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COMMUNICATION

Ligand effects on the magnetic anisotropy of tetrahedral cobalt complexes *

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The effect of ligands with heavy donor atoms on the magnetic anisotropy of the pseudo-tetrahedral cobalt complexes, Co(quinoline)₂I₂ (**1**) and Co(EPh₃)₂I₂ (**2-3**) (E = P, As) has been investigated. The axial zero-field splitting parameter *D* was found to vary from +9.2 cm⁻¹ in **1** to -36.9 cm⁻¹ in **2** and -74.7 cm⁻¹ in **3**. Compounds **2** and **3** exhibit slow relaxation of the magnetization up to 4 K under an applied dc field, indicating SMM behavior.

The field of single molecule magnets (SMMs) has witnessed a remarkable evolution over the past two decades and is gaining even more momentum from the expansion of the topic to organometallic compounds, lanthanides and mononuclear transition metal complexes.¹ The considerable progress in SMM research notwithstanding, there is a necessity for advances given that hysteresis has not been observed above 14 K² which is not yet suitable for practical applications.

During the quest for SMMs with enhanced properties, it has become obvious that magnetic anisotropy is the main criterion for developing slow relaxation of magnetization, a characteristic that is affected by the molecular symmetry, the ligand field and the single ion effects of spin-orbit coupling and zero-field splitting.³ Several routes have been employed to enhance the global anisotropy of molecular materials such as increasing single ion anisotropy via incorporating the heavier second and third row transition metal ions.⁴ This strategy has been found to lead to improved SMMs with higher barriers and higher temperature hysteresis, one example of which is a cyanide compound based on Mn₂Mo.⁵ Furthermore, recent reports of slow paramagnetic relaxation of the magnetization in transition metal-based mononuclear complexes provide ample evidence for the importance of geometrical control of the local anisotropy in metal complexes. Indeed, the rational design of low coordinate iron

complexes has led to an extraordinary example of a mononuclear SMM with an energy barrier that even surpasses the benchmark Mn₁₂-acetate compound.^{1d}

Such seminal results are setting the stage for a new era of research on the topic of magnetic bistability in molecules.^{1d-u} Attaching heavier halides with their larger spin orbit coupling parameters to metal centers is known to enhance the magnetic anisotropy of metal complexes.⁶ Long and coworkers reported a family of SMMs, viz., [Co(EPh)₄]²⁻ (E = O, S and Se) for which the observed increased magnetic anisotropy of the complexes with heavier analogues was attributed to the softness of the ligand.^{1h, 1i} Magneto-structural studies of CoL₂X₂ (L = Phosphine, X = Cl or Br) complexes were recently reported revealing the presence of slow relaxation of the magnetization.^{1r, 1u}

Herein, we report a magnetic study of a series of mononuclear distorted tetrahedral cobalt complexes of general formula Co(L)₂I₂ (L = quinoline (**1**), triphenylphosphine (**2**) and triphenylarsine (**3**)). The group 15 donor atom was varied from the first row to the third row element in order to investigate the effect of the softness and larger spin orbit coupling constant of the ligand with heavier donor atoms on the global magnetic anisotropy of the metal complexes. The present complexes were synthesized following previously reported procedures.⁷

The crystal structure of **1** was previously reported^{7c} (Figure 2 left) which revealed a pseudo-tetrahedral local coordination environment around the central cobalt ion. The metal-ligand bond angles (Table S2) are slightly distorted with angles of I1-Co-I2 = 109.72(2)°, I1-Co-N1 = 108.51(7)°, and N1-Co-N2 = 101.8(1)°. Compound **2** exhibits a similar structure (Figure 1 center) with

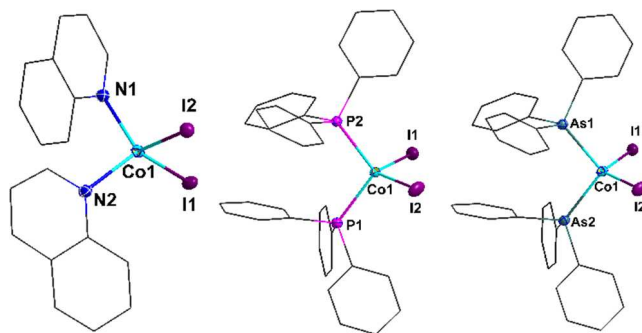


Figure 1. Molecular structures of compounds **1-3**. Phenyl rings are shown in a wire model and hydrogen atoms were omitted for clarity.

