HIGH-FREQUENCY AND -FIELD EPR OF OPEN CHAIN Mn(III) PORPHYRINOID COMPLEXES

S. Köhler, M. Bröring (Philipps U., Marburg, Germany, Chemistry); J. Krzystek (NHMFL)

Introduction

The study of the electronic structure of various 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. Cyclic analogues such as porphycenes, corroles and expanded porphyrins, have lately been subject to further investigations as well as a variety of acyclic salen complexes.[2] These two different types of ligand systems exhibit specific properties that are 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 high-frequency and -field EPR, which allows the determination of the zero-field splitting terms in the spin Hamiltonian. Comparison with the X-ray structures of the investigated compounds shows how these terms correlate with the geometry of the complexes.

Experimental

HFEPR experiments at multiple frequencies were performed at the EMR Facility and its 17-Tesla superconducting magnet. Polycrystalline samples were used first 'as is', and then also pressed into pellets to prevent torquing in the field.

Results and Discussion

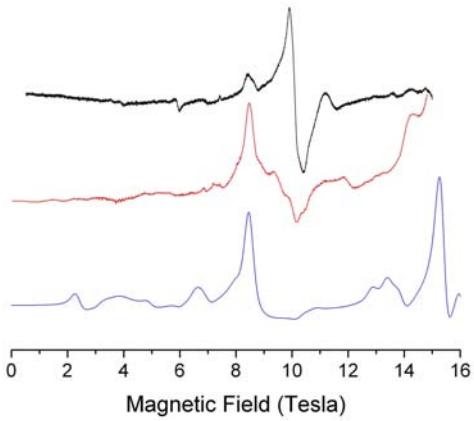

Figure 1. HFEPR spectra of OEBDPMnCl at 422 GHz and 10 K. The black trace shows the sample 'as is'; the red trace – constrained in a pellet, and the blue trace – a powder-pattern simulation using spin Hamiltonian parameters as in text.

Fig. 1 shows typical HFEPR spectra of the complex octaethylbidipyrrinatomanganese(III)chloride (OEBDPMnCl) . Pressing the sample into a pellet drastically changes spectral shape, which proves that the loose sample undergoes torquing in magnetic field. The pellet spectra were simulated using the following spin Hamiltonian parameters for OEBDPMnCl: $S = 2$, $D = -2.05$, $E = -0.22$ cm^{-1}, $g_{iso} = 2.00$. Preliminary simulations of the spectra obtained from the other complexes of this series yielded $D \sim -1.1$ cm^{-1} for OEBDPMnBr and -0.25 cm^{-1} for OEBDPMnI, each with significant rhombic factor E. 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, and its sign remains negative; however, the rhombicity of the zfs tensor is significant and not encountered in porphyrins.

Acknowledgements

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References

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