ROYAL SOCIETY OF CHEMISTRY

Journal Name

COMMUNICATION

Single ion magnetic anisotropy in a vacant octahedral Co(II) complex

Amit Kumar Mondal,[a] Jesús Jover,[b] Eliseo Ruiz*[b] and Sanjit Konar*[a]

www.rsc.org/

A rare example of pentacoordinate Co^{II} single-ion magnet based on a *P*-donor ligand with vacant octahedral coordination geometry is reported. Thorough magnetic measurements reveal the presence of field induced slow relaxation behavior with an easy-plane magnetic anisotropy. The combined theoretical and experimental studies disclose that direct and quantum tunneling processes become dominant at low temperature to relax the magnetization, however from the thermal dependence of relaxation time it can be observed that the optical or acoustic Raman processes become important to the overall relaxation process.

Single-molecule magnets (SMMs) have attracted substantial attention over the past few years because of their potential applications in data storage and quantum computing.[1] For SMMs the thermal energy barrier depends on the total spin and the easy axis anisotropy parameter.[2] As a consensus, high magnetic anisotropy has been considered as the most important criteria for constructing better SMMs. Nevertheless, tuning of anisotropy in polynuclear SMMs has been proven to be most challenging task as it depends on numerous factors such as ligand field strength, symmetry of the molecule and spin-orbit coupling. Therefore, considerable efforts have been devoted to develop a better control of the magnetic anisotropy with a new class of molecules, that is, mononuclear SMMs, also known as single-ion magnets (SIMs).[3]

Since the first report of slow magnetic relaxation behavior in a mononuclear Fe^{II} complex in 2010,[4a] transition metal based SIMs have experienced a rapid development.[4] A considerable effort has been directed to design and synthesize transition metal based SIMs with a variety of coordination numbers ranging from two to eight,

and with different geometries.[5] Among transition metal based single-ion magnets, Co^{II} complexes remain fascinating targets because of their non-integer spin ground state, which actually decreases the probability of quantum tunnelling of magnetization (QTM)[6] and also, because of their larger spin-orbit contribution in comparison with Fe^{II} systems. The first report of mononuclear Co^{II} complexes show slow magnetic relaxation are pentacoordinate systems having distorted square-pyramidal geometry with bis(imino)pyridine and thiocyanido ligands.[7] This discovery was followed by further development of Co^{II} based SIMs in various coordinate systems.[5]

Long and coworkers reported the first example of the tetrahedral Co^{II} SIM $[PPh_4]_2[Co(SPh)_4]$ which exhibits ZFS parameter (*D*) = -70 cm^{-1} and effective energy barrier (U_{eff}) = 21 cm^{-1}.[8] After that, various examples of tetrahedral systems have been reported in the literature and a very different ranges of *D* values (-5 to -160 cm^{-1}) and relaxation energy barriers (14 to 230 cm^{-1}) have been observed.[9] These studies showed that the presence of heavier donor atoms such as S, Se, P or I increase the magnetic anisotropy of Co^{II} centers in the resulting complexes.[9] The geometry of the metal centre plays a very important role to influence the magnetic anisotropy and the slow magnetic relaxation behavior in Co^{II} SIMs. For example, in the reported tetrahedral Co^{II} SIM $[NHEt_3]_2[Co(pdms)]$ (pdms = 1,2-bis(methanesulfonamido)benzene), the tight bite angle of the ligand produces a large axial distortion at the Co^{II} center and, as a result large magnetic anisotropy and high energy barrier of 230 cm^{-1} are obtained.[10] Compare to tetracoordinate Co^{II} SIMs, pentacoordinate systems are much rarer.[4b-d] Only a few examples of pentacoordinate Co^{II} SIMs have been reported in the literature and all of them typically adopt square pyramidal or trigonal bipyramidal coordination geometries.[11] Herein, we report the first example of pentacoordinate Co^{II} SIM $[Co(L)_2Cl]\cdot ClO_4$ (**1**, where L = 1,2-Bis(diphenylphosphino)benzene) with a vacant octahedral coordination geometry. The magnetic anisotropy and slow magnetic relaxation behavior of the studied complex has been investigated in details.

