Co-ordination Chemistry of Mixed Pyridine–Phenol and Phenanthroline–Phenol Ligands; A Variable-temperature Electron Paramagnetic Resonance and Magnetic Susceptibility Study on Two Binuclear Copper(II) Complexes with $Cu_2(\mu\text{-}O)_2(\mu\text{-}1,3\text{-}O_2CMe)$ Cores*

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The EPR spectra (characteristic of triplet species) of the complexes $[Cu_2L^1_2(\mu\text{-}1,3\text{-}O_2CMe)][PF_6]$ **1** [HL^1 = 6-(2-hydroxyphenyl)-2,2′-bipyridine] and $[Cu_2L^2_2(\mu\text{-}1,3\text{-}O_2CMe)][PF_6]$ **2** [HL^2 = 2-(2-hydroxyphenyl)-1,10-phenanthroline], previously structurally characterised as containing $Cu_2(\mu\text{-}O)_2$ cores in which the phenolate oxygen atoms of L^1 and L^2 bridge both copper(II) centres, have been successfully modelled using a perturbation-theory approach. The Cu ··· Cu distances calculated from the spectra are in reasonable agreement with the values given by the crystal structures. By measuring the variation in intensity of the spectrum of **1** with temperature it was established that **1** is antiferromagnetic with $J = 52 \pm 8\ cm^{-1}$. Variable-temperature magnetic susceptibility measurements on **1** and **2** confirm the presence of moderate antiferromagnetic couplings, although the presence of a mononuclear impurity in each case precludes use of the Bleaney–Bowers equation to obtain more accurate values of J.

We have recently been interested in the study of polydentate ligands containing mixed pyridine–phenol and phenanthroline–phenol donor sets.[1–3] In our initial studies on the N,N,O-terdentate ligands 6-(2-hydroxyphenyl)-2,2′-bipyridine (HL^1) and 2-(2-hydroxyphenyl)-1,10-phenanthroline (HL^2) it became apparent that the presence of a terminal phenolate donor on the ligand allows formation of polynuclear phenolate-bridged complexes. In particular we recently reported the syntheses of $[Cu_2L^1_2(\mu\text{-}MeCO_2)][PF_6]$ **1** and $[Cu_2L^2_2(\mu\text{-}MeCO_2)][PF_6]$ **2** and their crystal structures, which consist in both cases of two near-planar CuL fragments stacked parallel to each other such that both phenolate donors bridge both copper(II) centres, giving a $Cu_2(\mu\text{-}O)_2$ core which is additionally bridged by a μ-1,3-acetate ligand.[1,3] Oxygen-bridged binuclear copper complexes have received considerable attention recently as models for the active site of type three copper proteins such as tyrosinase and haemocyanin,[4] and also because of interesting magnetic properties arising from interactions between the copper centres mediated by the bridging atom.[5] We have accordingly undertaken variable-temperature EPR and magnetic susceptibility studies on **1** and **2**, the results of which are reported here.

Experimental

Complexes **1** and **2** were prepared as previously described;[1,3] the former was recrystallised from dichloromethane and the latter from acetonitrile–diethyl ether. The samples used for the magnetic studies were handled with plastic spatulas, since even brief contact with metal spatulas could result in samples having anomalously high susceptibilities. The EPR spectra were recorded on a Bruker ESP-300E spectrometer equipped with an Oxford Instruments variable-temperature facility. The solvent used was tetrahydrofuran–CH_2Cl_2 (2:1 v/v) for **1**, or dimethylformamide–tetrahydrofuran (2:1 v/v) for **2**; the sample concentration was 1.3 mmol dm^{-3}. Magnetic susceptibilities were measured over a range of temperatures using a Faraday balance calibrated with $HgCo(NCS)_4$ as described previously.[6] The data are subject to an error of ±3%.

