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Moderately strong antiferromagnetic exchange coupling in a dinuclear complex containing a μ-hydroxo-μ-carboxylatodicopper(II) core †

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The dinuclear complex $[Cu_2L_2(\mu\text{-}OH)(\mu\text{-}C_6H_5CO_2)][ClO_4]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) has been synthesized and characterized by X-ray crystallography and from temperature-dependent susceptibility measurements which established a moderately strong, intramolecular, antiferromagnetic exchange coupling ($J = -66\ cm^{-1}$, $H = -2JS_1 \cdot S_2$, $S_1 = S_2 = \frac{1}{2}$) and a magneto–structural correlation between the Cu–O–Cu angle and J for complexes containing a Cu^{II}_2 μ-hydroxo-μ-carboxylato core.

Intramolecular exchange coupling in complexes containing a di-μ-hydroxodicopper(II) core has been shown to be either antiferro- or ferro-magnetic in nature yielding a singlet or a triplet ground state.[1] A linear correlation has been reported[2] for the coupling constant, J, and the Cu–$O_{hydroxo}$–Cu angle, α, equation (1). At angles > 97.5° the exchange interaction is found

$$2J = -74.53\alpha + 7270\ cm^{-1} \qquad (1)$$

to be anti-ferromagnetic and at $\alpha < 97.5°$ it is ferromagnetic.

In contrast, dinuclear complexes containing a μ-hydroxo-μ-carboxylatodicopper(II) core have been reported to be exclusively ferromagnetically coupled to date.[3,4,5] Table 1 lists the structurally characterized compounds for which temperature-dependent susceptibility measurements have been carried out. Here we report the first example of such complexes exhibiting a moderately strong antiferromagnetic coupling.

A reaction mixture of $Cu(ClO_4)_2 \cdot 6H_2O$, 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and sodium benzoate (1 : 1.3 : 0.7) in methanol was briefly heated to 50 °C after addition of a few drops of piperidine. Upon cooling to 0 °C blue-green crystals suitable for X-ray crystallography precipitated. Elemental analysis of this material indicated the stoichiometry $[Cu_2L_2(OH)(C_6H_5CO_2)][ClO_4]_2$ **1**.‡

The structure of one of the two crystallographically independent dinuclear dications in crystals of **1** is shown in Fig. 1; the second has very similar metric dimensions.§

The Cu^{II} ions are each in a distorted square-pyramidal ligand environment where two amine nitrogens, a μ_2-bridging hydroxide and a symmetrically *syn,syn*-co-ordinated carboxylate group occupy the four basal co-ordination sites and one amine nitrogen is in the apical site. The average basal Cu–N_{amine} bonds are shorter (by 0.12 to 0.17 Å) than the apical Cu–N_{amine} bonds as is always observed in square-pyramidal copper(II) complexes containing the macrocyclic ligand L.[7] Interestingly, the vacant sixth co-ordination site *trans* to the apical Cu–N_{amine} bond is occupied by one bridging oxygen atom of a ClO_4 group [O(8) interacts weakly with Cu(1) and Cu(2) and O(18) with Cu(3) and Cu(4)]. These Cu···$OClO_4$ interactions are very weak at 2.79 to 2.98 Å and are probably electrostatic rather than covalent. The second ClO_4^- anion forms a weak O–H···O hydrogen-bonding contact to the bridging hydroxide [O(1)···O(19) 2.97 Å].

The electronic spectrum of **1** in methanol is also consistent with a square-pyramidal CuN_3O_2 chromophore since it displays two weak d–d transitions in the visible region at 638 nm ($\varepsilon = 134\ dm^3\ mol^{-1}\ cm^{-1}$) and at 1054 (55)[8] in agreement with a $(d_{x^2-y^2})^1$ ground state of the copper(II) ions.

