A Cu-Zn-Cu-Zn HETEROMETALLOMACROCYCLE SHOWS SIGNIFICANT ANTIFERROMAGNETIC COUPLING BETWEEN PARAMAGNETIC CENTRES MEDIATED BY DIAMAGNETIC METAL

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Introduction

An unprecedented antiferromagnetic exchange mediated by two -O-Zn-O- bridges, with the singlet-triplet splitting $J = 35\ cm^{-1}$, was observed between two copper centers separated by 5.7062(9) Å in the heterometallomacrocyclic complex of diethanolamine (H_2L) $[Cu_2Zn_2(NH_3)_2Br_2(HL)_4]Br_2 \cdot CH_3OH$.

Experimental

The X-Ray structure of $[Cu_2Zn_2(NH_3)_2Br_2(HL)_4]Br_2 \cdot CH_3OH$ has been determined in this work[1]. Magnetic susceptibility (Fig. 1) and magnetization measurements were performed by using a SQUID magnetometer. EPR spectra (Fig. 2) were taken at the 15/17 Tesla EMR facility of the NHMFL over the temperature range 3 – 300K, at frequencies 95 to 380 GHz.

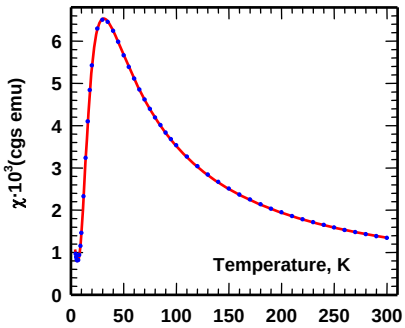

Fig. 1. Experimental (blue) and calculated (red) magnetic susceptibility

Results and Discussion

The temperature dependence of the magnetic susceptibility was fitted to the spin Hamiltonian $\mathbf{H} = J_{ab}\mathbf{S}_a\mathbf{S}_b$ with the exchange integrals $J_{ab} = 35(1)\ cm^{-1}$. High-Field EPR spectra due to the S = 1 excited state were fitted to the spin Hamiltonian

$$\mathbf{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D\{\mathbf{S}_z^2 - (1/3)S(S+1)\} + E(\mathbf{S}_x^2 - \mathbf{S}_y^2)$$

with $g_x = 2.053$, $g_y = 2.055$, $g_z = 2.251$, $|D| = 101 \cdot 10^{-4}\ cm^{-1}$, $|E| = 6 \cdot 10^{-4}\ cm^{-1}$.

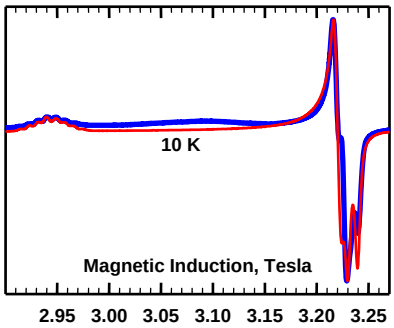

Fig. 2. EPR spectra at 10.0 K, 92.767 GHz (blue). Red: simulated triplet state spectrum

Conclusions

In view of the molecular structure of the title compound, a pathway for the exchange interaction involves orbitals of the tetrahedral zinc atom. The value of the exchange integral reported here is the highest so far in a system containing -O-Zn-O- bridges. In addition to the magnetic dipole-dipole interactions, the anisotropic exchange interactions must contribute to the zero-field splitting parameters. The results of this study have already been published in [1], while the EPR and magnetic properties of a closely related tetranuclear copper complex have been described in [2].

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References

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[2] Buvaylo, E.A., *et al.*, Inorganic Chemistry, **44**, 206-216 (2005).