CHAPTER 5

AN INVESTIGATIVE STUDY FOR ESTIMATION OF ZERO FIELD SPLITTING AND HYPERFINE COUPLING IN Co(II) COMPLEXES USING *AB INITIO* CASSCF METHOD

INTRODUCTION

Cobalt is another d-block transition metal which is on focus regarding the high-spin transition metal complexes acting as SMMs, iron [1,2], manganese [3,4] and nickel [5] being the other widely used transition metals. Majority of the high-spin Co(II) complexes studied are of tetrahedral or pseudotetrahedral coordination [6–8]. Higher coordination with five or six is limited and they are of square-pyramidal, trigional-bipyramidal, octahedral as well as trigonal prismatic geometry. It is interesting to note that usually the complexes with pseudotetrahedral geometry exhibit the highest spin-reversal barriers with U_{eff}=118 cm^{-1} [9]. The first Co(II) complex showing U_{eff}=62 cm^{-1} was a distorted pseudotetrahedral with solely an *N, O*-donor environment.

Section 5A Prediction of D-tensor and hyperfine coupling in [CoN_2X_2] and [$Co(PPh_3)_2X_2$] using CASSCF method

5A.1 Theory

In this work also we have studied Co(II) complexes with N and P donor environment along with halide contribution to the metal ion. The D-tensor and the hyperfine coupling are predicted for these complexes. D enters for S > 1/2 systems and is the zero field splitting constant which depends on the exact symmetry of the paramagnetic center. The hyperfine coupling tensor, A, describes the interaction between the unpaired electron(s) in the molecular system and the magnetic moments of the nuclei.

Co(II) in high-spin state with tetracoordinate environment is taken for study. The complexes are as follows: [$Co(quin)_2Cl_2$] **(1)**, [$Co(quin)_2Br_2$] **(2)**, [$Co(PPh_3)_2Cl_2$] **(3)** and [$Co(PPh_3)_2Br_2$] **(4)**, where the abbreviation quin is quinolone. We have computed the D-tensor and the hyperfine coupling constants of these complexes. The theory of D-tensor was discussed in earlier chapters. In case of hyperfine coupling the total hyperfine tensor (A_{Tot}) has contribution both from Fermi contact and spin dipolar hyperfine interaction.

The isotropic term is actually the combination of the Fermi contact term and the pseudo-contact term which is actually the spin-orbit correction term [10].

$$A_{\mu\vartheta}^{A} = A_{\mu\vartheta}^{(A;c)} + A_{\mu\vartheta}^{(A;d)} + A_{\mu\vartheta}^{(A;SO)}$$

The spin Hamiltonian (SH) is $\hat{H}_{HFC} = \hat{S}A^{A}\hat{I}^{(A)}$. Here $\hat{S}$ is the operator of the spin of the ground state.and $\hat{I}$ is the nuclear spin orperator of the corresponding nucleus which is taken as nucleus `A`. When we consider an orbitally non-degenerate many-electron ground state of the system represented by a set of 2S+1 states $|0SM\rangle$ we can calculate the isotropic and dipolar parts of the hypeferfine coupling as

$$A_{\mu\vartheta}^{(A;c)} = \delta_{FC}\frac{8\pi}{3}\frac{\alpha}{2}\frac{1}{S}g_e\beta_N g_N^{(A)}\langle 0SS|\sum_i S_{zi}\delta(r_{iA})|0SS\rangle$$

And

$$A_{\mu\vartheta}^{(A;d)} = \frac{\alpha}{2}\frac{1}{S}g_e\beta_N g_N^{(A)}\langle 0SS|\sum_i S_{zi}\, r_{iA}^{-5}\{\delta_{PC}r_{iA}^{2} - 3r_{iA,\mu}r_{iA,\vartheta}\}|0SS\rangle$$

Where, g_e is the free electron g-tensor, α is the hyperfine structure constant, β_N is the nuclear mageton, $g_N^{(A)}$ is the nuclear g-value of A nucleus, r_{iA} is the $|r_i - R_A|$ with r_i being the position of the i^{th} electron and R_A is the position of the A^{th} nucleus.