The single-crystal X-ray analysis reveals that the complex **1** crystallizes in the orthorhombic *P*ccn space group (Table S1). The

[a] *Department of Chemistry, Indian Institute of Science Education and Research (IISER), Bhopal Bypass Road, Bhauri, Bhopal-462066, India.*
E-mail: skonar@iiserb.ac.in
[b] *Departament de Química Inorgànica i Orgànica and Institut de Recerca de Química Teòrica i Computacional, Universitat de Barcelona, Diagonal 645, E-08028 Barcelona, Spain. E-mail: eliseo.ruiz@qi.ub.es*

molecular structure of complex **1** is shown in Fig. 1. The ligand coordinates to the Co^{II} centre in a bidentate fashion and the geometry at the Co^{II} centre is best described as vacant octahedral. The four equatorial positions are occupied by the four *P*-atoms of the ligands and the axial site is occupied by the chloride ion. The SHAPE analysis[12] of complex **1**, which has been carried out to ascertain the coordination geometry adopted by the Co^{II} centre, reveals that the complex can be best described as vacant octahedral (minimum CShM value of 0.693, Table S3) when compared to the square pyramidal geometry (minimum CShM value of 1.374, Table S3). There are extensive intermolecular hydrogen-bonding interactions in complex **1** which support the construction of supramolecular two dimensional arrangements (Fig. S1-S2 and Table S4).
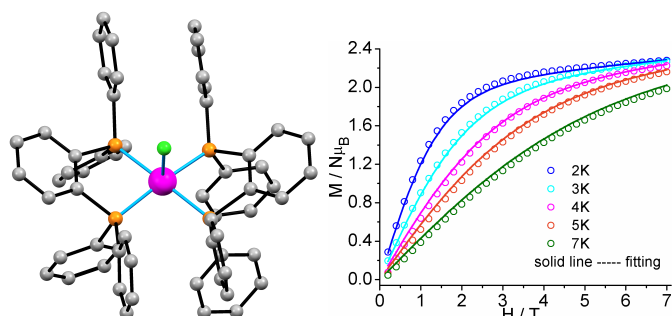
Fig. 1 View of the molecular structure of complex **1** (left), hydrogen atoms are omitted for clarity; *M*/Nμ_B *vs. H* plots for complex **1** at the indicated temperatures (right). The solid lines are the best fit.

The purity of as-synthesized product is confirmed by the good agreement of bulk phase powder X-ray diffraction patterns with the simulated counterparts (Fig. S3). Variable temperature magnetic susceptibility studies have been carried out under direct current (DC) and an applied field of 0.1 T. The $\chi_M T$ value (χ_M = molar magnetic susceptibility) obtained is 2.93 cm^3 K mol^{-1} at room temperature, larger than the 1.87 cm^3 mol^{-1} K corresponding to the spin-only value for high-spin Co^{II} centre. This value falls within the range of 2.1-3.4 cm^3 mol^{-1} K obtained for an anisotropic Co^{II} centre having substantial orbital contribution.[13] The $\chi_M T$ value remains almost constant when decreasing the temperature from 300 to 100 K; below that value $\chi_M T$ decreases and reaches a minima of 1.74 cm^3 mol^{-1} K at 2 K (Fig. S4). The decline of $\chi_M T$ value can be attributed to the inherent anisotropy of the Co^{II} center. The magnetization data (*M*/Nμ_B *vs. H*) have been collected and found to reach the highest value of 2.27 Nμ_B at 2 K and at 7 T (Fig. 1). This experimental value is lower than the theoretical saturation value of 3.3 for an *S* = 3/2 system. The magnetization value does not saturate even at the maximum applied field and all the isotherm magnetization plots do not fall on the same master curve, which indicates the presence of anisotropy in the system (Fig. S4). The spin Hamiltonian shown in eqn (1) has been used to qualitatively estimate the anisotropy parameters

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

In eqn (1), the *D* and *E* terms indicate the single-ion axial and rhombic ZFS parameters, respectively. The PHI program[14] was used to obtain the *D* and *E* parameters by concurrent fitting of $\chi_M T$ *vs. T* and *M*/Nμ_B *vs. H* plots. The best fitting produces *D* = 48.5(3) cm^{-1}, *E* = 0.76(5) cm^{-1} and g = 2.31. The ZFS parameters have also been

obtained with electronic structure CASSCF calculations using the ORCA[15] and MOLCAS[16] packages (Table 1). In both cases the calculations suggest a quadruplet (3/2) ground state. Both computational methods provide positive and similar *D* values and very low *E/D* values. These calculated values are found to be in excellent agreement with those obtained from the fitting of the experimental data. Additionally, similar spin-free excitation energies, Kramers's doublets distribution and g tensors are found in both calculations (Tables S5-S6).