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the angles I1-Co-I2 = 111.44(1)°, I1-Co-P1 = 109.04(2)°, and P1-Co-P2 = 108.25(2)°. Compound **3** is isostructural with **2** (Figure 1 right) [I1-Co-I2 = 116.80(2)°, I1-Co-As1 = 108.44(2)°, As1-Co-As2 = 105.15(2)°]. The metal-ligand bond distances in compounds **1-3** (Table S 2) are in the range of previously reported four coordinate cobalt complexes.^{1r} The angular distortion from ideal tetrahedral geometry was estimated by calculating the angular distortion parameter $\delta = 2 \cdot Td - (\alpha + \beta)$ where $\alpha = L-Co-L$ and $\beta = X-Co-X$ angles. Compound **1** was found to be a compressed pseudo-tetrahedral molecule ($\delta = +7.48$) whereas **2** ($\delta = -0.69$) and **3** ($\delta = -2.95$) exhibit flattened geometries.

Magnetic measurements were performed on samples of crushed single crystals at 1000 Oe over the temperature range of 1.8-300 K. DC magnetic susceptibility data (see Fig. 2) revealed that the room temperature χT values for **1-3** are 2.55, 2.66, and 2.63 cm³ K/mol, respectively. These values are significantly higher than the expected value of 1.875 cm³ K/mol for an isotropic S = 3/2 center with g = 2. The χT values for all compounds slowly decrease upon lowering the temperature down to ~100 K and then rapidly drop to a minimum of 0.52, 1.39, and 1.52 cm³ K/mol at 2 K for **1-3** respectively. Both the higher room temperature χT values and the rapid decrease in the low temperature regime are a signature of appreciable magnetic anisotropy for the complexes.

The anisotropic nature of the Co(II) centers in **1-3** is further evidenced by the lack of saturation in the magnetization versus field data even at 7 T (Figure S5-S7). The field-dependent magnetization data for **1-3** at temperatures between 1.8 and 4.5 K (Figure S5-S7 inset) exhibit a non-superposition of the iso-field lines which also supports the presence of significant zero-field splitting. Attempts to determine zero-field splitting parameters of **1** by fitting the field-dependent magnetization data using ANISOFIT2.0⁸ resulted in a D value of +9.2 cm⁻¹ with E = 0.01 although with a low correlation factor which is likely due to intermolecular interactions. The positive sign supports the recent reports of angular dependence of the zero-field splitting parameters (ZFS) which predict a positive D for a compressed pseudo-tetrahedral coordination environment.⁹ The fitting results of the ZFS parameters for **1-3** are summarized in Table 1 along with analogous tetrahedral cobalt complexes. Compound **2** was found to exhibit an axial zero field splitting parameter, D of -36.9 cm⁻¹ with E = 0.2 cm⁻¹. The analogous complexes Co(PPh₃)₂X₂

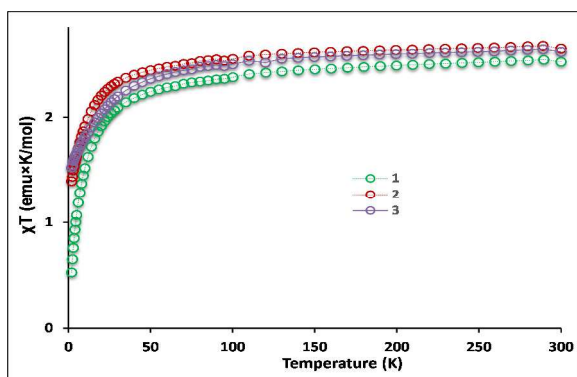


Figure 2. Variable temperature DC magnetic susceptibility data for **1-3**.