The value for $A_{\mu\vartheta}^{(A;c)}$ and $A_{\mu\vartheta}^{(A;d)}$ is correct only if the Hellmann-Feynman theorem is satisfied.

Thus the isotopic and dipolar hyperfine coupling constants are given by the perturbing operators as below

$$\hat{H}_{SI}^{(c)} = \frac{\alpha}{2}\frac{8\pi}{3}g_e\beta_N\sum_A g_N^{(A)}\sum_i s_i\hat{I}^{(A)}\delta(r_{Ai})$$

$$\hat{H}_{SI}^{(d)} = \frac{\alpha}{2}g_e\beta_N\sum_A g_N^{(A)}\sum_i \frac{s_i\hat{I}^{(A)}}{r_{iA}^{3}} - 3\frac{(s_i r_{iA})(\hat{I}^{(A)}r_{iA})}{r_{iA}^{5}}$$

where $\hat{s}_i$ is spin operator for the ith electron and $\hat{I}^{(A)}$ is the spin operator for the Athnucleus.

The hyperfine interaction in Co(II) ion is characterized by interaction between unpaired electrons and the nuclear spin in Co.

5A.2 Computational Details

We have used the Dmol^3 program package for optimization. Geometry optimizations were done in DFT level using the TZVPP basis set for the cobalt ion, dunning-DZP for the halide ions and SV basis set for the smaller atoms like carbon, hydrogen etc. The functional used is B3LYP. The single point calculations for the D-tensor were carried out in the *ab initio* CASSCF method (Complete Active Space Self-Consistent Field Method). We have preferred the CASSCF method in this work as it is fully variational which renders the calculation of analytical gradients very easy.

CASSCF is a multiconfigurational SCF method. In this method the orbitals are categorized into three subspaces: (i) the doubly occupied internal orbitals in all configuration state function (CSFs), (ii) the partially occupied or the active orbitals and (iii) the external virtual orbitals which are empty in all CSFs. A CASSCF(N,M) wavefunction is the one where N denotes the number of electrons in active orbitals and M is the number of active orbitals. It is considered that all the spin eigen functions for N-electrons in the M orbitals are included in the configuration interaction step. Also the energy is made stationary with respect to variations in the MO and CI coefficients. For any configuration the unpaired electrons may possibly be coupled into various ways resulting in total spin S. a configuration state function is actually a given linear independent spin-coupling inside a given configuration. For an open-shell system with N number of unpaired electrons and spin being S we have

$$f_N^S = \binom{N}{\frac{1}{2}N - S} - \binom{N}{\frac{1}{2}N - S - 1}$$

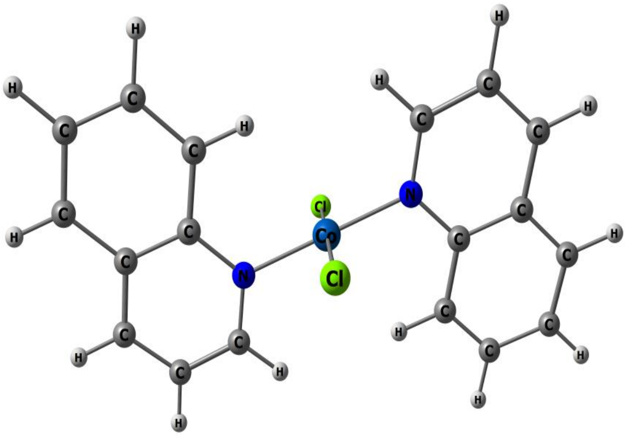
A system with spin as S, there are *2S+1* magnetic sublevels *M=S, S-1, ….–S.* here all the sublevels are degenerate as long as the Hamiltonian of the system is spin-independent. For a non- relativistic approach M=S is chosen for each of the states. Since S and M being quantum numbers, the electronic levels of a given system is identified according to the irreducible representations (irrep) of the point group. Though CASSCF weavefuntions are reasonably elaborate, they are still self-consistent wavefunctions. The active electrons experience the average electric field exerted by the metal nucleus and the other core-electrons and electrons of the ligand. CASSCF wavefunctions are the suitable one for this because they have the proper symmetry of the Hamiltonian in terms of spin symmetry and space. Also their number equals to the number of possible ligand field excited states. Unlike in density functional method symmetry generated states may not be formed.

