

The Effect of Subtle Changes in Geometry on the Zero-Field Splitting in Co Tetrahedral Complexes

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Mononuclear transition metal complexes are ideal for studying the relationship between spin relaxation processes and zero-field splitting. By studying the same complex crystallized with different counterions, we gain insight into how small geometry changes induced by packing effect the zero-field splitting. Herein we present a series of pseudotetrahedral $[\text{Co}(\text{C}_3\text{S}_5)_2]^{2-}$ complexes with varying deviations from D_{2d} symmetry. Complete active space self consistent field calculations with corrections from second order perturbation theory (CASSCF/CASPT2) were performed for the quartet and doublet states including excitations in the full d manifold. Through the use of an effective spin Hamiltonian, the static magnetic properties were computed and compared with experimental measurements. We are able to use d-orbital splitting model to provide an explanation of how the structural distortions affect the observed dynamic magnetic properties.