A Novel μ-Phenolato Binuclear Copper(II) Complex Where Two Basal Planes are Nearly Orthogonal

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The crystal structure and magnetic properties of the μ-phenolato binuclear copper(II) complex, $[Cu_2(L)(C_6H_5CO_2)_2]PF_6$ are reported, where H(L) represents 2,6-bis[N-(2-diethylaminoethyl)-N-ethyl-aminomethyl]-4-methylphenol; this complex is unique in that two basal planes containing the copper ion are nearly orthogonal.

Recently progress has been made towards understanding the mechanism of the interaction between paramagnetic centres in polymetallic compounds. According to recent theoretical work,[1—3] the energy separation between singlet and triplet states in binuclear copper(II) complexes, $-2J$, can be expressed as shown in equation (1), where J_F and J_{AF} represent the ferromagnetic and antiferromagnetic contributions, respectively, both being defined as positive. Several workers have reported that J_{AF} depends on two important factors: (i) the Cu–O–Cu angle(θ),[1—4] and (ii) the dihedral angle(ϕ) between two basal planes.[5] Generally J_{AF} increases with increasing θ and with increasing ϕ (in the range 130—180°). These facts have been rationalized in terms of the 'orbital model' developed by Hoffmann et al.[1] In several cases, however, J_{AF} is very low when $\theta > 120°$ and $\phi \approx 180°$. This has been explained in terms of the 'orbital countercomplementary effect' proposed by Nishida et al.[6] Here we report the first example of a crystal structure where two basal planes containing the copper(II) ion are nearly orthogonal, and discuss the relationship between the $-2J$ value and the dihedral angle near 90°.

$$-2J = -J_F + J_{AF} \qquad (1)$$

The ligand, 2,6-bis[N-(diethylaminoethyl)-N-ethyl-aminomethyl]-4-methylphenol [abbreviated as H(L)] was synthesised as follows: an ethylacetate solution of 2,6-bis-(chloromethyl)-p-cresol (0.02 mol) was added dropwise an ethylacetate solution containing N,N,N'-triethylethylenediamine (0.04 mol) at 3 °C, and the resulting solution stirred for 2 hours. After the addition of triethylamine (0.04 mol), the solution was refluxed for 2 hours. The precipitated white triethylamine hydrochloride was removed, the filtrate was evaporated to dryness, and the residue was diluted with methanol. The methanol solution obtained above was used for the preparation of the copper(II) complex without further purification. The copper(II) complex, $Cu_2(L)(C_6H_5CO_2)_2PF_6$ was obtained from a methanol solution of the ligand, copper(II) benzoate, triethylamine, and NH_4PF_6. Green

H(L)
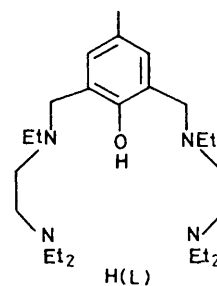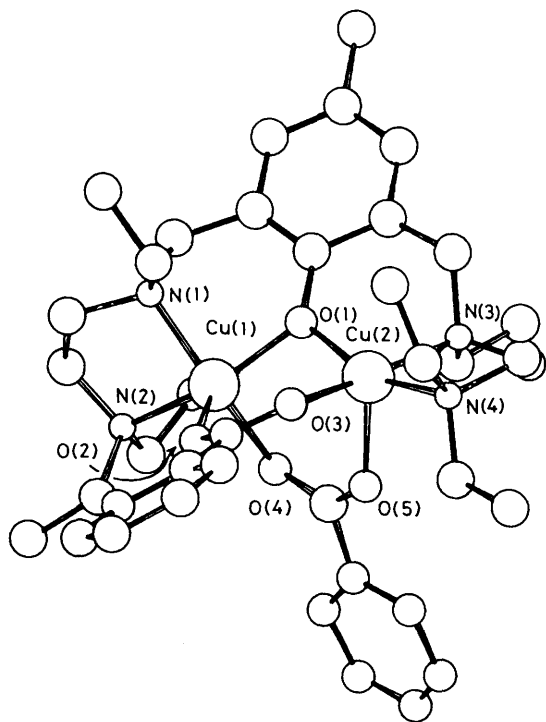
Figure 1. Perspective drawing of the complex. Selected bond distances(Å) and angles(°): Cu(1)–Cu(2) 3.297(3); Cu(1)–O(1) 1.976(10); Cu(1)–N(1) 2.030(11); Cu(1)–N(2) 2.088(14); Cu(1)–O(2) 2.139(9); Cu(1)–O(4) 1.994(9); Cu(2)–O(1) 2.002(9); Cu(2)–N(3) 2.018(12); Cu(2)–N(4) 2.118(13); Cu(2)–O(3) 1.949(9); Cu(2)–O(5) 2.107(10); Cu(1)–O(1)–Cu(2) 112.0(3).
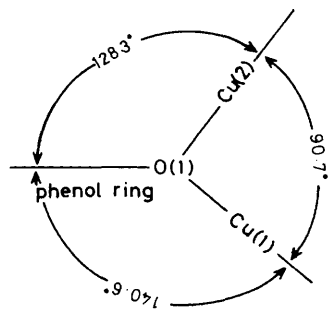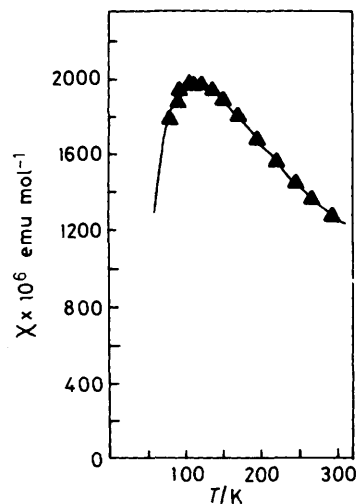