The Co(II) ion in these four complexes has d^7 configuration. The wavefunction is CASSCF(7,10) where there are 7 electrons in active orbitals and 10 active orbitals. All the 3d and 4d orbitals of the cobalt atom are considered. This (7,10) active space is used to calculate all the states arising from a d^7 configuration. For connection between ligand field theory and quantum chemistry, the orbitals in the active space must be predominantly of metal d-character. Here we have ensured this by selecting proper MOs as an initial guess. It is taken care of that the active orbitals are dominated to a significant extent by the basis functions of the metal d-character. In our case of using ORCA for performing the CASSCF method, it has the advantage that it is allowed to average over any number of states for any number of irreps and multiplicities. This is imperative because optimization of each irrep or multiplicity individually may result in several sets of molecular orbitals that are orthonormal within their own set but not orthonormal within different sets.

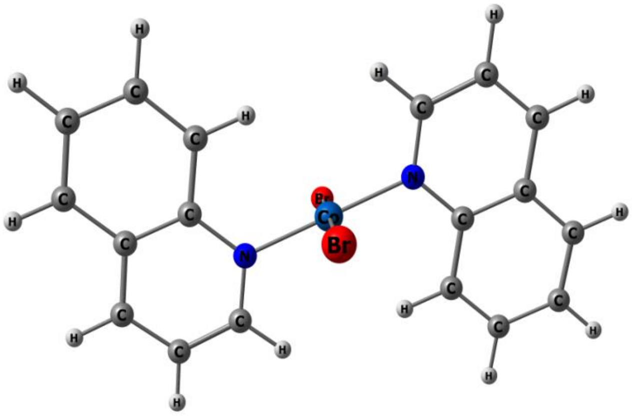
In the single point calculation for the magnetic properties the same basis sets and functional is used as in the case of optimization. A quasi-degenerate perturbation theory was used for the prediction of the zero-field splitting parameter ZFS. This perturbation theory utilizes a Breit-Pauli approximation form with a spin-orbit coupling operator (SOMF).

Unlike the D-tensors for the complexes which were calculated using the *ab inito* method, we have predicted the hyperfine coupling using the DFT method. The *ab initio* method for calculation of the hyperfine has not produced satisfactory results. Hence only DFT calculations were done in this regard. There are several studies where DFT is the sole method utilized for calculation of hyperfine coupling constant (HFC) [11–15].

