High-Frequency EPR and Ligand Field Theory Analysis of Hexachlororhenate(IV) Salts

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Introduction

Second and third row transition metals differ significantly in their electronic properties from their first row counterparts. The difference stems from two sources: first, the *d* orbitals are more diffuse; and, secondly, the spin orbit coupling is stronger due to the larger mass of the second and third row ions. High-frequency electron paramagnetic resonance (HFEPR) was utilized to elucidate the electronic structure of a series of hexachlororhenate(IV) salts of protonated organic cations.[1] The two cations used in this study are 2,2-bipyrimidinium **(1)**, and 2-imidazalpyridine **(2)**. The crystal structures of **1** and **2** are shown in Fig. 1.

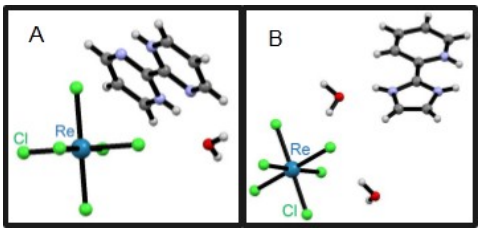

Fig. 1 Crystal structure of **1** (A) and **2** (B).

Experimental

A series of high-field EPR measurements were conducted on a ground solid sample of **1** pressed into a KBr pellet. The experiment was conducted using the homodyne quasi-optical EPR instrument outfitted with a 15/17T superconducting magnet in the EMR facility.[2]

Results and Discussion

EPR spectra recorded at 211 GHz of **1** and **2** are shown in Fig. 2. The spectra reveal a considerable anisotropy which seems to contradict what is expected for a nearly octahedral, homoleptic ligand field shown for both complexes in Fig. 1. In order to gain insight into the substantial anisotropy, the angular overlap model was employed.[3] The chlorines are separated into three groups (A, B and C, as illustrated in Fig. 3), bonding strengths (e_σ) of the A and B groups were then varied, while C was kept constant. Physically, this corresponds to slight tetragonal elongations/contractions along A and B. These calculations indicate the extreme sensitivity of zero field splitting to slight geometric distortions in 5d ions.

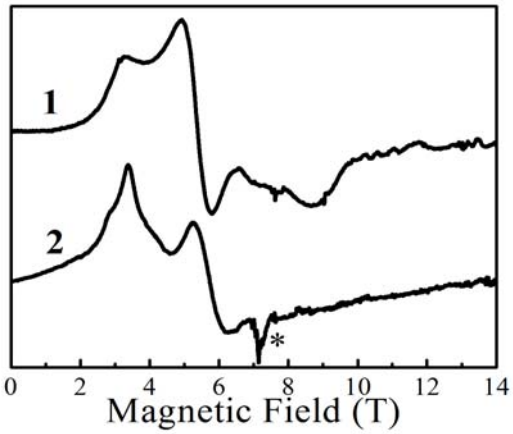

Fig. 2 EPR spectra of **1** and **2** recorded at 211 GHz.

Conclusions

Small distortions from crystal packing can lead to big changes in magnetic anisotropy.

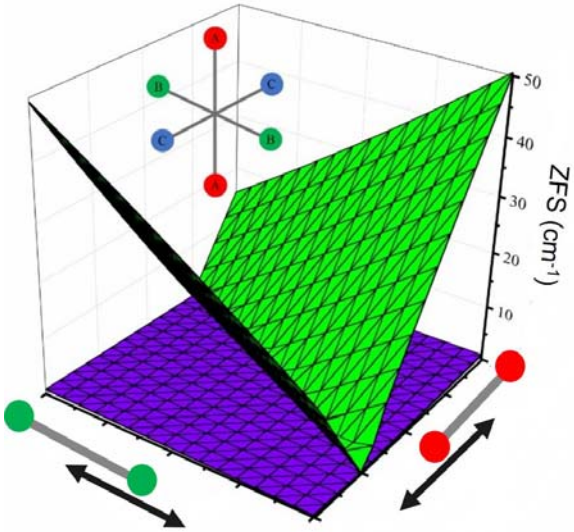

Fig. 3 Magnetic anisotropy (ZFS) as a function of slight compression/elongation of atom groups A and B. The green surface is the result for Re(IV) as the central atom; the purple surface shows the response of the isoelectronic Mn(IV) ion for comparison.

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