High-Frequency and -Field EPR of a Mono-Nuclear Complex of Rhenium(IV)

J. Martinez-Lillo, J. Faus, M. Julve, F. Lloret (U. of Valencia, Spain, Dept. of Inorganic Chemistry & Institute of Molecular Science); S. Nellutla, J. Krzystek (NHMFL, EMR)

Introduction

In a previous Research Report\(^1\) we summarized HFEPR experiments performed on a powdered sample of a mononuclear complex containing the heavy metal rhenium, \((\text{NBu}_4)_2[\text{ReCl}_4(\text{ox})]\) (1), where \(\text{NBu}_4^+\) = tetra-\(n\)-butylammonium cation, \(\text{ox} = \text{oxalate dianion.}\) The motivation driving these experiments has been to acquire information on the magnetic anisotropy of this complex since it is used to synthesize a polynuclear cluster \((\text{NBu}_4)_4[\text{Ni}\{\text{ReCl}_4(\text{ox})\}_3]\), which shows properties of a single-molecule magnet.\(^2\) The results have been ambiguous, however, due to a strong torquing experienced by the polycrystalline material. We have thus concentrated our effort on a single crystal of the same compound.

Experimental

A single crystal of (1) of approximate dimensions of 1x0.5x0.5 mm\(^3\) was mounted on a goniometer in the superheterodyne 240 GHz spectrometer of the EMR Facility and its associated 12.5-Tesla superconducting magnet.

Results and Discussion

A HFEPR spectrum of (1) for three orientations of the single crystal relative to the magnetic field is shown in Fig. 1. For each orientation there appear two resonances, in agreement with the crystal structure.\(^3\) In addition to the well-resolved hyperfine struture due to the \(I = 5/2\) nuclear spin of rhenium, the spectrum is characterized by a strong anisotropy due to the effects of a large zero-field splitting acting on the \(S = 3/2\) electron spin wavefunction of Re(IV). An analysis of the rotational pattern of the resonances (not shown) leads to the conclusions listed below.

Conclusions

(a) The measure of magnetic anisotropy in complex (1), expressed by the zero-field splitting parameter \(D\) is much larger than the energy quantum available in our spectrometers, which puts a lower limit on its magnitude as \(|D| > 20\ \text{cm}^{-1}\), in agreement with magnetometric data;\(^4\) (b) the sign of \(D\) is negative, which means that the ground spin multiplet is \(M_S = \pm 3/2\) and the excited \(M_S = \pm 1/2\) multiplet is positioned > 40 cm\(^{-1}\) above it; (c) the observed resonances are intra-Kramers transitions driven within the \(M_S = \pm 3/2\) multiplet; (d) the zfs tensor exhibits a pronounced rhombicity, with the ratio \(E/D \geq 1/10\), which makes the nominally forbidden \(\Delta M_S = \pm 3\) intra-Kramers transition appear in the spectrum. These results will be useful in modeling the magnetic properties of polynuclear clusters of Re(IV) using (1) as a building block.

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References