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Synthesis and X-ray Structural Characterization of Cu(I) and Cu(II) Derivatives of a New Symmetric Tripodal Ligand $N(CH_2CH_2\text{-}py)_3$, (py = 2-pyridyl)

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The coordination environments observed for the active sites of the Type I 'blue' copper proteins [1–3] and the observations of positive reduction potentials for the copper centers in other redox active copper metalloproteins [1, 4] has prompted interest in the study of copper(I) and copper(II) ions in non-planar coordination geometries with thioether and/or unsaturated nitrogen donor ligands. To this end, a number of studies of copper complexes utilizing 'tripodal' tetradentate ligands have been reported. These include symmetric tripodal ligands $N((CH_2)_n{-}L)_3$ where L is a donor group such as thioether [5–8], benzimidazole [9], pyrazole [10] or imidazole [11] groups.

We have reported structural studies of Cu(I) and Cu(II) complex of tripodal N_2S_2 ligands [12–14]. Related to these systematic investigations of structural, electronic, redox and reactivity trends in such Cu(I)–Cu(II) chelates, we now report preliminary studies on complexes of the ligand $N(CH_2CH_2py)_3$, py = 2-pyridyl (tepa), which represent the first structural studies on both Cu(I) and Cu(II) complexes of symmetric tripodal N_4 ligands.

The ligand tepa was synthesized by reaction of excess 2-vinyl pyridine with ammonium acetate in methanol followed by chromatography on alumina. The complex $Cu^I(tepa)BPh_4$(I) forms by reaction of cupric nitrate with tepa in MeOH followed by reduction and precipitation with excess $NaBPh_4$. Recrystallization from CH_2Cl_2–Et_2O affords yellow–brown crystals. $Cu^{II}(tepa)(Me\text{-}Im)(PF_6)_2$(II), (Me-Im = 1-methyl imidazole) was isolated by reaction of cupric nitrate, tepa and Me-Im in MeOH, followed by precipitation with excess PF_6^-. Purification was effected in acetone–Et_2O.

Compound I crystallizes in monoclinic space group Cc with the unit cell parameters a = 16.310(3), b = 12.799(2), c = 18.315(3) Å, β = 100.82(1)°, V = 3755.3 Å^3 and Z = 4. A total of 3002 unique reflections have been refined to a R value of 0.055. The Cu(II) complex II crystallized in the monoclinic space group $P2_1/n$ with a = 10.466(2), b = 22.498(7), c = 14.002(5) Å, β = 110.2(2)°; V = 3093.8 Å^3, and Z = 4. A total of 3211 unique reflections have been refined to an R value of 0.052 (MoKα, λ = 0.71069 Å).

An ORTEP drawing including selected bond angles and distances of I appears in Fig. 1. The Cu(I) complex is four-coordinate containing the symmetric tripodal N_4 ligand. The coordination geometry is pseudo-tetrahedral, distorted toward pyramidal with the Cu atom 0.31 Å above the N2–N3–N4 plane. The pyramidal nature of the complex allows a fifth ligand to coordinate in the corresponding Cu(II)

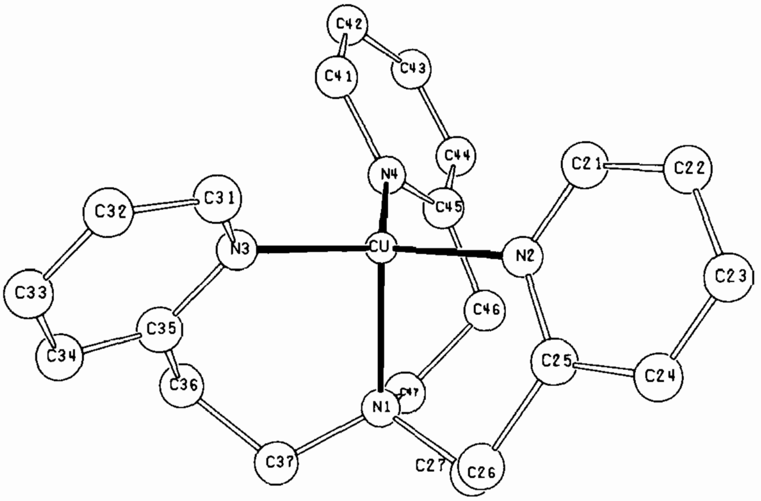

Fig. 1. ORTEP diagram of the Cu(tepa)$^+$ unit, showing the atom labelling scheme. Relevant bond lengths (Å) and angles (deg) are: Cu–N1, 2.192(6); Cu–N2, 2.021(5); Cu–N3, 2.012(5); Cu–N4, 2.022(5): N1–Cu–N2, 99.2(2); N1–CuN3, 99.8(2); N1–Cu–N4, 97.4(2); N2–Cu–N3, 111.9(2); N2–Cu–N4, 121.2(2); N3–Cu–N4; 120.0(2).