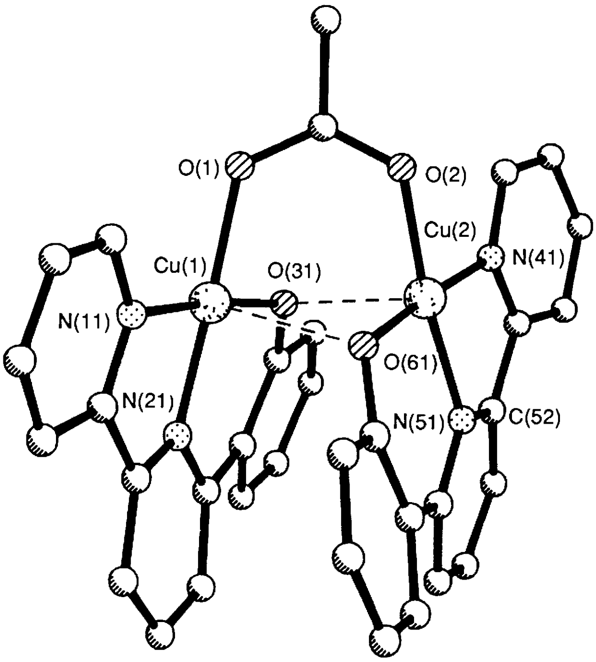

Fig. 1 Crystal structure of complex **1** (taken from ref. 1)

Results and Discussion

The core structure of complex **1** is recalled in Fig. 1; the

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* *Non-SI unit employed:* $G = 10^{-4}\ T$.

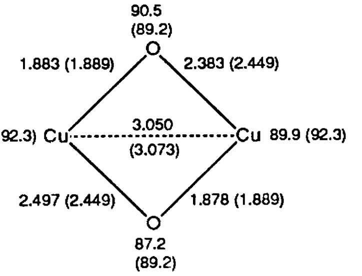

Fig. 2 Dimensions of the $Cu_2(\mu\text{-}O)_2$ cores in complexes **1** and **2** (figures for **2** in parentheses); distances in Å, angles in °

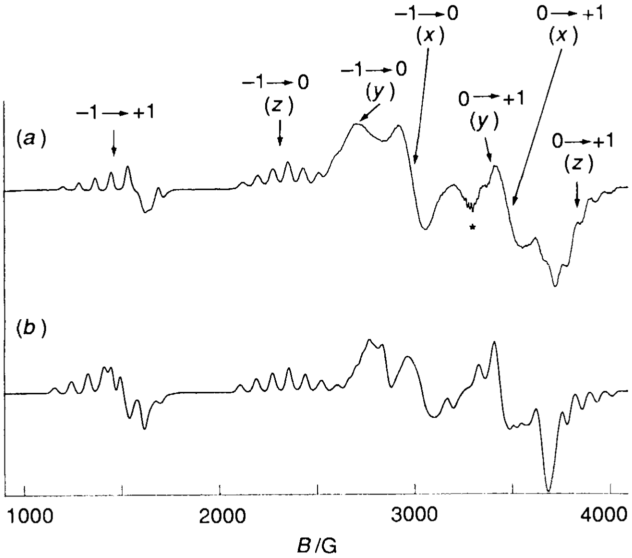

Fig. 3 Observed (*a*) and calculated (*b*) EPR powder spectra of complex **1**

structure of **2** is generally similar.[3] Relevant structural parameters are in Fig. 2. The EPR spectra at 90 and 77 K respectively, shown in Figs. 3(*a*) and 4(*a*), are typical of dimeric copper(II) species. The spectra are unusually well resolved with the three expected transitions easily identified and labelled in the Figures. With arbitrary axis assignments these are: $-1 \longrightarrow +1$ (features around 1500 G); $-1 \longrightarrow 0$ (*z* component, positive-going multiplet; *y* component, divergence-like feature; *x* component, negative-going feature), and $0 \longrightarrow +1$ (*y* component, positive-going feature with partially resolved structure; *x* component, divergence-like feature; *z* component, negative-going multiplet).

The separation of the *z* multiplets, 1424 and 1493 G for complexes **1** and **2** respectively, provides estimates of the zero-field splitting parameter, 2*D*. Assuming that both multiplets correspond to the same effective *g* values and that *D* is due solely to electron–electron dipolar coupling, we have $D = (g_{eff})^2\mu_B{}^2/r^3$ and r = 3.10 and 3.01 Å, in reasonable agreement with the Cu ••• Cu distances from the crystal structures, 3.050 and 3.073 Å.

