High-Field EPR Study on Asymmetric Atomic Chain Complex $Cr_3(dpa)_4ClBF_4$

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Introduction

Peak splitting at ~100 K from our previous High-Frequency EPR study on symmetric $Cr_3(dpa)_4Cl_2 \cdot CH_2Cl_2$ indicated the dynamic behavior of the central Cr, hopping between two stable positions. This is consistent with XRD data of the ellipsoid electron density for the central Cr [1]. In order to verify this assignment, similar trichromium chain with fixed position for the central Cr is desired. Asymmetric $Cr{\equiv}Cr\cdots Cr(dpa)_4ClBF_4$, was synthesized in which the chloride anion from one Cr end was selectively removed and replaced with a weakly coordinating tetrafluoroborate anion. This ligand change on one Cr end side of the molecule, however, changes the geometry of the molecule from the XRD data, making the $Cr{\equiv}Cr\cdots Cr$ chain very asymmetric and removes ellipsoid of the central Cr as well (Fig. 1a).

Experimental

HF-EPR measurements on powder and single crystal sample were made using home-built multi-frequency homodyne spectrometer and superheterodyne spectrometer, respectively, at the National High Magnetic Field Laboratory, Tallahassee, FL.

Results and Discussion

Molecular structure of $Cr_3(dpa)_4ClBF_4$ is shown in Fig. 1a. The chromium chain is asymmetric with central Cr having a fixed position. The HF-EPR spectra of a polycrystalline sample are shown in Fig. 1b at microwave frequency 203.2 GHz at 290 K. Various well resolved peaks allow us to simulate the spectra by SPIN program, with spin Hamiltonian parameters: S = 2, $g_x = g_y = 1.994$, $g_z = 1.998$, D = –1.62 cm^{-1} and E = – 0.34 cm^{-1}. This is very similar to those for its parent compound $Cr_3(dpa)_4Cl_2$,[2] indicating the symmetry of chromium chain has little

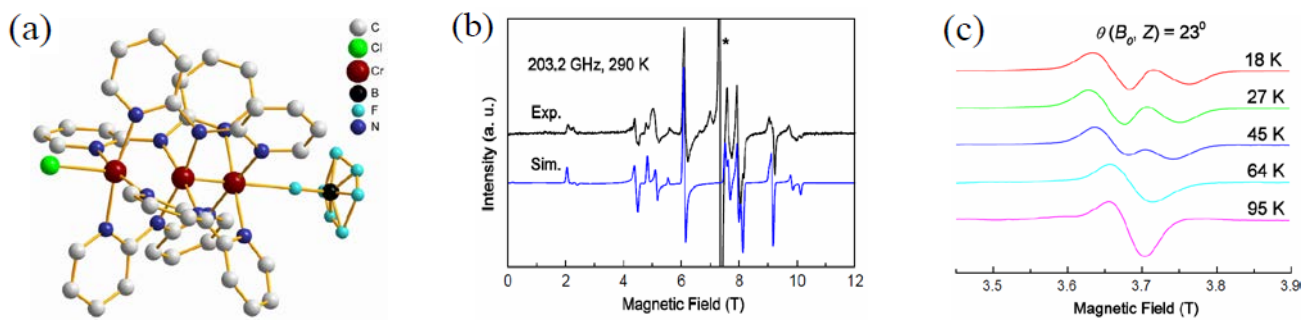

Figure 1. (a) Molecular structure of $Cr_3(dpa)_4ClBF_4$; (b) HF-EPR spectra of $Cr_3(dpa)_4ClBF_4$: the black and blue lines are experiment and simulation, respectively; (c) peak splitting at ~45 K with magnetic field 23^0 from chain axis.

effect on the spin Hamiltonian parameters. Fig. 1c does show a peak splitting at ~45 K. However, the temperature at which the peak starts to split is very anisotropic. It ranges from 65 K when the magnetic field is 77^0 from the Z axis, $\theta\,(B_0, Z) = 77^0$ to less than 10 K, when $\theta\,(B_0, Z) = 15^0$. This mechanism of peak splitting is very different from that for $Cr_3(dpa)_4Cl_2$, since there is no anisotropy for splitting temperature for the latter compound.

Conclusions

The removal of the chain symmetry has little effect on the spin Hamiltonian parameters for trichromium complex. However, the dynamics of the central Cr along the chain was removed.

Acknowledgements

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References

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[2] Wang, J., *et al*., Polyhedron, **30**, 3058-3081 (2011).