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# Investigation of easy-plane magnetic anisotropy in P-ligand square-pyramidal $Co^{II}$ single ion magnets

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**In this work we report the first two pentacoordinated $Co^{II}$-$P_4X_1$ Single Ion Magnets (SIMs) based on P-donor ligands. The tetradentate ligand tris[2-(diphenylphosphino)ethyl]phosphine allows the obtention of the isostructural square pyramidal $[Co(PP_3)Cl]\cdot ClO_4$ (1) and $[Co(PP_3)Br]\cdot ClO_4$ (2) complexes. Consistent theoretical and experimental studies indicate that these complexes have a high spin (S=3/2) ground state and suggest that the relaxation dynamics is governed by ground state quantum tunneling, whereas its temperature dependence is directed by optical or acoustic Raman processes.**

Single-molecule magnets (SMMs) are molecules that exhibit a slow relaxation of their magnetization from a pure molecular origin. When one of these molecules contains only one metal ion they are referred as single-ion magnets (SIMs). The study of these systems has experienced a huge increase in recent times due to their promising properties in molecular spintronics,[1] high-density information storage,[2] and qubits for quantum computation.[3] In SMMs and SIMs the thermal energy barrier for the reversal of the magnetization ($U$) depends on the total spin (S) and the easy axis anisotropy parameter ($D$). $U$ can be quantified as $|D|S^2$ and $|D|(S^2 - 1/4)$ for integer and half-integer spins, respectively.[4] A substantial effort has been devoted to the preparation of new molecules to better understand different phenomena that effect slow relaxation behaviour. The early examples of SMMs were based on polynuclear transition metal complexes[5] but more recently low-nuclearity lanthanide complexes[6] and even mononuclear lanthanide[7] and transition-metal complexes[8] have been reported to show SMM behaviour. Mononuclear transition metal complexes are significant because the relaxation process concerning the ground state, or the contribution of some excited states, can be tuned via variation of the ligand field around the metal center. The most remarkable feature of SIMs lies in the possible estimation and design of their magnetic anisotropy based on the ligand field theory. Among 3d-SIMs, $Co^{II}$ complexes are mostly important due to the presence of non-integer spin ground state, which decreases the probability of quantum tunnelling of magnetization (QTM).[9] The first mononuclear $Co^{II}$ complexes showing slow magnetic relaxation were reported for pentacoordinate systems having distorted square-pyramidal geometry with bis(imino)pyridine and thiocyanido ligands.[10] After this discovery other $Co^{II}$-based SIMs, with different coordination environments, have been developed. Among those, only a few examples correspond to pentacoordinated $Co^{II}$ SIMs, which are mainly formed by different combinations of multidentate *N*-donor and monodentate halido/pseudohalido ligands. In contrast, and despite the similarity between nitrogen and phosphorus, the usage of P-donor ligands to produce $Co^{II}$ pentacoordinate SIMs has not been yet achieved. We report herein the first two $Co^{II}$ SIMs displaying a pentacoordinate arrangement. These complexes, with general formula $Co^{II}$-$P_4X_1$: $[Co(PP_3)Cl]\cdot ClO_4$ (**1**) and $[Co(PP_3)Br]\cdot ClO_4$ (**2**) where $PP_3$ = tris[2-(diphenylphosphino) ethyl]phosphine, have been synthesized and the influence of the metal coordination geometry on the magnetic anisotropy has been investigated. The single-crystal X-ray analysis of **1** and **2** reveals that both complexes are isostructural and crystallize in the triclinic *P*-1 space group (Fig. 1 and Table S1). The tripodal $PP_3$ ligand coordinates in a tetradentate fashion, with one of the P atoms occupying the axial position, while the fifth position is taken by the halide ion (X = Cl (**1**) and Br (**2**)). The geometry at the $Co^{II}$ centre is best described as a distorted square pyramid; the calculated $\tau$ values for **1** and **2** are 0.331 and 0.354, respectively (Table S2).[11] Additional SHAPE[12] analysis of these complexes confirms that both are better described as square pyramids (1.14 and 1.41 for **1** and **2**) than as trigonal bipyramids (3.31 and 3.29 for **1** and **2**, Table S3). In both complexes, substantial $\pi\cdots\pi$ interactions and intermolecular hydrogen-bonding are found, favoring the formation of a supramolecular two dimensional arrangement (Fig. S1-S2 and Table S4-S5).

