MAGNETIC AND VARIABLE FREQUENCY EPR STUDIES OF PENTA-NUCLEAR Cu^{2+} POLYOXOMETALATE

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Introduction

The class of Cu^{2+}-containing, sandwich-type polyoxometalates is well-known and to date numerous complexes have been reported, but most of these polyanions are dimeric and contain three or four Cu^{2+} centers [1]. This report presents the magnetic properties and EPR spectroscopy [2] of a new penta-copper substituted polyoxoanion $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ (**Cu_5**). **Cu_5** consists of two $A\text{-}\alpha\text{-}[SiW_9O_{34}]^{10-}$ Keggin moieties which are linked via two adjacent W-O-W bonds and stabilized by a central $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$ fragment leading to a structure with idealized C_{2v} symmetry (see Fig. 1). The Cu^{2+} ions in **Cu_5** are at the corners of a rectangular pyramid.

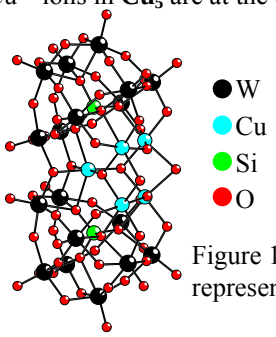

Figure 1. Ball-and-stick representation of **Cu_5**.

Experimental

Magnetic susceptibility data were collected on Quantum Design MPMS XL SQUID Magnetometer and Q-band (~35 GHz) EPR data were collected on Bruker Elexsys 500 at the Department of Chemistry and Biochemistry, FSU. EPR measurements at high frequencies were done on home-built homodyne instrument at the National High Magnetic Field Laboratory, Tallahassee, FL.

Results and Discussion

Magnetic susceptibility data for **Cu_5** is shown in Fig. 2. as a plot of χT vs T. Steady decrease of χT as temperature, T, decreases, suggests the presence of antiferromagnetic interactions between Cu^{2+} ions. Saturation below 50 K at ~0.39 emu-K/mol implies a spin $S_T = 1/2$ ground state, where S_T is the total spin value of the cluster. Analysis of the data according to the exchange spin Hamiltonian shown in Eq.1, provides the exchange constants as: $J_a = -51 \pm 6$ cm^{-1}, $J_b = -104 \pm 1$ cm^{-1}, $J_c = -55 \pm 3$ cm^{-1} and $g = 2.035 \pm 0.002$.

$$\hat{H}_{exch} = -2J_a[\hat{S}_1\bullet\hat{S}_2 + \hat{S}_3\bullet\hat{S}_4] - 2J_b[\hat{S}_1\bullet\hat{S}_3 + \hat{S}_2\bullet\hat{S}_4] - 2J_c[\hat{S}_1\bullet\hat{S}_5 + \hat{S}_2\bullet\hat{S}_5 + \hat{S}_4\bullet\hat{S}_5 + \hat{S}_3\bullet\hat{S}_5] \quad (1)$$

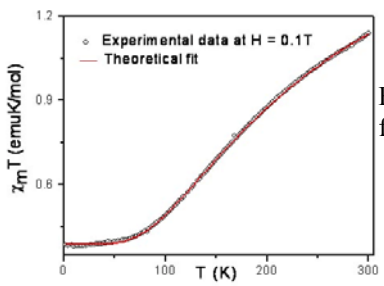

Figure 2. χT vs T for **Cu_5**.

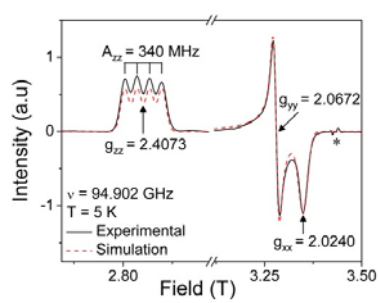

Figure 3. 95GHz EPR of **Cu_5**.

Figure 3 shows a 95 GHz powder spectrum of **Cu_5** at 5 K and it is a typical Cu^{2+} spectrum, with a four line hyperfine structure (A_{zz}) on the low-field Zeeman peak (g_{zz}). The unpaired electron is assigned to the apical copper centre [2]. The spectra at all frequencies were reproduced satisfactorily with the Hamiltonian parameters: $g_{zz} = 2.4073 \pm 0.0005$, $g_{yy} = 2.0672 \pm 0.0005$, $g_{xx} = 2.0240 \pm 0.0005$, $|A_{zz}| = 340 \pm 20$ MHz (0.0113 cm^{-1}) implying that there is no net exchange field on the apical copper. The g-values are consistent with a $3d_{x^2-y^2}$ type molecular orbital ground state, as expected for a Cu^{2+} in an elongated rhombic-octahedral co-ordination with oxygen. A qualitative analysis of the g- and A_{zz} values, using the Crystal field – Molecular orbital theory [3], yields $\alpha^2 = 0.71$, where α is the molecular orbital coefficient of the ground state, indicating a moderate (~ 30%) contribution from the oxygen orbitals.

Conclusions

Magnetic and EPR measurements reveal that the pentameric copper core of **Cu_5** exhibits strong antiferromagnetic interactions resulting in a spin $S_T = ½$ ground state, with a localized unpaired electron spin density. **Cu_5** can therefore be considered as a model system for a 5-spin electronically coupled, spin-frustrated system.

Acknowledgements

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References

[1] see for e.g.: Kortz, U. et. al. *Inorg. Chem.* **2001**, *40*, 4742.
[2] Nellutla, S. et. al. *Inorg. Chem.* **2005**, *44*, 9795.
[3] Hathaway, B. J. et. al. *Coord. Chem. Rev.* **1970**, *5*, 143.