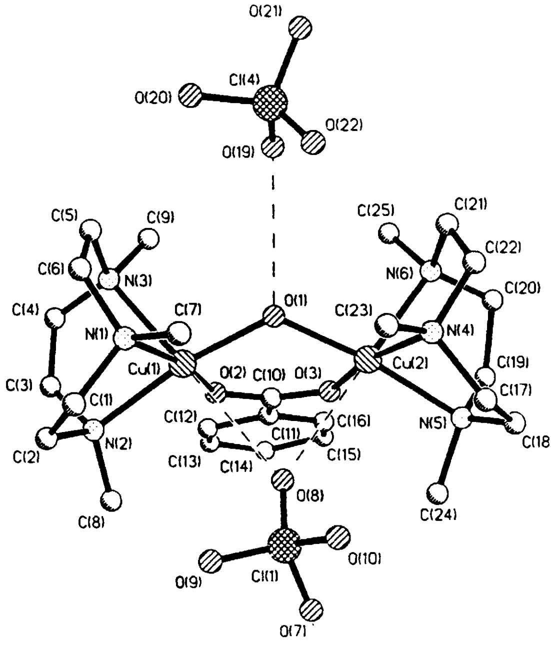

Fig. 1 Structure of $[Cu^{II}_2L_2(\mu\text{-}OH)(\mu\text{-}C_6H_5CO_2)][ClO_4]_2$ **1**. Selected bond lengths (Å) and angles (°) for one crystallographically independent molecule: Cu(1)–N(1) 2.09(1), Cu(2)–N(4) 2.11(1), Cu(1)–O(8) 2.97(1), Cu(1)–N(2) 2.09(2), Cu(2)–N(5) 2.12(2), Cu(2)–O(8) 2.92(1), Cu(1)–N(3) 2.27(2), Cu(2)–N(6) 2.24(2), O(11)···O(4) 2.97(1), Cu(1)–O(1) 1.93(1), Cu(2)–O(1) 1.95(1), Cu(1)–O(2) 1.98(1), Cu(2)–O(3) 1.99(1); Cu(1)–O(1)–Cu(2) 123.6(5)

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† *Non-SI unit employed:* $\mu_B \approx 9.274\,02 \times 10^{-24}\ J\ T^{-1}$.

‡ Blue-green crystals of $[Cu_2L_2(\mu\text{-}OH)(\mu\text{-}C_6H_5CO_2)][ClO_4]_2$ were obtained by the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.38 g, 1.0 mmol) and L (0.22 g, 1.3 mmol) in methanol (20 dm^3). After addition of sodium benzoate (0.10 g, 0.7 mmol) and three drops of piperidine the solution was heated to 50 °C for 5 min. Upon cooling to 0 °C for 12 h, blue-green crystals of X-ray quality precipitated in 68% yield (0.55 g) (Found: C, 37.1; H, 5.9; N, 10.3. Calc. for $C_{25}H_{48}Cl_2Cu_2N_6O_{11}$: C, 37.20; H, 6.00; N, 10.40%). UV/VIS (MeOH): λ_{max} 229 nm (ε 14.0 × 10^3 $dm^3\ mol^{-1}\ cm^{-1}$), 281 (12.8 × 10^3), 638 (134) and 1054 (55).

§ Crystal data. $C_{25}H_{48}Cl_2Cu_2N_6O_{11}$, $M = 806.7$, orthorhombic, space group $P2_12_12_1$, $a = 16.132(3)$, $b = 16.290(3)$, $c = 27.078(5)$ Å, $U = 7116(2)$ Å^3, $Z = 8$, $D_c = 1.504$ g cm^{-3}, $F(000) = 3352$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 1.406$ mm^{-1}, ψ-scan absorption correction, crystal dimensions 0.5 × 0.6 × 0.4 mm, 4371 observed diffractometer data [$F > 4.0\sigma(F)$]. Structure solved by direct methods and refined by full-matrix least-squares analysis by using the SHELXTL PLUS package.[6] Due to the low data-to-parameter ratio (5.6:1) hydrogen-atom positions are not included; all non-hydrogen atoms were refined with anisotropic thermal parameters to $R = 0.073$, $R' = 0.076$, $w^{-1} = \sigma^2(F) + 0.0003F^2$. Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Table 1 Comparison of structural and magnetic properties of dinuclear complexes containing the μ-hydroxo-μ-carboxylatodicopper(II) core

Complex[a]	J/cm^{-1} [b]	α(Cu–O–Cu)/°	β/° [c]	Cu ··· Cu/Å [d]	Ref.
$[Cu_2(\mu\text{-}OH)(\mu\text{-}MeCO_2)(phen)_2][NO_3]_2\cdot H_2O$	+55.5[e]	103.4	122.8	3.017	3
$[Cu_2L'(\mu\text{-}OH)(\mu\text{-}MeCO_2)][ClO_4]_2\cdot MeOH$	+1.3	109.3	117.5	3.156	4
$[Cu_2(\mu\text{-}OH)(\mu\text{-}H_2O)(\mu\text{-}MeCO_2)(bipy)][ClO_4]_2$	+19	103.8	118.1	3.035	5
$[Cu_2L_2(\mu\text{-}OH)(\mu\text{-}C_6H_5CO_2)][ClO_4]_2$	−66	124 (av.)	134.8	3.43	This work
			141.9	3.46	

[a] phen = 1,10-phenanthroline, L′ = a hexaimidazole dinucleating ligand and bipy = 2,2′-bipyridine. [b] Spin Hamiltonian convention: $H = -2JS_1\cdot S_2$ ($S_1 = S_2 = \frac{1}{2}$). [c] Dihedral angle between the basal planes of the two Cu polyhedra. [d] Intramolecular Cu ··· Cu distance. [e] T 80–300 K.

