

Self-assembly preparation, structure and magnetic studies of a novel dinuclear copper(II) complex: $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-OAc})(\mu\text{-L})][\text{BF}_4]_2$ [L = bis-1,3-(*cis,cis*-1,3,5-triaminocyclohexane)xylylidene]

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The crystal structure of a novel dinuclear copper(II) complex, with the bridging ligand bis-1,3-(*cis,cis*-1,3,5-triaminocyclohexane)xylylidene has been obtained; the complex was prepared using a single-pot reaction of copper(II) salts, isophthalaldehyde and *cis,cis*-1,3,5-triaminocyclohexane.

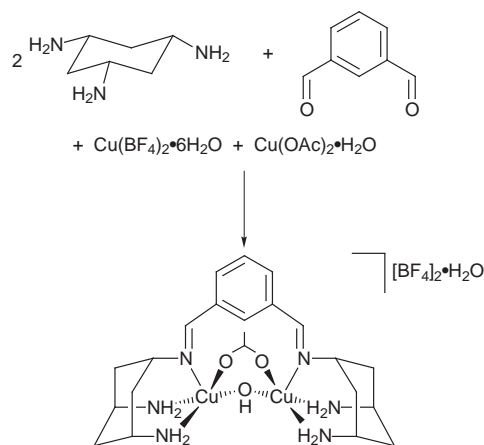
cis,cis-1,3,5-Triaminocyclohexane (tach) is a versatile N_3 face-capping ligand in bioinorganic chemistry.¹ Complexes of tach (and its derivatives) have received considerable interest as effective bioinorganic model complexes,² *in vivo* chelating agents³ and highly efficient catalysts for the hydrolytic cleavage of DNA.⁴ Recently, attention has focused on the use of bis(tach) ligands as potential binucleating ligands.⁵ Herein, we report the preparation and characterization of a dinuclear copper(II) complex containing a novel bis-1,3-(*cis,cis*-1,3,5-triaminocyclohexane)xylylidene ligand.

We have previously reported that Schiff-base derivatives of tach (prepared from tach and benzaldehyde derivatives) readily complex to 3d transition-metal ions. This complexation is accompanied by the selective hydrolysis of two of the three imine bonds to give unusual monoimine, diamine–tach metal complexes in good yields.¹ We have now extended this synthetic route to prepare the first bridging bis(tach) complex $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-OAc})(\mu\text{-L})][\text{BF}_4]_2$ [L = bis-1,3-(*cis,cis*-1,3,5-triaminocyclohexane)xylylidene]. The complex is prepared in a convenient ‘one-pot’ synthesis using a solution of isophthalaldehyde, tach and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O} - \text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Scheme 1. High dilution conditions are not required and the synthesis proceeds smoothly over a period of 48 h to give the product in *ca.* 30% yield.[†]

The crystal structure of $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-OAc})(\mu\text{-L})][\text{BF}_4]_2$ (Fig. 1) ‡ shows the dicopper(II) cation with the bridging bis-1,3-(*cis,cis*-1,3,5-triaminocyclohexane)xylylidene ligand. The two copper(II) ions are further bridged by hydroxo and acetato groups. The cation has near mirror plane symmetry (there is no

crystallographic mirror symmetry, which is broken by a single water molecule of crystallization). Each copper(II) ion has a square pyramidal co-ordination geometry, with the basal plane described by the two amino nitrogen atoms of the tach moiety and the oxygen atoms of the acetato and hydroxo groups. The third nitrogen atom of tach occupies the axial position [Cu2–N4 2.282(9), Cu1–N1 2.261(10) Å]. The Cu–N (imine)–C (imine) angles of 130.9(7) and 131.1(9)° indicate some steric strain in the structure, presumably between the bridging *m*-xylyl group and the $\text{Cu}(\mu\text{-OH})(\mu\text{-OAc})\text{Cu}$ moiety. The angle between the acetato and xylyl planes is 25.6(3)°. The $\text{Cu} \cdots \text{Cu}$ separation is 3.491(10) Å (which is comparable to that observed in the oxygen-carrying protein haemocyanin⁷) and the Cu–(OH)–Cu angle is 131.2(3)°. This is the largest angle reported for a Cu–(μ-OH)(μ-OAc)Cu moiety. Two non-co-ordinated tetrafluoroborate anions and a single water molecule, hydrogen bonded to one of the amino groups of tach, complete the structure.