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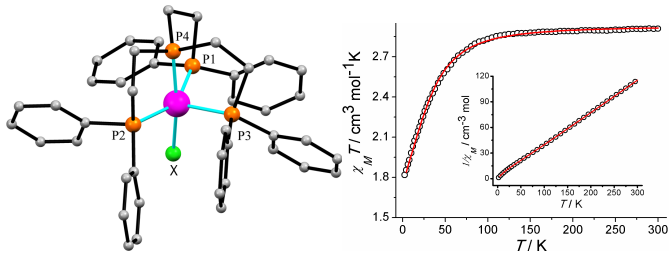


**Fig. 1** View of the molecular structures for complexes **1** and **2**, where X = Cl (**1**) and X = Br (**2**); hydrogen atoms are omitted for clarity; $\chi_M T$ *vs.* *T* plot measured at 0.1 T for complex **1** (left). The red line is the best fit.

The purity of the as-synthesized products has been confirmed by the good agreement between the experimental and simulated bulk phase powder X-ray diffraction patterns based on the single crystal structure data (Fig. S3). Magnetic susceptibility measurements have been performed under direct current (DC) and an applied field of 0.1 T. At room temperature, $\chi_M T$ values ($\chi_M$ = molar magnetic susceptibility) of 2.90 and 2.84 $cm^3$ K $mol^{-1}$ have been obtained for **1** and **2**, respectively. These values are larger than the spin-only value of 1.87 $cm^3$ $mol^{-1}$ K for a high-spin $Co^{II}$ ion but, nevertheless, they fall within the usual range of 2.1-3.4 $cm^3$ $mol^{-1}$ K found for highly anisotropic $Co^{II}$ ions with a significant orbital contribution.[13] Upon cooling from 300 K, the $\chi_M T$ values of **1** and **2** remain constant down to 100 K, below which they decrease, reaching a value of 1.81 and 1.78 $cm^3$ $mol^{-1}$ K at 2 K, respectively (Fig. 1 and S5). The decrease of the $\chi_M T$ curves at low temperature is mainly due to the intrinsic magnetic anisotropy of the $Co^{II}$ center. Reduced magnetization data ($M/N\mu_B$ *vs.* *H*) have been collected and those attain the highest values of 2.42 and 2.35 $N\mu_B$ for **1** and **2** at 2 K and 7 T (Fig. S4-S5). These values are well below the theoretical saturation for an *S* = 3/2 system ($M_{sat}$ = 3.3 for g = 2.2). A spin Hamiltonian of eqn (1) is used to describe the magnetic anisotropy qualitatively:

$$H = g\mu_B S \times B + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (1)$$

where the *D* and *E* terms represent the single-ion axial and rhombic ZFS parameters. The PHI code[14] has been employed to quantify the anisotropy parameters of the $Co^{II}$ centres by fitting of the $\chi_M T$ *vs.* *T* plots. The best fits of the magnetic susceptibility data give *D* = 46.4 $cm^{-1}$, *E* = 10.1 $cm^{-1}$, and g = 2.31 for **1**; *D* = 40.7 $cm^{-1}$, *E* = 9.3 $cm^{-1}$, and g = 2.28 for **2**. Similar values are found for the anisotropy parameters with electronic structure CASSCF calculations, carried out with either ORCA[15] and MOLCAS[16] (Table 1). In all cases the calculations indicate a quadruplet (3/2) ground state. The quasi-degenerate perturbation theory (QDPT) implemented in ORCA produces very similar results to those obtained by the fit of experimental data although the computed *D* values seem to be slightly underestimated for both complexes **1** and **2**. The SO-RASSI approach included in the MOLCAS package produces also quite similar *E* and *D* values for both complexes, again in good agreement with those obtained from the experimental fit. Other useful computational information, such as the computed low-lying spin-orbit energy states and the orientation of the g- and *D*-tensors, can be found in the ESI (Table S6-S9 and Fig. S6). The relative energy order of the 3d orbitals has been extracted from the ORCA calculation using the *ab initio* ligand field theory (AILF) method.[17] The final d-orbital splitting for complexes **1** and **2**, which allows the prediction of the lowest energy transitions, is shown in Fig. 2. As may be observed the last doubly occupied orbital is $d_{yz}$ (or $d_{xz}$, because those cannot be distinguished) and the first semioccupied orbital is $d_{xy}$ for both complexes. Since these orbitals have a different $|m_l|$ value, the contribution to the *D* value should be positive[18] in complete agreement with the experimental fit. The d-orbital splitting allows the rationalization of the difference in the magnitude of *D* between both complexes. The presence of a chloride ligand produces a 1746.1 $cm^{-1}$ energy gap while with bromide the gap slightly increases to 1806.1 $cm^{-1}$; since the energy gap is smaller for complex **1** it should have a higher *D* value, as observed both in experiments and calculations.

