

Molecular Magnetic Building Blocks

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Funding Grants: G.S. Boebinger (NSF DMR-1157490, DMR-1644779); J.R. Long (NSF CHE-1800252); R. Clérac (ANR & CNRS)

The fundamental coordination chemistry of 4d and 5d transition metal ions remains much less explored and underdeveloped in comparison to their lighter 3d analogs. Recent results showing the promise of heavier transition metal ions in advanced molecule-based magnetic materials has sparked interest in engineering their physical properties, notably their magnetic anisotropy.

This study reports the first transition metal complexes featuring mixed fluorine and cyanide ligands, namely *trans*-[M^{IV}F₄(CN)₂]²⁻ (where M = Re, Os). These complexes were isolated using a novel synthetic approach relying on silicon-mediated fluoride abstraction (see top of Figure). A strong and significant enhancement of the magnetic anisotropy for the Re^{IV} complex, as compared to the parent [ReF₆]²⁻ anion, is demonstrated by combined analysis of high-field electron paramagnetic resonance (HF-EPR) spectroscopy (see lower Figure) and magnetization measurements.

This ligand-field engineering methodology paves the way toward the realization of new transition metal complexes featuring extremely strong magnetic anisotropy, complexes that could serve as useful building-blocks for the design of high-performance molecule-based magnetic materials.

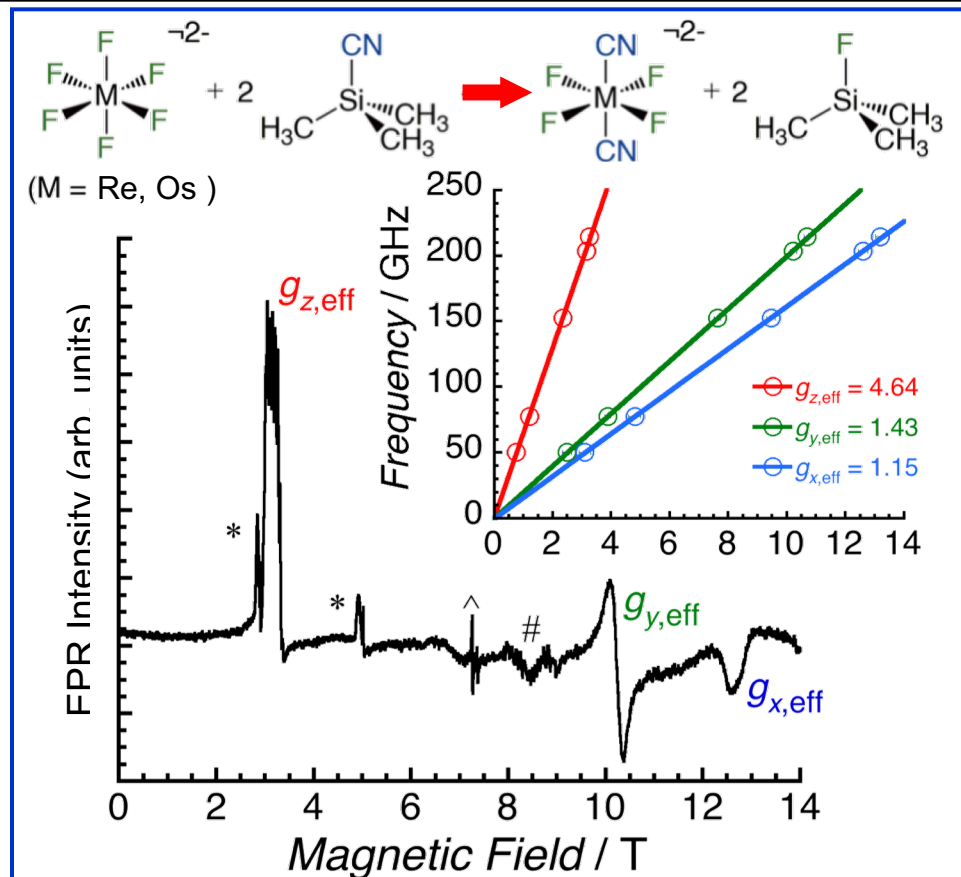


Figure. (top) Synthetic approach for targeted substitution of fluoride ligands for cyanide, yielding *trans*-[M^{IV}F₄(CN)₂]²⁻, starting from M^{IV}F₆. (lower) HF-EPR spectrum (203.2 GHz & 5 K), with the inset showing peak positions deduced from measurements at several frequencies (*, ^ & # denote impurity signals).

Facilities and instrumentation used: EMR Facility (15/17T SC magnet and spectrometer).

Citation: J.-L. Liu, K.S. Pedersen, S.M. Greer, A. Mondal, S. Hill, F. Wilhelm, A. Rogalev, A. Tressaud, E. Durand, J.R. Long, R. Clérac, *Access to Heteroleptic Fluorido-Cyanido Complexes with a Large Magnetic Anisotropy via Fluoride Abstraction*, *Angew. Chem.* (online March 2020); <https://doi.org/10.1002/anie.201914934>