Structural Features of Di-μ-5,7,7-trimethyl-4,8-diazaundec-4-ene-1,11-diolato(1−)-*ONN'O'*-dicopper(II) Perchlorate, a Diamagnetic Copper(II) Compound; *X*-Ray Crystal and Molecular Structure

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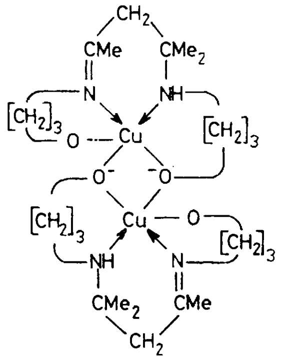
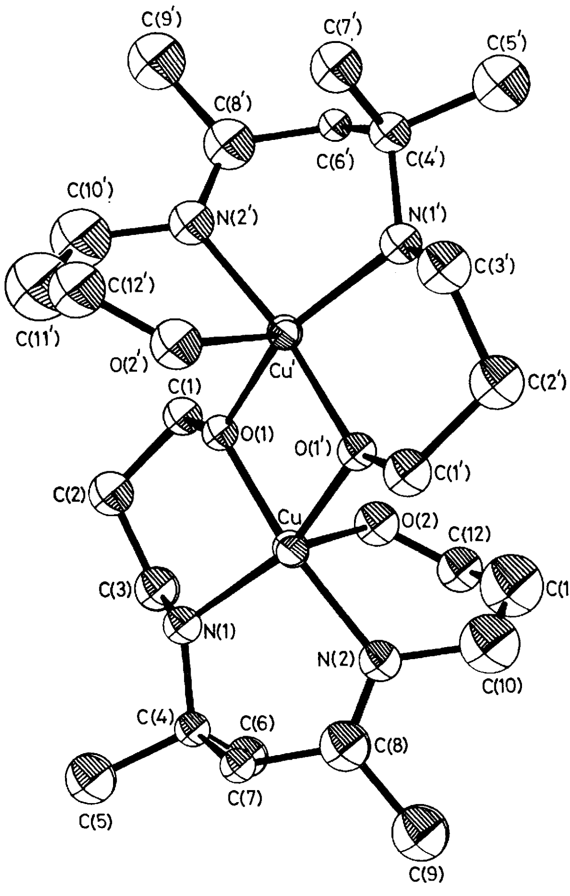
Summary The title compound is almost unique in showing complete spin-pairing at room temperature but has a molecular structure, determined by *X*-ray diffraction, characteristic of similar, but paramagnetic, compounds.

ONE feature of the co-ordination chemistry of copper(II) which has received long and detailed attention is the phenomenon of spin-pairing. It has been of interest for its own sake,[1] for the light thrown on mechanisms of electronic overlap,[2] and more recently for the insight small spin-paired molecules might give into the state of so-called 'Type III' copper[3] in 'blue' cuproproteins. A surprising feature of these enzymes is the complete diamagnetism of the Type III centres, a result which has not, with the exception of tetrakis-(1,3-diphenyltriazene)dicopper(II)[4] and some tetrakis(arylazo-oxime)dicopper(II) compounds,[5] been duplicated in small molecule chemistry. We now report the structure of a dimeric copper(II) complex (I) which is completely diamagnetic at room temperature. It shows that such a compound does not require extraordinary ligands or structural arrangements and can be readily contemplated as occurring in proteins.



(I)

The compound is prepared from copper(II) perchlorate hexahydrate and 3-amino-propan-1-ol using acetone (also a reactant) as solvent. A dark green semicrystalline compound separates after two days and can be reprecipitated from hot acetone–ethanol. Crystallisation by all the common techniques produced only thin, randomly stacked, plates but persistence eventually provided a 0·25 × 0·25 × 0·02 mm sample which could be used for data collection by *X*-ray diffractometry. *Crystal data*: $C_{12}H_{25}ClCuN_2O_6$, $M = 392$; orthorhombic, $a = 19{\cdot}704(9)$, $b = 12{\cdot}735(3)$, $c = 13{\cdot}508(4)$ Å, $U = 3389$ Å^3, space group $= P_{bca}$, $D_c = 1{\cdot}54$ g cm^{-3}, $D_m = 1{\cdot}6$ g cm^{-3} by flotation, $Z = 8$; λ (Mo-K_α) $= 0{\cdot}7107$ Å. The structure analysis by conventional methods suffered from the lack of data (602 intensities $> 2\sigma$ were used) and has been refined to $R = 0{\cdot}10$ assuming an isotropic description of the non-hydrogen atoms and $R = 0{\cdot}087$ for an anisotropic description. The compound has a centrosymmetric dimeric cation (Figure) based on two oxo bridges in a central Cu_2O_2 group.



