

A Dinuclear Copper(II) Complex bridged Simultaneously by End-on Azido, Bromo and Diazole (N₂) Groups exhibiting Strong Ferromagnetic Exchange. X-Ray Structure and Magnetic Properties

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The tetradentate ligand 2,5-di-(2'-methylpyridylthio)thiadiazole (DPTD) forms a dinuclear, triply bridged, copper(II) complex, involving end-on μ_2 -1,1-azido, μ_2 -bromo and μ_2 -1,2-thiadiazole (N₂) bridges, which exhibits a strong ferromagnetic interaction between adjacent copper centres, a feature present only in a very limited number of dicopper(II) complexes.

The synthesis of bulk ferromagnetic materials presents a special challenge in chemistry, and may lead to useful molecular-based organic or inorganic magnets, with practical applications in the realm of high-temperature superconducting materials. Several approaches, which have produced simple ferromagnetic compounds, include: (i) creating a superexchange bridged polynuclear complex with strict orthogonality between metal ion centres, *e.g.* Cr³⁺/Ni²⁺, VO²⁺/Cu²⁺;¹ (ii) coupling organic nitroxide radicals to transition metal ion centres;² (iii) using the principle of accidental orthogonality in *e.g.* bridged species like Cu-(X)_n-Cu (*n* = 1, 2; X = Cl, OH, N₃), and generating dinuclear complexes with bridge angles less than the critical angle,^{3,4} (iv) utilising the spin-polarizing effect of the μ_2 -1,1 azide bridge.¹

The number of complexes that have been characterized both structurally and magnetically, which exhibit a net ferromagnetic interaction, is very limited, and is less than 5% of dinuclear complexes. In dihydroxy-bridged dicopper(II) complexes, the crossover from ferromagnetic to antiferromagnetic behaviour is at *ca.* 97.5°,³ and theoretical calculations have shown that for a less electronegative bridge like azide the critical angle for accidental orthogonality is at *ca.* 103°.⁴ However, in a separate study the spin-polarization effect is presumed to dominate the situation for all azide bridge angles.⁵ The dilemma stems, in part, from the paucity of μ_2 -1,1 azide bridged complexes that have been characterized both structurally and magnetically.

The tetradentate (N₄), dinucleating ligand 2,5-di-(2'-methylpyridylthio)thiadiazole (DPTD) was obtained by treat-

ing 2,5-dimercapto-1,3,4-thiadiazole with 2-picolychloride hydrochloride in the presence of sodium metal in dry methanol-ethanol. A dinuclear copper(II) complex, [Cu₂(DPTD)(μ_2 -Br)(μ_2 -N₃)Br₂].MeCN **1** was obtained as brown crystals by reacting CuBr₂, DPTD and NaN₃ (excess) in acetonitrile-methanol at room temp. The structure of **1** has been determined (see Fig. 1†).

The two copper(II) centres are best described as distorted square-pyramidal and are bound in a triply bridged arrangement involving an axial bromo-bridge, and equatorial azido- and thiadiazole-(N₂) bridges. The azido ligand is linked to both copper centres in an end-on (μ_2 -1,1) fashion, with a

† Crystal data for Cu₂N₈C₁₆S₃H₁₅Br₃: brown, *M* = 782.33, monoclinic, space group *P*2₁/*n*, *a* = 8.437(5), *b* = 25.146(8), *c* = 11.858(4) Å, β = 92.68(3)°, *T* = 25 °C, *V* = 2513(2) Å³, *Z* = 4, *D_c* = 2.068 g cm⁻³, Mo-K α , λ = 0.71069 Å, *F*(000) = 1512. The 4530 independent reflections with $2\theta < 50.0^\circ$ were measured with a Rigaku diffractometer with graphite monochromatized Mo-K α radiation and 2349 reflections [*I*_{net} > 2.00 σ (*I*_{net})] were used in the analysis. The structure was solved by direct methods with weighting based on counting statistics. The non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure and hydrogen atoms placed in calculated positions and included, but not refined, in the last round of least squares analysis. A well-defined acetonitrile molecule was found in the asymmetric unit. Final residuals of *R* = 0.076 and *R_w* = 0.073 were obtained for observed reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

