

An Unusual Axial Co-ordination of Phenolate Oxygen to Copper(II): Crystal Structure of Chloro{2-[bis(2-pyridylmethyl)aminomethyl]-4-nitrophenolato}copper(II)

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A tripod ligand possessing two pyridine moieties and a phenolato group as pendants forms a mononuclear complex with an axial copper(II)-phenolate co-ordination in a square-pyramidal environment.

Copper complexes of ligands containing phenolic hydroxyl groups are of interest because of their relevance to copper enzymes such as tyrosinase¹ and galactose oxidase.² The former catalyses the hydroxylation of monophenols to diphenols and the two-electron oxidation of catechol to quinone while the latter catalyses the stereospecific oxidation of a broad range of primary alcohol substrates to the corresponding aldehydes. Karlin *et al.*³ recently reported phenolate-bridged dinuclear copper(II) complexes as analogues for the ligand probe derivatives of the active sites of tyrosinase and haemocyanin. In order to understand the physico-chemical properties of these dinuclear systems Karlin and co-workers^{4,5} have also explored the chemistry of the mononuclear analogues of the binucleating ligands. A very recent report on the crystal structure of galactose oxidase⁶ reveals a unique mononuclear copper site with two histidine nitrogens, a tyrosine oxygen and an acetate ion forming an almost perfect square and another tyrosine oxygen in the axial position to complete the square pyramid. We report here the isolation and X-ray crystal structure of a mononuclear copper(II) complex with an axial copper(II)-phenolate bond which may mimic the axial copper(II)-phenolate bond in galactose oxidase.

The tetradentate tripod ligand, 2-[bis(2-pyridylmethyl)aminomethyl]-4-nitrophenol (Hbnpn) was prepared according to the literature method.⁷ The copper complex was prepared by treating a methanolic solution (10 cm³) of the ligand (2 mmol) with CuCl₂·2H₂O (2 mmol) in methanol (4 cm³) and triethylamine (2 mmol) in methanol (2 cm³). The green precipitate formed was filtered off, dried and recrystallized from methanol (yield 90%). Dark green rectangular parallelepiped crystals of [Cu(bnpn)Cl] obtained were found suitable for X-ray diffraction.

The compound is a neutral species and its X-ray structure (Fig. 1)† reveals the co-ordination of the copper atom by two pyridine nitrogens, the tertiary amine nitrogen, the phenolate oxygen and the chloride ion. The geometry around copper(II) is best described as square pyramidal with a very small trigonal bipyramidal component, $\tau = 0.16$ [$\tau = (\beta - \alpha)/60$, where $\beta = \text{Cl-Cu-N}(9)$ 169.6° and $\alpha = \text{N}(2)\text{-Cu-N}(16)$ 160.1°]; for a perfect tetragonal and trigonal-bipyramidal geometries the value of τ is zero and unity respectively.¹² The basal plane is comprised of two pyridine and one tertiary amine nitrogen atoms and the chloride ion. As in other similar copper(II) complexes,^{13,14} the two pyridine nitrogens in the present complex are *trans* to each other. Copper is 0.223 Å above the

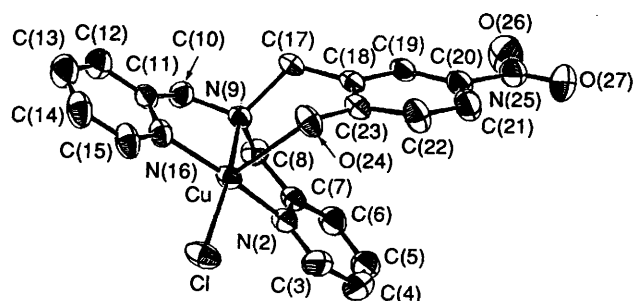


Fig. 1 Perspective ORTEP drawing of [Cu(bnpn)Cl] with atom numberings. The relevant bond lengths and bond angles are: Cu-N(2) 1.986(24), Cu-N(9) 2.060(25), Cu-N(16) 1.997(23), Cu-O(24) 2.268(25) and Cu-Cl 2.256(13) Å; N(2)-Cu-N(9) 82.9(1), N(2)-Cu-N(16) 160.1(1), N(9)-Cu-N(16) 82.3(1), O(24)-Cu-N(2) 100.1(1), O(24)-Cu-N(9) 91.7(1), O(24)-Cu-N(16) 93.5(1), Cl-Cu-O(24) 98.7(1), Cl-Cu-N(16) 95.9(1), Cl-Cu-N(9) 169.6(1), Cl-Cu-N(2) 96.4(1)°

plane and is axially co-ordinated to the phenolate oxygen [Cu-O(24) 2.268(25) Å].