**Table 1**. ORCA and MOLCAS CASSCF+RASSI computed *D*, $|E/D|$ and g-values for complexes **1** and **2**. ΔE indicates the first excitation energy computed in the spin-free state of the $Co^{II}$ complexes.

| Complex | $D_{fit}$ ($cm^{-1}$) | $D_{calc}$ ($cm^{-1}$) | $\lvert E/D\rvert_{calc}$ | ΔE ($cm^{-1}$) | $g_{xx}$, $g_{yy}$, $g_{zz}$ |
|---|---|---|---|---|---|
| **1**[a] | 46.4 | 40.1 | 0.24 | 1568.7 | 2.03, 2,27, 2,55 |
| **1**[b] | 46.4 | 45.6 | 0.24 | 1638.3 | 2.04, 2,29, 2,56 |
| **2**[a] | 40.7 | 38.3 | 0.24 | 1559.9 | 2.03, 2.28, 2.55 |
| **2**[b] | 40.7 | 36.9 | 0.24 | 1635.2 | 2.04, 2,30, 2,56 |

[a] ORCA. [b] MOLCAS.

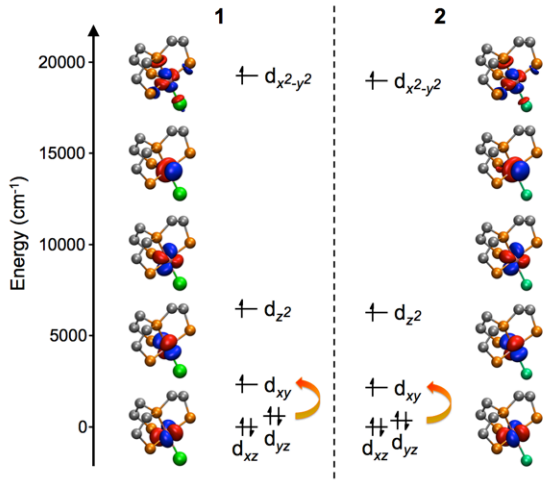


**Fig. 2** $Co^{II}$ core and computed d-orbitals for complexes **1** (left) and **2** (right). Orbital relative energies are given in $cm^{-1}$. Color code: Co = pink C = gray, P = orange, Cl or Br = green; outer C and H atoms have been omitted for clarity. The curvy orange arrows indicate the lowest energy transitions.

As mentioned above complexes **1** and **2** constitute a new class of $Co^{II}$ SIMs and therefore the impact of the P-donor atoms on the magnetic properties is difficult to assess. We have carried out an exploration of the Cambridge Structural Database (CSD) looking for other pentacoordinate $Co^{II}$ complexes containing $P_4$ ligands (either mono or polydentate) and one halide, which could be compared to complexes **1** and **2**. For those complexes, 7 in total, we have carried out a CASSCF calculation equivalent to those of **1** and **2**, and we have also computed their SHAPE analysis regarding the typical 5 vertexes polyhedra (Table 2, entries 1-7). The computed *D* value for all these $Co^{II}$-$P_4X_1$ complexes is positive independently of the ligand arrangement or nature, suggesting that the presence of a P-donor ligand tends to produce easy-plane complexes. CSD refcode DIZQAF (Entry 1 in Table 2) has a negative D value but other parameters derived from the calculations indicate it should be positive (see ESI).

**Table 2**. SHAPE analysis and computed *D* values for the studied Co(II)-$L_4X_1$ complexes.

| Entry | Structure | vOC-5 | TBPY-5 | SPY-5 | *D* ($cm^{-1}$) | *E*/*D* |
|---|---|---|---|---|---|---|
| 1 | DIZQAF | 6.77 | 0.74 | 4.89 | -32.8[a] | 0.28 |
| 2 | JIPCER01 | 0.74 | 5.76 | 1.10 | 53.3 | 0.12 |
| 3 | NIZDOP | 3.76 | 1.04 | 2.49 | 52.4 | 0.12 |
| 4 | RUTSUU | 4.62 | 2.01 | 3.69 | 86.4 | 0.28 |
| 5 | UFUCUV | 6.51 | 1.01 | 5.11 | 53.0 | 0.08 |
| 6 | VAKFAR | 0.77 | 4.29 | 1.50 | 36.6 | 0.10 |
| 7 | VAKFEV | 0.72 | 5.91 | 1.37 | 46.8 | 0.15 |
| 8 | FAWYUX | 2.08 | 5.50 | 1.39 | 107.0[a] | 0.29 |
| 9 | NADTUH | 2.01 | 4.54 | 0.30 | 113.6 | 0.15 |
| 10 | NUQMAP | 2.73 | 3.46 | 1.07 | 104.0 | 0.10 |
| 11 | RUJSOE | 2.76 | 2.40 | 1.18 | -71.9[a] | 0.31 |
| 12 | XOBFEZ | 2.93 | 5.76 | 0.63 | -65.9[a] | 0.30 |