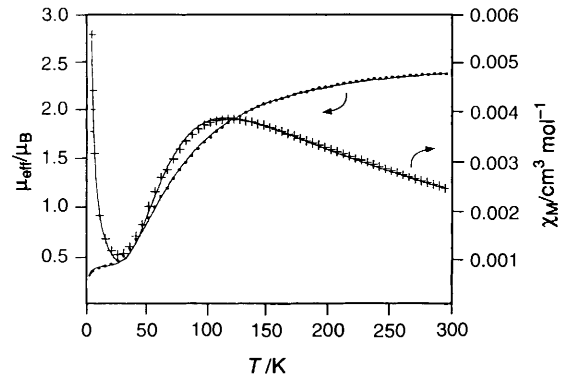

Fig. 2 Temperature dependence of the molar susceptibility, χ_M (+), and of the magnetic moment, μ_{eff} (■), of a powdered sample of **1**. The solid lines represent a fit to the Bleaney–Bowers[9] equation

The molar susceptibility of a powdered sample of **1** has been measured in the temperature range 2–293 K at 1.0 T on a SQUID magnetometer (Quantum Design) and was corrected for underlying diamagnetism by use of tabulated Pascal's constants and for a temperature-independent paramagnetism of 60×10^{-6} cm^3 mol^{-1} per Cu^{II}. The solid lines in Fig. 2 represent a best fit of the data to the isotropic Heisenberg, Dirac, van Vleck exchange model ($H = -2JS_1\cdot S_2$, $S_1 = S_2 = \frac{1}{2}$). Numerical values for the exchange parameter J, the g factor and a paramagnetic monomeric impurity $p(S = \frac{1}{2})$ of −66 cm^{-1}, 2.21 and 6.2%, respectively were obtained from a non-linear least-squares fitting procedure. From these data it is concluded that a moderately strong, intramolecular, *antiferromagnetic* interaction between the two Cu^{II} ions exists in the dinuclear cation of **1** leading to a singlet ground state. This contrasts with the magnetism of three other dinuclear complexes containing the μ-hydroxo-μ-carboxylatodicopper(II) core (Table 1) for which a *ferromagnetic* coupling (triplet ground state) has been reported.[3–5]

All complexes in Table 1 can be viewed as dinuclear square-pyramidal copper(II) species where the magnetic $d_{x^2-y^2}$ orbitals are intramolecularly bridged by one hydroxo and one *syn,syn*-bound carboxylate and, hence, the effective magnetic exchange pathway should be the same in all cases. As has been pointed out by several authors[3,10,11] combination of the two bridging ligands between $d_{x^2-y^2}/d_{x^2-y^2}$ magnetic orbitals is non-complementary (Fig. 3). Following the discussion in the paper by Christou *et al.*[5] we have attempted to correlate the Cu–O–Cu angle, α, and the sign and magnitude of the magnetic coupling constant J. In Fig. 4 we show (*i*) the well established correlation between J and the Cu–O–Cu angle of di-μ-hydroxodicopper(II) species and (*ii*) a similar correlation for the present series of complexes. It is noted that the ferromagnetic coupling for $[Cu^{II}_2(\mu\text{-}OH)(\mu\text{-}MeCO_2)(phen)_2][NO_3]_2\cdot H_3O$[3] appears to be too large but this value is the least reliable one of the series in Table 1 because the temperature dependence of the susceptibility was measured only in the range 80 to 300 K.

As predicted,[5] large Cu–O–Cu angles (> 110°) lead to antiferromagnetic coupling. It is also noted that the overall effect is much larger for the complementary di-μ-hydroxodicopper(II) series than for the complexes containing a non-complementary μ-hydroxo-μ-carboxylatodicopper(II) core.

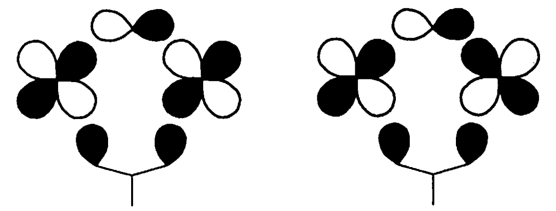

Fig. 3 Schematic representation of the antisymmetric (left) and symmetric (right) combinations of the magnetic orbitals of the μ-hydroxo-μ-carboxylatodicopper(II) core in **1**, showing the 'non-complementary' nature of the overlap

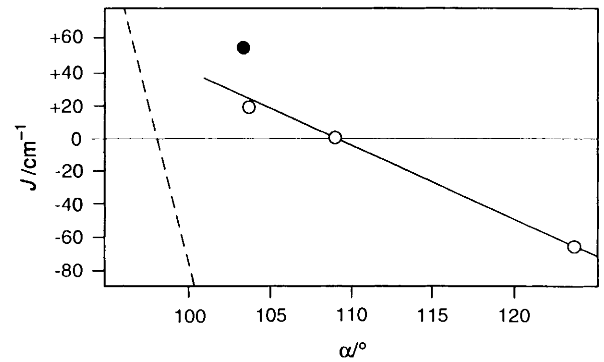

Fig. 4 Magneto-structural correlations between the coupling constant J and the Cu–O$_{hydroxo}$–Cu bond angle α for di-μ-hydroxodicopper(II) (– – –) and μ-hydroxo-μ-carboxylatodicopper(II) complexes (——). Open circles denote accurate determinations of J from susceptibility measurements in the temperature range 2–300 K; the filled circle represents a value from an 80–300 K measurement

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