

## A Novel Tetranuclear Copper(II) Complex with Three Different Types of Azide, exhibiting Weak Antiferromagnetic Exchange

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The antiferromagnetically coupled, tetranuclear copper(II) complex  $[\text{Cu}_4(\text{pap})_2(\mu\text{-}1,1\text{-N}_3)_2(\mu\text{-}1,3\text{-N}_3)_2(\mu\text{-MeOH})_2(\text{N}_3)_4]$  **1** contains a unique structural arrangement with two  $\mu\text{-}1,1$ -azide intramolecular bridges, and two  $\mu\text{-}1,3$ -azide intermolecular bridges linking pairs of copper(II) centres, in addition to four terminal azide groups.

The azide group is a versatile ligand which can bond to metal centres in three ways: as a terminal ligand *via* one nitrogen donor, as a bridge in the  $\mu\text{-}1,1$ -mode *via* one nitrogen donor, and in the  $\mu\text{-}1,3$ -mode *via* both of the peripheral nitrogen donor atoms. Combinations of  $\mu\text{-}1,3$ -azide and terminal azide in the same complex are rare (Ni),<sup>1</sup> and while combinations of  $\mu\text{-}1,1$ -azide and terminal azide are more common in copper<sup>2,3</sup> and nickel<sup>4-6</sup> chemistry, but still rare, the presence of both  $\mu\text{-}1,1$ -azide and  $\mu\text{-}1,3$ -azide in the same complex is most unusual (Cu,<sup>7</sup> Ni<sup>8</sup>). The magnetic properties of the azide bridge are dependent upon its mode of bonding, with symmetric  $\mu\text{-}1,3$ -azides normally propagating antiferromagnetic exchange (Cu,<sup>9-11</sup> Ni<sup>12,13</sup>), and the  $\mu\text{-}1,1$ -azide propagating ferromagnetic exchange (Cu,<sup>14,15</sup> Ni<sup>6,16-18</sup>), particularly at small ( $<108^\circ$ ) bridge angles. However recent studies with  $\text{N}_4$  diazine complexes have shown that for angles  $> \approx 108^\circ$  the  $\mu\text{-}1,1$ -azide is an antiferromagnetic bridge,<sup>2,19</sup> and if ligand constraints (*e.g.* bite, steric effects *etc.*) can be incorporated into the complex structure very large azide bridge angles ( $>120^\circ$ ) can be produced.<sup>2</sup>

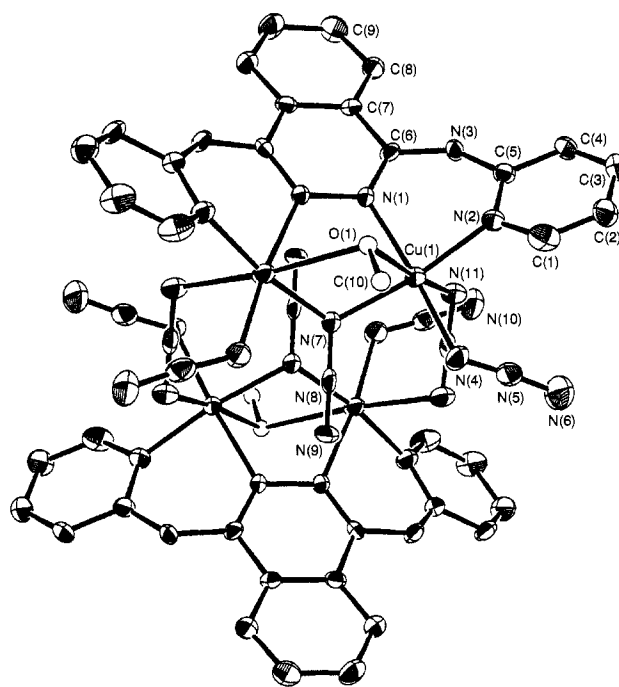
Reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with the  $\text{N}_4$  diazine ligand pap† in dichloromethane-methanol, followed by the addition of a slight excess of  $\text{NaN}_3$  dissolved in water led to the formation of green crystals of **1** suitable for structural determination.§¶ The structure of  $[\text{Cu}_4(\text{pap})_2(\mu\text{-}1,1\text{-N}_3)_2(\mu\text{-}1,3\text{-N}_3)_2(\mu\text{-MeOH})_2(\text{N}_3)_4]$  (Fig. 1) is remarkable in that three different bonded azide groups are present. Each pair of six-coordinate copper(II) centres, which are bonded to one ligand, are bridged equatorially by an intramolecular  $\mu\text{-}1,1$ -azide, with a bridge angle of  $107.9(5)^\circ$ . Two  $\mu\text{-}1,3$ -azide bridges link the two anti-dinuclear complex units *via* axial interactions [Cu(1)–N(11) 2.469(8) Å], and four terminal azide ligands fill the remaining equatorial coordination positions. A distant bridging methanol [Cu(1)–O(1) 2.740(2) Å] completes the six-coordination. The intradinuclear copper–copper separation [3.207(3) Å] is smaller than the interdinuclear separations [5.517(4), 6.382(3) Å] as would be expected. The ligand is slightly bent, with dihedral angles between the pyridine mean planes and the phthalazine mean plane of  $29.0^\circ$ . The basal  $\text{N}_4$  donor set is almost flat with N–Cu–N angles in the range  $85.9\text{--}98.1^\circ$ , and the copper centre is displaced slightly from the mean  $\text{N}_4$  plane towards the axial azide nitrogen by 0.11 Å.

