High-Frequency and High-Field EPR of Mono- and Poly-Nuclear Complexes of Rhenium(IV)

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Introduction

Since the discovery of discrete molecular species exhibiting the phenomenon of single-molecule magnetism, much work has been devoted to their preparation and characterization. The need for a larger magnetic anisotropy, higher spin ground states, and a better understanding of quantum tunneling effects through synergy of heterometal spins, moved synthetic chemists toward the heterometallic single-molecule magnets, including those containing the heavy metal rhenium (Re).[1] The motivation behind the current effort is a corroboration of the magnetic data on the mononuclear and polynuclear Re(IV) complexes. In particular, it was desired to determine the sign and magnitude of the zero-field splitting parameters in both kinds of systems, since those obtained from magnetometry are the result of multiparameter fits through approximate models. Consequently, accurate values for them are not ensured and other more appropriate techniques have to be used.

Experimental

Several structurally characterized magnetic samples are subject of the present study. We started with a mononuclear complex $(NBu_4)_2[ReCl_4(ox)]$ (**1**), where NBu_4 = tetra-*n*-butylammonium cation, ox = oxalate dianion, and the tetranuclear compound $(NBu_4)_4[Ni\{ReCl_4(ox)\}_3]$ (**2**), for which the former complex is a precursor. Approx. 10 mg of polycrystalline material in each case was used, and the experiments performed at the EMR Facility and its associated 17-T superconducting magnet.

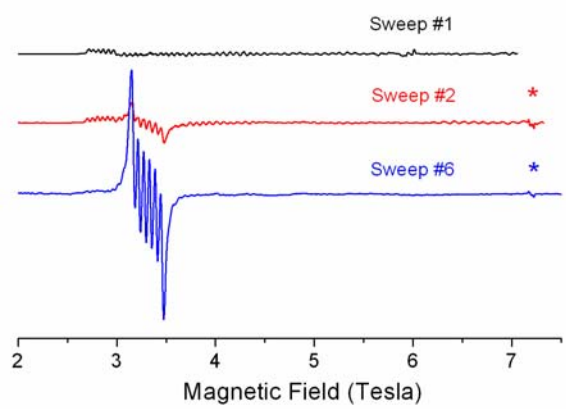

Fig. 1 EPR spectra at 201 GHz of complex **1** at 20 K are dominated by a hyperfine structure with a ca. 560 G constant characteristic for the I = 5/2 nuclear spin of rhenium. Strong torquing effects are observed when sweeping the field.

Results and Discussion

Both complexes delivered very rich EPR spectra. Those of the mononuclear complex **1** are dominated by the hyperfine structure characteristic for both naturally occurring isotopes ^{185}Re and ^{187}Re (nuclear spin number I = 5/2, see Fig. 1), while the spectra of the tetranuclear cluster **2** (not shown) are governed by the fine structure. The failure to observe inter-Kramers transitions within the ground S = 3/2 spin state of the mononuclear complex **1** in the experimentally available frequency-field space puts a lower limit on the zfs parameter D as 20 cm^{-1}, which goes along a magnetometric estimate[2] of the same value in the $AsPh_4^+$ analog as 60(5) cm^{-1}. On the other hand, the fine structure observed in **2** agrees qualitatively with the same parameter as measured by magnetometry (–0.46 cm^{-1}) for the ground S = 11/2 spin state of polynuclear complex **2**.

Conclusions

Further HFEPR experiments are currently in progress to determine a precise value of D for **2**. Complex **1** requires higher frequencies than currently available at both Mm- and Sub-mm Wave and EMR Facilities, and is a candidate for Far-Infrared Magnetic Resonance Spectroscopy when it is developed in the NHMFL.

Acknowledgements

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References

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[2] Chiozzone, R., *et al.*, Inorg. Chem.**, 38**, 4745-4752 (1999).