High-Frequency and -Field EPR of Octahedral Low-Spin Chromium(II)

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Introduction

Nearly thirty years ago, Nobel Laureate Sir Geoffrey Wilkinson and his co-workers reported the synthesis and structural characterization of a series of early transition metal complexes of the then novel ligand 1,2-bis(dimethylphosphino)ethane (dmpe).[1] These complexes had the general formula $[MX_2(dmpe)_2]$, where M = Ti, V, Cr, Mn, or Fe, and X = Cl or Me (methyl). The Cr(II) ($3d^4$) complex, $[CrCl_2(dmpe)_2]$, was unusual in that it exhibited a low-spin, S = 1, ground state, in contrast to typical 6-coordinate, roughly octahedral Cr(II) complexes, which are high-spin, S = 2. Chromium(II) has been relatively unstudied by HFEPR, in contrast to the isoelectronic ion Mn(III).[2] As an extension of our studies on analogous Ti(II) complexes, we have investigated $[CrCl_2(dmpe)_2]$ by HFEPR. The original crystal structure was solved at room temperature; to match more closely the spectroscopic conditions, and to provide higher quality structural data for computational analysis, a low temperature (100 K) crystal structure was also determined.

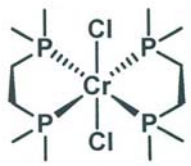

Fig. 1. Line drawing of $[CrCl_2(dmpe)_2]$.

Experimental

The EMR Facility and its 15/17 T superconducting magnet was used in the experiments. Rigorously air-free procedures were used at all stages for this air-sensitive complex.

Results and Discussion

Powder $[CrCl_2(dmpe)_2]$ generated a strong HFEPR response. Both the spectra and their frequency dependence could be very adequately simulated using a spin Hamiltonian for a triplet (S = 1) state: D = +7.39(2) cm^{-1}, E = 0, $g_\perp$ = 1.989(4), $g_\parallel$ = 1.991(6) (Fig. 2). The lack of any rhombic zero-field splitting (zfs) is surprising given that the chelating diphosphine ligands effect two distinct sets of P-Cr-P bond angles: 83° (within chelate) and 97° (between chelates). Oftentimes, we find rhombic zfs to be present and/or greater than expected based simply on the molecular structure; here it is absent despite the structure. The D value is very different from that for spin quintet Cr(II) complexes such as $[Cr(H_2O)_6]^{2+}$ in several forms[3, 4] and *trans*-$[Cr(NCCH_3)_4(FBF_3)_2]$,[5] both of which gave $D \approx -2$ cm^{-1}.

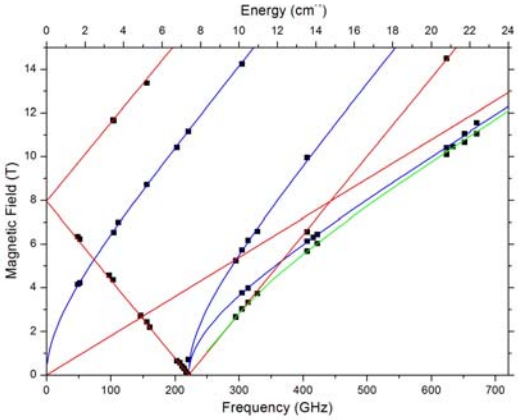

Fig. 2. 2D field/frequency map of resonances in powder sample of $[CrCl_2(dmpe)_2]$ (squares) and its simulation using spin Hamiltonian parameters as in text. Blue lines: external magnetic field perpendicular, red lines: field parallel, green lines: off-axis turning points.

Conclusions

This study is the first definitive zfs determination for a spin triplet Cr(II) complex. Related complexes have exhibited spin-crossover behavior,[6] so the relation of zfs in this complex to its electronic structure will be of interest.

Acknowledgements

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