HFEPR and Magnetic Studies on an Octanuclear Copper Complex with C_{3i} Symmetry and Paramagnetic Ground State

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Introduction

Coordination compounds of high nuclearity, their chemical and physical properties as well as catalytic activity have been subject to extensive studies in recent years [1]. An interesting subgroup of them are close-packed metal cores of high symmetry (Fig. 1) which can be often self-assembled by using simple multifunctional ligands. In this work, a novel octanuclear copper complex of N-*tert*-butyl-diethanolamine, $[Cu_8O(tbDea)_6(H_2O)_2](BF_4)_2$, **1**, belonging to that rare class was investigated.

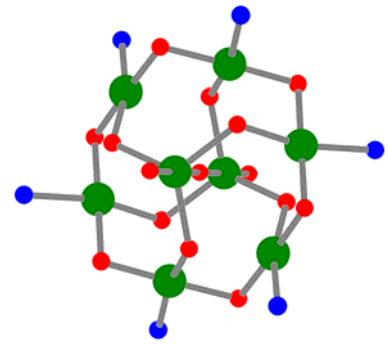

Figure 1. The structure of the octanuclear core in **1**. Red: O; Blue: N;

Experimental

High-field and -frequency EPR spectra were recorded on the 17 T transmission EPR instrument of the NHMFL EMR facility at frequencies *ca*. 52-432 GHz and at low temperatures. Magnetic susceptibility was measured at Wroclaw University using a SQUID magnetometer.

Results and Discussion

According to the molecular symmetry, the magnetic data (Fig. 2) were interpreted in terms of the spin Hamiltonian [1]:

$$\begin{aligned}\hat{\mathbf{H}} = {} & J_A(\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2\,\hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_3\,\hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_4\,\hat{\mathbf{S}}_5 + \hat{\mathbf{S}}_5\,\hat{\mathbf{S}}_6 + \hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_6) + \\ & J_B(\hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_3\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_5\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_2\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_4\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_6\,\hat{\mathbf{S}}_8) + \\ & J_C(\hat{\mathbf{S}}_2\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_4\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_6\,\hat{\mathbf{S}}_7 + \hat{\mathbf{S}}_1\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_3\,\hat{\mathbf{S}}_8 + \hat{\mathbf{S}}_5\,\hat{\mathbf{S}}_8) + J_D\,\hat{\mathbf{S}}_7\,\hat{\mathbf{S}}_8\end{aligned} \qquad [1]$$

Standard "giant spin" Hamiltonian was used for evaluation of the EPR spectra (Fig. 3). A zero-field splitting parameter D value of 0.23 cm^{-1} for the low-lying S = 3 state was found.

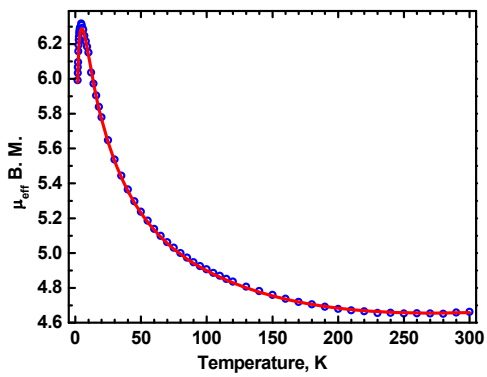

Figure 2. The effective magnetic moment in **1**. Circles: experimental; line: calculated.

Conclusions

Although most exchange integrals in Hamiltonian [1] are antiferromagnetic, the ground state of the system consists of the paramagnetic S = 2 and S = 3 states at practically the same energy. The experimental magnitudes of the exchange integrals J_A through J_D in equation [1] were qualitatively reproduced by the Density Functional Theory calculations [2]. Some of the EPR signals observed at very high microwave frequencies indicate zero-field splitting of ~14 cm^{-1} between the states involved and they must correspond to transitions between different S states [2].

Acknowledgements

This work has been supported by the Foundation for Science and Technology (FCT), Portugal (projects PTDC/QUI-QUI/102150/2008, PTDC/QUI-QUI/121526/2010 and PEst-OE/QUI/UI0100/2013; fellowships SFRH/BPD/42000/2007 and SFRH/BPD/63710/2009).

References

[1] Stamatatos, T., *et al*., *Chem. Commun.*, **47**, 274 (2011).
[2] Nesterov, D.S., *et al*., *Chem. Commun.*, submitted.

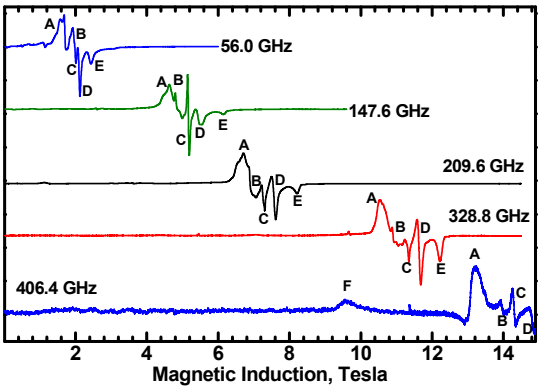

Figure 3. EPR spectra of **1** recorded at 10 K.