We have used the perturbation theory approach of Boyd *et al.*,[7] in which it is assumed that the zero-field splitting is entirely dipolar in origin and that the principal axes of the *g* and hyperfine matrices are coincident. The orientation of the major axis of the zero-field splitting matrix is determined by the polar angle ζ and the azimuthal angle η, relative to the *g*-matrix principal axes. Simulation of a spectrum requires ten parameters, g_x, g_y, g_z, A_x, A_y, A_z, ζ, η, *r*, and the component linewidth. No hyperfine structure is resolved on the *x* and *y* components and A_x and A_y were arbitrarily set to 10×10^{-4} cm^{-1}, which is a typical value for compounds of this type.[7] The *g* components were adjusted to fit the average locations of the $-1 \longrightarrow 0$ and $0 \longrightarrow +1$ pairs of *x*, *y* and *z* features, and *r* was adjusted to match the separation of the *z* multiplets. The multiplet splittings are somewhat different with $a(-1 \longrightarrow +1) > a(-1 \longrightarrow 0) > a(0 \longrightarrow +1)$; the relative spacings proved to be quite sensitive to the angle ζ; accordingly ζ and A_z were adjusted to give the best reproduction of the multiplet spacings. The position of the half-field resonance is strongly dependent on the angle ζ and would be best fit with ζ near zero (where the relative hyperfine couplings are poorly reproduced); furthermore, with ζ ⩾ 30°, the *y*- (or *x*-) $0 \longrightarrow +1$ feature should show resolved hyperfine structure. The major effect of the angle η is to change the relative separations of the pairs of *x* and *y* features; accordingly, this parameter was adjusted to minimise the (still substantial) error in these separations. The angle η also determines the size of the hyperfine splitting on the *x*- and *y*- $(0 \longrightarrow +1)$ features; although no splitting is resolved in the experimental spectra, the *y* feature is somewhat 'lumpy' and the *x* feature is broad, suggesting unresolved splitting. In simulations, the *y* feature shows substantial splitting for η = 0; this splitting decreases with increasing η (at constant ζ), and, for η > 45°, becomes noticeable on the *x* feature. By both of these criteria the spectra are best reproduced with η approximately equal to 45°.

The final parameters are given in Table 1. Computer simulations based on these parameters are shown in Figs. 3(*b*) and 4(*b*). Although the simulations give a reasonable qualitative account of the experimental spectra, there are significant discrepancies: the half-field features in the simulations are *ca.* 50 G lower than in the experimental spectra and the separations of the *x* and *y* components are about 13% too small.

Detailed interpretation of these spectra is complicated by the non-coincidence of the principal axes of the interaction matrices. The geometry of the copper centres may be considered as nearly square planar (with a substantially weaker axial ligand), which suggests that the *g* and hyperfine matrices for each centre should share principal axes; however, if we assume that the local *z* axes are normal to the co-ordination planes, they are 17 and 22° apart for the L^1 and L^2 complexes, respectively; similarly, if we define the local *x* axes by the Cu–O (acetate) vectors, they differ by 29 and 37°, respectively. The difficulties

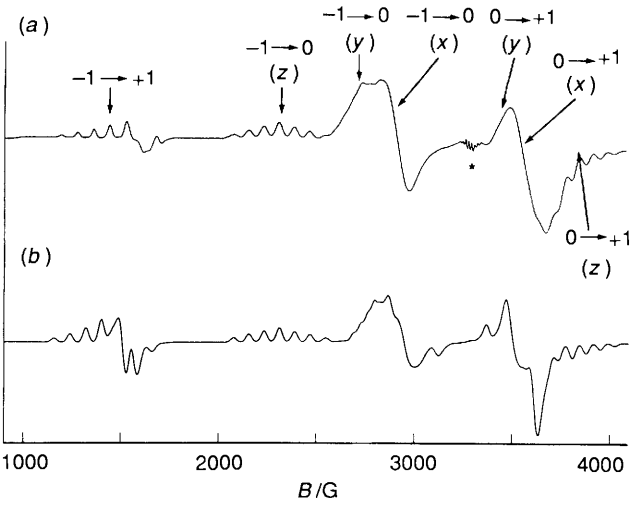

Fig. 4 Observed (*a*) and calculated (*b*) EPR powder spectra of complex **2**

Table 1 The EPR parameters for complexes **1** and **2**

Complex	g_x	g_y	g_z	A_z*	ζ/°	*r*/Å
1	2.026	2.209	2.332	198	26	3.134
2	1.997	2.094	2.242	178	24	3.035

* In units of 10^{-4} cm^{-1}.

