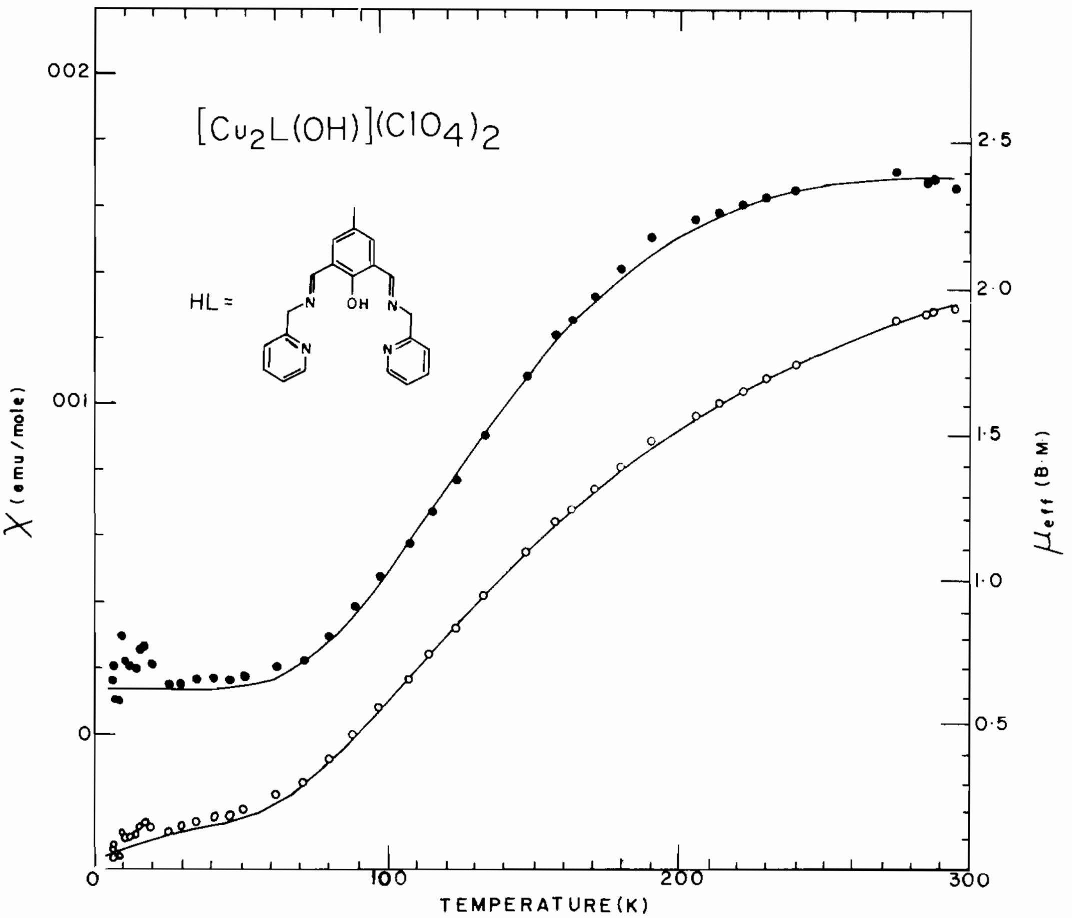

Fig. 3. Magnetic susceptibility (●) and effective magnetic moment (○) corrected for a 1.8% paramagnetic impurity and plotted as a function of temperature for $[Cu_2LOH](ClO_4)_2$).

TABLE I. Fitted Magnetic Parameters for the Two Complexes Using Eqn. 2 as Described in Text.

	g	J (cm^{-1})	J′ (cm^{-1})	Paramagnetic impurity
$[Cu_2LCl]Cl_2 \cdot 2H_2O$	2.09 ± 2	−42 ± 2	−1.1 – 0.1	1.75%
$[Cu_2LOH\text{-}(ClO_4)_2$	2.16 ± 2	−160 ± 5		1.8%

results in a one dimensional interaction in the crystalline lattice. The structural linkage of binuclear units also affects the magnetic properties of the complex by allowing a weak magnetic coupling of neighboring binuclear units. Weak interactions of this type may be accounted for by applying a molecular field correction [16] to the data as in eqn. 3.

$$\chi' = \frac{\chi}{1 - (2zJ'/Ng^2\mu_B^2)\chi} \qquad (3)$$

where χ' is the exchange influenced susceptibility actually measured and χ is the exchange corrected susceptibility. The term zJ' gives an estimate of the extent of the molecular field interaction between binuclear centers and z is the number of interacting neighbors.

A simple curve fitting routine was used to determine the magnetic parameters for the binuclear compounds using eqn. 2 (and correcting with eqn. 3, if necessary) and the best fitted parameters are listed in Table I. The quality of the fits is illustrated by the theoretical curves drawn through the points in Figs. 2 and 3 using the parameters listed in Table I.

The antiferromagnetic behavior for the complexes reported here is attributed to a spin–spin interaction propagated *via* the direct bridging exchange pathway. It appears that the hydroxy ligand is more efficient medium for the propagation of magnetic exchange. However, an unambiguous assignment of the mechanism is not possible without structural data for the μ-hydroxo complex. We are currently trying to fill this gap as well as preparing addition complexes with other types of exogenous bridging ligands. Studies on related binucleating systems, however, corroborate the efficiency of the hydroxo-bridge for the propagation of magnetic coupling [21].

