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Magnetic Exchange in Amido-bridged Binuclear Copper(II) Complexes

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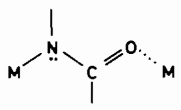
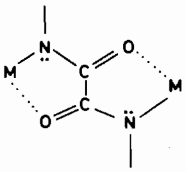
There has recently been a resurgence of interest in binuclear metal complexes containing similar (homobinuclear) and dissimilar (heterobinuclear) metal ions, because of their relevance as synthetic models of certain polymetallic metal–proteins [1]. Though the nature of the bridging group in the biological molecule is known in some cases from X-ray crystallography, in others it is not known and variable temperature magnetic susceptibility is an important technique for the identification of bridging groups such as imidazolate (histidine) [2, 3] by determination of the magnitude of the coupling constant, *J*. One group which can potentially bridge between metal centres in biological systems is the deprotonated amide bond in peptides, and this possibility has been suggested for the copper/heme a_3 site in cytochrome *c* oxidase [4]. In such a system, shown in structure A, the M–N and M...O bonds would need to be reinforced by participation of neighbouring donor atoms and by the tertiary structure of the protein.



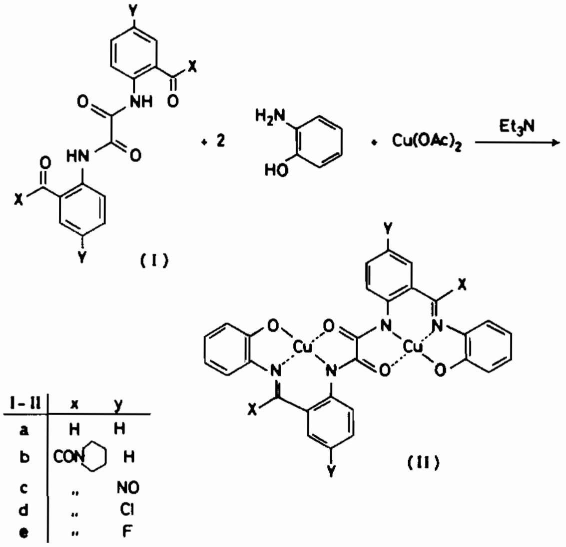
(A)



(B)

The oxamido system of structure B is a simple model which incorporates the precise bonding of the amide structure A within a more stable framework.

We have prepared a range of binuclear copper(II) complexes (II) containing such a bridging oxamide linkage. The complexes (II) can be readily formed from the oxamido-carbonyl compounds (I) [5, 6] by metal template condensation with *o*-aminophenol in the presence of copper(II) acetate and triethylamine. The complexes are insoluble in most organic solvents and it has not been possible, thus far, to obtain crystals suitable for structural determination.



(I)

(II)

I-II	x	y
a	H	H
b	CON	H
c	,,	NO
d	,,	Cl
e	,,	F

The magnetic susceptibilities of the complexes have been measured over the range 4.2–300 K using the Faraday method, and powder e.s.r. spectra were recorded in representative cases. Variations in the

TABLE I. Best-Fit Magnetic Parameters.[a,b,c]

Complex	μ_{eff} (B.M.) at 300 K (per molecule)	*g* (± 0.02)	*J* (cm^{-1}) (±5 cm^{-1})	% Monomer
IIa	1.72	2.10	−201	2.5
IIb·H_2O	1.72	2.10[d]	−205	6.8
IIc·$2H_2O$	1.73	2.20	−210	1.2
IId·H_2O	1.66	2.05	−205	5.2
IIe·H_2O	1.73	2.15	−210	7.8

[a] Singlet–triplet splitting = 2*J*. [b] T.I.P. (per molecule) = 120 × 10^{-6} cm^3 mol^{-1}. [c] Diamagnetic susceptibility determined for Zn(II) analogue of IIb. [d] E.S.R. (monomer) value = 2.11.