Table 1. ORCA (CASSCF) and MOLCAS (CASSCF+RASSI) computed *D*, |*E/D*| and g-values for complex **1**. ΔE indicates the first excitation energy computed in the spin-free state of the Co^{II} complex. The experimental fitted D_{fit} value is provided for comparison.

|	D_{fit} (cm^{-1})	D_{calc} (cm^{-1})	$|E/D|_{calc}$	ΔE (cm^{-1})	g_{xx}, g_{yy}, g_{zz}
ORCA	48.5(3)	47.0	0.01	324.2	2.29, 2.33, 2.42
MOLCAS	48.5(3)	42.5	0.03	368.2	2.27, 2.34, 2.43

The relative energies of the five 3d orbitals of the Co^{II} centre have been obtained from the ORCA CASSCF calculation, which employs the *ab initio* ligand field theory (AILF) procedure. The d-orbital splitting diagram, shown in Fig. 2, states that the lowest energy transition should take place between the last doubly occupied orbital d$_{yz}$ (or d$_{xz}$) and the first semioccupied orbital d$_{xy}$. This transition, which has the most important contribution to the *D* value, should be positive because the orbitals implied have different |m$_l$| values, as predicted by Gómez-Coca and coworkers.[19]
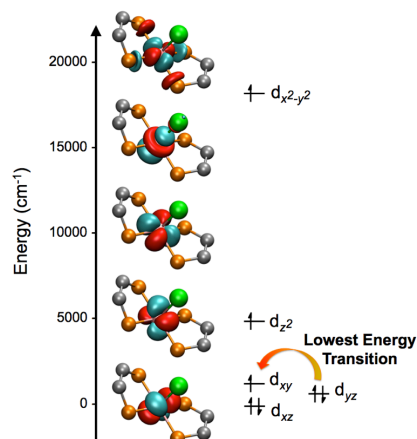
Fig. 2 Co^{II} core and computed d-orbitals for complex **1**. Orbital relative energies are given in cm^{-1}. Color code: Co = pink C = gray, P = orange, Cl = green; outer C and H atoms have been omitted for clarity.

In order to check the magnetic relaxation behavior of complex **1**, alternative-current magnetic susceptibility measurements have been carried out under a 3.5 Oe ac field. Complex **1** did not show any out-of-phase ac signal under a zero dc field. However, the temperature and frequency-dependent ac signals have been observed under a 2000 Oe dc field (Fig. 3 and S5). Additionally, frequency-dependent ac susceptibility data have been used to construct the Cole-Cole plots (Fig. S5), which have been fitted with a generalized Debye model[20] to produce *α* values within the ranges 0.07-0.29, and hence suggesting a narrow distribution of the relaxation time.[21]

The magnetic relaxation dynamics of complex **1** has been extracted from the MOLCAS calculation by computing the corresponding

COMMUNICATION
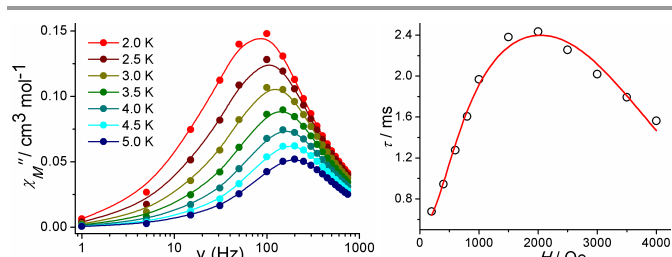
Fig. 3 Frequency dependency of the out-of-phase (χ_M'') (left) AC magnetic susceptibility plots for complex **1** at 2000 Oe; Field dependence of the relaxation time measured at 2 K. The red solid line represents the best fit using Equation (3).

dominant at low temperature to relax the magnetization. On the other hand, the thermal dependence of the relaxation time shows that the optical or acoustic Raman processes become also important to the overall relaxation process at higher temperatures.

