Structural Comparison of Cu^{I} and Cu^{II} Complexes displaying Analogous N_2S_2 Co-ordination; *X*-Ray Analyses of Tetraco-ordinate $[Cu(pma)]BPh_4$ and Pentaco-ordinate $[Cu(pma)SO_4]$ [pma = 2-pyridylmethylbis-(2-ethylthioethyl)amine]

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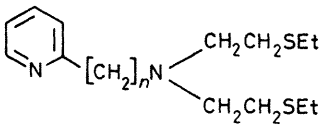
Summary The synthesis and *X*-ray structural characterization of the Cu^{I} and Cu^{II} complexes $[Cu(pma)]BPh_4$ and $[Cu(pma)SO_4]$ [pma = 2-pyridylmethylbis-(2-ethylthioethyl)amine] are reported, both display N_2S_2 co-ordination with the Cu^{I} complex exhibiting trigonal pyramidal geometry while the Cu^{II} derivative shows a distorted trigonal bipyramidal geometry which includes a co-ordinated sulphate group.

CO-ORDINATION complexes of Cu^{I} and Cu^{II} with nitrogen- and sulphur-donating ligands continue to be of interest as models for the redox active sites in the 'blue' copper oxidases and the 'blue' copper electron transfer proteins [1] Many of the unusual spectral and redox properties of the 'blue' copper proteins have been ascribed to the presence of distorted tetrahedral geometry and the particular ligand co-ordination [2–4] In order to understand better the nature of the Cu^{I}–Cu^{II} redox process, it is necessary to examine the

structural and chemical consequences of this metal in different oxidation states, but occupying similar co-ordination environments. This has led us to examine the co-ordination complexes of Cu^{I} and Cu^{II} with a new series of tripodal, tetradentate, N_2S_2 ligands, (**1**), which are designed



(1)

pma, $n = 1$

pea, $n = 2$

to impart pseudo-tetrahedral co-ordination geometry to the metal ion. We have previously communicated[5] the synthesis and structure of $[Cu(pea)]BPh_4$, demonstrating the feasibility of stabilizing a copper(I) complex in a pseudo-tetrahedral geometry with this ligand design. We report here the synthesis and preliminary *X*-ray structural study of both the Cu^{I} and Cu^{II} complexes of pma, $[Cu(pma)]BPh_4$ and $[Cu(pma)SO_4]$, in which a similar co-ordination geometry is adopted by the pma ligand in both structures, even though the co-ordination number is increased from four to five on going from Cu^{I} to Cu^{II}.

The ligand, pma, was synthesized by the reaction of 2-picolyl chloride hydrochloride and bis(2-ethylthioethyl)-amine hydrochloride in anhydrous MeOH in the presence of K_2CO_3. $[Cu(pma)]BPh_4$ was obtained by the reaction of pma with $Cu(MeCN)_4BF_4$ in MeOH under N_2, followed by addition of $NaBPh_4$. Recrystallization from CH_2Cl_2–MeOH yielded colourless crystals. Deep blue crystals of $[Cu(pma)SO_4]\cdot 7H_2O$ were obtained after the reaction of pma with $CuSO_4$ in water, upon addition of acetone and cooling.

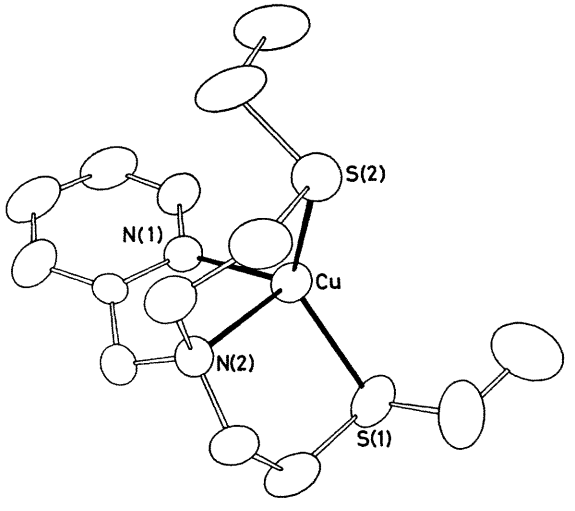


FIGURE 1. A perspective view of the $[Cu(pma)]^+$ unit, showing the atom labelling scheme for the copper co-ordination sphere. Relevant bond lengths (Å) and angles (deg) are: Cu–S(1), 2·230(5); Cu–S(2), 2·275(5); Cu–N(1), 2·035(10); Cu–N(2), 2·158(8); S(1)–Cu–S(2), 122·1(2); S(1)–Cu–N(1), 127·6(3); S(1)–Cu–N(2), 90·5(3); S(2)–Cu–N(1), 109·9(3); S(2)–Cu–N(2), 90·4(3); N(1)–Cu–N(2), 82·9(3).

