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# Magnetostructural Correlations in Ferromagnetic and Antiferromagnetic Isomers of a Binuclear Copper(II) Complex.
## The Importance of the Geometry of the Bridging Alkoxo Oxygen Atom

G. D. FALLON, K. S. MURRAY*

*Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia*

W. MAZUREK and M. J. O'CONNOR

*Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia*

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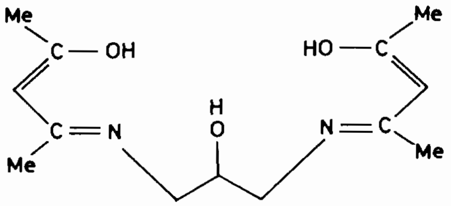
While considerable advances have recently been made in understanding the relationships between structural features and $J$ values in symmetrical dibridged copper(II) dimers, *e.g.* of the type $Cu_2(OH)_2^{2+}$, [1, 2] the same degree of understanding has not yet been achieved for asymmetrical dibridged systems. The latter compounds generallly contain an endogenous bridging group such as a phenoxo or alkoxo oxygen atom, often as part of a binucleating ligand, as well as an exogenous bridging group ($OH^-$, $Cl^-$, $CH_3CO_2^-$, *etc.*) [3]. There are, therefore, two potential superexchange pathways which can contribute towards the ferromagnetic and antiferromagnetic contributions that make up the observed $J$ value. In a paper on binuclear copper(II) complexes containing monoatomic exogenous bridging groups ($OH^-$, $Cl^-$, $Br^-$) and an alkoxo-bridging binucleating ligand based on 1,5-diamino-pentan-3-ol or 1,3-diamino-propan-2-ol we showed that small systematic variations could lead to quite diverse values of $J$, both antiferromagnetic and ferromagnetic [4]. However, crystal structures on key compounds were unfortunately not available which would allow us to make meaningful correlations between structure and magnetism.

A recent report by Nishida *et al.* [5] on the structure of an antiferromagnetically coupled copper(II) complex of the ligand **1** has provided the rate opportunity of being able to compare the structural features in a ferromagnetic isomer of the *same* molecule.



(**1**) $H_3$acaca

The complex $[Cu_2(apaca)(CH_3CO_2)]$, **2**, was studied as part of a range of binuclear complexes containing two-atom bridging from pyrazolate or acetate ions [6]. Preliminary results have been reported [7]. The same complex was subsequently reported by Nishida *et al.* except that their sample contained a molecule of water of hydration which the present complex does not. It is difficult to know with certainty from their report whether the $H_2O$ is bonded to one of the copper atoms, or whether it plays any significant role in the resulting structure.

## Experimental

### *Synthesis of $Cu_2(apaca)(CH_3CO_2)$*

A stock solution of the ligand $H_3$apaca was prepared by mixing acetylacetone (10 g, 0.1 mol) and 1,3-diaminopropan-2-ol (4.5 g, 0.05 mol) in 100 ml of ethanol/methanol (1:1). 5 ml (0.005 mol) of this solution was added to copper acetate (2.0 g, 0.01 mol) in ethanol (150 ml). The resulting blue solution was evaporated on a hot plate to a volume of 50 ml. After cooling, the dark blue crystalline product was filtered, washed with ethanol, dried and recrystallized from chloroform/ethanol. *Anal.* Found: C, 41.1; H, 5.1; N, 6.4; Cu, 29.3. Calc. for $C_{15}H_{22}N_2O_5Cu_2$: C, 41.2; H, 5.0; N, 6.4; Cu, 29.1%.

Magnetic susceptibilities between 300 and 4.2 K were measured on a Faraday balance as described previously [4].

