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Towards a Hemocyanin Model. Relation Between Molecular and Electronic Structure in Binuclear Complexes: Effect of Bridging Group Length and Angle Between Metal Planes*

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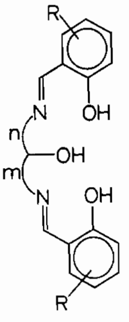
Interest in binucleating ligands centers around [1–5] their ability to hold pairs of metal atoms in close physical and electronic proximity. This permits strong magnetic interactions, doubles the number of electrons that can participate in catalysis and electron transfer [6–9]. With copper complexes, a major challenge is in modelling such properties as the 3.6 Å distance proposed for oxyhemocyanin from EXAFS [10, 11] and crystallographic [12] data and the strong magnetic coupling that appears to be present in oxyhemocyanin. Hemocyanin binds oxygen at the binuclear copper site, and is crucial to the electron transfer process in arthropods and molluscs [13]. The magnetic coupling between the metal atoms is strong [14]. Small molecule complexes can also catalyze such two-electron transfers [15–17], and there is a possible correlation between the redox properties and the strength of magnetic coupling between the metal atoms [17–18].



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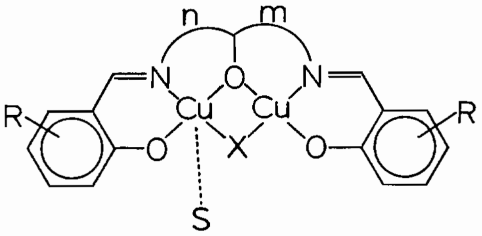
The binucleating ligand, LH_3 (**1**) has been shown to link copper and other metals in homo- and heterobinuclear complexes [19] closely enough to allow magnetic superexchange coupling when the metals are both paramagnetic.

Variation of the chain lengths, *n* and *m*, allow the two binding sites to differ, e.g. to favor planar or tetrahedral geometry. With copper, the extreme geometries can favor oxidation states II and I, while intermediate geometries may favor easy transition between the two states, an important consideration for electron transfer properties.



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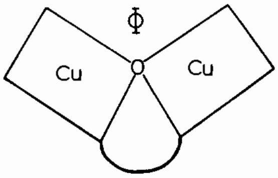

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The binuclear copper complexes, Cu_2LXS, (**2**) of this ligand type have an alkanolic oxygen as a common donor bridging the two metals, which are further linked by the di- or tri-atomic bridging ligand, X. S is a solvent molecule or other neutral ligand which is weakly bonded to one of the metal atoms in some of the complexes. The metal atoms are each in a distorted planar environment made up from a tridentate unit of L and one of the atoms of X. Though changes in the ligand geometry bring about a variety of distortions in the molecular geometry, the O_3N chromophores ('copper planes') remain at least approximately planar. The principal copper planes are joined like butterfly wings by the common O and by the polyatomic ligand X. The angle, ϕ (**3**), between the two copper planes gives a measure of the extent of the most dramatic distortion. As expected [19–21] this angle is found to exert a strong influence on the magnetic interaction.

When the entire molecule Cu_2LX approaches being flat, the copper planes and the bridging planes Cu–O–Cu and Cu–R–Cu are very approximately coplanar. Then the magnetic coupling is quite strong, as is observed in the pyrazole derivative [19], $[Cu_2$-

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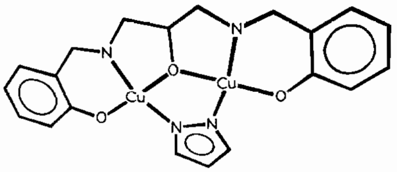
(Sal_2PrO)•pz], **4**, in which the singlet–triplet separation is in excess of 400 cm^{-1} ($-2J = 410$ cm^{-1}, $g = 2.11$), which makes for interesting comparison with dicopper proteins [14]. Another important feature of this complex is that X constitutes a two-atom bridge. The coupling is not so strong when X is a three atom chain or the molecules are bent, as revealed by a systematic study of binuclear complexes [$Cu_2(Sal_2PrO)X$].



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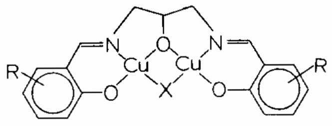

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The binuclear complexes **5** exhibit interactions ranging from antiferromagnetic to ferromagnetic. In cases with coordinated solvent molecules, one of the copper atoms has four strong bonds to L^{3-} and X^-, in an approximate plane; a fifth bond, to the solvent molecule, completes a distorted square pyramid, the other copper atom is roughly planar. The stronger interactions occur when the molecules are less bent allowing better overlap of ligand and metal $d_{x^2-y^2}$ orbitals: values of <10° for ϕ correspond to singlet–triplet separations of around 170 cm^{-1}. None of the series **4** has very strong interactions because not both the Cu–O–Cu bridges and the Cu–O–C–O–Cu bridges can simultaneously orient for optimal superexchange overlap.

