Homoleptic 5d fluoride complexes as modules for molecular spin-architectures

Pedersen, Kasper Steen; Clerac, Rodolphe; Barra, Anne-Laure; Sibille, Romain; Probert, Michael; Meihaus, Katie; Dechambenoit, Pierre; Sørensen, Mikkel Agerbæk; Sigrist, Marc; Weyhermüller, Thomas; Weihe, Høgni; Piligkos, Stergios; Tressaud, Alain; Mutka, Hannu; Bill, Eckhard; Long, Jeffrey R.; Bendix, Jesper

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Introduction

Diffuse orbitals and large magnetic anisotropies resulting from strong spin-orbit coupling make complexes with central ions from the 4d and 5d series interesting modules for magnetic systems. The preponderance of homo- and heteroleptic cyanide complexes has been hard to challenge and only few exceptions have been reported. Although homoleptic fluoride complexes are well-described in the literature, they have, with a sole exception, not been employed as modules for molecular magnetic materials. This scarcity of hexafluorido-metallate-based magnetic materials may be due to the harsh synthetic conditions often required for the formation of fluorodometallates and to their common inherent lability, outside hydrofluoric acid solutions, towards e.g. hydrolysis. The combination of the apparent kinetic inertness and the potential strong magnetic anisotropy of 5d systems, led us to explore MF₂⁻ as possible modules for molecule-based magnetic materials.

Hexafluoridometallate modules

Combined analysis of inelastic neutron scattering, high-field and X-band EPR spectroscopies, and magnetic measurements unravels the magnetic anisotropy of (PPh₃)₂ReF₆·2H₂O. Neglecting hyperfine interactions and Zeeman terms with higher order in S, the employed Hamiltonian reads:

$$\hat{H} = g \mu_B \hat{S} + D \hat{S}^2 - J \hat{S} \cdot \hat{S} + E \hat{S} \cdot \hat{S}$$

Quantification of magnetic anisotropy

Example: Long-range order in the Fe³⁺-Re⁴⁺ chain

Conclusions

We presented the use of the simple 5d homoleptic fluoride complexes as modules for magnetic systems. This is exemplified by the chemically robust [ReF₆]⁻²⁻ ion, which additionally provides pronounced magnetic anisotropy and mediation of sizable magnetic super-exchange interactions.