IR data are in accord with the structural features, with three sharp  $\nu_{\text{as}}$  azide bands at 2102, 2049 and 2012  $\text{cm}^{-1}$ . The high-energy band is consistent with the  $\mu\text{-}1,1$ -azide bridge,<sup>2,19</sup> while the lower-energy bands are consistent with terminal and  $\mu\text{-}1,3$ -azide groups respectively. The room temperature magnetic moment ( $\mu_{\text{eff}} = 1.49 \mu_{\text{B}}$  at 303 K) indicates that the spin coupling is dominated by antiferromagnetic exchange between the copper(II) centres. A plot of  $\chi_{\text{Cu}}$  *versus* temperature is illustrated in Fig. 2. As is typical of a weakly antiferromagnet-

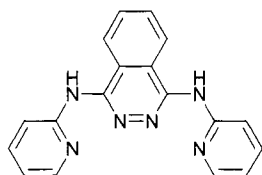
ically coupled dicopper(II) complex the susceptibility rises to a maximum ( $\approx 75$  K) and drops at higher temperatures. Fitting of the magnetic data to the Bleaney–Bowers equation<sup>20</sup> [eqn. (1)] was found to be impossible with  $\theta$  values close to 0 K.

$$\chi_{\text{m}} = \frac{N\beta^2 g^2}{3k(T - \theta)} [1 + 1/3 \exp(-2J/kT)]^{-1} (1 - \rho) + \frac{[N\beta^2 g^2] \rho}{4kT} + N\alpha \quad (1)$$

In fact experimental values of susceptibility are about half of those calculated on the basis of  $T_{\chi_{\text{max}}}$  (*e.g.* assuming  $-2J \approx 75 \text{ cm}^{-1}$ ;  $\mu_{\text{RT}} > 1.7 \mu_{\text{B}}$ ). If the equatorial, magnetically active bridges (phthalazine and azide) stabilized different spin ground states (antiferromagnetic–ferromagnetic combination), then because of the additive nature of the exchange ( $J_{\text{T}} = J_{\text{AF}} + J_{\text{F}}$ )<sup>14</sup> the Bleaney–Bowers equation would apply. However, the case for the combination of two parallel, different bridges, both of which stabilize the same type of ground state *e.g.* a singlet state, has not been thoroughly examined. Four structurally documented cases involving pap complexes with parallel combina-



**Fig. 1** Structural view of  $[\text{Cu}_4(\text{pap})_2(\mu\text{-}1,1\text{-N}_3)_2(\mu\text{-}1,3\text{-N}_3)_2(\mu\text{-MeOH})_2(\text{N}_3)_4]$  **1**. Bond lengths ( $d/\text{\AA}$ ): Cu(1)–Cu(1') 3.207(3), Cu(1)–N(1) 2.021(7), Cu(1)–N(2) 2.006(7), Cu(1)–N(4) 1.978(8), Cu(1)–N(7) 1.983(7), Cu(1)–N(11) 2.469(8), Cu(1)–O(1) 2.740(2), N(7)–N(8) 1.23(1), N(8)–N(9) 1.13(1), N(10)–N(11) 1.184(8). Bond angles/ $^\circ$ : N(1)–Cu(1)–N(2) 86.9(3), N(1)–Cu(1)–N(4) 172.4(3), N(1)–Cu(1)–N(7) 85.9(3), N(1)–Cu(1)–N(11) 95.2(3), N(2)–Cu(1)–N(4) 96.0(3), N(2)–Cu(1)–N(7) 171.3(3), N(2)–Cu(1)–N(11) 87.4(3), N(4)–Cu(1)–N(7) 90.6(4), N(4)–Cu(1)–N(11) 92.0(3), N(7)–Cu(1)–N(11) 98.1(3), Cu(1)–N(1)–N(1) 116.7(2).



tions of  $\mu$ -diazine ( $N_2$ ) and  $\mu$ -1,1-azide bridges and with azide bridge angles in the range 107.9–108.7° now exist, none of which comply with eqn. (1)  $\{[Cu_2(pap)(\mu-N_3)Cl_3] \cdot CH_2Cl_2,^2 [Cu_2(pap)(\mu-N_3)(N_3)(NO_3)(MeOH)]NO_3 \cdot MeOH,^2 [Cu_2(pap)(\mu-N_3)Br_3] \cdot CH_2Cl_2,^{19}$  and **1**).