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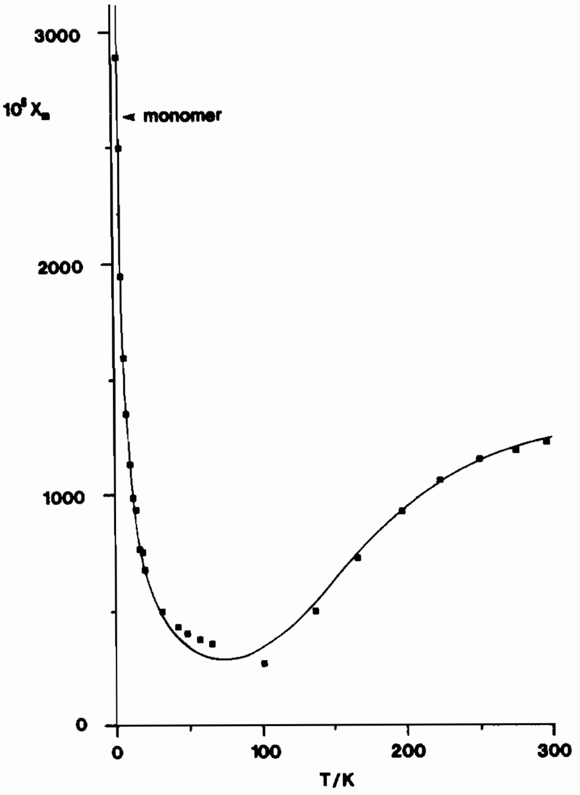

Fig. 1. Susceptibility per molecule of (IIa) as a function of temperature. The steep increase at low temperatures is due to paramagnetic mononuclear impurity. The solid line is the best fit to theory using the parameters in Table I.

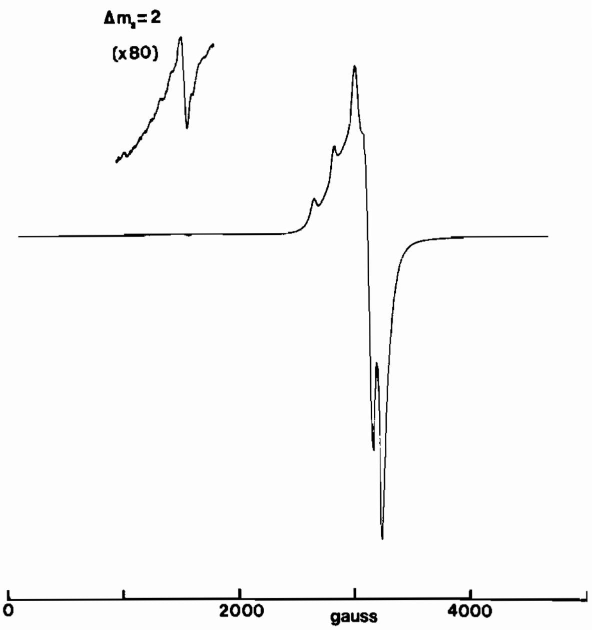

Fig. 2. X-band e.s.r. spectrum of powdered sample of complex (IIb) at 140 K. The main line at *ca.* 3100 gauss is due to monomeric impurity and the $\Delta M_s = 2$ line due to dipolar coupled Cu(II) pairs. The exchange-coupled binuclear species is e.s.r. inactive.

imine and ring substituents, X and Y, were made to see if such variations affected the strength of the exchange coupling. The magnetic parameters are given in Table I and the susceptibility *vs.* temperature curve for complex (IIa) is shown in Fig. 1. At room temperature the molecular susceptibility is reduced below the spin-only value due to strong antiferromagnetic coupling. The susceptibility decreases between 300 and 100 K as expected for population of a singlet spin state but below this it shows a minimum followed by a very steep increase. This unusual feature is due to the presence of a small percentage of a monomeric complex of (II) in which only one of the metal sites is occupied. The solid line in Fig. 1 is the best-fit calculated value using the Heisenberg–Dirac–Van Vleck expression for ($S = ½$: $S = ½$) coupling modified to include a small paramagnetic contribution [7]. The g and J values for this and some other derivatives are given in Table I.