vOC-5: vacant octahedron, TBPY-5: trigonal bipyramid, SPY-5: spherical square pyramid. [a] See full explanation in the ESI.

Another interesting feature consists of checking whether the magnetic behavior of complexes **1** and **2** can be modulated by replacing the P-donor ligand by an equivalent structure containing N-donor atoms *i.e.* $Co^{II}$-$N_4X_1$ complexes. This has been already achieved by replacing a ($NN_3^{Me}$) with an equivalent ($NS_3^{iPr}$) ligand in mononuclear trigonal bipyramidal $Co^{II}$ complexes.[19] In that case, the decrease of the sigma donor ability in the equatorial plane produces an increase in absolute value in the magnetic anisotropy. Searching the CSD reveals there are not many $Co^{II}$-$N_4X_1$ complexes (5) adopting a square pyramid shape similar to **1** and **2** (Table 2, entries 8-12). Among those, only one contains a neutral $P_4$ tetradentate ligand and a chloride where one of the nitrogen atoms takes the axial position (CSD refcode FAWYUX, entry 6 in Table 2, Fig. S7). The computed D value for this complex is positive (107.0 $cm^{-1}$), indicating that the square pyramid arrangement shown in complexes **1** and **2** seems to produce also easy plane $Co^{II}$-$N_4X_1$ complexes, although more examples should be needed to extract a general conclusion. As may be observed, two complexes have negative D values (Table 2, entries 11-12); nevertheless, the E/D value is in the limit (0.3), and thus the sign of D for those complexes is not well defined and may well be positive, as hinted by other computed features (see ESI).

To probe the magnetic relaxation dynamics of both complexes, AC magnetic susceptibility measurements have been performed in the temperature range of 1.8-10 K at a 3.5 Oe ac field. No out-of-phase ac susceptibility ($\chi_M''$) signal was observed under a zero dc field. Nevertheless, upon application of a 2000 Oe dc field, all complexes show temperature and frequency-dependent ac signals, typically observed for field-induced 3d-SIM species (Fig. 3 and S8-S10). Furthermore, the Cole-Cole plots (Fig. 3 and S10) have been constructed from the frequency-dependent ac susceptibility data. The fit of the $\chi_M''$ *vs* $\chi_M'$ data at each temperature, using the generalized Debye model,[20] produces values of $\alpha$ within the ranges 0.03-0.22 (**1**) and 0.05-0.25 (**2**), showing a narrow distribution of the relaxation time. The effective energy barrier ($U_{eff}$) and relaxation times ($\tau_0$) have been determined using the Arrhenius equation (2):[21]

$$\ln(1/\tau) = \ln(1/\tau_0) - U_{eff}/kT \qquad (2)$$

The best fit of equation (2) using the available data produces $U_{eff}$ = 37.8 K and $\tau_0 = 8.2 \times 10^{-6}$ s for **1**, and $U_{eff}$ = 34.5 K and $\tau_0 = 6.7 \times 10^{-6}$ s for **2** (Fig. S11).

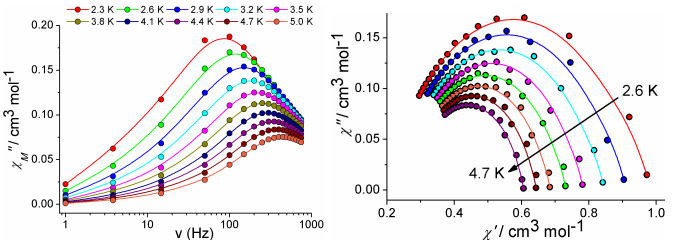


**Fig. 3** Frequency dependency of the out-of-phase ($\chi_M''$) (left) AC magnetic susceptibility plots for complex **1** at 2000 Oe; Cole-Cole plots for complex **1** (right). Solid lines represent the best fit.

