HFEPR and Magnetic Studies on a Hexanuclear Manganese Complex

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Introduction

The study of multinuclear manganese complexes remains of interest to numerous groups, partly because of the potential connection to the {Mn4Ca} moiety in the oxygen evolving cluster of Photosystem II, and partly for their potential to serve as single-molecule magnets (SMMs) in nanoscale electronics. Recently, we discovered a fascinating, highly symmetrical hexanuclear manganese complex of perfluoropinacolate ($pin^F)_6$, [1]), $[Mn_6O_4(OH)_4(pin^F)_6(THF)_4K_4]$, containing two Mn(IV) and four Mn(III) ions. EPR and magnetic studies were undertaken to further characterize this very unusual species.

Experimental

The HFEPR spectra were recorded on the homodyne instrument of the EMR facility equipped with a 15/17T SC magnet. Magnetic susceptibility measurements were performed using a SQUID magnetometer at the Department of Chemistry, Wroclaw University, Poland.

Results and Discussion

The hexamer (inset in **Fig.1**) consists of four Mn^{3+} ions located in the equatorial plane of an octahedron and two Mn^{4+} ions on the axis of the octahedron, giving rise to 10,000 spin microstates $|S,M_S>$. If the atoms in plane are numbered 1, 2, 3, 4 and those on the axis 5 and 6, then according to the molecular symmetry, all in-plane exchange interactions 1-2, 2-3, 3-4 and 4-1 are equal.

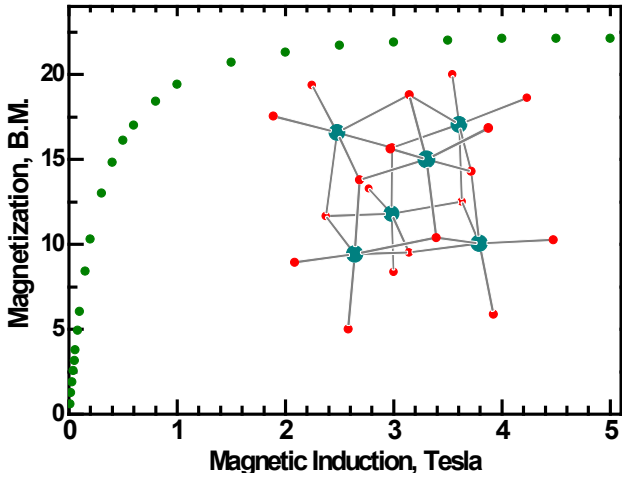

Fig.1 Magnetization as a function of the magnetic field. The core of the molecule is shown in the inset: Mn: ●; O:●.

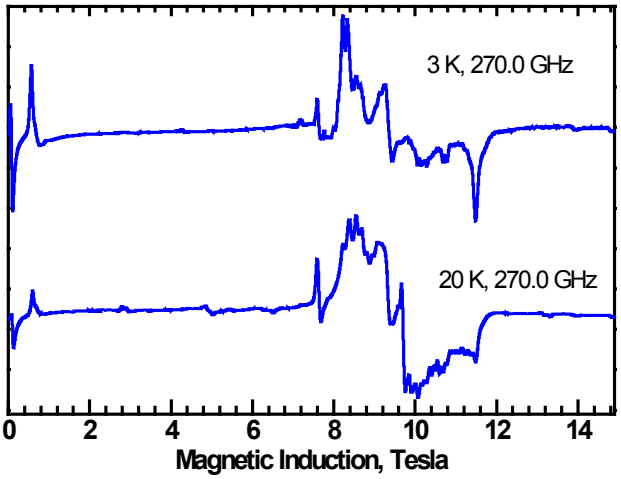

Fig.2 EPR spectra recorded at 270 GHz and 3 and 20 K.

Interactions 5-1, 5-3, 6-2, 6-4 are equal. Interactions 5-2, 5-4, 6-1, 6-3 are also equal but may be different from those in the former group. Analysis of the magnetic data revealed that all exchange interactions in the system are ferromagnetic resulting in an S = 11 ground state with magnetization of 22 μ_B per molecule at high magnetic fields (**Fig.1**). A pattern of multiple splittings in the central part of the HFEPR spectra (**Fig.2**) is consistent with a high-spin state.

Conclusions

A new ferromagnetic hexameric complex with a ground spin state S = 11 was prepared. Its AC susceptibility is currently being investigated to determine whether the complex may be a single-molecule magnet.

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References

[1] Cantalupo, S.A., *et al*. Angew. Chem. Int. Ed., **51**, 1000-1005 (2012).