### *Crystal Structure Determination*

The cell dimensions: $a = 12.029(8)$, $b = 12.262(8)$, $c = 12.291(8)$ Å, $\beta = 104.6(3)°$, $U = 1754.4$ Å$^3$; $Z = 4$, $D_c = 1.66$, $D_m = 1.65(2)$ g cm$^{-3}$ (by flotation), space group $P2_1/n$. Single crystal X-ray diffraction data were collected on a Philips PW1100 diffractometer with graphite-monochromated Cu-K$\alpha$ radiation for reflections with $6° < 2\theta < 120°$. 2267 absorption corrected data with $F > 6\sigma(F)$ were used in the solution and refinement of the crystal structure. The structure was solved by direct methods and refined with anisotropic thermal parameters for Cu, all other atoms isotropic and hydrogen included in geometrically calculated positions with a common thermal parameter, to $R = 0.053$, $R_w = \Sigma\omega^{1/2}\Delta/\Sigma\omega^{1/2}|F_o| = 0.061$, with $\omega^{-1} = \sigma^2(F)$ and $\Delta = \| F_o| - |F_c\|$.

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*Author to whom correspondence should be addressed.

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TABLE I. Comparisons of Magnetism and Structure for **2** and **3**.

| | $Cu_2(apaca)(CH_3CO_2)$ **2** (this work) | $[Cu_2(apaca)(CH_3CO_2)]\cdot H_2O$ **3** (ref. 5) |
|---|---|---|
| $\mu_{Cu}(\mu_B)$, 295 K | 1.93 | 1.64 |
| $J$ ($cm^{-1}$) | +18.9 | −82.5 |
| *Bond Lengths* (Å) | | |
| Cu1–Cu2 | 3.237(1) | 3.502(2) |
| Cu1–O1 | 1.943(4) | 1.946(1) |
| Cu1–O3 | 1.929(4) | 1.902(6) |
| Cu1–O5 | 1.887(4) | 1.903(6) |
| Cu1–N2 | 1.910(4) | 1.936(7) |
| Cu2–O2 | 1.946(4) | 1.930(6) |
| Cu2–O3 | 1.924(4) | 1.913(6) |
| Cu2–O4 | 1.895(4) | 1.893(6) |
| Cu2–N1 | 1.919(4) | 1.896(7) |
| *Bond Angles* (°) | | |
| Cu1–O3–Cu2 | 114.3(2) | 133.3(3) |
| Cu1–O3–C9 | 109.8(3) | N.G.[a] |
| Cu2–O3–C9 | 111.4(3) | N.G. |
| O1–Cu1–O3 | 91.9(2) | 94.2(3) |
| O1–Cu1–O5 | 88.6(2) | 85.5(2) |
| N2–Cu1–O3 | 86.4(2) | 86.1(3) |
| N2–Cu1–O5 | 94.6(2) | N.G. |
| O2–Cu2–O3 | 92.0(2) | 95.1(3) |
| O2–Cu2–O4 | 88.1(2) | 85.6(2) |
| N1–Cu2–O3 | 86.0(2) | 84.8(3) |
| N1–Cu2–O4 | 95.3(2) | 94.5(3) |
| Dihedral angle between planes Cu1, N2, O3, C9, C10 and Cu2, N1, O3, C9, C8 | 119.2 | N.G. |

[a] N.G. = not given.

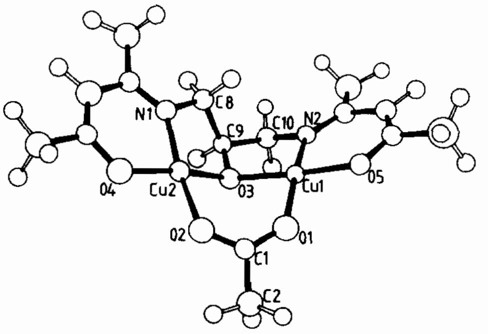

Fig. 1. Molecular structure of $[Cu_2(apaca)(CH_3CO_2)]$, **2**; geometrical details are given in Tables I and II.

## Results and Discussion

The molecular structure of $[Cu_2(apaca)(CH_3CO_2)]$, **2** is shown in Fig. 1 and the magnetic data are displayed in Fig. 2. Comparisons of magnetic properties and geometric details with those of $[Cu_2(apaca)(CH_3CO_2)]H_2O$, **3**, are given in Tables I and II.

