A Copper–Copper Bond by Intent

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The ESR spectra for a series of binuclear trigonal bipyramidal copper complexes show that the SOMO is largely composed of the two equivalent d_{z^2} orbitals on copper; the temperature independence of the ESR parameters shows that this is a relatively strong bond, and since the unpaired electron is antibonding, the σ-bond must be even stronger; these results are contrasted with the more common situation that arises when the electron is shared between two $d_{x^2-y^2}$ type orbitals.

The majority of Cu[II] complexes have a SOMO that is predominantly $d_{x^2-y^2}$ on copper, with relatively stong 'square-planar' σ-bonding in the x–y plane and weak σ-bonding along z. The inverse, with the SOMO primarily using the d_{z^2} orbital is relatively rare, both in chemistry and in biology.

When Cu[II] complexes are held close together in pairs in the $(d_{x^2-y^2})^1$ configuration the spins normally couple to give a triplet-state and for close pairs spin-exchange results in each electron experiencing an average environment (giving 7 hyperfine components from the I = 3/2 nuclei if the ligand environments are the same). This is the normal situation, and there is a range of such pairs known.[1] However for the $(d_{z^2})^1$ configuration σ-overlap is more favourable and strong Cu–Cu bonding can result in electron pairing to give strong σ-bonding.

On addition of an extra electron, the pairs with $(d_{x^2-y^2})^1$ configuration may give a delocalised or localised product depending on the extent of overlap and the tendency for the ligands to move. If the exchange is fast, all ligands will relax equally to suit the distributed electrons, but if it is slow, asymmetric relaxation will trap the electron on one side. In the former a seven-line spectrum will be observed, and in the latter, a four-line spectrum similar to that for the monomeric Cu[II] complex will be detected.[2] However, for the $(d_{z^2})^1$ configurations, the σ-bond will be retained, and the electron will be in the σ* (d_{z^2}–d_{z^2}) orbital, with a distribution that reflects the nature of the ligands. In the present examples, the two halves are identical and so a seven-line spectrum is detected.

Three structurally characterised complexes containing the dinuclear couple $(Cu_2)^{3+}$ encapsulated in the ligands 1–3 have been investigated.[3] The paramagnetic properties of each are temperature independent: an effective moment of ca. 2.0 BM per complex in the range T = 4–300 K corresponding to the average valency Cu (3/2), and a seven line hfs in the range 4–150 K in the ESR (Fig. 1 and Table 1). No signals from monomeric species are seen in the ESR spectra, although the complexes are unstable in organic solvents, an intense signal in the g = 2 region developing on standing. The spectrum in Fig. 1 shows a weak shoulder due to this to the high field side of the parallel components. As expected for these complexes, the parameters for all three are similar. The X- and Q-band spectra were better defined for complexes of 1 and 2 than for 3 so the error limits are greater for 3. The results clearly establish the presence of two equivalent copper ions and a d_{z^2} contribution for each with a common z-axis for the local sites. These conclusions stem from the form of the spectra of the frozen solutions (Fig. 1) which show equal hyperfine interaction along the x and y axes and the form of the g values, which show $g_\perp > g_\parallel$ ca. 2.0. This is expected for the d_{z^2} configuration and rules out the $d_{x^2-y^2}$ configuration.

