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 \([\text{Co(C}_3\text{S}_5)_2]^{2-}\) 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.