Linear Cu–OH–Cu: Magnetic Silence for Dicopper(II) in Trigonal Bipyramidal Coordination Geometry

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A dicopper(II) μ-hydroxo cryptate with trigonal bipyramidal copper coordination geometry and linear Cu–O(H)–Cu bridge exhibits virtual diamagnetism arising from efficient antiferromagnetic exchange between d_{z^2} magnetic orbitals mediated *via* the $2p_z$ orbital of the hydroxo bridge.

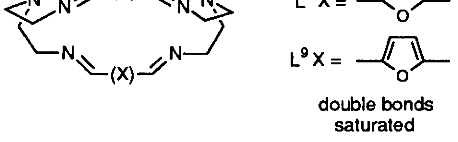
The coupled binuclear copper site as found, for example, in oxidase enzymes such as laccase, ascorbate oxidase and ceruloplasmin,[1] involved in multielectron redox reactions of molecular oxygen, has stimulated a large volume of work on synthesis of model dicopper compounds.[2] In most of these model compounds, the coordinate geometry of the copper(II) cation is square-based, so that orbital overlap considerations involved to explain the antiferromagnetic interaction relate to the $d_{x^2-y^2}$ magnetic orbital. As the high-resolution structure of ascorbate oxidase[3] shows that a likely candidate for the bridging ligand in the coupled site in ascorbate oxidase is hydroxo-, interest attaches to the dependance of magnetic interaction on geometric parameters such as Cu–OH–Cu bridge angle. For dihydroxo bridged systems, correlations of the degree of interaction with geometric parameters in the Cu–$(OH)_2$–Cu link have been developed.[4] Binuclear copper complexes bridged by a single hydroxo link are much rarer, but give rise to the strongest interactions so far discovered. In two structurally characterised cases,[5,6] which exhibit virtual magnetic silence arising from strong antiferromagnetic interaction, the Cu^{II} ions are in approximate square-planar geometry and Cu–Cu distances of 3.38 and 3.64 Å together with relatively large Cu–O–Cu angles of around 132 and 143° apply.

These observations have stimulated generalisations,[7] which suggest Cu–Cu distances below 3.5 Å and bridge angles of around 135° are prerequisite for strongly interacting dicopper(II) sites.

In the much less common trigonal bipyramidal geometry where the magnetic orbital is d_{z^2} the parameters governing magnetic exchange between bridged copper ions have not been established. However, naive arguments suggest that the unidirectional nature of the d_{z^2} orbital may lead to enhanced interaction, because of the efficient overlap which would result between O_{2p_z} and d_{z^2} at large values of the Cu-OH-Cu bridging angle. For a μ-hydroxo or μ-alkoxo bridge, for example, highly efficient exchange is to be expected when disposition of the d_{z^2} orbitals is colinear with O_{2p_z}.

In the series of azacryptands which we have recently synthesised,[8] magnetically silent dicopper(II) μ-hydroxo complexes have been obtained with the ligands L^1 and L^2.[9] Most of the other ligands fail to accommodate Cu^{II}, having a preference[10] for the lower oxidation state, Cu^I. However, while with L^1 and L^2 bright green microcrystalline products, $[Cu_2L(OH)]X_3$, ($L = L^1$ **1**; $L = L^2$ **2**; $X = ClO_4^-, CF_3SO_3^-$) could be isolated by treatment of the free cryptand with copper(II) salt followed by rapid removal of solvent, these products were not sufficiently stable in solution in the long term to permit the growth of crystals large enough for X-ray crystallographic investigation. The hydrolytically sensitive imine bonds were attacked on standing in solution for any length of time, resulting in ring opening and isolation of copper(II) complexes of the appropriate dipendant amine macrocycle. So we were unable to confirm our suspicion that the strong antiferromagnetic interaction derived from near linearity of the N_{br}–Cu–OH–Cu–N_{br} assembly, nor indeed the guess that the somewhat superior solution stability of the L^2 dicopper cryptate **2** derived from the existence of an OH ··· O(furan) hydrogen bond.