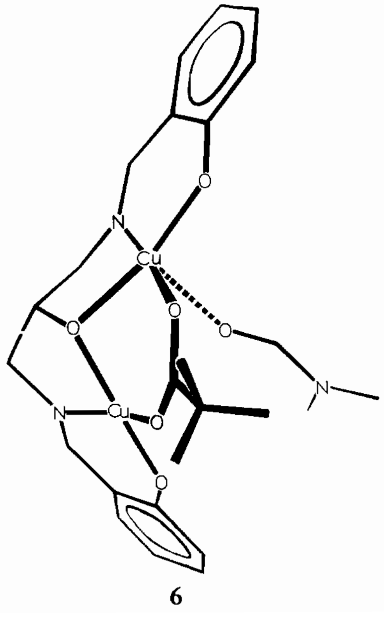
The stronger coupling can be attributed to the favorable superexchange overlap permitted by approximate coplanarity of the copper planes and the Cu–O–Cu and Cu–O–C–O–Cu bridging. When these planes are dramatically misaligned, as the pivalate complex [19] (X = pivalate, $(CH_3)_3C\cdot COO^-$), the coupling is quite small. In the pivalate complex, the analogous dihedral angle between the principal copper planes, ϕ, is dramatically increased to 60.5°, compared with the small value of less than 10° in the molecules described above. This bending is accompanied by virtual elimination of the coupling ($-2J \approx 10$ cm^{-1}). The dramatic bending of the molecule also brings the two Cu atoms much closer together (3.137(1) Å) than in the less distorted analogs with small ϕ, but the Cu–Cu separation is still too large to contribute significantly to the coupling. The bending is accompanied by a severe decrease in the Cu–O–Cu angle, but this angle is still much larger than the value where the trend towards ferromagnetic should produce essentially no coupling (Table I).

TABLE I.

X	pz	Propionate	Acetate	Pivalate, **6**
# atoms	2	3	3	3
Cu–O–Cu (°)	122.5	130.5	133.5	105.7
ϕ (°)	7.4	6.5	7.6	60.5
$-2J$ (cm^{-1})	410	177	175	10

Some of the [Cu_2LX] complexes exhibit ferromagnetic coupling, but no crystal structures are available, so that it is not yet known whether these constitute examples of even more values of the severe bending, ϕ. These include [Cu_2L(PhAc)-(2,3,4,6-tetrachlorophenol)] and [Cu_2L(PhAc)(X-pyNO)], where X′ = H, 2-CH_3 or 4-CH_3, PhAc = phenylacetate.

The Cu–Cu distance ranges aroud 3.5 Å for the mostly flat binuclear complexes, which compares with the 3.5 ± 0.2 Å value suggested from EXAFS data for the oxy and met forms of hemocyanin [12]. In [Cu_2(3-EtOSal$_2$PrO)($C_2H_5\cdot COO$)(H_2O)]H_2O with a coordinated water molecule, Cu–Cu = 3.473 Å, while in [$Cu_2(Sal_2PrO)(Cl_2CH\cdot COO)$], with no coordinated solvent molecules, Cu–Cu = 3.526 Å. In [$Cu_2(Sal_2PrO)((CH_3)_3C\cdot COO)$DMF], there is a solvent of crystallization, weakly bonded (2.384 Å). [$Cu_2(Sal_2PrO)(PhAc)]_2\cdot$(4-EtPhenol)$_2$,



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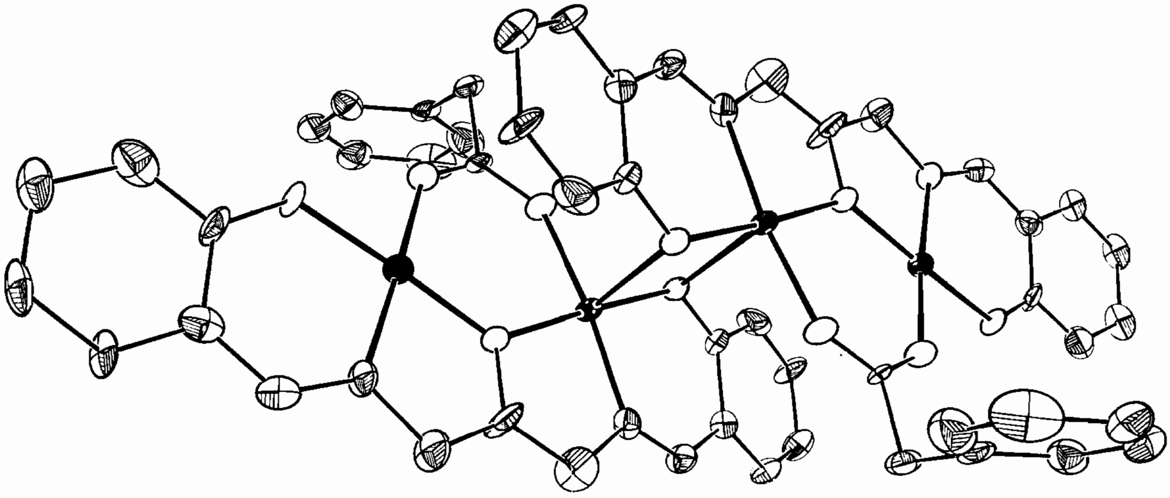

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with no coordinated solvent, is a tetranuclear molecule consisting of pairs of $[Cu_2(Sal_2PrO)(PhAc)]$ units linked via bridging phenolic oxygens, 7. The 4-ethylphenol molecules are not involved in the coordination.

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