were previously reported to exhibit significantly smaller D values (-11.6 cm⁻¹ for Cl and -13 cm⁻¹ for Br)^{1r, 1u, 10} as compared to the heavier iodide analogue **2**. A further increase in the magnitude of

the D value was observed for **3** (-74.7 cm⁻¹, E = -0.82 cm⁻¹) as a result of the incorporation of the heavier arsenic atom. The successive increase in the magnitude of D for **1-3** follows a similar trend to that observed for the Tp*NiX series (D = +3.93, -11.43, -22.81 cm⁻¹, for X = Cl, Br, I, respectively) which was found to be a result of the ligand spin-orbit coupling contribution based on CASSCF calculations.^{6a, 6b} In a pseudo-tetrahedral environment, the Co(II) center is expected to exhibit an orbitally nondegenerate ground state ⁴A₂, but the weak tetrahedral ligand field provides relatively low-lying excited states that enhance the second order perturbations of the ground state via spin-orbit coupling generating significant D values. In a tetragonally distorted d⁷ system, D is directly proportional to the total spin-orbit coupling in the system and inversely proportional to the axial crystal field splitting.¹¹ The two spin-orbit coupling parameter model has been previously used to explain the observed decrease in D value of a series of trigonally distorted nickel centers doped in CsMgX₃ crystals (X = Cl, Br, I) in order to take into account the strong covalency of the metal-ligand interaction in case of the heavier halides.^{6d} The observed trend in the present series can, thus, be attributed to the increased ligand spin-orbit coupling contribution in progression from the lighter nitrogen based to the heavier phosphorus and arsenic containing ligands. The relative ligand field strength differences could be another factor of interest. The magneto-structural studies of the family of mononuclear SMMs, [Co(EPh)₄]²⁻, recently reported by Long and coworkers, revealed a similar trend to the current series (D = -11.1, -62, -83 cm⁻¹ for E = O, S or Se respectively) which was tentatively attributed to the softness of the ligand field.¹¹ An early report by Orgel and coworkers revealed a decreasing ligand field strength; P(n-C₃H₇)₃ > Piperidine > As(n-C₃H₇)₃ which does not follow the observed trend in the D values of the present series.¹² More detailed experimental and computational studies are underway to elucidate the nature of the contributions of each of these effects.

The large negative D values in **2** and **3** imply very large energy gaps between the ±3/2 and ±1/2 M_s levels with substantial predicted energy barriers of 73.8 and 149.4 cm⁻¹ for spin reversal. The dynamic magnetic properties were studied in the absence of a field and under an applied field to check for slow relaxation of the magnetization. The AC susceptibility measurements of compound **1** did not reveal an out-of-phase signal under a zero or applied DC field. Compound **2** exhibits a field induced out of phase AC signal up to 2.5 K as depicted in Figure 4. The frequency dependent AC measurements of **2** were conducted under different applied DC fields in order to determine the optimum field which was found to be 1000 Oe (fig. S10). The frequency dependent measurements at different temperatures in the range of ν (1-1500 Hz) were measured over the temperature range 1.8-2.9 K under 1000 Oe DC field (fig 3). The data were fit using a Debye model.¹³

Table 1. Zero-field splitting parameters and energy barriers for mononuclear cobalt complexes with C_{2v} local symmetry.

