Unusually Large Zero-Field Splitting of Cr(III) Elucidated by High-Frequency Electron Paramagnetic Resonance (HF-EPR)

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Introduction

Detailed magnetic characterization of two new Cr(III) polyoxometaltes (POMs), **I** and **II**, is of high interest because these are rare instances of Cr (III), a $3d^3$ ion, in a well-defined geometry with six covalently bonded oxo ligands. Each Cr (III) ion is surrounded by many diamagnetic atoms which magnetically insulate the Cr ions from each other, the nearest neighbor Cr (III) ion distance being ≈ 8 Å. This situation is particularly suitable for characterization by electron paramagnetic resonance (EPR), since the lack of dipolar couplings with the nearest neighbors should lead to narrow EPR peaks and thus higher precision for the measurement of magnetic parameters.

Experimental

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E500 spectrometer equipped with X and Q-band microwave sources (9.5 and 34 GHz respectively). High-frequency EPR measurements (239.2 GHz) were conducted at the Florida State University National High Magnetic Field Laboratory (FSU-NHMFL) in Tallahassee, FL, using its 12.5 T SC magnet.

Results and Discussion

Figure 1 (a) shows the room temperature, X-band powder EPR spectrum of **I** (middle segment, red trace). The absence of 9 peaks expected for an S = 3/2 ion in a distorted octahedral symmetry immediately suggested that the *D*-value must be much larger than the X-band microwave quantum. Computer simulations using a locally developed program (middle segment, black trace), were in good agreement with the experimental data, and yielded : $S = 3/2$, $g_z = 1.97$, $g_{x,y} = 1.92$, $|D| = 2.3\ cm^{-1}$ (2.5 T), and $|E| = 0.123 cm^{-1}$ (0.134 T). Figure 1 (b) shows the 239.2GHz experimental spectrum of **I** (middle segment, red trace) and the simulated spectra (middle segment, black trace).. Although the spectrum becomes increasingly complicated at such high frequencies, it is seen that there is fine agreement between the experimental and simulated spectra.

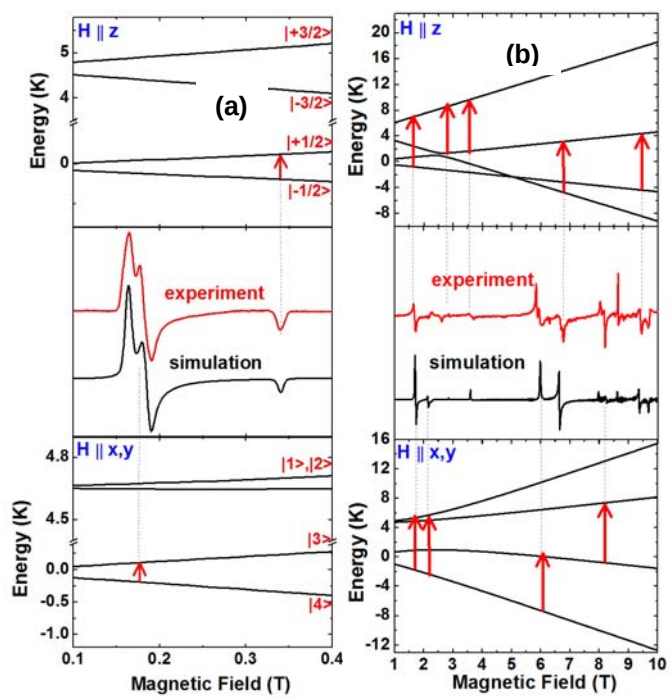

Figure 1. The experimental and simulated EPR spectra of **I**. The top and bottom portions show the energy level diagrams for H || z (principal symmetry axis of the molecule) and the perpendicular x, y directions along with the Ms eigenstates. The red arrows mark the EPR transition assignments. (a) X-band (b) HF-EPR (239.2 GHz).

Conclusions

Precise information on the spin state and the magnetic parameters (zero-field splitting, the *D* and *E* parameters, and g tensors) of two new Cr(III) POMs was found, including their signs. Typically Cr (III) complexes show small zero-field splitting since the ground state and excited states are generally well separated; however, in these new compounds the zero-field parameters were found to be unexpectedly large, thus the presented EPR data should be of high theoretical interest.

Acknowledgements

This work is supported by the National Science Foundation, Grant # DMR-0701462.