Crystal data: $[Cu^{I}(pma)]BPh_4$, triclinic, space group $P\bar{1}$, $a = 11{\cdot}455(2)$, $b = 13{\cdot}718(2)$, $c = 11{\cdot}296(2)$ Å, $\alpha = 88{\cdot}93(4)$, $\beta = 85{\cdot}84(4)$, $\gamma = 71{\cdot}28(3)°$, $U = 1676{\cdot}7$ Å^3, $Z = 2$. A total of 2555 symmetry-independent reflections contributed to the solution, which was refined to a current $R = 0{\cdot}099$. $[Cu^{II}(pma)SO_4]$, triclinic, space group $P\bar{1}$, $a = 11{\cdot}415(1)$, $b = 12{\cdot}673(1)$, $c = 9{\cdot}806(1)$ Å, $\alpha = 101{\cdot}18(1)$, $\beta = 94{\cdot}28(1)$, $\gamma = 71{\cdot}00(1)°$, $U = 1315{\cdot}7$ Å^3, $Z = 2$. The structural analysis was based on 3859 symmetry-independent reflections and the current $R = 0{\cdot}058$.†

The stereochemistry of the $[Cu^{I}(pma)]^+$ unit is shown in Figure 1, which illustrates the distortion about the Cu^{I} centre from tetrahedral toward trigonal pyramidal geometry. The Cu^{I} ion is displaced 0·08 Å from the basal plane generated by S(1), S(2), and N(1), toward the apical N(2). The overall geometry is similar to that previously reported for $[Cu(pea)]^+$.[5] The $[Cu^{II}(pma)SO_4]$ unit is shown in Figure 2, which illustrates the essentially trigonal bipyramidal co-ordination geometry assumed by the copper atom. The basal plane is defined by the two sulphide sulphurs and the pyridyl, N(1), donors of the pma ligand while the axial positions are defined by the amine nitrogen, N(2), and an oxygen from the sulphate group. The pma ligand maintains an overall trigonal pyramidal arrangement of donor atoms about the Cu^{II} ion analogous to that observed for the Cu^{I} species.

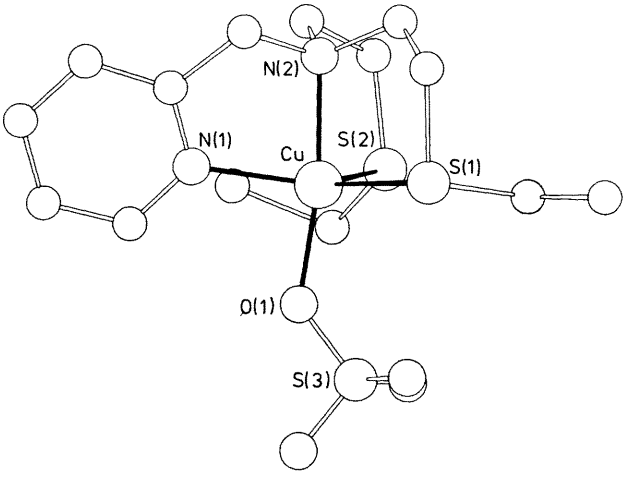


FIGURE 2. A perspective view of the $[Cu(pma)SO_4]$ unit, showing the atom labelling scheme for the copper co-ordination sphere. Relevant bond lengths (Å) and angles (deg) are: Cu–S(1), 2·385(1); Cu–S(2), 2·461(2); Cu–N(1), 2·021(5); Cu–N(2), 2·033(4); Cu–O(1), 1·909(4); S(1)–Cu–S(2), 108·20(7); S(1)–Cu–N(1), 129·4(1); S(2)–Cu–N(1), 120·2(1); N(2)–Cu–O(1), 170·8(2); S(1)–Cu–N(2), 87·6(1); S(1)–Cu–O(1), 100·3(1); S(2)–Cu–N(2), 87·6(1); S(2)–Cu–O(1), 96·0(2); N(1)–Cu–N(2), 82·3(2); N(1)–Cu–O(1), 88·9(2).

The most significant difference between the copper(I) and copper(II) complexes is the expansion of the basal plane in the Cu^{II} complex to accommodate the oxygen-donor capping the $Cu(pma)^{2+}$ pyramid. The Cu^{II} ion is displaced 0·19 Å toward the apical oxygen of the sulphate group, a displacement of 0·27 Å through the basal plane from the Cu^{I} position in $[Cu(pma)]^+$.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The observations that the configuration and mode of co-ordination of the tetradentate pma ligand remain similar in both Cu^{I} and Cu^{II} derivatives is unique, since in other structural studies of Cu^{I} and Cu^{II} complexes of identical ligands, gross geometrical changes are observed [6] This is important because it shows that pma and related ligands may be suitable for studies in which one wishes to define and constrain the co-ordination environment of the copper ion, as may occur in the 'blue' copper proteins

Electrochemical studies by cyclic voltammetry show that $[Cu(pma)SO_4]\cdot 3H_2O$ undergoes a reversible one-electron reduction, $E_{1/2} = +0{\cdot}30$ V *vs* standard calomel electrode (80% MeOH–H_2O, 0·1 M $Bu^{n}_{4}NClO_4$, carbon electrode) The electronic spectra of blue solutions in MeOH show peaks at 335 nm (ϵ 4200 l mol^{-1} cm^{-1}), 700 nm (ϵ 280), and 825 nm (ϵ 370) The e s r spectrum (MeOH) is rhombic $g_1 = 2{\cdot}20$, $A_1(Cu) = 144 \times 10^{-4}$ cm^{-1} These results also suggest that the Cu^{I}pma/Cu^{II}pma system may be a good chemical and structural model for the active site of the 'blue' copper proteins and substantiates the importance of further investigations of ligands of this type

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