High-Frequency and -Field EPR Investigation of Square-Pyramidal Manganese(III) Complexes

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Introduction

[Mn(HphpzH)X] complexes, where H2phpzH = 3(5)-(2-hydroxyphenyl)-pyrazole and X = Cl− (1) or Br− (2) are mononuclear manganese(III) compounds in which the Mn(III) ion assumes a square-pyramidal geometry. Intermolecular hydrogen bonds are present thus forming ladder-like chains. Temperature-dependent susceptibility and magnetic specific heat measurements on 1 and 2 show the presence of antiferromagnetic S = 2 chains, the magnetic interaction being described by the anisotropic Heisenberg model with a predominantly planar (XY) type of crystal field anisotropy. In addition, the magnetic specific-heat data evidence the occurrence of long-range magnetic ordering between chains in 1 and 2 below about 1.5 K.1 The aim of this work is to determine accurately the magnetic anisotropy of the above complexes represented by the zero-field splitting parameters, D and E, using HFEPR. Of particular interest is the sign of D, since the manganese(III) ion is mostly known for its Ising-type anisotropy (D < 0),2 whereas previous magnetometric analysis so far has indicated XY-type anisotropy (D > 0).

Experimental

The EMR Facility with its 17-T superconducting magnet was used in this experiment. Polycrystalline samples of 1 and 2 were either used ‘as is’ or pressed into pellets.

Results and Discussion

A representative EPR spectrum of 1 is shown in Figure 1. The powder pattern is not ideal despite immobilizing the crystallites in a pellet pressed under pressure, but can be approximately simulated using spin Hamiltonian parameters corresponding to a quintet (S = 2) spin state, and specified in the Figure 1 caption. Moreover, simulations clearly indicate a negative sign of D, analogous to all other known Mn(III) complexes of the same or similar geometry as 1. Complex 2 also produces EPR spectra (not shown), which can be simulated using smaller zfs parameters of about D = −1.4, E = −0.14 cm−1, giso = 2.00.

Conclusions

The EPR results on complexes 1 and 2 brought about spin Hamiltonian parameters that are quite typical for Mn(III) complexes of a square-pyramidal geometry in which the apical position is occupied by either a Cl− or a Br− ion. In particular, the negative sign of D has to be taken into consideration when reevaluating the magnetic properties of the S = 2 antiferromagnetic chains formed by the complexes in the solid state.

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References