

A Cu–Zn–Cu–Zn heterometallomacrocyclic shows significant antiferromagnetic coupling between paramagnetic centres mediated by diamagnetic metal†

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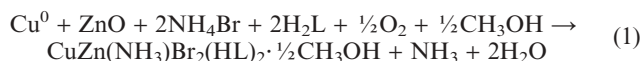
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An unprecedented antiferromagnetic exchange mediated by two –O–Zn–O– bridges, with singlet–triplet splitting $J = 35.0 \text{ cm}^{-1}$, was observed between two copper centers separated by $5.7062(9) \text{ \AA}$ in the heterometallomacrocyclic diethanolamine (H₂L) complex $[\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HL})_4]\text{Br}_2 \cdot \text{CH}_3\text{OH}$.

Modern magnetochemistry of bimetallic complexes allows in many cases the prediction of the magnetic interaction in a complex, based on the nature of the magnetic orbitals and the bridging geometry.¹ Because of the long distance of $\sim 5.7 \text{ \AA}$ between copper atoms in a novel heterometallomacrocyclic (Fig. 1), one would not expect any significant exchange coupling. Nevertheless, the compound in which $\{\text{Zn}(\text{NH}_3)\text{Br}\}^+$ entities alternate with copper aminoalkoxo $\{\text{Cu}(\text{HL})_2\}$ fragments in a puckered cyclic $\text{Cu}_2\text{Zn}_2\text{O}_4$

structure, and the copper atoms are joined by triatomic –O–Zn–O– bridges, does show remarkable antiferromagnetic exchange. Exchange interactions between paramagnetic metal centres mediated by a diamagnetic metal ion are known.^{2–6} However, the reported values of magnetic coupling are small,^{2,4–6} while in the case of stronger coupling,³ exchange pathways exist that are alternative to those involving a diamagnetic Pd atom. To the best of our knowledge, the compound $[\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HL})_4]\text{Br}_2 \cdot \text{CH}_3\text{OH}$ (**1**) shows the strongest exchange interaction reported to date that is mediated by diamagnetic metal atoms. The synthesis,[†] and the X-ray crystal structure[‡] of **1** are described, and the EPR spectra in frozen solution and the solid state[¶] and magnetic properties^{||} are discussed.

The interaction of copper powder with ZnO, diethanolamine and ammonium bromide in methanol exposed to air, with molar ratios Cu : ZnO : H₂L : NH₄Br of 1 : 1 : 2 : 4 yielded a compound with the formula $\text{CuZn}(\text{NH}_3)\text{Br}_2(\text{HL})_2 \cdot \frac{1}{2}\text{CH}_3\text{OH}$. In the reaction, dioxygen was reduced to H₂O while Cu⁰ was oxidized to Cu²⁺:



The single-crystal X-ray diffraction study conclusively proved the identity of the complex as $[\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HL})_4]\text{Br}_2 \cdot \text{CH}_3\text{OH}$. The crystal lattice of **1** is built of the tetranuclear metallomacrocyclic cations $[\text{Cu}_2\text{Zn}_2(\text{NH}_3)_2\text{Br}_2(\text{HL})_4]^{2+}$, bromide anions and methanol molecules (Fig. 1). The four metal atoms lie in one plane and are linked together by bridging oxygen atoms of the four diethanolamine groups to form a rhombus with edge lengths of $3.4274(6)$ (Cu···Zn') and $3.4422(7)$ (Cu···Zn) Å. Each copper centre is surrounded by two alkoxo oxygen atoms and two amine N atoms of the monodeprotonated diethanolamine ligands in a square-planar geometry [Cu–O/N bond lengths in the range $1.934(2)$ – $2.038(2)$ Å]. The two axial positions of each copper centre are occupied by weakly bound hydroxyl groups of the ligands [Cu–O distances $2.459(2)$ and $2.564(2)$ Å]. The geometry around the copper atom can therefore be best described as elongated octahedral, owing to the Jahn–Teller effect in the d⁹ electronic configuration. The zinc atom forms three quite short bonds to bridging oxygen atoms, O(1) and O(3) of HL ligands and to the ammonia nitrogen atom. The Zn–O/N bond lengths span the range $1.967(2)$ – $2.010(2)$ Å, while the Zn–Br bond is longer at $2.3707(6)$ Å, resulting in a distorted tetrahedral geometry (Fig. 1). In this cyclic structure, there are no bridging ligands between the

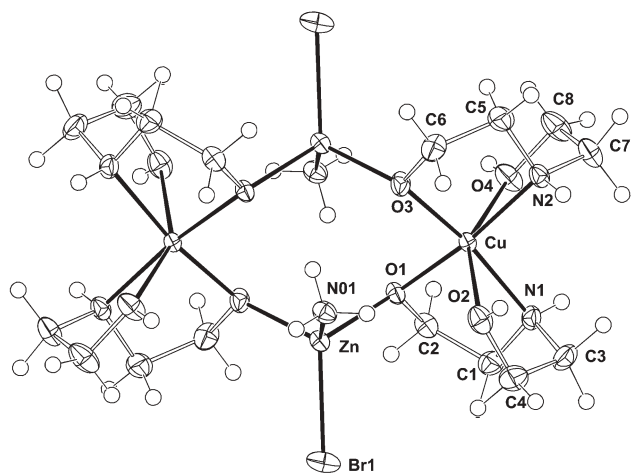


Fig. 1 The molecular structure of **1**.