We have now synthesised the more chemically robust octaamine ligand, L^9, obtained from L^2 by BH_4^- reduction.[9] Crystals of its μ-hydroxo dicopper(II) cryptate, $[Cu_2L^9(OH)]X_3 \cdot H_2O$ **3** ($X = CF_3SO_3^-$)† can be obtained by treatment of the ligand with copper(II) salt in basic solution followed by slow solvent evaporation. This bright-green product shows the expected sharp relatively high frequency IR ν_{OH} absorption at 3554 cm^{-1}. The electronic spectrum in H_2O solution or in the solid state shows the characteristic splitting of d–d absorption into two roughly equal intensity components *ca.* 700 and 860 nm, indicative of trigonal bipyramidal geometry. In addition there is, as always with μ-hydroxo dicopper(II) complexes, an intense ($\varepsilon \approx 4000$ mol dm^{-3} cm) near-UV ligand-to-metal charge-transfer absorption, close to 360 nm in this instance.



Variable temperature magnetic susceptibility investigations of **3** made with an Oxford Instruments magnetic susceptibility balance showed a tiny room-temperature moment, which reduced further on cooling to 4 K (Fig. 1). The increase in susceptibility at low temperature indicated a paramagnetic impurity, estimated from the data at 4 K as 1.3% assuming Curie-law behaviour and a *g* value of 2. Fitting of the interaction to the Bleaney–Bowers equation (including the impurity),[11] assuming a diamagnetic correction of -602×10^{-6} cgsu per complex, yielded a magnetic exchange parameter, -2 J, of (880 ± 70) cm^{-1}, using a *g* value of 2.07 and temperature-independent-paramagnetism (TIP) of 95×10^{-6} cgsu per Cu^{2+} ion. In agreement with these results, the ESR spectrum in frozen solution shows only ill-defined absorption associated with the small proportion of paramagnetic impurity.

X-Ray crystallographic structure determination‡ shows (Fig. 2) each copper ion coordinated to three imine nitrogens, a bridgehead amine, and the expected bridging hydroxide [O(1)]. The furan oxygen atoms are not coordinated to copper but there is a hydrogen bond between one ring and the central hydroxide [O(1)–O(11), 2.819(7) Å]. There are no significant interactions between the cation and the triflate anions or solvate water molecules. The copper ions have reasonably good trigonal bipyramidal geometry, although the copper ions lie slightly out of the plane of the three imine nitrogens, in the direction of the hydroxo-bridge. The Cu–O–Cu angle is 174° and the copper ions lie nearly, but not exactly on the N(1)–N(2) line [appropriate angles: N(1)CuN(2) = 179°, Cu(1)Cu(2)N(1) = 178°, N(1)CuO(1) = 178° and O(1)CuN(2) = 179°]. So, to a first approximation our prediction of linearity

