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Chemical Communication

Modulation of Coordination Environment: A Convenient Approach to Tailor Magnetic Anisotropy in Seven Coordinate Co(II) Complexes

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The possibility to control magnetic anisotropy by tuning contribution of second order perturbation to spin-orbit coupling through modulation of coordination environment is investigated. Subtle variation of the coordination environment triggers remarkable deviation in the axial zero field splitting parameter of seven coordinate Co(II) complexes.

Large uniaxial magnetic anisotropy is widely recognized as an essential criterion for enhancement of blocking temperature of magnetization reversal in single molecular magnets (SMM).[1] Even single ion species with strong uniaxial anisotropy are reported to behave as SMM with large energy barrier for magnetization reversal.[2] In view of this, efforts to rationally manipulate the magnetic anisotropy of molecular species have intensified during the last few years.[3] However, parameters governing magnetic anisotropy are poorly understood and intricate control over magnetic anisotropy has remained one of the most formidable challenges.

It is well established that magnetic anisotropy is primarily induced by spin-orbit coupling which is operative as a first order perturbation or as second order perturbation. In transition metal complexes, orbital degeneracy is lifted by crystal field splitting and Jahn-Teller effect. Thus, orbital angular momentum is quenched and this in turn minimizes spin-orbit interaction. Recent studies have established that in low coordinate 3d complexes with a symmetric and weak ligand environment, quenching of orbital angular momentum is significantly reduced as the d-orbitals lie within a narrow energy gap. Increasing magnetic anisotropy by adopting unconventional coordination geometry has emerged as a promising strategy for enhancing energy barrier for magnetization reversal in SMMs.[4-5] For example, due to large uniaxial anisotropy in mononuclear two coordinate Fe(I) complex, record energy barrier for magnetisation reversal has

been observed.[5] However, low coordinate species are stable only under inert atmosphere and this severely limits their possible utility in different applications. In this context, an approach to induce magnetic anisotropy in high coordinate transition metal species is highly desirable.

Contribution to spin-orbit coupling through second order perturbation may occur through spin-orbit interaction of an orbitally non-degenerate ground state with a low lying orbitally degenerate excited state. Thus, even in species with orbitally non-degenerate electronic ground state, there is a possibility to both induce and control magnetic anisotropy by appropriate manipulation of excited state energy levels. This approach allows designing magnetically anisotropic building blocks with higher coordination number. In this regard, seven coordinate pentagonal bipyramidal (PBP) 3d complexes are found to be particularly appealing as a few examples with large uniaxial anisotropy have been already reported.[6-15]

PBP Fe(II) and Ni(II) complexes formed by the planer pentadentate acyclic ligand 2,6-diacetylpyridine bis(benzoyl hydrazone) (dapbhH$_2$) have strong uniaxial anisotropy and associated with characteristic large negative axial zero field splitting parameters (D).[10-16] However, the zero field splitting parameters of Co(II) complexes of dapbhH$_2$ were found to be large positive and all of them show slow relaxation of magnetization under a small applied field. The origin of this large positive D parameter lies in spin-orbit coupling stemming from mixing of the ground electronic level with two excited electronic levels. Thus, in principle it should be possible to control magnetic anisotropy by tuning the mixing of ground electronic state with the excited electronic states. Therefore, it is anticipated that appropriate modulation of the coordination environment can act as a promising approach to control magnetic anisotropy. However, without comprehensive understanding of the electronic states involved in spin-orbit mixing, it is not viable to undertake such investigations. Therefore, systematic studies on coordination environment mediated control of magnetic anisotropy are very rare.[17]

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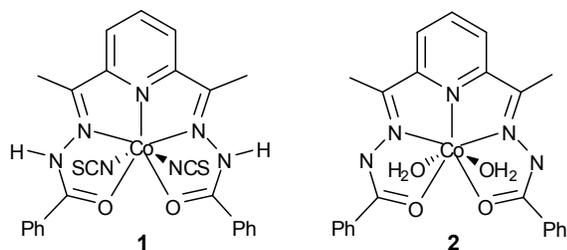
Chart 1: Seven coordinate Co(II) complexes 1 and 2.

Figure 2: Temperature dependence of $\chi_M T$ between 2-300K for **1** (left) and **2** (right). The circles represent experimental data and the solid line represent best fit obtained by using PHI program.