Fig. 4 Lowest two Kramer's doublets and *ab initio* computed relaxation mechanism for complex **1**. The thick black lines imply KDs as a function of their magnetic moment along the main anisotropy axis. Red lines indicate the magnetization reversal mechanism. The blue lines correspond to ground state QTM and thermally assisted-QTM via the first excited KD, and green lines show possible Orbach relaxation processes. The values close to the arrows indicate the matrix elements of the transition magnetic moments (above 0.1 an efficient spin relaxation mechanism is expected).[19b]

Kramer's doublets (KDs) (Fig. 4). As may be observed, the spin relaxation mechanisms for the studied complex show a plausible pathway via a direct quantum tunneling (QTM) in the ground state, the matrix elements of the transition magnetic moments to go from state 1- to 1+ are 1.56, much higher than the 0.1 value associated to an efficient relaxation mechanism. The relaxation through a thermally-assisted QTM via the first excited states seems to be at the edge of the operating conditions although the second KDs is found at relatively low energies of 85.1 cm^{-1}. The third KD lies slightly higher in energy (approx. 433 cm^{-1}), and thus that state should not be expected to participate in the spin relaxation mechanism. However, the matrix elements connecting the first and third KDs show that the thermally-assisted QTM relaxation and the Orbach processes should allow the spin relaxation through this pathway as well. Despite the computed results the Raman relaxation process seems to be operating preferentially since the U_{eff} value obtained in the fitting of the Cole-Cole plots, which translates to less than 30 cm^{-1}, is much lower than the thermal barrier obtained in the calculations.

To examine the contribution of different relaxation processes involved in magnetic relaxation behaviour, the field and temperature dependence of the relaxation time have been measured. The first two terms in eqn (2) represent the contributions of the direct and QTM processes, whereas the third term corresponds to the weakly field dependent Raman and Orbach mechanisms and hence kept as constant, *C*, in eqn (2).[22]
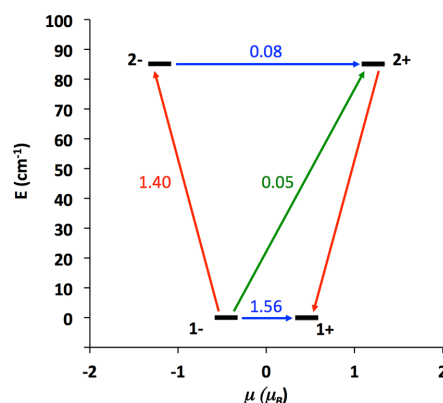
$$\tau^{-1} = AH^4T + B_1 / (1+B_2H^2) + C \qquad (2)$$

As may be observed from the field dependence study of relaxation time at 2 K (Fig. 3 (right)), the fitting of these curves are good and the values of different parameters *A*, B_1, B_2 and *C* have been collected in Table S7. It may be seen that the contribution of the ground state quantum tunneling, which plays the leading role at low field, is suppressed under an external dc field. Additionally the relaxation becomes rapid in higher dc field as the direct process becomes predominant. Additionally, the temperature dependence of τ can be described by including different thermally active processes (Orbach and Raman processes) and a field-dependent mechanism contribution τ_{FDM}^{-1}. The temperature dependence of τ at 2000 Oe was studied and the relaxation time can be well described by eqn (3) with the values of effective energy barrier (U_{eff}) = 40.3 K, relaxation time (τ_0) = 5.8 × 10^{-6} s and *n* = 4.3 (Fig. S5). The obtained *n* value is close to the previously reported value by Colacio *et al.*[23]

$$\tau^{-1} = \tau_{FDM}^{-1} + bT^n + \tau_0^{-1} \exp(-U_{eff}/k_BT) \qquad (3)$$

The detailed study of the field and temperature dependence of the relaxation time indicates that direct and QTM processes become

In conclusion, this paper presents the first example of a pentacoordinate Co^{II} SIM with rare vacant octahedral coordination geometry. Both magnetic measurements and detailed *ab initio* theory calculations reveal that the direct and quantum tunneling processes become dominant at low temperature to relax the magnetization and additionally the optical or acoustic Raman processes become also important to the overall relaxation process for the studied complex.