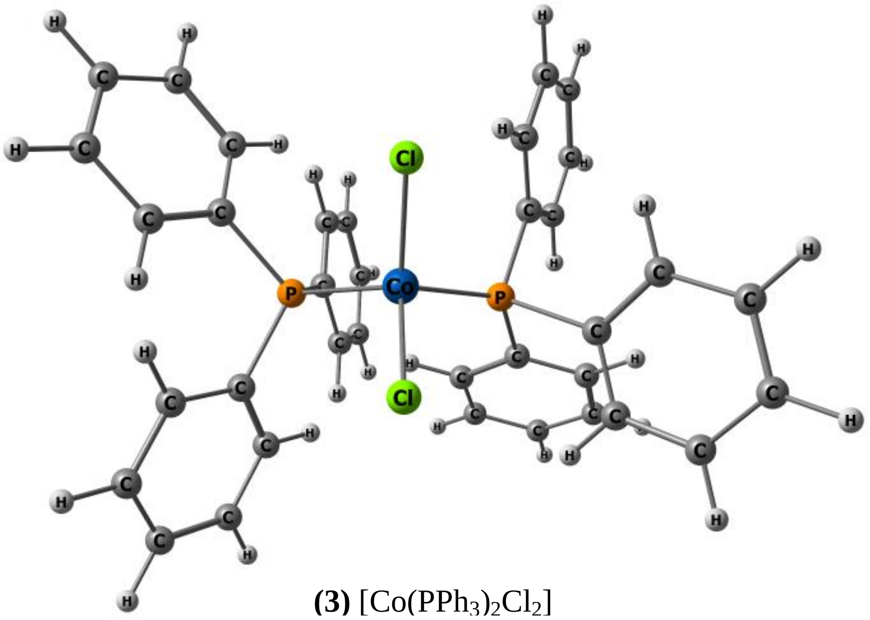
5A.3 Results and discussion



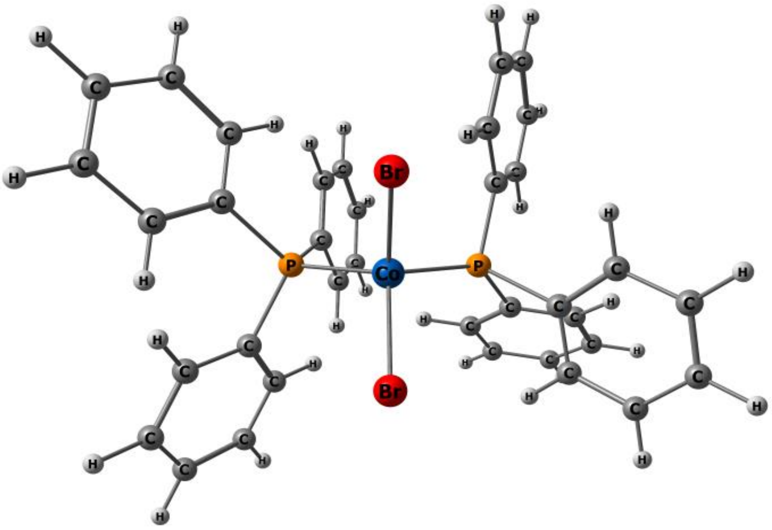
(1) [Co(quin)$_2$Cl$_2$]



(2) [Co(quin)$_2$Br$_2$]



(3) [Co(PPh$_3$)$_2$Cl$_2$]



(4) [Co(PPh_3)$_2$$Br_2$]

Figure 5A.1: Optimized geometries of the Co(II) complexes

Table 5A.1: Calculated D-tensors by *ab initio* method

Sl. No	Name of the Complex	Theoretical D-tensor (in cm^{-1})
(1)	[Co(quin)$_2$$Cl_2$]	6.2
(2)	[Co(quin)$_2$$Br_2$]	7.4
(3)	[Co(PPh_3)$_2$$Cl_2$]	-14.8
(4)	[Co(PPh_3)$_2$$Br_2$]	-12.5

Table 5A.1 shows the D-tensors in the four complexes by performing *ab initio* CASSCF methods. The quinoline containing complexes have positive D-tensor values. The positive D-tensor supports the recent reports of angular dependence of the zero-field splitting in case of a pseudotetrahedral environment [16,17].

The phosphine containing complexes [Co(PPh_3)$_2$$X_2$] have negative D-tensor values. There is successive increase in the magnitude of D while coming from [Co$N_2$$X_2$] to [Co($PPh_3$)$_2$$X_2$]. This trend is similar to that observed in TpNiX series (D = +3.93, 11.43, 22.81 cm-1, for X = Cl, Br, I, respectively). This was found so due to ligand spin-orbit coupling contribution which is based on the CASSCF calculations [18,19].