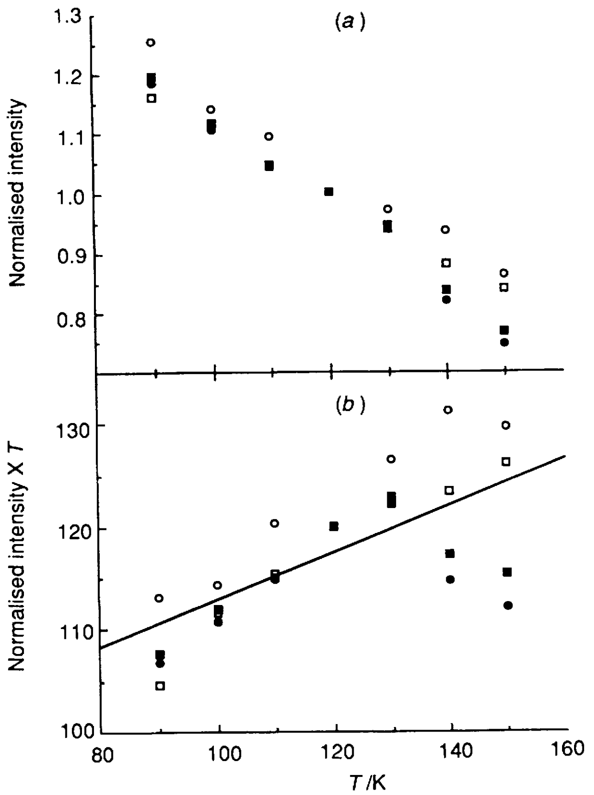

Fig. 5 (*a*) EPR intensities for complex **1**, scaled to 1.0 at 120 K, *vs.* temperature; (*b*) intensities × *T*. *vs.* *T*. Squares and circles represent different data sets; open symbols represent double integrations, filled symbols peak-to-peak amplitudes

Table 2 Magnetochemical measurements for complexes **1** and **2**

Complex 1			Complex 2		
T/K	$10^3\chi$/ emu mol^{-1} [a]	μ [b]	T/K	$10^3\chi$/ emu mol^{-1} [a]	μ [b]
66.7	5.15	1.66	65.1	4.96	1.61
72.0	5.07	1.71	80.3	4.37	1.68
99.3	3.85	1.75	100.2	3.58	1.69
120.0	3.49	1.83	120.6	3.31	1.79
140.0	3.13	1.87	140.2	3.00	1.83
159.8	2.90	1.92	159.6	2.77	1.88
179.3	2.67	1.95	179.4	2.45	1.87
198.6	2.34	1.93	199.5	2.27	1.90
217.1	2.19	1.95	218.6	2.11	1.92
237.9	1.90	1.90	238.3	1.95	1.93
255.5	1.81	1.92	256.7	1.87	1.96
275.2	1.67	1.92	276.4	1.72	1.95
300.8	1.56	1.94	299.6	1.65	1.99

[a] Accuracy: ±3%. [b] Magnetic moment per copper(II) ion, *i.e.* per half of formula weight.

encountered in obtaining completely satisfactory simulations of the spectra are almost certainly due in large part to this problem. In addition difficulty in obtaining accurate simulations is not surprising considering the low symmetry around the copper ions in the dimer. Attempts to improve the simulations by using the perturbation approach of Carr *et al.*,[8] which allows for non-coincident local axes but assumes that the singlet and triplet states are degenerate, were unsuccessful as anticipated from the known singlet–triplet splitting.

If we average the local coordinate systems based on the X-ray structures, the Cu ··· Cu vector, which should be the major axis of the *D* matrix, is oriented at $\zeta = 35$ and 39°, $\eta = 24$ and 32°, for complexes **1** and **2**, respectively. The angle η is difficult to evaluate since the choice of x axis is rather arbitrary. These values of ζ are significantly larger than those obtained from analysis of the EPR spectra, suggesting that the copper co-ordination planes may be more nearly face-to-face in solution than in the crystals. The Cu ··· Cu distances from the EPR analyses are in quite good agreement with those from the crystal structures.

