

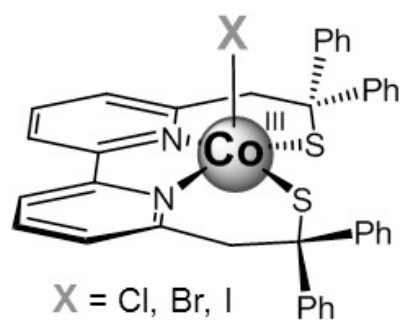
# An Experimental and Theoretical Investigation on Penta-coordinated Cobalt(III) complexes with an Intermediate $S = 1$ Spin State: How Halide Ligands Affect their Magnetic Anisotropy

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Understanding the factors that control the magnitude and symmetry of the magnetic anisotropy should facilitate the rational design of mononuclear metal complexes in the quest of single molecule magnets based on a single metal ion with high blocking temperatures and large energy barriers. The best strategy is to define magneto-structural correlations through investigation of series of metal complexes. Since the main contribution to the magnetic anisotropy arises from spin-orbit coupling (SOC) effect in metal ion-based systems, current studies particularly focus both on the use of ligands and metal ions possessing a large SOC. We herein report on an unique series of halide  $\text{Co}^{\text{III}}$  complexes,  $(\text{CoX})$  with  $X = \text{Cl}, \text{Br}$  and  $\text{I}$ , which possess a rare intermediate  $S = 1$  spin ground state. These  $\text{Co}^{\text{III}}$  complexes are attractive species as they possess a remarkable large axial zero-field splitting ( $D$  parameter). Single-crystal X-ray structures reveal that  $\text{CoBr}$  and  $\text{CoI}$  complexes are isostructural to the previously described  $\text{CoCl}$  complex<sup>[1]</sup>. They display distorted penta-coordinated square pyramidal geometries with the halide located in the  $\text{Co}^{\text{III}}$  axial position. Large positive  $D$  values of 35, 26 and 18  $\text{cm}^{-1}$  have been found for  $\text{CoCl}$ ,  $\text{CoBr}$  and  $\text{CoI}$ , respectively. To rationalize this trend, theoretical calculations based on both density functional theory (DFT) and complete active space self-consistent field methods have been successfully carried out. Both sign and magnitude of  $D$  are remarkably predicted by these theoretical approaches. DFT calculations also show that the resulting  $D$  values originates from a balance of several contributions and that many factors including structural differences and halide nature should be taken into account to explain the trend of  $D$  in this series of complexes<sup>[2]</sup>.

**S=1**



$$D^{\text{Cl}} = +35 \text{ cm}^{-1}$$

$$D^{\text{Br}} = +26 \text{ cm}^{-1}$$

$$D^{\text{I}} = +18 \text{ cm}^{-1}$$

- 1) M. Gennari, B. Gery, N. Hall, J. Pécaut, M.-N. Collomb, M. Rouzières, R. Clérac, M. Orio, C. Duboc, *Angew. Chem. Int. Ed.* **2014**, 53, 5318
- 2) D. Brazzotto, M. Gennari, S. Yu, J. Pécaut, M. Rouzières, R. Clérac, M. Orio, C. Duboc, *Chemistry*, **2015**, press