Slightly higher energy barriers are found with the electronic structure calculations, which allow the location of the lowest Kramer's doublets (KDs) responsible for the relaxation process (Fig. S12). The spin relaxation mechanisms for both complexes show a plausible pathway via a direct quantum tunneling (QTM) in the ground state. The relaxation through a thermally-assisted QTM via the first excited states seems also possible since the second KDs are found at relatively low energies of 83.8 and 79.9 $cm^{-1}$. On the other hand, the third KD lies much higher in energy (aprox. 1700 $cm^{-1}$) for both complexes, and thus those states are not expected to participate in the spin relaxation process. The computed spin relaxation mechanisms also indicate that the Orbach processes cannot be completely ruled out and can play a significant role under certain conditions.

In order to acquire a deeper understanding of the magnetic relaxation behaviour, the relaxation times have been reassessed considering the different relaxation processes. The two terms in equation (3) represent the strongly field dependent (related to QTM) and weakly field dependent (Raman, Orbach, etc.) processes (kept as constant, *C*, in equation (3)).[22]

$$\tau^{-1} = B_1 / (1+B_2H^2) + C \qquad (3)$$

The relaxation time has been studied starting from its field dependence at 2 K (Fig. S13 (left)) and is well defined by this method. Since the $\tau$ parameter becomes larger for stronger fields (Fig. S13 (left)), the direct term has not been taken into consideration. $\tau_{QTM}$ has been calculated to be $1.36 \times 10^{-4}$ s and $1.18 \times 10^{-4}$ s for **1** and **2,** respectively, using equation (3). These values suggest the presence of substantial contribution of ground state quantum tunneling in the relaxation process, as observed in the electronic structure calculations. The temperature dependence of the relaxation time at 0.2 T was studied (Fig. S13 (right)), including the thermally active Orbach and Raman processes.[22] The relaxation time is well defined by the method with a single power law (equation (4)).

$$\tau^{-1} = \tau_{QTM}^{-1} + bT^n \qquad (4)$$

Values of n = 5.8 and 5.3 are obtained for complexes **1** and **2**, respectively (note that the $\tau_{QTM}$ values have been kept fixed at $1.36 \times 10^{-4}$ s and $1.18 \times 10^{-4}$ s for **1** and **2,** respectively), which are close to the value reported by Colacio *et al.*[23] The Orbach relaxation pathway is not applicable for the studied complexes because the energy barriers obtained from ac susceptibility measurements are lower than the energy gap between the $M_S = \pm 1/2$ and $M_S = \pm 3/2$ doublets. Hence, the combined study of field and temperature dependence of the relaxation time suggests that quantum tunneling is the leading process to relax the magnetization at low temperature. Nevertheless, this relaxation mechanism is directed

by the optical or acoustic Raman processes which elucidate the thermal dependence of the relaxation time.

In summary, this work describes the magnetic anisotropy of the first two pentacoordinate $Co^{II}$ SIMs based on P-donor ligands. The experimental fit of the magnetic data indicates that the square pyramid arrangement of the ligands around the metal center produces positive D values, as confirmed by the electronic structure calculations. Both experimental and computational approaches indicate that the main relaxation process of the magnetization of these compounds is the quantum tunneling through the ground state.

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## Notes and references

†Electronic Supplementary Information (ESI) available: magnetic plots, PXRD, computational details, computed low-lying spin-orbit energy states and magnetic axes are provided.

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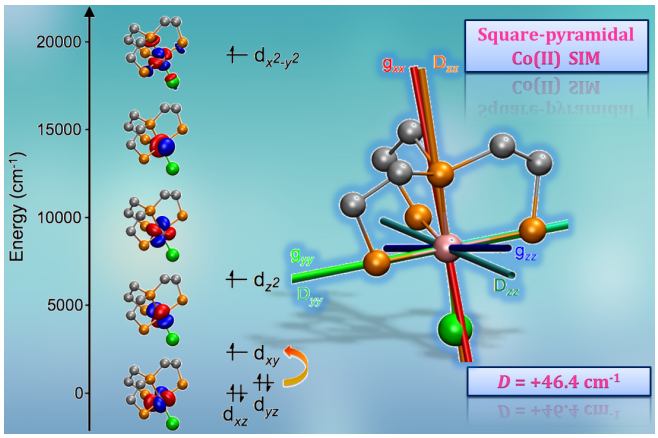


Field induced slow magnetic relaxation behavior has been studied for the first two P-donor ligand-based square-pyramidal $Co^{II}$ complexes with an easy-plane magnetic anisotropy using combined experimental and theoretical studies.