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Distorted Tetrahedral Complexes of Copper(I) and Copper(II) Displaying N_2S_2 Co-ordination. *X*-Ray Crystal Structure of [2-(2-Pyridyl)ethyl]-bis[2-(ethylthio)ethyl]aminecopper(I) Tetraphenylborate

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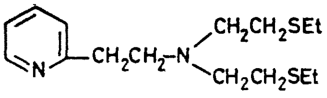
Summary Reaction of the appropriate copper starting material with the new N_2S_2 ligand [2-(2-pyridyl)ethyl]-bis[2-(ethylthio)ethyl]amine (pea) (**A**) which is constrained to pseudo-tetrahedral co-ordination, yields the Cu^I and Cu^{II} derivatives, $[Cu(pea)]^+$ and $[Cu(pea)]^{2+}$; the Cu^{II} species shows low energy *d–d* absorption bands suggesting a distorted co-ordination geometry and the *X*-ray structure of the Cu^I derivative confirms a pseudo-tetrahedral co-ordination environment.

THE 'blue' copper oxidases and the related 'blue' copper electron transfer proteins have been studied extensively, in part because of the 'unusual' spectral and redox properties of their copper centres.[1,2] Recently an *X*-ray structural determination at 2·7 Å resolution has shown that the copper centre in spinach plastocyanin is co-ordinated to two histidine, one methionine, and one cysteine residue in a distorted tetrahedral geometry.[3] This finding has helped to focus attention on the chemistry of copper ions with nitrogen–sulphur ligands.

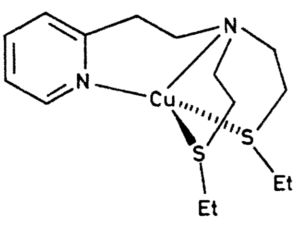
In spite of the results for plastocyanin, it is clear that important differences do exist in the nature of the 'blue' sites in various proteins and systematic studies are needed to elucidate the details of co-ordination geometry, donor atoms set, spectral, and redox relationships in copper(I) and copper(II) complexes.[1]

Our interest has also focused on the co-ordination chemistry of Cu^I, since it is an intimate part of the copper redox couple and its chemistry is rather undeveloped.[4] We have synthesized new N_2S_2 ligands which are designed to impart pseudotetrahedral geometry upon metal ions and allow for systematic studies.[1] Here, we report the synthesis and preliminary results of a structural study of a stable Cu^I derivative of one such tetradentate ligand. The Cu^{II} analogue has also been synthesized and its spectral properties are consistent with a pseudotetrahedral geometry.

The ligand [2-(2-pyridyl)ethyl]bis[2-(ethylthio)ethyl]-amine (pea) (**A**) was synthesized *via* the acid-catalysed addition[5] of bis[2-(ethylthio)ethyl]amine† to 2-vinyl-pyridine and purified by chromatography on silica gel in diethyl ether.



(A)



(B)

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† Made by the reaction of ethanethiol in methanol with bis(2-chloroethyl)amine in the presence of base, and purified as the hydrochloride salt.

Mixing equimolar solutions of pea with aqueous copper(II) nitrate gave an intense blue solution. Addition of $NaBPh_4$ resulted in spontaneous reduction giving a colourless precipitate (*ca.* 30%) which was recrystallized from CH_2Cl_2–MeOH to give analytically pure $[Cu(pea)]^+[BPh_4]^-$.‡ This Cu^I derivative can be made in higher yield using $Cu(MeCN)_4(BF_4)$ followed by metathesis to give the tetraphenylborate salt. The Cu^{II} complex, $[Cu(pea)]^{2+}[BF_4^-]_2$, was made in 70% yield by reaction of pea with $Cu(BF_4)_2 \cdot 6H_2O$ in methanol. Precipitation with Et_2O followed by recrystallization from acetone–Et_2O gives a bright blue crystalline solid.‡

Crystal data: $[Cu(pea)][BPh_4]$, triclinic, space group $P\bar{1}$, with $a = 11{\cdot}274(3)$, $b = 11{\cdot}556(4)$, $c = 14{\cdot}285(4)$ Å, $\alpha = 88{\cdot}95(3)$, $\beta = 76{\cdot}87(2)$, $\gamma = 86{\cdot}93(3)°$, $Z = 2$. The structure analysis is based on 3492 independent reflections ($I_{obs}) > 2{\cdot}58\sigma(I_{obs})$ (Mo-K_α, $\mu = 7{\cdot}68$ cm^{-1}) and R is currently 0·034.§