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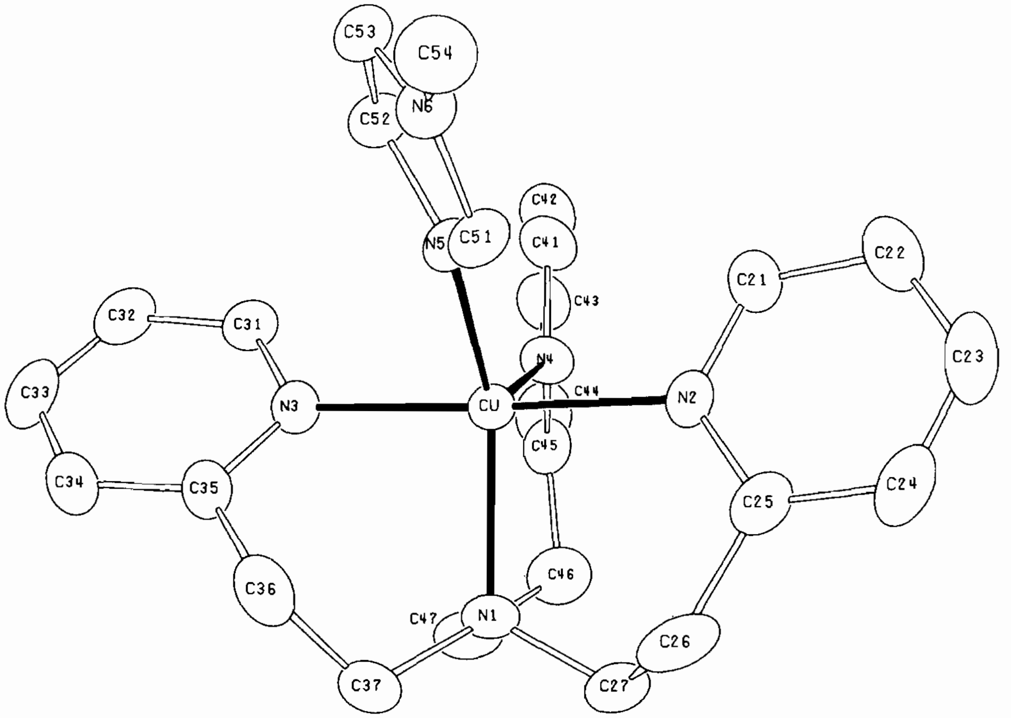

Fig. 2. ORTEP diagram of the Cu(tepa)(Me-Im)$^{+2}$ unit, showing the atom labelling scheme. Relevant bond lengths (Å) and angles (deg) are: Cu–N1, 2.101(4); Cu–N2, 2.027(5); Cu–N3, 2.039(5); Cu–N4, 2.197(5); Cu–N5, 2.002(5); N1–Cu–N2, 94.3(2); N1–Cu–N3, 88.3(2); N1–Cu–N4, 98.1(2); N1–Cu–N5, 145.0(2); N2–Cu–N3, 174.8(2); N2–Cu–N4, 93.1(2), N2–Cu–N5, 87.2(2); N3–Cu–N4, 91.0(2); N3–Cu–N5, 88.1(2); N4–Cu–N5, 116.8(2).

complex II, shown in Fig. 2. There, we have a distorted trigonal bipyramidal configuration, with N1, N4 and N5 from Me-Im comprising the trigonal plane. The axial positions consist of the pyridyl N2 and N3 atoms.

The complexes are both well behaved electrochemically. Cyclic voltammetric experiments (dimethylformamide, graphite, 0.1 *M* (N-Bu)$_4$NPF$_6$) show one electron processes for the Cu(I) (oxidation) and Cu(II) (reduction) complexes at $E_{1/2}$ = 0.29 V and $E_{1/2}$ = 0.26 V *vs.* NHE respectively. The effects of the presence of Me-Im, as well as Cl^-, NO_3^- etc. on the Cu(I) and Cu(II) coordination chemistry are being studied. Redox, epr, structural, reactivity and electronic spectral properties of these and related complexes are also under investigation.

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