High-Frequency and -Field EPR of Open Chain Mn(III) Porphyrinoid Complexes

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Introduction

Electronic structure of manganese(III) complexes is of great interest because of their particular properties in such diverse fields as biochemistry, molecular magnetism or catalysis.[1] Especially porphyrinoid complexes have been widely utilized and extensively characterized. Lately, cyclic analogues such as porphycenes, corroles and expanded porphyrins, as well as a variety of acyclic salen complexes, have been subject to further investigations.[2] These two types of ligand systems exhibit properties correlated to their structural and magnetic features. In order to combine the characteristics of both classes of substances we have synthesized a set of open chain tetrapyrrole complexes of manganese(III). The introduction of different axial ligands permits a directed variation of the electronic and magnetic properties. One of the best techniques for elucidating to the above-mentioned features is HFEPR, through the zero-field splitting terms in the spin Hamiltonian. We previously[3] described HFEPR experiments performed on polycrystalline samples, which suffered from field-induced torquing problems, thus producing less then ideal spectra. In this report we present far superior spectra obtained in a methylene chloride glass.

Experimental

HFEPR experiments were conducted at the EMR Facility and its 17-Tesla superconducting magnet. Polycrystalline material was dissolved in CH_2Cl_2 at a concentration of 100–150 mM, and the solution cooled down to form a low-temperature glass.

Results and Discussion

Fig. 1 shows a typical HFEPR spectrum of the complex octaethylbidipyrrinatomanganese(III) bromide (OEBDPMnBr) in a CH_2Cl_2 glass. The spectra at several frequencies could be well simulated using the following spin Hamiltonian parameters for OEBDPMnBr: $S = 2$, $D = -1.40$, $E = -0.09$ cm^{-1}, $g_{iso} = 2.00$. Simulations of the spectra obtained from the other complexes of this series yielded $D = -2.29$, $E = -0.23$cm^{-1} for OEBDPMnCl and $D = +0.45$ cm^{-1}, $E \sim 0$ for OEBDPMnI. The magnitude of the axial zero-field splitting term D thus follows the order known for Mn(III) complexes with regular porphyrins: Cl > Br > I, while its sign changes from negative for the chloride and bromide to positive for the iodide. The rhombicity of the zfs tensor is significant in two of the investigated complexes and not encountered in porphyrins. The changes in the D magnitude can be explained by the ligand-field theory; the rhombicity is linked to the reduced symmetry of investigated complexes in comparison with porphyrins.

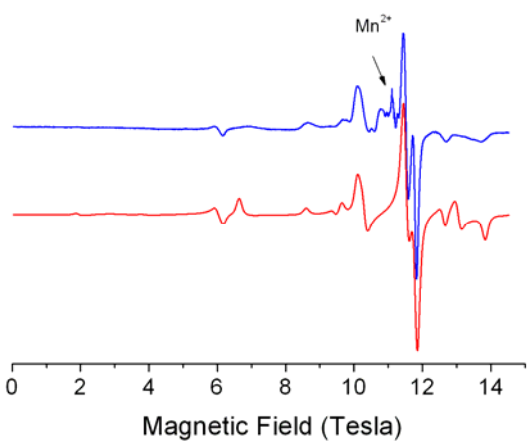

Figure 1. HFEPR spectra of OEBDPMnBr at 312 GHz and 20 K. The blue trace shows the experimental spectrum; the red trace – a powder-pattern simulation using spin Hamiltonian parameters as in text.

Acknowledgements

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References

[1] Loewen, P.C., *et al.*, Cell. Mol. Life. Sci., **61**, 192-208 (2004); Sorokin, A., *et al.*, Science, **268**, 1163-1166 (1995); Novak, A.M., *et al.*, Nature, **365**, 141-143 (1993).
[2] Adam, W., *et al.*, J. Am. Chem. Soc., **121**, 1879-1882 (1999); Gray, H.B., *et al.*, Chem. Comm., 1957-1958 (2000).
[3] Köhler, S., *et al.*, NHMFL Annual Report (2006).