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† Electronic supplementary information (ESI) available: Simulated and experimental EPR spectra, table of magnetic susceptibilities, and details of calculation of the dipole–dipole interaction. See <http://dx.doi.org/10.1039/b509810f>

two copper atoms or between the two zinc atoms, and the Cu...Cu' distance is 5.7062(9) Å. The heterometallomacrocyclic is further stabilized by intramolecular N-H...O hydrogen bonds. Intermolecular hydrogen bonds involving OH and NH groups of the ligands, ammonia, and uncoordinated bromide anions link the tetranuclear cations together resulting in the formation of an extended three-dimensional network. The non-coordinated methanol molecules are disordered in the crystal lattice with no short H-bond contacts to other components.

The temperature dependence of the magnetic susceptibility shown in Fig. 2 is typical of an antiferromagnetic exchange interaction of moderate strength between copper(II) ions. As is commonly observed in antiferromagnetic complexes,^{1,7,8} the presence of a monomeric impurity is evident at the lowest temperatures through a slight increase in χ_M . The data were fitted to the equation

$$\chi_M = \frac{N\mu_B^2 g^2}{3kT} \frac{3 \exp(-J/kT)}{1 + 3 \exp(-J/kT)} (1 - \rho) + \frac{N\mu_B^2 g^2}{3kT} \frac{3}{4} \rho + N\alpha \quad (2)$$

where the exchange integral J corresponds to the Hamiltonian $H = JS_1S_2$, ρ is the fraction of the monomeric impurities and other symbols have their usual meaning. The best data fit (solid line in Fig. 2) gave $J = 35.0(1) \text{ cm}^{-1}$, $g = 2.08(1)$, $\rho = 0.01$ and $N\alpha = 121(3) \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. Fixing g to 2.12, the average of g_x , g_y and g_z as obtained from EPR, and assuming the generally accepted value of $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for $N\alpha$ resulted in an only slightly different J value of $35.7(1) \text{ cm}^{-1}$.

Interpretation of the X-band EPR spectra was not possible because of the extensive overlap of the 'parallel' and 'perpendicular' features (ESI†). Fortunately, application of high-frequency EPR resolved that difficulty. Both the X-band and high-frequency powder spectra (Fig. 3.), taken over the temperature range 300–15 K seemed to be non-indicative of metal–metal interactions. Narrow 'parallel' and 'perpendicular' resonances showing no visible hyperfine structure were observed (Fig. 3.), with $g_x = 2.053$, $g_y = 2.055$ and $g_z = 2.251$ (parameters found from a 377 GHz spectrum, see ESI†). Below ~40 K the spectra intensity decreased with decreasing temperature and at 10 K a spin-triplet spectrum appeared with its 'parallel' part split into eight lines separated by about 85 G. Upon further cooling below 4 K, the 8-line structure was replaced by a 4-line hyperfine pattern with a splitting of 174 G, corresponding to $A_z = 183 \times 10^{-4} \text{ cm}^{-1}$, and with $g_x = 2.051$, $g_y = 2.055$ and $g_z = 2.248$, characteristic of a single-copper

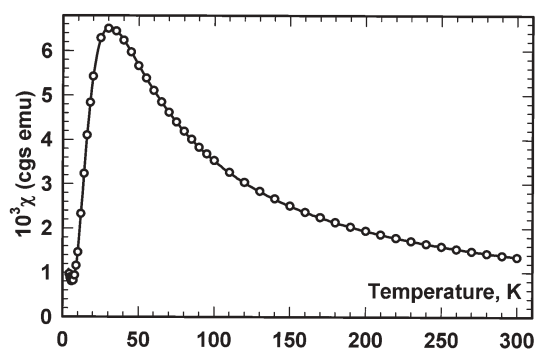


Fig. 2 Experimental (circles) and calculated (solid line) magnetic susceptibility per $\frac{1}{2}$ of the molar mass.

