A Mononuclear Fe(III) Single Molecule Magnet with a 3/2–5/2 Spin Crossover

The air stable complex [(PNP)FeCl₂] (1) (PNP = N[2-P(CHMe₂)₂-4-methylphenyl]₂–), prepared from one-electron oxidation of [(PNP)FeCl] with ClCPh₃, displays an unexpected $S = 3/2$ to $S = 5/2$ transition above 80 K as inferred by the dc SQUID magnetic susceptibility measurement. The ac SQUID magnetization data, at zero field and between frequencies 10 and 10²Hz, clearly reveal complex 1 to have frequency dependence on the out-of-phase signal and thus being a single molecular magnet with a thermally activated barrier of $U_{\text{eff}} = 32–36$ cm⁻¹ (47–52 K). Variable-temperature Mössbauer data also corroborate a significant temperature dependence in $\delta$ and $\Delta E_Q$ values for 1, which is in agreement with the system undergoing a change in spin state. Likewise, variable-temperature X-band EPR spectra of 1 reveals the $S = 3/2$ to be likely the ground state with the $S = 5/2$ being close in energy. Multiedge XAS absorption spectra suggest the electronic structure of 1 to be highly covalent with an effective iron oxidation state that is more reduced than the typical ferric complexes due to the significant interaction of the phosphine groups in PNP and Cl ligands with iron. A variable-temperature single crystal X-ray diffraction study of 1 collected between 30 and 300 K also reveals elongation of the Fe–P bond lengths and increment in the Cl–Fe–Cl angle as the $S = 5/2$ state is populated. Theoretical studies show overall similar orbital pictures except for the $d(\bar{z}²)$ orbital, which has the most sensitivity to change in the geometry and bonding, where the quartet (4B) and the sextet (6A) states are close in energy.