Notes and references

†Electronic Supplementary Information (ESI) available: synthetic procedure, computational details, PXRD pattern, magnetic plots, additional figures and plots are provided.
§
1   (*a*) L. Bogani and W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179; (*b*) R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer and F. Balestro, *Nature,* 2012, **488**, 357.
2   (*a*) F. Neese and D. A. Pantazis, *Faraday Discussions*, 2011, **148**, 229; (*b*) E. K. Brechin, *Chem. Commun.*, 2005, 5141.
3   (*a*) R. J. Blagg, C. A. Muryn, E. J. L. McInnes, F. Tuna and R. E. P. Winpenny, *Angew. Chem. Int. Ed.*, 2011, **50**, 6530; (*b*) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 14236; (*c*) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nat. Chem.*, 2011, **3**, 538; (*d*) F. Habib and M. Murugesu, *Chem. Soc. Rev.*, 2013, **42**, 3278; (*e*) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110; (*f*) J. J. Le Roy, L. Ungur, I. Korobkov, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2014, **136**,

COMMUNICATION   Journal Name

8003; (*g*) P. Zhang, Y. N. Guo and J. Tang, *Coord. Chem. Rev.*, 2013, **257**, 1728; (*h*) V. E. Campbell, H. Bolvin, E. Rivière, R. Guillot, W. Wernsdorfer and T. Mallah, *Inorg. Chem.*, 2014, **53**, 2598; (*i*) L. Ungur, J. J. Le Roy, I. Korobkov, M. Murugesu and L. F. Chibotaru, *Angew. Chem. Int. Ed.*, 2014, **53**, 4413; (*j*) A. J. Brown, D. Pinkowicz, M. R. Saber and K. R. Dunbar, *Angew. Chem. Int. Ed.*, 2015, **54**, 5864; (*k*) A. K. Mondal, S. Goswami and S. Konar, *Dalton Trans.*, 2015, **44**, 5086; (*l*) S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, *Chem. Sci.*, 2016, **7**, 5181; (*m*) S. Goswami, A. K. Mondal and S. Konar, *Inorg. Chem. Front.*, 2015, **2**, 687.

4   (*a*) W. H. Harman, T. D. Harris, D. E. Freedman, H. Fong, A. Chang, J. D. Rinehart, A. Ozarowski, M. T. Sougrati, F. Grandjean, G. J. Long, J. R. Long and C. J. Chang, *J. Am. Chem. Soc.*, 2010, **132**, 18115; (*b*) G. A. Craig and M. Murrie, *Chem. Soc. Rev.*, 2015, **44**, 2135; (*c*) A. K. Bar, C. Pichon and J.-P. Sutter, *Coord. Chem. Rev.*, 2016, **308**, 346; (*d*) J. M. Frost, K. L. M. Harriman and M. Murugesu, *Chem. Sci.*, 2016, **7**, 2470.

5   (*a*) P. H. Lin, N. C. Smythe, S. I. Gorelsky, S. Maguire, N. J. Henson, I. Korobkov, B. L. Scott, J. C. Gordon, R. T. Baker and M. Murugesu, *J. Am. Chem. Soc.*, 2011, **133**, 15806; (*b*) J. M. Zadrozny, M. Atanasov, A. M. Bryan, C. Y. Lin, B. D. Rekken, P. P. Power, F. Neese and J. R. Long, *Chem. Sci.*, 2013, **4**, 125; (*c*) J. Vallejo, I. Castro, R. R. García, J. Cano, M. Julve, F. Lloret, G. D. Munno, W. Wernsdorfer and E. Pardo, *J. Am. Chem. Soc.*, 2012, **134**, 15704; (*d*) R. Ruamps, R. Maurice, L. Batchelor, M. Boggio-Pasqua, R. Guillot, A. L. Barra, J. J. Liu, E. Bendeif, S. Pillet, S. Hill, T. Mallah and N. Guihery, *J. Am. Chem. Soc.*, 2013, **135**, 3017; (*e*) S. Gómez-Coca, E. Cremades, N. Aliaga-Alcalde and E. Ruiz, *Inorg. Chem.*, 2014, **53**, 676; (*f*) A. K. Bar, C. Pichon and J. Sutter, *Coord. Chem. Rev.*, 2016, **308**, 346; (*g*) Y.-Y. Zhu, M.-S. Zhu, T.-T. Yin, Y.-S. Meng, Z.-Q. Wu, Y.-Q. Zhang and S. Gao, *Inorg. Chem.*, 2015, **54**, 3716; (*h*) C. Mathonière, H.-J. Lin, D. Siretanu, R. Clérac and J. M. Smith, *J. Am. Chem. Soc.*, 2013, **135**, 19083; (*i*) Y. Y. Zhu, C. Cui, Y. Q. Zhang, J. H. Jia, X. Guo, C. Gao, K. Qian, S. D. Jiang, B. W. Wang, Z. M. Wang and S. Gao, *Chem. Sci.*, 2013, **4**, 1802; (*j*) J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese and J. R. Long, *Nat. Chem.*, 2013, **5**, 577; (*k*) R. Herchel, L. Váhovská, I. Potočňák and Z. Trávníček, *Inorg. Chem.*, 2014, **53**, 5896; (*l*) Y.-Z. Zhang, S. Gómez-Coca, A. J. Brown, M. R. Saber, X. Zhang and K. R. Dunbar, *Chem. Sci.*, 2016, **7**, 6519; (*m*) R. Boča, J. Miklovič and J. Titiš, *Inorg. Chem.*, 2014, **53**, 2367; (*n*) D. Brazzolotto, M. Gennari, S. Yu, J. Pécaut, M. Rouzières, R. Clérac, M. Orio and C. Duboc, *Chem. Eur. J.*, 2016, **22**, 925.