Complex 1 is EPR silent as a solid at both room temperature and 100 K. Subsequent magnetic susceptibility studies (Fig. 2) §



Scheme 1 Single-step synthesis of a dicopper(II) complex with novel bridging bis(tach) ligand

† A solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.13 g, 0.65 mmol) and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.22 g, 0.65 mmol) in methanol (25 mL) was added to a solution of *cis,cis*-1,3,5-triaminocyclohexane (0.16 g, 1.30 mmol) in methanol (25 mL). A solution of isophthalaldehyde (86 mg, 0.65 mmol) in methanol (5 mL) was then added and the resulting deep blue solution was refluxed for 48 h. Slow evaporation of the solvent at room temperature yielded the product as royal blue crystals (0.28 g, 28%). M.p. 200 °C (decomp.) [Found: C, 34.15; H, 4.85; N, 10.65. Calc. for $\text{C}_{22}\text{H}_{40}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_6\text{O}_5 \cdot (\text{H}_2\text{O})$: C, 34.35; H, 5.25; N, 10.95%]. IR (cm^{-1} , in KBr): 3434s, 3338m, 3277m, 3229m, 3140m, 2919m, 1636m, 1577m, 1424m, 1084s, 894m, 668m. FAB Positive ion mass spectrum (nitrobenzyl alcohol matrix): $m/z = 541$ ($M^+ - 2\text{BF}_4^- - \text{H}_2\text{O} - \text{OH}^-$), 499 ($M^+ - 2\text{BF}_4^- - \text{H}_2\text{O} - \text{OAc}^-$).

‡ $\text{C}_{22}\text{H}_{38}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_6\text{O}_4$, $M = 751.28$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 14.824(9)$, $b = 14.967(6)$, $c = 13.937(5)$ Å, $U = 3092(3)$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 14.63 \text{ cm}^{-1}$, $T = 293 \text{ K}$, $R_F = 0.053$, $wR_F = 0.125$ for 2570 unique reflections. CCDC reference number 186/1062. See <http://www.rsc.org/suppdata/dt/1998/2449/> for crystallographic files in .cif format.

§ Magnetic susceptibility measurements were measured on a Quantum Design MPMS7 SQUID magnetometer with a powdered sample of the copper dimer. Measurements were made in the temperature region 2–300 K and at external field strengths of 5.0, 1.0 and 0.5 T. Each curve was identical once corrected for inherent diamagnetism and for temperature independent paramagnetism of $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per copper(II) ion. Fig. 2 shows the plot of molar susceptibility ($\chi_m/\text{cm}^3 \text{ mol}^{-1}$) versus temperature at a field of 1.0 T. The solid line represents the best fit to the modified Bleaney–Bowers expression (1).⁸ The best fit was

$$\chi_m = \left(\frac{N g_{\text{iso1}}^2 \beta^2}{3kT} \right) \times \left(1 + \left(\frac{1}{3} \right) \exp \left(\frac{-2J}{kT} \right) \right)^{-1} + pS(S+1) \frac{N g_{\text{iso2}}^2 \beta^2}{3kT} \quad (1)$$

obtained for $2J = -152.1 \text{ cm}^{-1}$, $p = 0.0106$, $g_{\text{iso1}} = 2.21$ and $g_{\text{iso2}} = 2.10$ (g_{iso1} = isotropic Landé factor for the dimer, g_{iso2} = isotropic Landé factor for the paramagnetic impurity, p = fraction of paramagnetic impurity).

Table 1 Comparison of the structural properties of dinuclear copper(II) complexes containing the Cu(μ -hydroxo)(μ -carboxylato)Cu moiety

Complex*	$2J/\text{cm}^{-1}$	Cu–O–Cu $^{\circ}$	Ref.
[Cu ₂ (μ -OH)(μ -OAc)(phen) ₂][NO ₃] ₂ ·H ₂ O	111	103.4	9(d)
[Cu ₂ (μ -OH)(μ -OAc)(μ -H ₂ O)(bipy) ₂][ClO ₄] ₂	38	103.8	9(b)
[Cu ₂ (μ -OH)(μ -OAc)(μ -L')][ClO ₄] ₂ ·MeOH	2.6	109.3	9(c)
[Cu ₂ (μ -OH)(μ -OAc)(tmen) ₂][ClO ₄] ₂	–55.6	120.1	9(e)
[Cu ₂ (μ -OH)(μ -OPh)(L'') ₂][ClO ₄] ₂	–132	124	9(a)
[Cu ₂ (μ -OH)(μ -OAc)(μ -L)][BF ₄] ₂	–152.1	131.2	This work

* L' = 1,3-Bis{4-[bis(1-methylimidazol-2-yl)(methoxy)methyl]imidazol-2-yl}benzene, L'' = 1,4,7-trimethyl-1,4,7-triazacyclononane.