The Co(II) complexes with d^7 electronic configuration has $^4A_2$ ground state and $^4T_2$ and $^4T_1$ excited states when they are tetrahedrally coordinated. The $^4T_2$ state is split into $^4B_2$ and ^4E terms since there is deviation from the ideal tetrahedral geometry. Hence there is mixing of these two terms with the $^4A_2$ ground state term, thereby resulting in mixing between the two lowest quartet states. Hence there is significant magnetic anisotropy by spin-orbit coupling in the [Co(PPh$_3$)$_2$X$_2$] complexes. The significant D values is attributed to the relatively low-lying excited states in case of these tetrahedrally coordinated geometries, that enhances the second order perturbations of the ground state via spin-orbit coupling. Due to the increased ligand spin-orbit coupling contribution from nitrogen to heavier phosphorus, the present trend of increased magnitude of the D-tensor is observed. The corresponding ligand field strength differences can also be another factor in this regard.The greater magnitude of the D-tensor in the [Co(PPh$_3$)$_2$X$_2$] complexes implies large energy gaps between the $\pm {}^3/_2$ and $\pm {}^1/_2\, M_S$ levels for spin reversal.

The spin polarization effect of the Co atom plays a significant role in prediction of the hyperfine coupling constant (HFC). At the point of its corresponding nucleus the isotropic hyperfine coupling is directly proportional to the spin density. Also we can say that the core shell spin polarization contributions to the isotropic HFC have been found to be proportional to the spin population in the 3d orbital of Co(II) ion. And they are comparatively independent of other details of the bonding. However the valence shell spin polarization has large contribution towards both isotropic and dipolar HFC. This is the reason that in these complexes there are mixing of the split excited state term with the $^4A_2$ ground state term. The HFCs are significant as compared to other transition metal and heteroatom ligand containing complexes. Table 5A.2 shows the calculated A_{Tot} and its contribution from isotropic and spin-dipolar terms.

Table 5A.2: Calculated hyperfine coupling constant, A_{Tot}

Sl. No	**Complexes**	**Isotropic hyperfine coupling contribution, (A_{iso}) (in MHz)**	**Spin dipolar hyperfine coupling contribution, (A_{dip}) (in MHz)**	**Total hyperfine coupling constants (A_{Tot}) (in MHz)**
(1)	$[Co(quin)_2Cl_2]$	-21.5	-15.8	-37.3
(2)	$[Co(quin)_2Br_2]$	-18.2	-10.2	-28.4
(3)	$[Co(PPh_3)_2Cl_2]$	-36.8	-29.6	-66.4
(4)	$[Co(PPh_3)_2Br_2]$	-16.9	-11.4	-28.3

The density functional calculations based on perturbational methods may overestimate or underestimate the isotropic effect depending on the type of functional used. Here we have used B3LYP functional. When we used the hybrid functional it was seen that the A_{iso} is overestimated for these complexes.

We can safely conclude that in these types of electronic configurations *ab initio* CASSCF method is the most suitable one because in DFT the second-order and spin dipolar contributions are underestimated. In such cases DFT shows the predomination of the Fermi contact contribution. We can see that for heavier ligands and higher ligand spin densities, the influence of the spin-orbit contribution to the hyperfine coupling is significant. This is in agreement with the experimental observations. Hence for lighter ligands the contribution from the SOC part is negligible and the basis set at the non relativistic level gives fairly small spin-orbit contribution. From the Lüwdin spin density which is calculated along side, it is evident that it is as large as 15-18% on each of the phosphorus, i.e. in the phosphine containing complexes. So this ligand carries significant spin density and hence there is reasonable approximation towards the ligand hyperfine coupling.