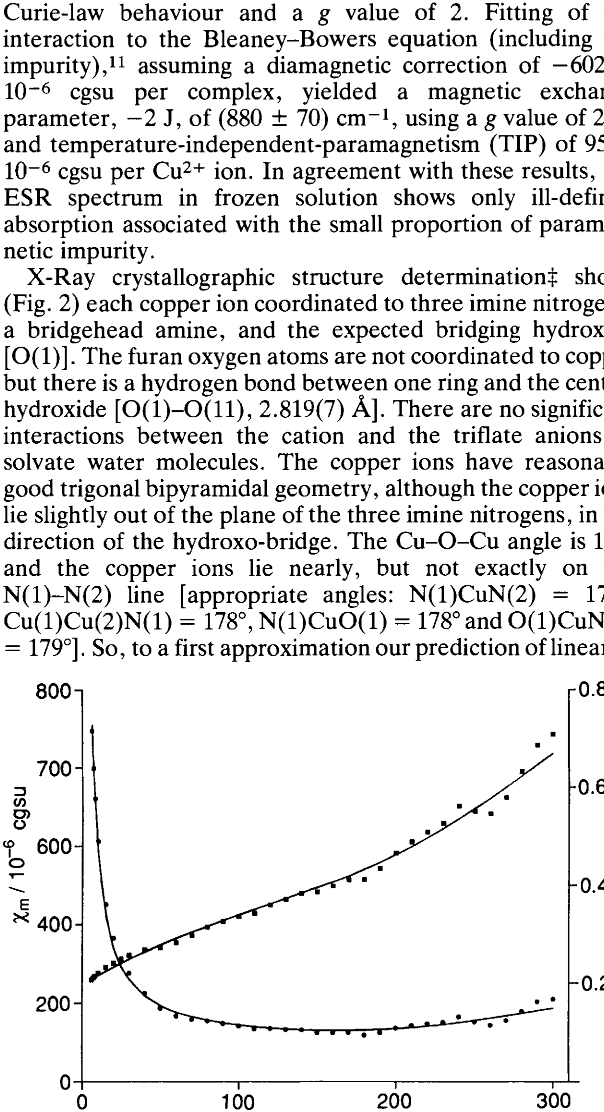


Fig. 1 Temperature variation of magnetic susceptibility and effective magnetic moment for [**3**] assuming $g = 2.07$, TIP = 95×10^{-6} cgsu per Cu ion, $-2J$ = (880 ± 70) cm^{-1}. Calculated curves ——; χm (experimental) ●; μ (experimental) ■.

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† Satisfactory element analyses were obtained. FAB-MS peaks: base peak $[Cu_2L^9](CF_3SO_3)$ at *m/z* = 843; intense cluster $[Cu_2L^9(OH)](CF_3SO_3)_2$ centred on *m/z* = 1009.

‡ *Crystal data*: $[Cu_2(L^9)OH](CF_3SO_3)_3 \cdot H_2O$, $C_{33}H_{51}N_8O_{14}F_9S_3Cu_2$, green block, crystal dimensions $0.56 \times 0.42 \times 0.30$ mm, monoclinic, $a = 12.434((3)$, $b = 16.919(4)$, $c = 22.300(4)$ Å, $\beta = 92.23(1)$, $U = 4688(2)$ Å^3, $\mu = 1.147$ mm^{-1}, space group $P2_1/n$, $Z = 4$, $F(000) = 2416$. Data were collected at 143 K on a Siemens P4 four-circle diffractometer using graphite-moderated Mo-Kα radiation ($\lambda = 0.71073$ Å). Using 2° ω-scans at 5° min^{-1}, 7273 reflections were collected in the range $4 < 2\theta < 47°$, 6914 unique reflections ($R_{int} = 0.0169$) were used in the refinement. The structure was solved by direct methods.[12] Hydrogen atoms were inserted at calculated positions with a common, fixed isotropic temperature factor, except for those on the hydroxo bridge and the disordered water solvate molecule. All the data were used for refinement of 611 parameters on F^2 which converged with $wR2 = 0.168$, Gof = 1.065 (and conventional $R1 = 0.059$ for $I > 2\sigma\ I$). All programs used in the structure refinement are contained in the SHELXL-92[13] package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