6   M. Murrie, *Chem. Soc. Rev.*, 2010, **39**, 1986.

7   T. Jurca, A. Farghal, P. H. Lin, I. Korobkov, M. Murugesu and D. S. Richardson, *J. Am. Chem. Soc.*, 2011, **133**, 15814.

8   J. M. Zadrozny and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 20732.

9   (*a*) M. R. Saber and K. R. Dunbar, *Chem. Commun.*, 2014, **50**, 12266; (*b*) S. Vaidya, A. Upadhyay, S. K. Singh, T. Gupta, S. Tewary, S. K. Langley, J. P. S. Walsh, K. S. Murray, G. Rajaraman and M. Shanmugam, *Chem. Commun.*, 2015, **51**, 3739; (*c*) L. Smolko, J. Černák, M. Dušek, J. Miklovič, J. Titiš and R. Boča, *Dalton Trans.*, 2015, **44**, 17565; (*d*) M. Sundararajan, D. Ganyushin, S. Ye and F. Neese, *Dalton Trans.*, 2009, 6021.

10   Y. Rechkemmer, F. D. Breitgoff, M. van der Meer, M. Atanasov, M. Hakl, M. Orlita, P. Neugebauer, F. Neese, B. Sarkar and J. van Slageren, *Nat. Commun.*, 2016, **7**, 10467.

11   (*a*) F. Habib, O. R. Luca, V. Vieru, M. Shiddiq, I. Korobkov, S. I. Gorelsky, M. K. Takase, L. F. Chibotaru, S. Hill, R. H. Crabtree and M. Murugesu, *Angew. Chem. Int. Ed.*, 2013, **52**, 11290; (*b*) R. Ruamps, L. J. Batchelor, R. Guillot, G. Zakhia, A. -L. Barra, W. Wernsdorfer, N. Guihéry and T. Mallah, *Chem. Sci.*, 2014, **5**, 3418; (*c*) F. Shao, B. Cahier, N. Guihéry, E. Rivière, R.

Guillot, A.-L. Barra, Y. Lan, W. Wernsdorfer, V. E. Campbell and T. Mallah, *Chem. Commun.*, 2015, **51**, 16475; (*d*) A. K. Mondal, J. Jover, E. Ruiz and S. Konar, *Chem. Commun.*, 2017, **53**, 5338; (*e*) A. K. Mondal, J. Jover, E. Ruiz and S. Konar, *Chem. Eur. J.*, 2017, **23**, 12550; (*f*) T. J. Woods, M. F. Ballesteros-Rivas, S. Gjmez-Coca, E. Ruiz and K. R. Dunbar, *J. Am. Chem. Soc.*, 2016, **138**, 16407; (*g*) F. Shao, B. Cahier, E. Rivière, R. Guillot, N. Guihéry, V. E. Campbell and T. Mallah, *Inorg. Chem.*, 2017, **56**, 1104; (*h*) C. Rajnák, J. Titiš, O. Fuhr, M. Ruben and R. Boca, *Inorg. Chem.*, 2014, **53**, 8200; (*i*) A. K. Mondal, T. Goswami, A. Misra and S. Konar, *Inorg. Chem.*, 2017, **56**, 6870.