Figure 2

prisms obtained were recrystallized from an acetonitrile–methanol solution.†

Figure 1 shows the perspective drawing of the complex.‡ Two copper(II) ions are bridged by phenoxide and two benzoate groups. Based on the bond distances, bond angles, and the best plane calculations, the geometries around the

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† A satisfactory analysis (C, H, N) has been obtained.

‡ *Crystal data* for [Cu$_2$(L)(C$_6$H$_5$CO$_2$)$_2$]PF$_6$, M = 934.0, monoclinic space group $P2_1/c$, a = 14.504(7), b = 13.667(6), c = 21.563(7) Å, β = 90.23(2)°, U = 4274 Å^3, Z = 4, D_c = 1.45 g cm^{-3}, $F(000)$ = 1944, μ(Mo-K$_\alpha$) = 11.4 cm^{-1}, T = 293 K. Crystal dimensons 0.2 × 0.2 × 0.4 mm; data were collected in the range 3° ≤ 2θ ≤ 55° by 2 θ–θ scan technique; intensities were corrected for Lorentz and polarization effects. The structure was solved by a combination of direct methods (MULTAN) and Fourier synthesis, and refined by block-diagonal least-squares procedures. A total 3078 unique reflections with F > 3σ(F) were refined to conventional values of $R(R_\omega)$ of 0.082 (0.098). Disorder was observed for the PF$_6$ ion. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Figure 3. Variation with temperature of the molar susceptibility (per Cu) of the complex. ▲ ▲ ▲ Experimental value. ——— Calculated value from Bleaney–Bowers equation for values of g = 2.165, $-2J$ = 126.4 cm^{-1}, and N$_\alpha$ = 60 × 10^{-6} emu/mol.

copper ions are best described as a square pyramid; the apical positions are occupied by O(2) and O(5) for Cu(1) and Cu(2), respectively. It should be noted here that the basal planes as defined above [the planes containing Cu(1), O(1), N(1), N(2), and O(4) and Cu(2), O(1), N(3), N(4), and O(3)] are nearly orthogonal, as illustrated in Figure 2. This is the first example of a binuclear copper(II) complex where two basal planes are nearly perpendicular to each other. The angle Cu(1)–O(1)–Cu(2) is 112.0(3)°. Magnetic susceptibility measurements (81.3—292.2 K) (*cf.* Figure 3) revealed that the $-2J$ value (the energy separation between singlet and triplet state) is 126.4 cm^{-1} based on the Bleaney–Bowers equation.[7]

Based on the recent works on the super-exchange interaction,[1—4,8] it can be concluded that contribution from the benzoate bridge to J_{AF} is negligible in this case, because one of the two oxygen atoms of carboxylate bridge co-ordinates to the copper ion at the apical position of the square pyramid. Thus, the small $-2J$ value observed should be attributed to J_{AF} by the phenoxide bridge. Kahn *et al.*[5] have reported that J_{AF} is highly dependent on the dihedral angle(ϕ) for di-μ-hydroxo copper(II) complexes; the value approaches zero when ϕ ~130° with decreasing from 180°, and increases again when ϕ <130°. At present it is not clear if their conclusion is applicable to other systems, but our present result, at least seems to be consistent with the results by Kahn. More detailed elucidation on the $-2J$ value of binuclear copper(II) complexes where ϕ is near 90° is now in progress.

References

1 P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 1975, **97**, 4884.
2 O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834.
3 B. Chiari, O. Piovesana, T. Tarantelli, and P. F. Zanazzi, *Inorg. Chem.*, 1987, **26**, 952.
4 D. J. Hodgson, *Prog. Inorg. Chem.*, 1975, **19**, 173.
5 M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. L-Abaul, and J. M-Frere, *Inorg. Chem.*, 1979, **18**, 1675.
6 Y. Nishida, M. Takeuchi, K. Takahashi, and S. Kida, *Chem. Lett.*, 1985, 631; Y. Nishida and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1986, 2633.
7 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, A*, 1952, **214**, 451.
8 Y. Nishida, H. Shimo, H. Maehara, and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1985, 1945.