These binuclear complexes may have some applications as models of the chemical and physical properties of the methemocyanin–azide complex that has been reported as strongly antiferromagnetically coupled and is diamagnetic at room temperature [22]. Other ligands will be used as probes of the exchange dependence on bridging ligand and structure.

References

1 F. L. Urbach, *Met. Ions Biol. Syst., 13,* 73 (1981).

2 R. R. Gagne, R. P. Kreh and J. A. Dodge, *J. Am. Chem. Soc., 101,* 6917 (1979).

3 R. Robson, *Inorg. Nucl. Chem. Lett., 6,* 125 (1970).
R. Robson, *Aust. J. Chem., 23,* 2217 (1970).
N. H. Pilkington and R. Robson, *Aust. J. Chem., 23,* 2225 (1970).
B. F. Hoskins, R. Robson and H. Schapp, *Inorg. Nucl. Chem. Lett., 8,* 21 (1972).
W. D. McCadyen, R. Robson and H. Schaap, *Inorg. Chem., 11,* 177 (1973).
B. F. Hoskins, R. Robson and D. Vice, *J. Chem. Soc., Chem. Commun.,* 392 (1973).
I. E. Dickson and R. Robson, *Inorg. Chem., 13,* 1301 (1974).
B. F. Hoskins, R. Robson and G. A. Williams, *Inorg. Chim. Acta, 16,* 121 (1976).
W. D. McFayden and R. Robson, *J. Coord. Chem., 5,* 49 (1976).

4 H. Okawa, *Bull. Chem. Soc. Jpn., 43,* 3019 (1970).
H. Okawa and S. Kida, *ibid., 44,* 1172 (1971).
H. Okawa and S. Kida, *ibid., 45,* 1759 (1972).
H. Okawa, S. Kida, Y. Muto and T. Tokii, *ibid., 45,* 2480 (1972).
H. Okawa, M. Honda and S. Kida, *Chem. Lett.,* 1027 (1972).
H. Okawa, T. Tokii, Y. Nonaka, Y. Muto and S. Kida, *Bull. Chem. Soc. Jpn., 46,* 1462 (1973).
H. Okawa, T. Tokii, Y. Muto and S. Kida, *ibid., 46,* 2464 (1973).
H. Okawa, I. Ando and S. Kida, *ibid., 47,* 3041 (1974).
T. Ichinose, Y. Nishida, H. Okawa and S. Kida, *ibid., 47,* 3045 (1974).

5 J. J. Grzybowski, P. H. Merrell and F. L. Urbach, *Inorg. Chem.,* (1978).

6 G. S. Vigee and K. M. Moore, *Inorg. Chim. Acta, 66,* 125 (1982).

7 E. I. Solomon, in 'Copper Proteins', T. G. Spiro, Ed., Wiley, New York (1981).

8 J. A. Larrabee and T. G. Spiro, *J. Am. Chem. Soc., 102* 4217 (1980).
J. M. Brown, L. Powers, B. Kincaid, J. A. Larrabee and T. G. Spiro, *J. Am. Chem. Soc., 102,* 4210 (1980).

9 Y. Nishida, K. Takahashi, H. Kuremoto and S. Kida, *Inorg. Chim. Acta, 54,* L103 (1981).
M. G. Simmons, C. L. Merrill, I. J. Wilson, L. A. Bottomley and K. M. Kadish, *J. Chem. Soc., Dalton,* 1827 (1980).

10 T. N. Sorrell and C. J. O'Connor, *Inorg. Chem.,* submitted.
V. McKee, J. V. Dagdigian, R. Bau and C. A. Reed, *J. Am. Chem. Soc.,* 881 (1981).

11 V. H. Crawford, H. W. Richardson, J. R. Wasso, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem., 15,* 2107 (1976).

12 K. J. Hodgson, *Prog. Inorg. Chem., 19,* 173 (1975).

13 S. G. N. Roundhill, D. M. Roundhill, D. R. Bloomquist, C. Landee, R. D. Willett, D. M. Dooley and H. B. Gray, *Inorg. Chem., 18,* 831 (1979).

14 W. E. Marsh, K. C. Patil, W. E. Hatfield and K. J. Hodgson, *Inorg. Chem., 22,* 511 (1983).

15 F. Ullman and K. Brittner, *Ber. Dtsch. Chem. Ges.,* 1909, 2539.

16 C. J. O'Connor, *Prog. Inorg. Chem., 29,* 203 (1982).

17 C. J. O'Connor, C. L. Klein, R. J. Majeste and L. M. Trefonas, *Inorg. Chem., 21,* 64 (1982).

18 C. J. O'Connor, E. J. Cucauskas, B. S. Deaner and E. Sinn, *Inorg. Chim. Acta, 32,* 29 (1979).

19 R. J. Majeste, C. L. Klein and E. D. Stevens, *Acta Cryst., C39,* 52 (1983).

20 B. Bleaney and K. D. Bowers, *Proc. Reg. Soc., London, A214,* 451 (1952).

21 T. N. Sorrell, D. L. Jameson and C. J. O'Connor, *Inorg. Chem., 23,* 190 (1984).

22 E. I. Soloman, in 'Copper Proteins', T. G. Spiro, Ed., John Wiley & Sons, New York, chapter 1 (1981).