Compound	D (cm ⁻¹)	U _{eff} (K)	T ₀	ref
CoN ₂ Cl ₂	-5.16	-	-	9b
CoN ₂ I ₂	+9.2	-	-	This work
CoP ₂ Cl ₂	-11.6	37.1	1.2x10 ⁻⁹	1r, 10
CoP ₂ Br ₂	-12.5	37.3	9.4x10 ⁻¹¹	1u
CoP ₂ I ₂	-36.9	30.6	4.65x10 ⁻¹⁰	This work
CoAs ₂ I ₂	-74.7	32.6	1.5x10 ⁻⁸	This work

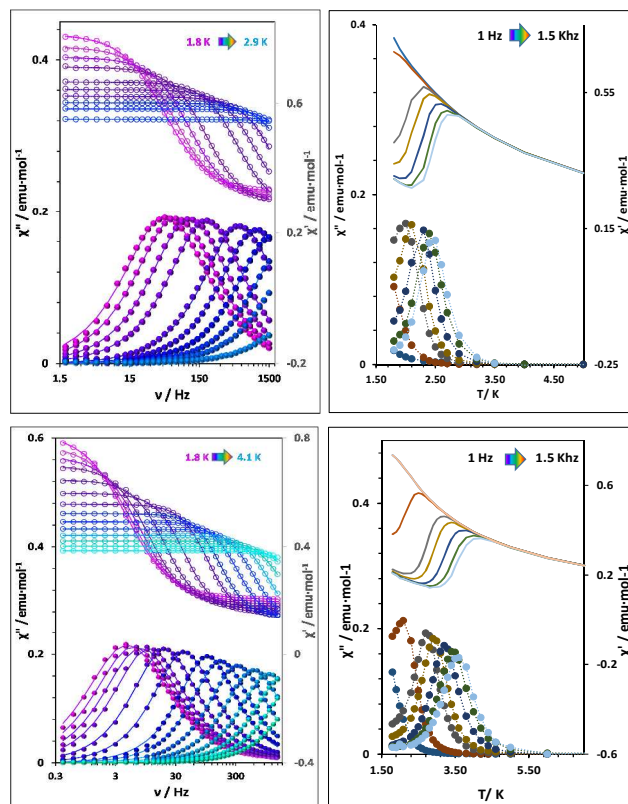


Figure 3. Temperature (right) and frequency (left) dependence of the AC susceptibility of **2** (top) and **3** (bottom). In-phase (open) out-of-phase (solid).

The linear regime of the Arrhenius plot which corresponds to a thermally activated relaxation via Orbach process¹¹ gave an energy barrier of 30.6 K and pre-exponential factor, $\tau_0 = 4.65 \times 10^{-10}$ s for **2**. The AC susceptibility measurements of compound **3** revealed a similar field induced AC signal under optimum field of 1000 Oe up to 4.5 K (fig 5). The fitting of the frequency dependence data gave an energy barrier of 32.6 K and $\tau_0 = 1.5 \times 10^{-8}$ s. The observed enhancement in the energy barrier of the heavier arsenic-based complex, **3** as compared to the phosphine-based analogue **2** (30.6 K \rightarrow 32.6 K) is significantly smaller than the corresponding increase in the D value ($-36.9 \text{ cm}^{-1} \rightarrow -74.7 \text{ cm}^{-1}$). Surprisingly, a comparison of **2** with the previously reported chloride and bromide analogues reveals a decrease in the energy barrier despite the significantly larger negative D value. The relaxation event in **3** is still much slower due to the larger magnitude of the pre-exponential factor.

The present series of mononuclear cobalt complexes further supports the hypothesis that ligands with heavier and softer main group donor atoms significantly enhance the global magnetic anisotropy of the metal complexes as evidenced by the increased ZFS parameters. This fact notwithstanding, the dynamic magnetic properties reveal only a minor effect on the magnitude of the energy barrier to reversing the magnetization. A similar observation was recently reported for the $[\text{Co}(\text{EPh})_4]^{2-}$ family of SMMs. More detailed experimental and computational studies are in progress to identify the different factors leading to such an enhancement of zero-field splitting parameters and the underlying issues causing the lack of concomitant increase in the energy barriers.

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