The axial co-ordination of the phenolate ion is in contrast to the equatorial co-ordination encountered in all salicylaldehyde-derived copper(II) complexes^{15,16} and in the copper(II) complexes^{4,5} of the tripod ligand *N,N*-bis(2-pyridylethyl)-2-methylaminophenol analogous to Hbnpn, with chloride or azide co-ordination in the equatorial position. Obviously, it is the introduction of the -NO₂ group *para* to the phenolic group

† Crystal data. C₁₉H₁₇CuClN₄O₃, $M = 448.35$, triclinic, space group $P\bar{1}$ (no. 2), $a = 6.938(1)$, $b = 11.782(6)$, $c = 12.678(3)$ Å, $\alpha = 114.56(3)$, $\beta = 92.70(2)$, $\gamma = 95.36(2)$ °, $U = 934.23$ Å³, $F(000) = 458$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 13.87$ cm⁻¹, crystal dimensions 0.23 × 0.31 × 0.68 mm. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares to $R = 0.048$ using 3824 observed reflections with $I_o \geq 3.0\sigma(I_o)$. All the positions of hydrogens were obtained from Fourier difference synthesis and refined isotropically. The SHELX 400 system of programs⁸ was used for structure analysis and refinement. For absorption corrections a FORTRAN program⁹ written based on North *et al.*¹⁰ was used. The molecular structure was drawn using ORTEP.¹¹ Atomic coordinates and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

which brings about a change in the site of co-ordination of the phenolate ion, *viz.* equatorial to axial, even though the co-ordination geometry is approximately the same in both [Cu(bppn)Cl] as well as the azide⁵ complex for which the crystal structure ($\tau = 0$) is known. Whereas one of the pyridines in the azide⁵ complex takes up the axial position, in [Cu(bppn)Cl] both the pyridine donors occupy equatorial sites. Consequently, the $N_{py}-Cu-N_{py}$ angle changes from 95.5° in the azide complex to 160.1° in [Cu(bppn)Cl]. However, this angle is less than that for other copper(II) complexes containing two pyridine donor groups ($168-178^\circ$) and adopting a square-pyramidal geometry.^{13,14} The weak co-ordination of the chloride ion in the equatorial position is evident from the long Cu-Cl bond [$2.256(13)$ Å]; it is longer than the axial Cu-Cl bond in [Cu(tpma)Cl]⁺ [tpma = tris(2-pyridylmethyl)amine],¹⁷ [Cu(bipa)Cl]⁺ {bipa = bis[2-(1-methylimidazolyl)methyl](2-pyridylmethyl)amine}¹⁸ and [Cu(tmima)Cl]⁺ {tmima = tris[2-(1-methylimidazolyl)methyl]amine}¹⁸ complexes.

The reflectance spectrum of [Cu(bppn)Cl] exhibits a broad ligand-field band around $13\,700\text{ cm}^{-1}$. However, in dimethylformamide (dmf) two ligand-field bands ($14\,000$ and $10\,200\text{ cm}^{-1}$) were observed, the position and the band separation being characteristic of square-pyramidal geometry.¹⁹ This is also supported by the axial EPR spectra* both in the polycrystalline state and in cryogenic dmf solution.

Though there are mononuclear copper(II) complexes with other types of oxygen donors, for example ether oxygen in the axial position,²⁰ there seems to be no report available for the phenolate O⁻ co-ordinating to mononuclear copper(II). The only such bonds reported so far are in binuclear²¹ compounds. Further, the crystal structure²² of a tyrosylhistidinate complex of Cu^{II} reveals a long axial Cu^{II}-O(phenol) bond [$2.601(4)$ Å], formed by the phenolic oxygen but from the neighbouring molecule. Hence to our knowledge the present structure is the first structurally well characterized mononuclear copper(II) complex possessing an axial phenolate(O)-Cu^{II} bond.

Studies on the electrochemistry of [Cu(bppn)Cl] and other similar complexes with one or two nitrophenolate groups and varying nitrogen-donor atom set are under progress.

Acknowledgements

We thank Department of Science and Technology, New Delhi for a generous research grant (No. SP/S1/I04/86). One of the

authors (U. R.) acknowledges University Grants Commission, New Delhi for a Fellowship.

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* For the polycrystalline sample at room temperature, $g_{\parallel} = 2.269$, $g_{\perp} = 2.073$, $A_0 = 13 \times 10^{-4}\text{ cm}^{-1}$. In dmf at 77 K, $g_{\parallel} = 2.244$, $A_{\parallel} = 179 \times 10^{-4}\text{ cm}^{-1}$, $g_{\perp} = 2.070$, $A_{\perp} = 33 \times 10^{-4}\text{ cm}^{-1}$.