HFEPR of Chromium(IV) Siloxide

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Introduction

Chromium alkoxide and siloxide complexes have been explored for their coordination chemistry and magnetism and as precursors for heterogeneous catalysts. Siloxide ligands in particular are able to coordinate chromium in oxidation states ranging from II to VI, with the chromium(V) siloxide oxidation state being more elusive. The Nocera group has previously examined the [1] alkoxide ligand $^{t}Bu_2MeCO$ (ditox) with the goal of enforcing a pseudotetrahedral ligand field about chromium(IV). Since the magnetic properties of these complexes are of considerable interest, we report herein the first EPR results on the recently crystallographically and spectroscopically characterized [2] analogous homoleptic chromium(IV) siloxide complex, $Cr(DTBMS)_4$ (DTBMS = $^{t}Bu_2MeSiO^{-}$, **1**).

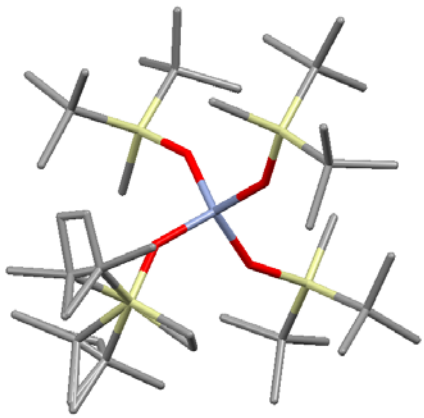

Figure 1. A stick diagram of **1** based on x-ray structure.

Experimental

Air-sensitive crystals of **1** were ground under argon, and loaded into EPR sample holders as powder. The experiments used both the DC Facility and its 25-T resistive "Keck" magnet, and the EMR Facility and its 15/17 T SC magnet.

Results and Discussion

High-Frequency and -Field EPR (HFEPR) on complex **1** delivered very accurate values of the spin Hamiltonian parameters of Cr(IV) in the pseudotetrahedral coordination: $S = 1$, $D = +0.556$ cm^{-1}, $E = 0$, $\boldsymbol{g} = [1.94, 1.94, 1.91]$ for the dominant species. Due to its intrinsic high resolution, HFEPR also detected two other spin triplets in the sample, one with larger, and the other smaller zero-field splitting (zfs) than the dominant species. The slight differences among the spin triplet species, and their temperature dependence may be related to disorder in the material. The published crystal structure [2] shows disorder in the *t*-Bu groups of DTBMS (See Fig. 1). Small structural changes, such as even the orientation of the siloxide ligand, which could also be temperature dependent, can affect the zfs of high-spin complexes.

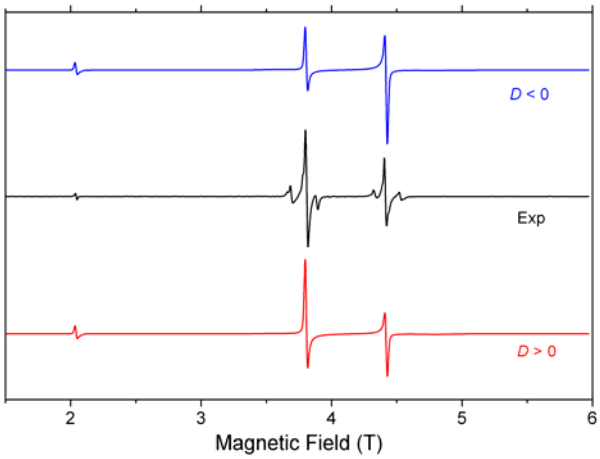

Figure 2. HFEPR spectrum of **1** at 10 K and 112 GHz (black trace) with simulations using spin Hamiltonian parameters of the dominant species as in text (color traces). Blue: negative *D*; red: positive *D*.

Conclusions

This work is the first, to our best knowledge, HFEPR characterization of Cr(IV) in a (pseudo)tetrahedral coordination. The magnetic parameters obtained through this method will be subsequently used in future quantum chemical calculations to correlate with the geometric and electronic structure. This in turn may have a bearing on understanding the catalytic properties of Cr(IV).

Acknowledgements

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References

[1] Groysman, S., *et al.,* Inorg. Chem., **49**, 10759-10761 (2010).
[2] Marshak, M.P., *et al.,* Inorg. Chem., **52**, 1173-1175 (2013).