12   S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell and D. Avnir, *Coord. Chem. Rev.*, 2005, **249**, 1693.

13   F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*; Dover Publications: Mineola, NY, 2008.

14   N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164.

15   F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73.

16   G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady and L. Seijo, *Comput. Matter Sci.*, 2003, **28**, 222.

17   L. F. Chibotaru, L. Ungur and A. Soncini, *Angew. Chem. Int. Ed.*, 2008, **47**, 4126.

18   F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 32997.

19   (*a*) S. Gómez-Coca, E. Cremades, N. Aliaga- Alcalde and E. Ruiz, *J. Am. Chem. Soc.*, 2013, **135**, 7010; (*b*) S. Gómez-Coca, D. Aravena, R. Morales and E. Ruiz, *Coord. Chem. Rev.*, 2015, **289**, 379.

20   (*a*) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341; (*b*) Y.-N. Guo, G.-F. Xu, Y. Guo and J. Tang, *Dalton Trans.*, 2011, **40**, 9953.

21   (*a*) S. Xue, Y. N. Guo, L. Zhao, P. Zhang and J. Tang, *Dalton Trans.*, 2014, **43**, 1564; (*b*) P. H. Lin, T. J. Burchell, R. Clérac and M. Murugesu, *Angew. Chem., Int. Ed.*, 2008, **47**, 8848; (*c*) G. F. Xu, Q. L. Wang, P. Gamez, Y. Ma, R. Clérac, J. Tang, S. P. Yan, P. Cheng and D. Z. Liao, *Chem. Commun.*, 2010, **46**, 1506; (*d*) M. T. Gamer, Y. Lan, P. W. Roesky, A. K. Powell and R. Clérac, *Inorg. Chem.*, 2008, **47**, 6581; (*e*) R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru and R. E. P. Winpenny, *Nat. Chem.*, 2013, **5**, 673; (*f*) E. K. Brechin, J. Yoo, M. Nakano, J. C. Huffman, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 1999, 783; (*g*) E. Colacio, J. Ruiz-Sánchez, F. J. White and E. K. Brechin, *Inorg. Chem.*, 2011, **50**, 7268; (*h*) S.-Y. Lin, L. Zhao, Y.-N. Guo, P. Zhang, Y. Guo and J. Tang, *Inorg. Chem.*, 2012, **51**, 10522; (*i*) I. Oyarzabal, A. R.-Diéguez, M. Barquín, J. M. Seco and E. Colacio, *Dalton Trans.*, 2017, **46**, 4278.

22   M. Atzori, L. Tesi, E. Morra, M. Chiesa, L. Sorace and R. Sessoli, *J. Am. Chem. Soc.*, 2016, **138**, 2154.

23   E. Colacio, J. Ruiz, E. Ruiz, E. Cremades, J. Krzystek, S. Carretta, J. Cano, T. Guidi, W. Wernsdorfer and E. K. Brechin, *Angew. Chem., Int. Ed.*, 2013, **52**, 9130.

Table of Contents

Pentacoordinate Co(II) SIM with Vacant octahedral geometry
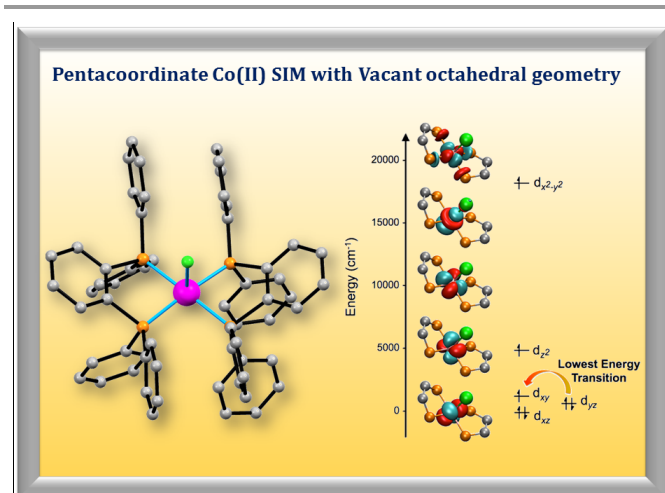
An experimental and theoretical investigation of magnetic anisotropy and single-ion magnetic behavior in vacant octahedral Co(II) complex.