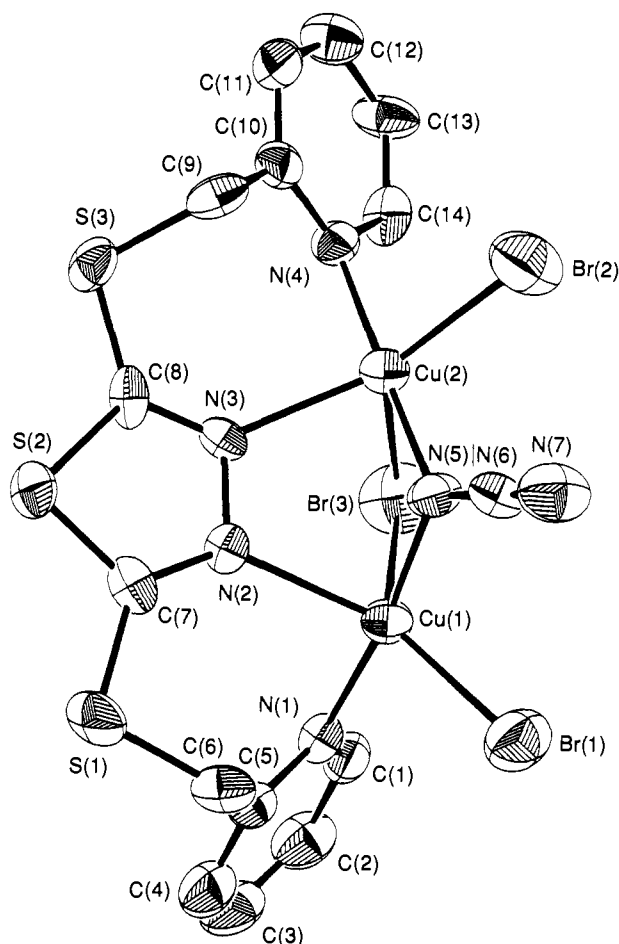


Fig. 1 Structural view of $[\text{Cu}_2(\text{DPTD})(\mu_2\text{-Br})(\mu_2\text{-N}_3)\text{Br}_2]\cdot\text{MeCN}$ **1**. Bond lengths (\AA): Cu(1)–Br(1) 2.384(4), Cu(1)–Br(3) 2.571(4), Cu(1)–N(1) 1.94(1), Cu(1)–N(2) 2.26(1), Cu(1)–N(5) 1.98(2), Cu(2)–Br(2) 2.363(3), Cu(2)–Br(3) 2.620(4), Cu(2)–N(3) 2.22(1), Cu(2)–N(4) 1.99(2), Cu(2)–N(5) 1.98(2), Cu(1)–Cu(2) 3.138(3). Bond angles ($^\circ$): Cu(1)–Br(3)–Cu(2) 74.4(1), Cu(1)–N(5)–Cu(2) 105.0(8), Cu(1)–N(5)–N(6) 127(1), Cu(2)–N(5)–N(6) 127(1), Br(1)–Cu(1)–N(2) 138.7(4), N(1)–Cu(1)–N(5) 172.3(7), Br(2)–Cu(2)–N(3) 145.6(4), N(4)–Cu(2)–N(5) 178.9(6).

copper–copper separation of 3.138(3) \AA and a Cu(1)–N(5)–Cu(2) bridge angle of 105.0 $^\circ$, which lies at the upper limit of the range reported for bis, end-on (μ_2 -1,1) azido copper(II) complexes,^{4–9} and mixed μ_2 -1,1 azido and μ_2 -hydroxo complexes.¹⁰ The angle at the bromine bridge (74.4 $^\circ$) is comparable with those reported for other similar, axially bromine bridged di-copper(II) complexes involving related tetradentate (N_4) diazole ligands.^{11,12} The axial copper–bromine distances are slightly shorter than those observed in analogous dicopper complexes, while the copper–nitrogen (diazole) bonds are quite long, but comparable with those in the complex $[\text{Cu}_2(\text{DPTD})\text{Cl}_4]$ [2.21(2), 2.27(2) \AA].¹² The end-on azido bridge is roughly symmetrically disposed with respect to the dinuclear centre, with equal copper–nitrogen [N(5)] distances of 1.98(2) \AA , and Cu–N(5)–N(6) angles of 127(1) $^\circ$. Cu(1) and Cu(2) are displaced by 0.57(1) and 0.47(1) \AA from the mean plane of the four basal donors N(1), N(2), N(5), Br(1) and N(3), N(4), N(5), Br(2), respectively towards Br(3), and the two N_3CuBr mean planes are mutually inclined by 46.3 $^\circ$.