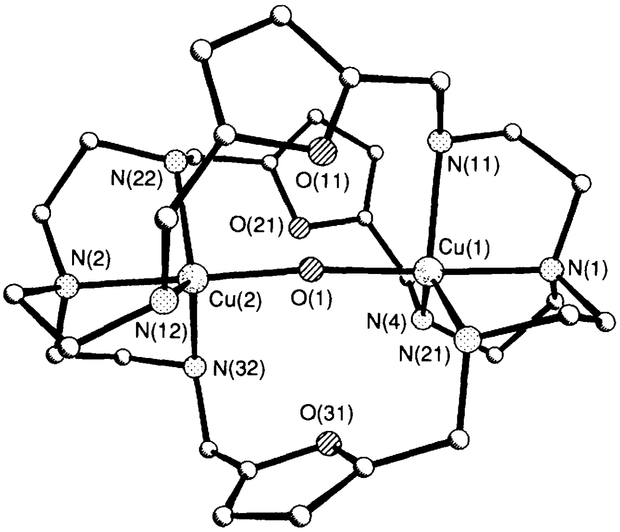

Fig. 2 View of the $[Cu_2L]^{3+}$ cation. Selected bond distances (Å): Cu–Cu 3.900(1); Cu(1)–N(1) 2.075(5), Cu(1)–O(1) 1.957(4), Cu(1)–N(11) 2.173(5), Cu(1)–N(31) 2.129(5), Cu(1)–N(21) 2.144(5), O1(H)···O(11)(furan) 2.819(7); Selected bond angles (°): N(11)Cu(1)N(31) 116.9(2), N(31)Cu(1)N(21) 124.9(2), N(21)Cu(1)N(11) 114.9(2), N(1)Cu(1)N(1) 84.2(2), N(1)C(1)O(1) 93.8(2).

based on magnetic silence is accurate. The copper–copper distance of 3.900(1) Å may be found surprisingly long by those used to interacting $d_{x^2-y^2}$ systems, but follows logically from the requirement for linear geometry together with a typical Cu–O bond distance of *ca.* 1.95 Å.

The observation of a short O···O distance between one of the furan oxygens and the bridging oxygen, representing a moderately strong hydrogen bond, is gratifying, as it rationalises the superior host properties of the furan-based cryptands for the $[Cu\text{–}OH\text{–}Cu]^{3+}$ assembly. The slight deviation of OH^- from the line of the Cu–Cu direction in fact derives from a small movement of the OH^- toward the furan O with which it is hydrogen bonded.

The establishment of geometric parameters for interacting d_{z^2} magnetic orbitals will be of interest to bioinorganic chemists modelling the dicopper biosite. Although square-based geometry characterises the majority of copper sites outside of biology, it must be remembered that atypical geometries are frequently utilised in biology, particular when redox chemistry or other special functions are to be facilitated.

We thank the SERC for support (to Q. L.) and for access to FAB-MS facilities at Swansea.

Received, 12th July 1993; Com. 3/04055K

References

1 A. Messerschmidt and R. Huber, *Eur. J. Biochem.*, 1990, **187**, 341.
2 T. N. Sorrell, in *Biological Inorganic Copper Chemistry*, ed. K. D. Karlin, J. Zubieta, Adenine, NY, 1985 p. 41; E. I. Solomon, M. J. Baldwin and M. D. Lowery, *Chem. Rev.*, 1992, **92**, 521.
3 A. Messerschmidt, A. Rossi, R. Ladenstein, R. Huber, M. Bolognesi, G. Gotti, A. Marchesini, R. Petruzelli and A. Finazzi-Agro, *J. Mol. Biol.*, 1992, **206**, 513.
4 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
5 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 3228.
6 P. L. Burk, J. A. Osborn, M.-T. Youinou, Y. Angus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, 1981, **103**, 1273.
7 See for example K. S. Murray, p. 27, in *Biological Inorganic Copper Chemistry*, eds. K. D. Karlin and J. Zubieta, Adenine, NY, 1985, p. 161; S. M. Nelson, p. 27.
8 D. McDowell and J. Nelson, *Tetrahedron Lett.*, 1988, 385.
9 D. J. Marrs PhD Thesis, OU, 1990; C. Harding, V. McKee, J. Nelson and Q. Lu, *Inorg. Biochem.*, 1992, 47; J.-M. Latour, Q. Lu, C. J. Harding, N. Martin, D. J. Marrs, V. McKee and J. Nelson, to be submitted.
10 M. McCann, W. Lu and J. Nelson, *Inorg. Biochem.*, 1993, **51**, 701.
11 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203.
12 G. M. Sheldrick, SHELXS-86, *Acta Cryst. Sect.*, **46**, 1990, 467.
13 G. M. Sheldrick, SHELXS-92, University of Göttingen.