Analysis of the hyperfine coupling constants, using the isotropic splitting to give relative signs, and assuming a positive value for 2B, the anisotropic component, gives A_{iso} ([65]Cu) ca. −87 G and 2B ca. +77 G. These values were obtained after correcting for orbital paramagnetism using the
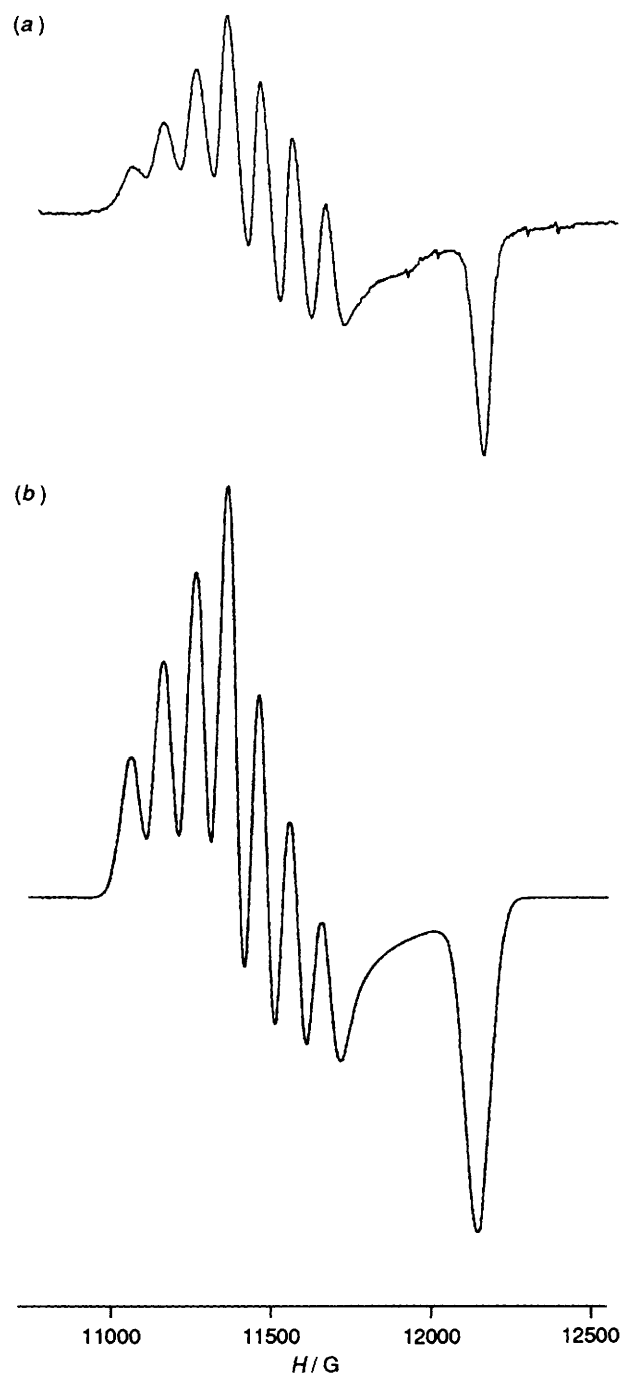

Fig. 1 Q-Band EPR (a) spectrum of frozen DMF solution of complex of 1 at 80 K and (b) simulation with the parameters in Table 1. The weak sharp features in the region of the perpendicular signal are due to a Mn field calibrant.

Table 1 Experimental EPR parameters for the three dimeric copper complexes

Complex	^{65}Cu hyperfine coupling			g-values		
	$A_{\|}$	$A_\perp$	A_{iso}	$g_{\|}$	$g_\perp$	g_{av}
1	±10	100	68.5	2.004	2.148	2.10
2	±10	107	65	2.005	2.145	2.10
3	±10	83	60	2.00	2.17	2.09
		(±2)	(±2)	(±0.005)	(±0.005)	(±0.005)

^{a} $G = 10^{-4}$ T

1

2

3
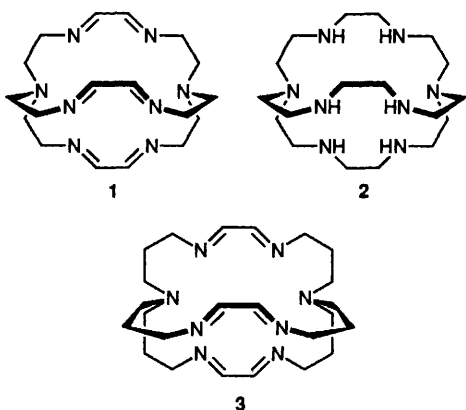
g-components and standard equations.[4] The A_{iso} value is *ca.* half the normal values found for monomeric Cu^{II} complexes. This requires that this splitting is primarily from spin-polarisation effects and that any direct admixture of 4S character must be small. The 2B value, compared with a calculated value of *ca.* +250 G for unit population, gives an approximate spin-density on each copper ion of 32%.[4] This, again, is a normal result and shows that delocalisation onto the ligands is

considerable, even though no hyperfine coupling to ligand nuclei could be resolved.

These results are comparable with those for the complexes whose structures have been fully determined by X-ray crystallography.[3] The local geometry (trigonal bipyramidal) is similar in each case, with Cu$\cdots$Cu distances in the range 2.40–2.45 Å. Use of the $(d_{z^2})^1$ configuration at each copper is dictated by the three-fold configuration in the *xy* plane, rather than the normal four-coordination. At a Cu$\cdots$Cu separation of about 2.4 Å, overlap of the colinear d_{z^2} orbitals results in the formation of a Cu–Cu bond of bond order one half.

Thus in these σ^* $(d_{z^2})^1$ complexes there is strong copper–copper σ-bonding 'by intent'. With the more common $(d_{x^2-y^2})^1$ dimers, magnetic interaction is present, but bonding is negligible, and the units are held together as a consequence of ligand structures.

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