Complex **1** has a room temperature magnetic moment (μ_{eff}) of 2.00 μ_{B} (300 K), ($\mu_{\text{B}} \approx 9.2740 \times 10^{-24} \text{ J T}^{-1}$), which is higher than values expected for uncoupled copper(II) ions and is indicative of a ferromagnetic interaction. Variable-temperature magnetic studies (4–300 K) on **1** show behaviour typical

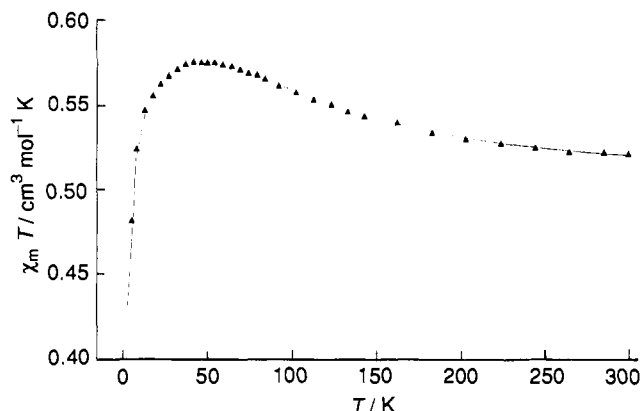


Fig. 2 Magnetic susceptibility data for **1**. The solid line was calculated from eqn. (1) with $g = 2.178(2)$, $2J = 118(3) \text{ cm}^{-1}$, $\rho = 0.0145$, $\theta = -1.15 \text{ K}$, $N\alpha = 73 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

of a system with a strong ferromagnetic exchange interaction and Fig. 2 illustrates a plot of $\chi_{\text{M}}T$ vs. T (χ_{M} = molar magnetic susceptibility per copper, T/K). At room temperature $\chi_{\text{M}}T$ is equal to 0.52 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$ and increases upon cooling, reaching a maximum (0.58 $\text{cm}^3 \text{ mol}^{-1} \text{ K}$) at 42 K and decreasing on further cooling. The magnetic data have been fitted to the Bleaney–Bowers expression¹³ [eqn. (1)] using the isotropic (Heisenberg) exchange Hamiltonian ($H = -2JS_1S_2$) for two interacting $S = 1/2$ centres (χ_{m} is expressed per mole of copper atoms, $N\alpha$ is the temperature-independent paramagnetism, ρ is the fraction of monomeric impurity and θ is a Weiss-like correction for intermolecular interactions). A non-linear regression analysis of the data was carried out with

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

ρ , $N\alpha$, and θ as floating parameters. The best-fit line is shown in Fig. 2 for $g = 2.178(2)$, $2J = 118(3) \text{ cm}^{-1}$, $\rho = 0.0145$, $N\alpha = 73 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, $\theta = -1.15 \text{ K}$ ($10^2R = 0.24$; $R = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2/\sum(\chi_{\text{obs}})^2]^{1/2}$). The small negative θ value indicates the presence of very weak intermolecular antiferromagnetic coupling, consistent with the rapidly diminishing values of $\chi_{\text{M}}T$ at temperatures approaching 0 K.

The copper magnetic orbitals ($d_{x^2-y^2}$) interact directly with the diazole bridge and the azide bridge, both of which would be expected to participate in spin exchange between the metal centres. The axial bromine bridge, being an orthogonal linkage, would not contribute significantly to the total exchange situation. Little data exist for exchange coupled thiadiazole dicopper(II) complexes of this type. X-Ray structural studies on the complex $[\text{Cu}_2(\text{DPTD})\text{Cl}_4]$ indicate an asymmetric, square-pyramidal structure involving two orthogonal chlorine bridges and an equatorial, magnetic diazole bridge linking the copper(II) centres.¹² Preliminary variable-temperature magnetic data indicate antiferromagnetic coupling with $-2J \approx 60 \text{ cm}^{-1}$. A similar diazole bridge exists in **1**, which, it is reasonable to assume, propagates antiferromagnetic coupling as well. Thus, the equatorial azide bridge might be expected to be responsible for stronger ferromagnetic coupling than indicated by the actual measured $2J$ value ($J_{\text{T}} = J_{\text{AF}} + J_{\text{F}}$).

Such strong ferromagnetic coupling involving a μ_2 -1,1 azide bridge, with such a large bridge angle, beyond the predicted level for ferromagnetic coupling, as determined by extended Hückel calculations,^{4,6} is most unusual and clearly indicates that more magnetostructural studies are necessary to establish the role of the azide bridge as a spin-exchange medium, and in particular the geometric circumstances in which ferromagnetic behaviour predominates, and if such behaviour can be controlled. Related complexes, involving μ_2 -1,1 azide bridges, are currently being studied, some of which are antiferromag-

netically coupled, while others are ferromagnetically coupled, and will be discussed elsewhere.

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