Origin of the Zero-Field Splitting in Mononuclear Octahedral MnIV complexes: A Combined Experimental and Theoretical Investigation

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Introduction
The aim of this work was to determine and understand the origin of the electronic properties of MnIV complexes, especially the zero-field splitting (ZFS), through a combined experimental and theoretical investigation on five mononuclear MnIV compounds, with various coordination spheres (N6, N3O3, N2O4 in both \textit{trans}- and \textit{cis}-configurations, and O4S2). In particular, high-frequency and -field EPR (HFEPR) spectroscopy was applied to determine the ZFS parameters of two of these compounds, MnL\textit{trans}-N2O4 and MnLO4S2.

Experimental
The experiments conducted at NHMFL used Virginia Diodes Inc. sub-THz wave sources and a 15/17-T SC magnet. The MnLO4S2 sample was ground and pressed into a pellet with \textit{n}-eicosane because of a strong torquing effect observed in neat powder. The electrostatic powder of MnL\textit{trans}-N2O4 was immobilized in an \textit{n}-eicosane mull.

Results and Discussion
While the X- and Q-band EPR spectra of MnL\textit{trans}-N2O4 were uninformative, the accurate values of the ZFS parameters were determined thanks to analysis of the HFEPR spectra: \(D = -0.997(6) \text{ cm}^{-1}\), \(E = -0.054(3) \text{ cm}^{-1}\), \(E/D = 0.054\) (see the two-dimensional field/frequency map in Fig. 1). Regarding the complex MnLO4S2, previous X-band EPR experiments found ZFS to be of moderate magnitude (\(D = +0.47 \text{ cm}^{-1}\), \(E/D = 0.09\). Unexpectedly, the HFEPR investigation led to a very different set of parameters: \(D = +2.289(5) \text{ cm}^{-1}\), \(E = +0.323(4) \text{ cm}^{-1}\) \(E/D = 0.141\), the magnitude of \(D\) being the largest ever measured for a MnIV complex. This work demonstrates that estimating the ZFS in absence of high frequency/field limit is risky at best. Specifically, ZFS values for MnIV resulting from low-frequency studies should thus be taken with caution, but the problem is of more general nature and concerns a larger number of high-spin (\(S > 1/2\)) Kramers (half-integer spin number) metal ions (non-Kramers ions are typically ‘EPR-silent’ in the same conditions).

Conclusions
The experiments carried out at the NHMFL were part of a combined experimental and theoretical study that defined and quantified the different contributions to the ZFS. On the experimental aspect, it highlights the fact that contrary to a common belief, ZFS in MnIV complexes can be of the same order of magnitude as that in MnIII.

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