The use of the zero-field splitting parameter to estimate electron–electron distances in triplet-state EPR spectra is somewhat questionable. The anisotropic part of the singlet–triplet exchange coupling is experimentally indistinguishable from electron–electron dipolar coupling, but exchange contributions appear to be unpredictably variable. Pilbrow and co-workers[7] suggested that anisotropic exchange may become important for $|J| > 30$ cm^{-1}, and Coffman and Pezeshk[9] have shown that exchange contributions may be important for r as large as 8–10 Å, but there are many cases where distances estimated assuming negligible exchange contributions are in good agreement with crystallographic values for r as small as 3–4 Å.[10] The relatively short Cu ··· Cu distance and large $|J|$ would suggest a significant anisotropic exchange contribution, and if so the value of r obtained from D may be much too small. However, the close agreement of r with the crystallographic values would then be fortuitous and we think it more likely that anisotropic exchange contributions are essentially absent in these cases.

For complex **1** two series of spectra were recorded over the temperature range 90–150 K, and intensities were determined by digital double integration or by measurement of peak-to-peak derivative amplitudes. The results of these measurements, scaled to the 120 K points, are shown in Fig. 5(*a*). If the triplet levels are not very much higher in energy than the singlet, the intensity of the spectrum should decrease linearly with increasing temperature as a result of changes in the Boltzmann distribution of population among the levels. Indeed, such a decrease is observed, but when the expected temperature dependence is factored out, as in Fig. 5(*b*), a small increase with increasing temperature is observed. If we assume that the normalised intensity is proportional to the triplet concentration as in equation (1), the slope of the least-squares line of Fig. 3(*b*)

$$[\text{Triplet}]/[\text{Singlet}] = 3\,e^{-J/kT} \qquad (1)$$

gives equation (2). With $T = 120$ K, we have $J \approx 624 \pm 90$ J mol^{-1} (52 ± 8 cm^{-1}).

$$\frac{1}{[\text{Triplet}]}\,\frac{d[\text{Triplet}]}{dT} = \frac{J/kT^2}{1 + 3\,e^{-J/kT}} = 0.0020 \pm 0.0004 \qquad (2)$$

The magnetochemical data for complexes **1** and **2**, presented in Table 2, show that both compounds have an antiferromagnetic interaction. Plots of χ^{-1} against temperature are linear for each compound, and give antiferromagnetic Weiss constants for **1** and **2** of 25.4 and 53.2 K respectively. However, the magnetic moment values are higher than expected for antiferromagnetically coupled binuclear species; for both compounds the room-temperature magnetic moment is close to 2 μ_B per Cu atom, and this does not fall below the spin-only value until about 100 K. We attribute this anomaly to the presence of a paramagnetic impurity, probably monomeric and having a lower molecular mass than those of the binuclear complexes. The presence of a monomeric impurity is confirmed by the presence of the weak signals marked * in the EPR spectra, which show nitrogen hyperfine coupling (these signals are completely absent in the simulated spectra). The samples used for the magnetic studies were analytically pure, and it seems likely therefore that these terdentate ligands can also form small amounts of mononuclear complexes with Cu^{II} which are analytically indistinguishable from the binuclear species. In the circumstances we think it not sensible to calculate J values from the Bleaney–Bowers equation.[11] Nevertheless the *J* value of 52 ± 8 cm^{-1} calculated for **1** from the variable-temperature EPR data is consistent with the overall picture provided by the magnetochemical results.

Acknowledgements

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References

1 J. C. Jeffery, E. Schatz and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 1921.
2 J. C. Jeffery and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 2119.
3 B. M. Holligan, J. C. Jeffery and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 3337.
4 D. Karlin and J. Zubieta (Editors), *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, Adenine Press, New York, 1983.
5 M. Melník, *Coord. Chem. Rev.*, 1982, **42**, 259.
6 M. A. Laffey and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1982, 313.
7 P. D. W. Boyd, A. D. Toy, T. D. Smith and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1973, 1549.
8 S. G. Carr, T. D. Smith and J. R. Pilbrow, *J. Chem. Soc., Faraday Trans. 2*, 1974, 497.
9 R. E. Coffman and A. Pezeshk, *J. Magn. Reson.*, 1986, **70**, 21.
10 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, 1974, **13**, 173.
11 B. B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

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