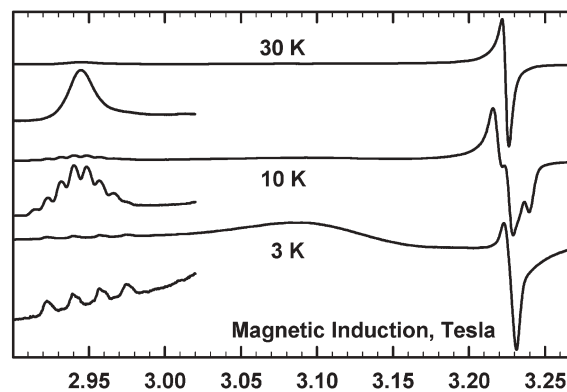


Fig. 3 EPR spectra (92.767 GHz) at the indicated temperatures.

impurity. The exact nature of that impurity is not known, but its g values, virtually identical to those of the triplet spectrum, indicate that it is a copper–diethanolamine complex. It is thus clear that the spectra observed above 10 K are due to a di-copper species and they do not exhibit fine and hyperfine splitting because of the long-range intermolecular exchange interactions. At a temperature of ca. 10 K, the molecules in the $S = 1$ state become sufficiently magnetically diluted in the now mainly diamagnetic lattice to show the hyperfine and fine structure. The eight-line pattern in the 'parallel' part of the 10 K spectrum is caused by combination of the hyperfine splitting due to two copper ions and the zero-field splitting being of comparable magnitudes. The hyperfine coupling constants A_x and A_y for copper (that typically are much smaller than A_z) could not be determined and the best simulations are obtained with their values fixed to zero. The fine splitting of the 'perpendicular' part of the spectrum is larger than in the 'parallel' region, thus indicating that the largest component of the zero-field splitting tensor is, at least approximately, perpendicular to the direction of g_z . The spin-triplet spectra were interpreted in terms of the spin Hamiltonian

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D \{ S_z^2 - \frac{1}{3} S(S+1) \} + E(S_x^2 - S_y^2) + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \quad (3)$$

The EPR parameters values are: $g_x = 2.053$, $g_y = 2.055$, $g_z = 2.251$, $|D| = 101 \times 10^{-4} \text{ cm}^{-1}$, $|E| = 6 \times 10^{-4} \text{ cm}^{-1}$, $A_x = A_y = 0$, $A_z = 94 \times 10^{-4} \text{ cm}^{-1}$. Separate coordinate frames were used for tensors \mathbf{g} and \mathbf{D} in that g_{zz} is perpendicular to D_{zz} .⁹ The sign of D can be determined from high-frequency EPR¹⁰ at low temperatures because the Zeeman energy is comparable to the Boltzmann energy, kT . Although in the present case this was complicated by very small magnitudes of the fine structure parameters, it is noteworthy that successful simulation of spectra at all frequencies (92–380 GHz) by using the same set of spin Hamiltonian parameters required a positive D (see ESI†). The dipole–dipole contribution to \mathbf{D} , \mathbf{D}_{dip} , calculated from the copper-centered point-dipole model¹¹ is $-152 \times 10^{-4} \text{ cm}^{-1}$. The discrepancy between the experimental and the calculated values may be caused by the contribution of the anisotropic exchange interactions^{12–15} and by the delocalisation of the unpaired electrons.¹⁶ To estimate the latter effect we calculated the dipole–dipole interaction assigning 0.25 of an electron to each of four points located half way between the respective copper atoms and

their equatorial ligands.¹⁶ This resulted in a slight decrease in D_{dip} to $-142 \times 10^{-4} \text{ cm}^{-1}$ (see also ESI†). The estimated exchange-induced zero-field splitting parameter D_{ex} (ESI) is about $-130 \times 10^{-4} \text{ cm}^{-1}$. Compared to the $\text{Cu}(\text{OH})_2\text{Cu}$ bridges,^{12–15} D_{ex} in **1** is inhibited more strongly than is the isotropic exchange interaction—the ratio D_{ex}/J may be as high as ~ 0.01 in the hydroxo-bridged dimers¹⁵ while it is no larger than 4×10^{-4} in **1**. The exchange contribution D_{ex} is associated with the interaction between an $x^2 - y^2$ orbital of one copper atom and an xy orbital of another copper atom.^{10,12–15} Such an interaction seems less likely to be transmitted through a system of σ bonds in the $\text{Cu}_2\text{Zn}_2\text{O}_4$ macrocycle than an interaction between the $x^2 - y^2$ orbitals of two copper atoms, which would determine the magnitude of the isotropic exchange integral, J . Broad, unresolved resonance appeared at the lowest temperatures (Fig. 3) at the effective g value close to the average of g_x , g_y and g_z . Because that signal increases slowly with the sample age, it is likely to be due to a decomposition product of **1**. A nicely resolved X-band EPR spectrum of **1** showing characteristic features of the spin-triplet state with a half-field signal detected at 160 mT is obtained from dmf solution at 77 K (not shown). The hyperfine structure due to two coupled Cu(II) centres, as well as the presence of $\Delta M_S = 2$ signals indicates that the cyclic structure is retained in solution.