A check on the g value is afforded by the appearance of an isotropic line at $g = 2.11$ in the room temperature powder e.s.r. spectrum of complex (IIb). This line, which arises due to the small amount of monomer present, is resolved into rhombic components at 140 K (Fig. 2), and has $g_z = 2.21, g_y = 2.07, g_x = 2.00$; $A_z = 180 \times 10^{-4}$ cm^{-1}, symptomatic of a $d_{x^2-y^2}$ ground state configuration. Five superhyperfine lines can be resolved on the x and y lines and are due to coupling to the two *cis* nitrogens of the ligand (A_N = 13 gauss). In the room temperature and 140 K spectra a weak 'half-field' line is observed at 1550 gauss, which shows Cu(II) hyperfine coupling at the lower temperature, the spacing between components being half of that displayed by the monomer line. This half-field line is a spin-forbidden $\Delta M_s = 2$ transition which arises through dipolar coupling of Cu(II) pairs and in the present case probably originates from adventitious stacking of the small percentage of monomer species in the solid such that the Cu(II) centres are some 5 Å distance apart [8]. It is important to note that, under the conditions used, the exchange-coupled complexes of structure (II) are e.s.r. inactive. Thus the spectrum does not exhibit lines at low and high-fields which are expected for triplet state molecules exhibiting large J values, as for example in the dinuclear copper(II) carboxylates [9, 10].

In Table I we see that the best-fits of the susceptibility data lead to a J value of *ca.* –210 cm^{-1}, which seems to be a characteristic of the oxamide bridge since there is little variation with substitution at positions X and Y. The π-molecular orbital system of the $-\overset{|}{N}-\underset{|}{\ddot{C}}-\ddot{O}-$ moieties are presumably suitably oriented to overlap with the magnetic orbitals of the two Cu(II) centres to yield an efficient pathway for superexchange. It is significant that the present J values are some of the largest known for Cu–Cu clusters bridged by multiatomic ligands, the nearest being the carboxylate ($J \sim -150$ cm^{-1}) and adenine ($J = -105$ cm^{-1}), while imidazolates ($J = -26$ to -81 cm^{-1}), oxalates ($J = 0$ to -37 cm^{-1}) and cyanates ($J = 0$) are considerably lower [3, 10–12]. There are one or two examples with very larger J values such that the compounds are diamagnetic; these contain triazenato [13] and bis-azido bridges [14]. The non-bridge part of the copper(II) coordination sphere and other stereochemical factors often markedly influence the size of J for a particular bridging group [12, 14]. Nevertheless we feel that a value of about -200 cm^{-1} will be close to that displayed by a bridging peptide linkage. The present magnetic and e.s.r. results further suggest that this kind of bridge must be seriously considered as a possibility in the Cu–Cu sites of the biological molecules. Further work is aimed at preparing heterobinuclear derivatives with amide bridges, *e.g.* of Cu(II)–Fe(III) or Cu(II)–Zn(II), to test these ideas in relation to mixed-metal active sites.

Acknowledgements

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References

1 P. J. Sadler, *Inorganic Perspectives in Biology and Medicine, 1,* 233 (1978).

2 M. F. Tweedle, L. J. Wilson, L. Garcia-Inigues, G. T. Babcock and G. Palmer, *J. Biol. Chem., 253,* 8065 (1978).

3 G. Kolks and S. J. Lippard, *J. Am. Chem. Soc., 99,* 5804 (1977).

4 J. T. Landrum, C. A. Reed, K. Hatano and W. R. Scheidt, *J. Am. Chem. Soc., 100,* 3232 (1978).

5 D. St. C. Black, C. H. Bos Vanderzalm and A. J. Hartshorn, *Inorg. Nucl. Chem. Letters, 12,* 657 (1976).

6 D. St. C. Black, G. I. Moss and L. C. H. Wong, *Tetrahedron Letters,* 2837 (1978).

7 A. P. Ginsberg, *Inorg. Chim. Acta, 4,* 45 (1971).

8 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev., 13,* 173 (1974).

9 J. H. Price, J. R. Pilbrow, K. S. Murray and T. D. Smith, *J. Chem. Soc. A,* 968 (1970).

10 J. Lewis, F. E. Mabbs, L. K. Royston and W. R. Smail, *J. Chem. Soc. A,* 291 (1969).

11 D. M. L. Goodgame and K. A. Price, *Nature, 220,* 783 (1968).

12 T. R. Felthouse, F. J. Laskowski and D. N. Hendrickson, *Inorg. Chem., 16,* 1077 (1977).

13 C. M. Harris, B. F. Hoskins and R. L. Martin, *J. Chem. Soc.,* 3728 (1959).

14 Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc., 101,* 3381 (1979).