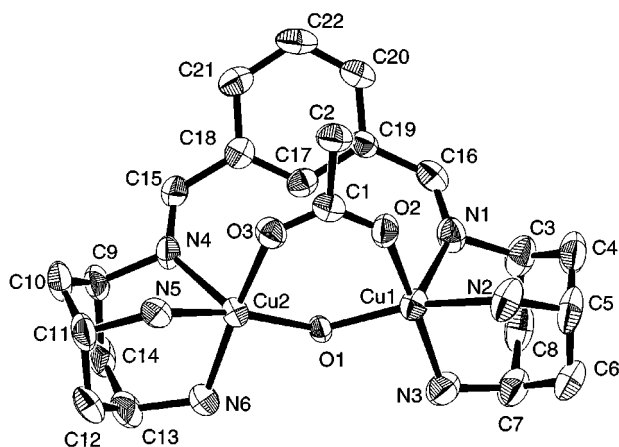


Fig. 1 An ORTEP⁶ representation of the cation in [Cu₂(μ -OH)(μ -OAc)(μ -L)][BF₄]₂ with 30% probability ellipsoids. The hydrogen atoms, tetrafluoroborate anions and water molecule have been omitted for clarity. Selected bond lengths (Å) and angles ($^{\circ}$): Cu(1)–Cu(2) 3.491(10), Cu(1)–O(1) 1.915(5), Cu(1)–O(2) 1.959(8), Cu(1)–N(1) 2.261(10), Cu(1)–N(2) 2.002(10), Cu(1)–N(3) 1.998(9), Cu(2)–O(1) 1.917(6), Cu(2)–O(3) 1.954(8), Cu(2)–N(4) 2.282(9), Cu(2)–N(5) 1.995(9), Cu(2)–N(6) 1.979(9); Cu(1)–O(1)–Cu(2) 131.2(3), O(1)–Cu(1)–O(2) 93.1(3), O(1)–Cu(1)–N(3) 87.2(3), O(2)–Cu(1)–N(2) 86.9(4), N(2)–Cu(1)–N(3) 90.6(4), Cu(1)–O(2)–C(1) 135.7(7), O(1)–Cu(2)–O(3) 94.3(3), O(1)–Cu(2)–N(6) 85.1(3), O(3)–Cu(2)–N(5) 87.1(3), N(5)–Cu(2)–N(6) 91.7(4), Cu(2)–O(3)–C(1) 133.9(8), Cu(1)–N(1)–C(16) 131.1(9), N(1)–C(16)–C(19) 127.7(11), C(18)–C(15)–N(4) 124.2(10), C(15)–N(4)–Cu(2) 130.9(7)

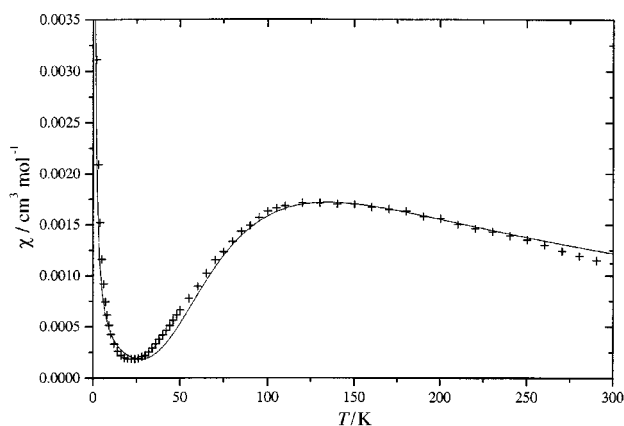


Fig. 2 Plot of molar susceptibility ($\chi_m/\text{cm}^3 \text{mol}^{-1}$) versus temperature at a field of 1.0 T of a powdered sample of [Cu₂(μ -OH)(μ -OAc)(μ -L)][BF₄]₂. The solid line is the best fit to the modified Bleaney–Bowers equation

gave a $2J$ value of -152.1 cm^{-1} . Thus the compound exhibits a strong intramolecular antiferromagnetic interaction between the copper(II) ions. Comparison of the magnetic coupling in this system with other Cu(μ -hydroxo)(μ -carboxylato)Cu systems⁹ shows that [Cu₂(μ -OH)(μ -OAc)(μ -L)][BF₄]₂ exhibits the largest degree of antiferromagnetic coupling reported for these

systems (Table 1). In the case of [Cu₂(μ -OH)(μ -OAc)(μ -L)][BF₄]₂ the rigidity of the ligand enforces a large Cu...Cu separation [3.491(10) Å] and large Cu–O–Cu angle [131.2(3) $^{\circ}$]. The $2J$ value of -152.1 cm^{-1} follows the magnetostructural correlation between the Cu–O–Cu angle and $2J$ recently reported by Wieghardt and co-workers.^{9a}

We have demonstrated that a dicopper bis(tach) complex can be readily prepared using a single-pot synthesis. Complex **1** is the first bridged bis(tach) complex to be crystallographically characterized.¹⁰ Furthermore, it is the rigidity of the ligand which is important in maintaining the relatively large Cu...Cu separation. Magnetic studies show that the complex exhibits strong intramolecular antiferromagnetic coupling between the two copper centers, which can be related to the large Cu–(μ -OH)–Cu angle.

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