Two new seven coordinate Co(II) complexes, [Co(dapbhH$_2$)(SCN)$_2$].3H$_2$O (**1**) and [Co(dapbh)(H$_2$O)$_2$] (**2**) were prepared starting from the parent compound [Co(dapbhH$_2$)(H$_2$O)(NO$_3$)]NO$_3$. The dapbhH$_2$ ligand is in neutral form in compound **1** while in compound **2**, the two hydrazide N-H protons are abstracted and the ligand is in dianionic form. Compound **1** crystallizes in a monoclinic P2$_1$2$_1$2$_1$ space group and compound **2** crystallizes in orthorhombic Cmc21 space group. Representative view of the molecular structures in compound **1** and **2** are depicted in Figure 1. As in case of the precursor complex, the central Co^{2+} atom in **1** and **2** are heptacoordinated with five of its coordination sites occupied by donor atoms from the planer pentadentate dapbh ligand. In compound **1**, the two of the axial positions are occupied by N atoms from thiocyanate ligands and thus the Co^{2+} center acquires distorted pentagonal bipyramidal geometry with a N$_5$O$_2$ coordination environment. In **2**, the two axial positions are occupied by two H$_2$O groups and the Co(II) centre has N$_3$O$_4$ coordination environment. Continuous shape analysis using shape software reveals that the geometry around Co^{2+} center in **1** and **2** are Johnson's pentagonal bipyramidal.[18] The five donor atoms from the pentadentate ligand form an ideal planer structure as the sum of the chelate angles and the bite angle measures 360.22° and 360.33° in **1** and **2** respectively. Careful analysis of the structural parameters within the dapbh-H$_2$ in **1** and **2** reveal good agreement with structural parameters observed in PBP Co(II)-dapbhH$_2$ complexes reported earlier.[12-14] However, the axial bonds in **1** (2.078(2) Å and 2.120(2) Å) are relatively shorter as compared to the axial bond lengths (2.097-2.793 Å) reported for other Co-dapbhH$_2$ complexes. The shorter axial bonds in **1** can be attributed to the better σ-donating ability of the SCN$^-$ ligand as compared to the axial ligands in other reported seven coordinate Co-dapbh-
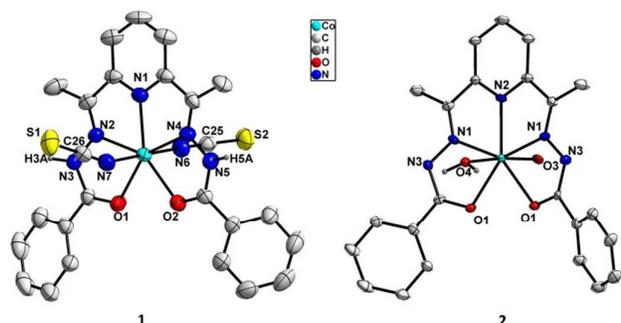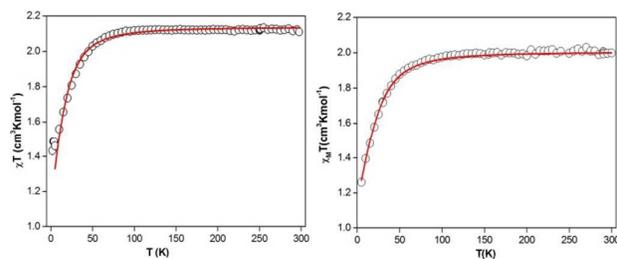
H$_2$ complexes. It is pertinent to note here that due to the presence of C$_2$ symmetry in **2**, the structural parameters observed for one half of the equatorial plane are identical for the other half. Thus, the equatorial coordination environment observed in **2** is more symmetric as compared to other PBP Co(II)-dapbhH$_2$ complexes reported so far. Moreover, the intermolecular H-bonding mediated packing diagram in **1** and **2** are significantly different as compared to the packing observed in earlier reported Co(II)-PBP complexes. In case of **1**, a helical one dimensional chain like packing is observed while in case of **2**, a zig-zag one dimensional chain like arrangement is observed (Figure S1 and S2).

Magnetization studies on polycrystalline samples of **1** & **2** were performed under a constant static field of 500 Oe between 2-300 K. Figure 2 depicts the variation of $\chi_M T$ between 2-300 K for **1** and **2** respectively. The expected $\chi_M T$ product for a magnetically isolated Co^{2+} center considering S = 3/2 and g = 2.0 is calculated to be 1.87 cm^{3}Kmol^{-1}. However at 300 K, the $\chi_M T$ product for **1** and **2** are found to be 2.11 and 1.93 cm^{3}Kmol^{-1} respectively, which are slightly higher as compared to the calculated value for an isotropic S = 3/2 center with g = 2.0. On lowering the temperature, $\chi_M T$ product does not change appreciably until 50 K for both **1** and **2**. However, on further cooling, $\chi_M T$ drops abruptly to reach a minimum of 1.43 cm^{3}Kmol^{-1} and 1.01 cm^{3}Kmol^{-1} at 2K for **1** and **2** respectively. Deviation of $\chi_M T$ product from the expected value and its rapid decrease at low temperature regime indicate the presence of significant orbital magnetic moment in PBP Co(II) complexes. Good quality fitting of the temperature dependence of $\chi_M T$ plots are obtained by using PHI program and it yields g = 2.13 for **1**; g = 2.06 for **2**.[19] Figure 3 depicts the field dependence of magnetization for **1** and **2** at 2, 5 and 10 K along with the calculated value for 2K for an isotropic system.