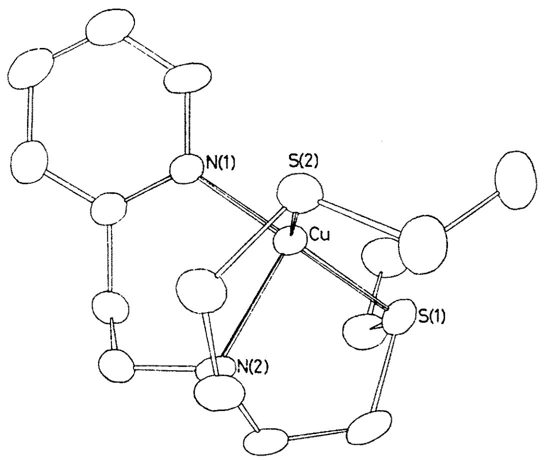

FIGURE 1. A perspective view of the cation $[Cu(pea)]^+$ (**B**) (ORTEP drawing) showing the atom labelling scheme for all non-hydrogen atoms. The relevant bond lengths and angles are: Cu–S(1), 2·247; Cu–S(2), 2·343; Cu–N(1), 2·000; and Cu–N(2), 2·192 Å; ∠S(1)–Cu–S(2), 121·0(1); ∠S(1)–Cu–N(1), 135·0(1); ∠S(1)–Cu–N(2), 91·8(1); ∠S(2)–Cu–N(1), 102·6(1); ∠S(2)–Cu–N(2), 88·9(1); and ∠N(1)–Cu–N(2), 100·1(1)°. E.s.d.s in the bond lengths average: Cu–S, 0·001; Cu–N, 0·003; S–C, 0·006; N–C, 0·006; and C–C, 0·009 Å.

The stereochemistry of the cation (**B**) is shown in Figure 1 which demonstrates the severely distorted tetrahedral geometry about the Cu^I centre, with a CuS(1)S(2)–CuN(1)N(2) dihedral angle of 87·1°. The sulphide donor groups are clearly non-equivalent, displaying distinct Cu–S distances: Cu–S(1) 2·247 and Cu–S(2) 2·342 Å. This distortion arises in part from the absence of the pseudo-mirror symmetry through the pyridyl ring and N(2) of the ligand group, to accommodate the co-ordination requirements of the central Cu^I ion, which lies 0·69 Å out of the plane formed by the pyridine ring. The presence of only two methylene groups between N(2) and the terminal thioether donor groups provides an additional source of distortion, producing a strained 5-membered chelate ring system which cannot approach the idealized tetrahedral value for the N(2)–Cu–S angles. The overall effect is to compress the idealized tetrahedron along its C_3 axis, expanding the N(1)–S(1)–S(2) face and drawing the Cu^I to 0·15 Å above this face.

The visible and near-i.r. electronic spectrum of $[Cu(pea)]^{2+}$ in acetone has been recorded and shows a distinct 'blue' band centred at 640 nm (ϵ 285 l mol^{-1} cm^{-1}) with a shoulder at *ca.* 900 nm (ϵ 140 l mol^{-1} cm^{-1}). Intense charge-transfer bands occur below 330 nm. The position and intensity of the 640 and 900 nm absorptions indicate that these can be assigned to *d–d* bands similar to those observed in other Cu^{II}–sulphide complexes[6] and pseudo-tetrahedral Cu^{II}–N_4 complexes,[7] with the copper–sulphide and copper–nitrogen charge-transfer bands occurring at much higher energies.[6] Figure 2 shows the e.s.r. spectrum of a frozen acetone solution of $[Cu(pea)][BF_4]_2$, exhibiting anisotropy with $g_\parallel = 2{\cdot}21$ and $A_\parallel(Cu) = 173 \times 10^{-4}$ cm^{-1}. These parameters are in the normal range for copper(II) complexes and in particular the value for $A_\parallel$(Cu) is quite distinct from that found in the 'blue' proteins.

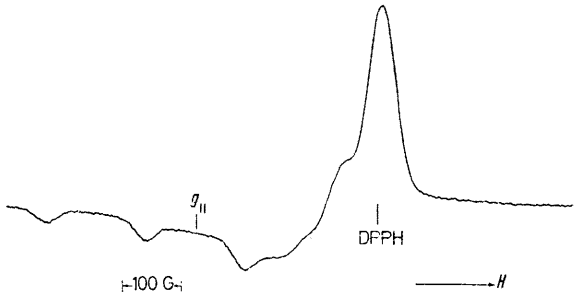

FIGURE 2. E.s.r. spectrum of $[Cu(pea)][BF_4]_2$ as a frozen solution in acetone at 77 K. DPPH = Diphenylpicrylhydrazyl.

Model studies indicate that pea cannot confer planar co-ordination upon a copper(II) ion and the absorption spectrum is also consistent with a distorted geometry. Along with other studies,[7,8] these results suggest that in addition to the donor atom type, the intimate details of the co-ordination geometry and the type of distortion observed contribute to the unusually low copper hyperfine coupling constants found in the proteins.

The structural results on the Cu^I complex and the implied pseudo-tetrahedral co-ordination geometry for $[Cu(pea)]^{2+}$ suggests that both copper(I) and copper(II) derivatives of pea are good structural models for the active sites of the

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‡ Satisfactory C, H, and N analyses were obtained for these compounds.

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

proteins. The stability of the copper(I) compounds[9] of these ligands will enable detailed examination of relationships between the two oxidation states of copper including structural, redox, spectral, and kinetic studies.

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