In conclusion, in view of the molecular structure of **1** a pathway for the exchange interaction must involve orbitals of the tetrahedral zinc atom. We suppose that it is the system of strong σ bonds that makes the $-\text{O}-\text{Zn}-\text{O}-$ bridges surprisingly efficient in enabling communication between copper atoms in the case studied. Interestingly, a cyclic molecule in which two copper atoms are joined by two $-\text{N}-\text{C}-\text{O}-\text{Zn}-\text{O}-$ bridges¹⁷ shows no exchange coupling. The compound reported here demonstrates that understanding of the mechanism by which the two electrons of the copper(II) ions feel the presence of each other through the filled d -orbitals of the diamagnetic transition metal atom still remains a challenge.

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Notes and references

† *Synthesis*: Copper powder (0.32 g, 5 mmol), ZnO (0.4 g, 5 mmol), NH_4Br (1.95 g, 20 mmol), CH_3OH (15 cm^3) and H_2L (1 cm^3) were heated to 50–60 °C and stirred until total dissolution of the Cu was observed (120 min). After cooling the resulting blue solution, a crude product precipitated immediately. It was filtered off and subsequently blue microcrystals of **1**, suitable for X-ray diffraction studies were formed within 1 h. They were collected by filter-suction and dried *in vacuo*. Mass collected: 1.6 g, yield 60%. Elemental analysis (%): calc. for $\text{C}_{17}\text{H}_{50}\text{Br}_4\text{Cu}_2\text{N}_6\text{O}_9\text{Zn}_2$: Cu 12.17, Zn 12.52, Br 30.61, C 18.98, H 4.64, N 8.05; found Cu 12.5, Zn 12.1, Br 30.8, C 19.3, H 4.3, N 7.7. The IR spectrum of **1** taken over the range 4000–400 cm^{-1} showed the expected ligand peaks. The spectrum also indicated the presence of hydrogen-bonded OH groups (3400–3500 cm^{-1}). Distinctive bands at 1260 cm^{-1} were assigned to N–H stretching in NH_3 molecules.

§ X-Ray structural analysis: Bruker SMART CCD diffractometer, graphite monochromator, Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), ω scans, XTAL3.7¹⁸ program set for structure solution (direct methods) and refinement

(full-matrix least squares on F). Significant electron density in later difference maps ($\sim 2.5e \text{ \AA}^{-3}$) was modeled as a methanol molecule disordered about the crystallographic inversion centre, the site occupancy factor of 0.5 being in agreement with that obtained from trial refinement. All the hydrogen atoms were refined (except for those on methanol which were not included in the model). **1**: $\text{C}_{17}\text{H}_{50}\text{Br}_4\text{Cu}_2\text{N}_6\text{O}_9\text{Zn}_2$, $M = 1060.11$, $T = 150 \text{ K}$, monoclinic, space group $C2/c$, $a = 20.959(4)$, $b = 9.625(2)$, $c = 18.365(3) \text{ \AA}$, $\beta = 101.415(4)^\circ$, $V = 3631.5(12) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc.}} = 1.939 \text{ g cm}^{-3}$, $\mu = 6.908 \text{ mm}^{-1}$, 38279 reflections collected, 9536 unique ($R_{\text{int}} = 0.065$), 5187 'observed', which were used in all calculations, $R = 0.035$, $wR = 0.032$ [$F > 4\sigma(F)$]. CCDC 278978. See <http://dx.doi.org/10.1039/b509810f> for crystallographic data in CIF or other electronic format.

¶ X-Band EPR spectra were recorded on a Bruker ESP 300E spectrometer equipped with the Bruker NMR gaussmeter ER 035M and the Hewlett-Packard microwave frequency counter HP 5350B. High-frequency EPR spectra were recorded on a home-built spectrometer at the EMR facility of NHMFL.¹⁹ The instrument was a transmission-type device in which waves are propagated in cylindrical lightpipes. The microwaves were generated by Gunn oscillator, operating at $95 \pm 3 \text{ GHz}$. Frequencies higher by a factor 2, 3, or 4 were obtained using a Schottky diode-based multiplier and appropriate high-pass filters. A phase-locked oscillator (Virginia Diodes) generating frequency of $52 \pm 4 \text{ GHz}$ and its 2nd, 4th and 6th harmonics were also used. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

|| Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at a magnetic induction of 0.5 T. Corrections for the sample holders were applied. Diamagnetic corrections for the molecule ($522 \times 10^{-6} \text{ cgs emu}$) were determined from Pascal's constants.

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