The most obvious difference between **2** and **3** is the non-coplanarity of the two Cu coordination spheres in **2**, folded relative to each other like a book, compared to the overall coplanarity of the binuclear moiety in **3**. This non-coplanarity leads to a smaller Cu——Cu distance, a smaller Cu–OR–Cu angle and to a pyramidal arrangement of bonds and non-bonding electrons around the alkoxo-oxygen atom O3. The latter feature is an important one and has been observed by us in one other related {Cu(OH)(OPh)-Cu} bridging system [8]. All other related 'co-planar' di-bridged systems based on 2,6-diformylphenol or metaxylylphenol backbones possess trigonal-planar geometry around the bridging-oxygen and display medium to strong antiferromagnetism [3, 4]. These compounds have Cu——Cu distances of 3.05–3.61 Å, depending on whether the exogenous bridge is mono- (*e.g.* $OH^-$) or multi-atomic (*e.g.* acetate,

TABLE II. Least-squares Plane (Cu1, Cu2, O1, O2 and O3).
Complex 2 $0.2640X + 0.7264Y - 0.6345Z - 3.0107 = 0$
Complex 3 $-0.1657X - 0.3915Y + 0.9124Z + 2.0596 = 0$

| | Deviation (A) | |
|---|---|---|
| | 2 | 3 |
| Cu1 | −0.359(1) | −0.017 |
| Cu2 | −0.284(1) | −0.007 |
| O1 | 0.467(4) | 0.011 |
| O2 | 0.041(4) | −0.004 |
| O3 | 0.135(4) | 0.017 |

1,3-azide), Cu–OR–Cu angles are in the range 100–137°. The O3–C9 vector of the bridging alkoxo or phenoxo group is likewise coplanar with the $Cu_2$-$O_2$ cycle in these structures and in **3**, but not in **2**.

The following magnetostructural correlations can be made based on the present data:

(i) Non-coplanarity of Cu coordination spheres and non-trigonal planar geometry on bridging alkoxo-oxygen generally leads to lower antiferromagnetic coupling and specifically to ferromagnetism in **2**.

(ii) The present geometrical feature in the endogenous-bridging pathway resembles the 'roof-shaped' feature of some dihydroxo bridged dimers [2, 9] (unfortunately O–H dependent angles are not usually determined which would reveal the geometry around the oxygen in these molecules).

(iii) The lowering of the antiferromagnetic contribution in **2** probably relates to (a) the development of accidental orthogonality of Cu magnetic orbitals as the Cu planes become non-coplanar [2, 9]; (b) the pyramidally disposed non-bonding electron pair on the bridging oxygen O3, will interact less effectively in any π-overlap with Cu orbitals than would be the case in **3** again leading to a less negative *J*. [It is noteworthy that a similar argument to (iii(b)) has recently been given to explain variations in *J* in Cr(III) dimers [10]. However the magnetic orbitals on Cr(III) are $t_{2g}$ (π) like and so such a dependence would be more likely relative to be seen than in Cu(II) centres, which are a $d_{x^2-y^2}$ magnetic orbital (in $C_{4v}$ symmetry)].

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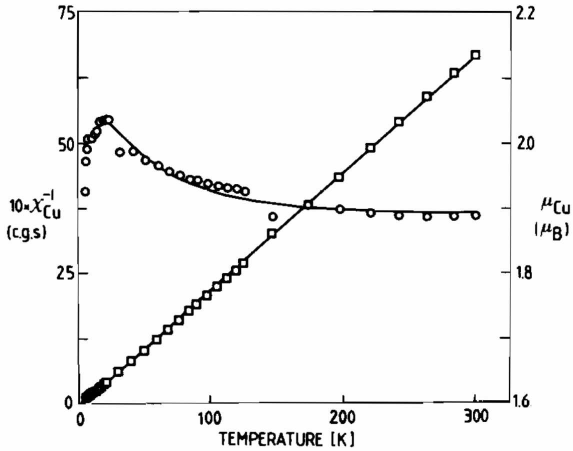

Fig. 2. Temperature dependence of $\chi_{Cu}^{-1}$ (□) and $\mu_{Cu}$ (○) for complex **2**. Solid lines are calculated for $g = 2.1$, $J = +18.9$ $cm^{-1}$.

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