FIGURE

The perchlorate ion has the expected geometry. Its role as a space-filling counter ion does not involve co-ordination to the metal in any way. The ligand is HO–$[CH_2]_n$–N=CMe–CH_2–CMe_2–NH–$[CH_2]_n$–O^- with $n = 3$. Each metal ion has a square-pyramidal co-ordination geometry; the two bridging oxygen atoms and the two nitrogen atoms are approximately coplanar whereas the hydroxy group is bound axially in an arrangement similar to that found for a number of amino-alcohols.[6] [A potential hydrogen-bonding contact, O(2) · · · O(4') = 2·75 Å, occurs with a perchlorate

Table

Structural parameter	Compound from 2-aminoethanol (II)	Compound from 3-aminopropan-1-ol (I)
Angle at bridging oxygen, ϕ^a	98·2 (1)°	102·7 (3)°
Tetrahedral distortion, τ^b	20·4°	18·7°
Distance of copper from basal donor plane	0·19 Å	0·08 Å
Intramolecular distance Cu-Cu′	2·929 (1) Å	3·045 (5) Å

[a] Ref. 8. [b] Ref. 10.

oxygen.] These include the related compound (II) prepared from a ligand in which $n = 2$. This has the other hydroxy group deprotonated,[7] *i.e.* it has the amino-linked oxygen donor, now the hydroxy group, bonded axially. Unlike (I) the compound obeys the Curie–Weiss relationship above 100 K, $\mu_{eff} = 1{\cdot}83$ B.M., thereby indicating the sensitive nature of the structure–spin-pairing relationship. Small differences between these two compounds must be seen as accounting for the marked change in magnetism. These differences arise from the presence of six-membered, rather than five-membered, chelate rings containing the oxygen atoms and the unexpected consequence that it is the ring involving the trigonal imino nitrogen, N(2), which occupies the out-of plane position and carries the hydroxy oxygen, O(2), to the apical site at each five-co-ordinate copper centre. The oxo donors of the central bridging arrangement lie in the equatorial plane as do the other donors on their rings, the sp^3-hybridised amino nitrogens, N(1). Some quantitative comparisons between (I) and (II), which may also be made with known empirical relationships,[8–11] are shown in the Table.

Previous investigations have shown that τ should be small if spin-pairing is to occur (in salicylaldiminato complexes) and, more pertinently, that ϕ should be $> 97{\cdot}6°$ for a singlet ground state[12] (in μ-hydroxo complexes). Diamagnetism is not, however, complete at room temperature when ϕ is as large as 104·1°[13] and indeed it must approach 108° if the linear relationship with the magnetic moment holds good. That $\mu_{eff} = 0$ for (I) at $\phi = 102{\cdot}7°$ does not impair the established correlation since the latter has been derived for μ-hydroxo compounds but it again indicates the sensitive nature of the relationship between bonding and spin-pairing.

Another pair of di-μ-oxo-bridged copper(II) compounds with the related tridentate ligands $NH_2–CMe_2–CH_2–CMe{=}N–[CH_2]_n–O^-$ show similar magnetic behaviour, a normal moment being observed when $n = 2$ and complete spin-pairing when $n = 3$.[14] For (I) and (II), and presumably for the pair based on the tridentate ligand, the major structural difference is the replacement of a five-membered chelate ring containing the bridging oxo groups (negligible spin-pairing) by a six-membered ring (complete spin-pairing). A similar, but less dramatic, effect has been observed for other related pairs of ligands.[15]

(*Received, 6th May* 1977; *Com.* 436.)

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