The only way that the variable-temperature magnetic data for **1**, and for the three other pap-azide complexes, could be made to fit eqn. (1) is to include large negative  $\theta$  values. A good data fit was obtained for **1** with  $g = 2.277(3)$ ,  $-2J = 47.6(5) \text{ cm}^{-1}$ ,  $\theta = -177(2) \text{ K}$  (Fig. 2). The large negative  $\theta$  value is unrealistic in terms of the normal minor adjustments that are made to magnetic data of this sort to account for small intermolecular association effects. Also, since there are no intermolecular contacts revealed in the structure of **1**, which could propagate any significant intermolecular spin interaction, it can be safely assumed that the necessity for such a correction implies more than one intramolecular spin exchange contact, and that it is antiferromagnetic in nature.

Mapping the magnetic bonding connections in **1** shows that there are only two bridge interactions, which would be expected to provide viable pathways for antiferromagnetic exchange. These include the phthalazine<sup>21</sup> and  $\mu$ -1,1-azides, which provide intramolecular bridges between the  $d_{x^2-y^2}$  copper centres. The intermolecular  $\mu$ -1,3-azides connect the copper centres *via* axial copper bonds, which are orthogonal to the active copper magnetic orbitals, and so at best would only be expected to provide a ferromagnetic term, which would be weak.

It is clear from this study with azides, and also from a reexamination of comparable pap complexes with hydroxide bridges,<sup>22</sup> that the Bleaney–Bowers equation is not an adequate description for weakly to moderately spin coupled dinuclear copper(II) complexes with a  $d_{x^2-y^2}$  ground state and parallel equatorial magnetic bridges, in which both bridges propagate antiferromagnetic exchange. Efforts are underway to rationalize this situation.

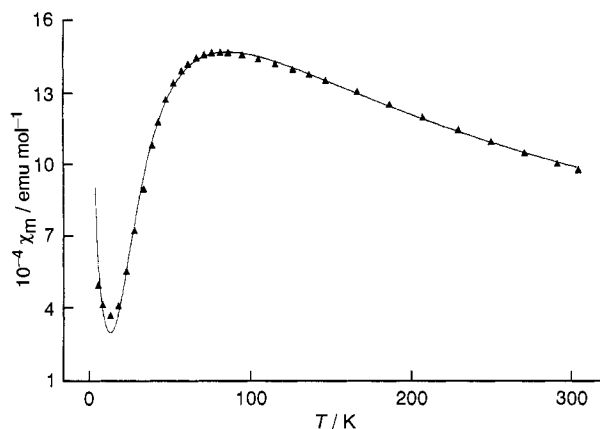


Fig. 2 Variable-temperature magnetic data for **1**.  $\blacktriangle$  Represents the experimental data, and the solid line the theoretical data calculated from eqn. (1)<sup>20</sup> with  $g = 2.277(3)$ ,  $-2J = 47.6(5) \text{ cm}^{-1}$ ,  $p = 0.0046$ ,  $TIP = 30 \times 10^{-6} \text{ emu}$ ,  $\theta = -177 \text{ (K)}$ ,  $10^2 R = 0.60$   $\{R = [\sum(\chi_{obs.} - \chi_{calc.})^2 / \sum \chi_{obs.}^2]^{1/2}\}$ .

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## Footnotes

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‡ pap = 1,4-bis(2-pyridylamino)phthalazine.

§ Found: C, 34.7; H, 3.0; N, 38.8. Calc. for  $Cu_2(C_{18}H_{14}N_6)(N_3)_4 \cdot CH_3OH \cdot 0.5H_2O$ : C, 35.1; H, 2.9; N, 38.8%.

¶ Crystal data for  $C_{19}H_{18}Cu_2N_{18}O$ : green, irregular crystal,  $M = 641.56$ . Monoclinic, space group  $C2/m$  (no. 12),  $a = 15.250(4)$ ,  $b = 15.356(7)$ ,  $c = 12.307(4) \text{ \AA}$ ,  $\beta = 119.70(2)^\circ$ ,  $\lambda(\text{Mo-K}\alpha) = 0.71069 \text{ \AA}$ ,  $T = 26 \text{ }^\circ\text{C}$ ,  $V = 2503(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.702 \text{ g cm}^{-3}$ . The 2314 independent reflections with  $2\theta < 50.2^\circ$  were measured on a Rigaku AFC6S diffractometer, with graphite monochromated Mo-K $\alpha$  radiation, and 1537 reflections [ $I_{net} > 2.0\sigma(I_{net})$ ] were used in the analysis. Hydrogen atoms were optimized by positional refinement, but fixed in the final round of least-squares. Final residuals of  $R = 0.054$  and  $R_w = 0.061$  were obtained for the 1537 significant reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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