Figure 1: Molecular structure of **1** and **2** as thermal ellipsoid plot with 50% probability. Aromatic and aliphatic hydrogen atoms are omitted for clarity.
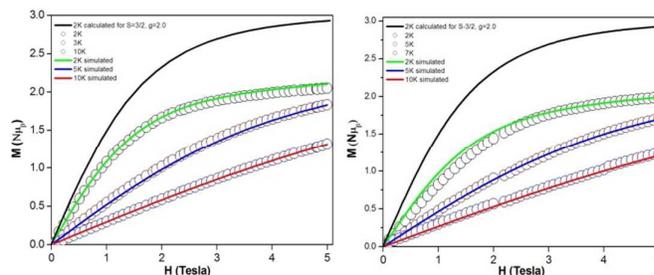
Figure 3: Field dependence of magnetization between 0-5 Tesla for 1 (left) and 2 (right) along with calculated magnetization behaviour for an isotropic S = 3/2 system. Circles represent experimental value and the solid lines are best fits obtained by using PHI program.

Although with increase of field strength, magnetization increases linearly initially, saturation magnetization Ms = 3 μB (for S = 3/2 and g = 2.0) was not achieved even at a field strength of 5 Tesla. Moreover, the calculated magnetization behaviour for an isotropic S=3/2 system at 2K deviated considerably from the experimental magnetization behaviour in both cases. Further, the reduced magnetization plots of both **1** and **2** at 2K, 5K and 10K do not superimpose on each other (Figure S7 and S8). The above observations unambiguously establish the presence of significant magnetic anisotropy in pentagonal bipyramidal Co^{2+} complexes, **1** and **2**. A spin Hamiltonian of equation 1 can be utilized to qualitatively describe magnetic anisotropy:

$$\hat{H} = D/3\ \hat{O}_2^0 +\ E\hat{O}_2^2 + g\mu_B\hat{S} \times B \qquad (1)$$

where μ_B, E, $\hat{S}$ and B represent Bohr magneton, rhombic ZFS parameter, spin and magnetic field vectors respectively while $\hat{O}_k^q$ is the equivalent operator as described by Stevens et al.[20] The best fits of the field dependant magnetization plots obtained by using PHI program yields D = 15.9 cm^{-1}, E = 0.0 cm^{-1} and g = 2.14 for **1**; D = 13.1 cm^{-1}, E = 0.0 cm^{-1} and g = 2.06 for **2**. The D values obtained for **1** and **2** are significantly lower than the D values reported for other PBP Co(II) complexes (Table 1). DFT calculations using the coupled perturbed method reveal ZFS parameters for **1** and **2** to be 14.6 cm^{-1} and 12.4 cm^{-1} respectively (Table 1).[21] These values are in good agreement with the experimental values obtained by fitting magnetization plots. Further, the DFT calculated decomposed excitations contributing towards D_{SOC} are listed in Table S5.

Table 1: DFT calculated spin-orbit and spin-spin contributions to total D-tensor values of **1** and **2**.

Complex	Total D-tensor (theoretical) (cm^{-1})	D_{SOC} (cm^{-1})	Dss (cm^{-1})
1	14.66328	12.353	2.32034
2	12.48633	10.251	2.2352

The smaller positive D parameter observed in compound **1** and **2** in comparison to other reported PBP Co(II) complexes can be explained in light of theoretical calculations. It is well established that the large positive D parameter in pentagonal bipyramidal Co(II) complexes originates from spin-orbit mixing of the ground quartet state with three excited state, two being quartets and the other is a doublet.[13] The quartet excited state with highest contribution to D represents an electronic configuration obtained by promoting an electron from the d_{xz} or d_{yz} orbital to the d_{z^2} orbital (Figure 4). On increasing the energy of the d_{z^2} orbital by employing better σ-donor apical ligands, the spin-orbit interaction between the ground quartet state with this excited quartet state is reduced. Thus the better σ-donor apical ligands in compound **1** reduce the positive D parameter by reducing the contribution of second order perturbation in spin orbit coupling. Careful analysis of earlier reported seven coordinate Co(II)-dapbhH$_2$ complexes revealed an identical underlying trend. The PBP complex, [Co(dapbhH$_2$)(im)$_2$] (im = imidazole) with a better σ-donor axial ligand has a relatively smaller axial ZFS parameter (D = 24.8 cm^{-1}) as compared to the complexes containing H$_2$O, NO$_3^-$, Br$^-$ and I$^-$ as axial ligands (D ≈ 30 cm^{-1}).

Table 2: D parameter of different PBP Co(II) complexes

Complex	D (cm^{-1})	References
[Co(bpy)$_{1.5}$(NO$_3$)$_2$]$_n$	68	6
[Co(L$_1$)Cl$_2$]	40	9
[Co(dapbhH$_2$)(H$_2$O)(NO$_3$)](NO$_3$)	32.4	13
[Co(dapbhH$_2$)I(NO$_3$)]I	30	15
[Co(dapbhH$_2$)Br(NO$_3$)]Br	30	15
[Co(L$_2$)](ClO$_4$)$_2$	26	7
[Co(L$_2$)](NO$_3$)$_2$	25	7
[Co(dapbhH$_2$)(im)$_2$]	24.8	14
[CoL$_{N5}$(H$_2$O)$_2$]Cl$_2$	24.6	14
[Co(L$_3$)](ClO$_4$)$_2$	23.1	7
[Co(dapbhH$_2$)(SCN)$_2$] (**1**)	15.9	This work
[Co(dapbh)(H$_2$O)$_2$] (**2**)	13.1	This work

bpy = 4,4'-bipyridine; L$_1$ = 3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene; L$_2$ = N,N'-bis(2-aminobenzyl)-1,10-diaza-15-crown-5; L$_{N5}$ = 2,13-dimethyl-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaphane-2,12-diene; L$_3$ = N,N'-bis(benzimidazol-2-ylmethyl)-1,10-diaza-15-crown-5

Another important contribution to the positive D parameter in PBP Co(II) complexes arise from spin orbit mixing of the ground quartet with an excited doublet state.[13] This doublet excited state refers to an electronic state obtained by either promoting an electron from d_{xy} to $d_{x^2-y^2}$ orbital or from $d_{x^2-y^2}$ to d_{xy} orbital (Figure 4). The energy gap between the d_{xy} and $d_{x^2-y^2}$ reduces when a symmetric equatorial field is applied. In compound **2**, the apical ligands are poor σ-donor and therefore significant spin-orbit mixing of the ground quartet with the excited quartet level described earlier is expected. However, the dapbhH$_2$ ligand in **2** is in dianionic form and both the anionic charges are conjugated. The metal-donor atom bond distances within the equatorial plane are found to be relatively shorter as compared to bond distances reported for other Co-dapbhH$_2$ complexes (Table S4). Therefore, the excited doublet state is expected to lie at higher energy. Moreover, due to the presence of C$_2$ symmetry, the equatorial dapbh ligand is structurally symmetric. This enforces a more symmetric equatorial coordination environment as compared to neutral dapbhH$_2$ ligand while the d_{xy} and $d_{x^2-y^2}$ lie within a narrow energy gap. Consequently, the positive contribution to D parameter originating from spin-orbit interaction of ground quartet state with excited doublet state is significantly reduced in **2**.
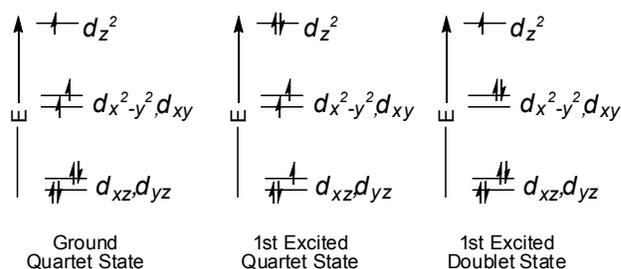

Figure 4: Electronic arrangement in the ground quartet, 1st excited quartet and 1st excited doublet states.

Results presented herein support earlier theoretical findings that the second order spin-orbit perturbation mediated control of magnetic anisotropy is possible by appropriate modulation of coordination environment.[13] It is observed that either by employing a better σ-donor apical ligand or by using a symmetric pentadentate equatorial ligand, it is possible to significantly decrease the positive contribution to D parameter. Earlier approaches to modulate axial ZFS parameter through modification of coordination environment primarily relied on covalent character of metal-ligand linkages.[17] However, for PBP Co(II)-dapbhH$_2$ complexes reported so far, no such trend based on hard/soft character of the donor ligands is observed.[15] Instead, the present approach of modulating magnetic anisotropy is based on tuning the contribution of second order perturbation to spin-orbit coupling in a predetermined fashion by modifying the energy of the excited levels. Thus, even in high coordinate species with no first order perturbation to magnetic anisotropy, there is a possibility to induce magnetic anisotropy by appropriately modulating the coordination environment. For example, in PBP Ni(II) complexes, reducing the contribution of SOC coupling of those excited states which contribute positive D parameters, may lead to further lowering of the overall D. Thus, proliferation of the present approach is anticipated to open fascinating frontiers for synthetic chemist to induce magnetic anisotropy in high coordinate species.

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