Section 5B Study of D-tensors in seven coordinated Co(II) complexes

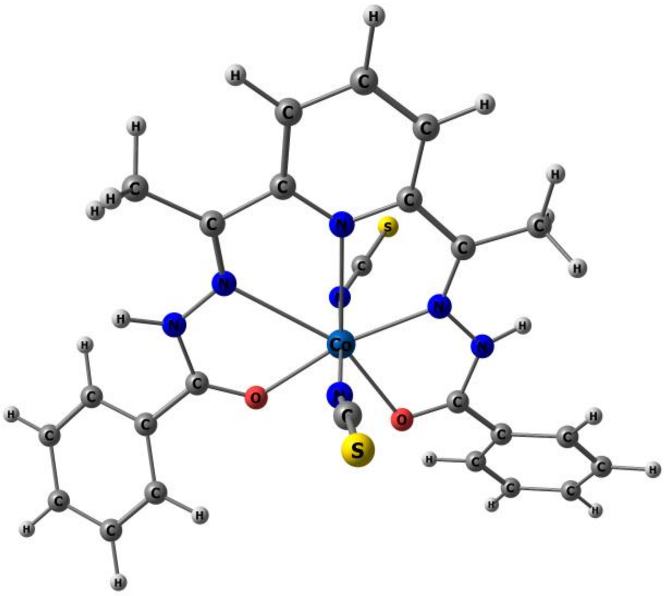
5B.1 Theory

We have theoretically calculated the D-tensors in two new seven coordinate Co(II) complexes, [Co(dapbhH_2)-$(SCN)_2$].$3H_2O$ **(5)** and [Co(dapbh)$(H_2O)_2$] **(6)** which were experimentally studied by Nayanmoni Gogoi *et.al.* [20]. The dapbh ligand stands for diacetylpyridinebis(benzoylhydrazone). The D-tensor values of these two dapbhH_2 complexes were found to be positive with large magnitude and this is found to be due to slow relaxation of magnetization when the applied magnetic field has insignificant strength. We have tried to tailor the magnetic anisotropy in these two systems by modulating the coordination environment. The large magnitude of positive D-tensor is due to the mixing of ground electronic states with the two excited electronic states. Thus by controlling this mixing of electronic levels the magnetic anisotropy of transition metal complexes can be manipulated.

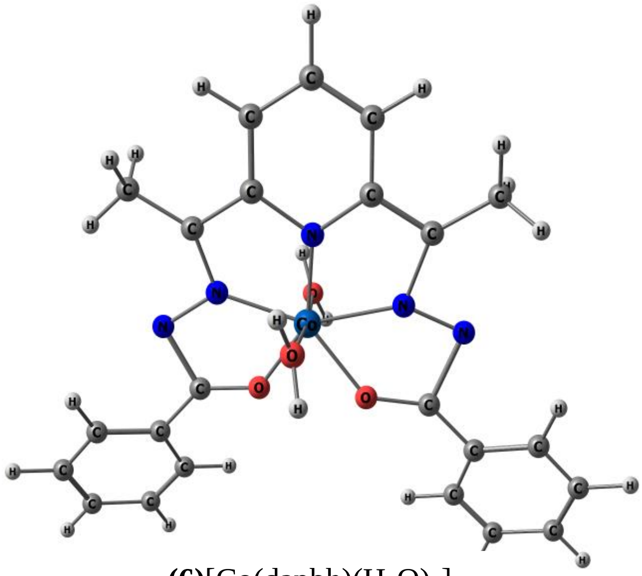
5B.2 Computational Details

DFT level single point calculations were carried on the experimental structures using the ORCA program package [21]. For the transition metal centre, i.e. Co(II) ion Stuttgart/Dresden ECPs (SDD) basis sets and the def2-TZVP Ahlrichs basis set for Coulomb fitting, i.e. def2-TZVP/J is used[22]. For all other atoms def2 basis set of the Ahlrich group along with TZVP basis set was used [23]. A hybrid DFT functional B3LYP was used for all DFT calculations [24]. Since both the complexes are open shell systems with spin multiplicity greater than 1, unrestricted Kohn-Sham (UKS) wavefunction was used. To be on the safe side of SCFconvergence of DFT calculation, *NoFinalGrid* keyword and spin-orbit operator based on mean-field approach are applied. For calculating contribution of spin-orbit coupling to the D-tensor, Coupled-Perturbed (CP) method is used as it uses revised pre-factors for the spin-flipterms. Meanwhile for evaluating spin-spin contribution to D tensor, Breit-Pauli type operatoris used along with canonical orbitals for the spin-density of the system.

5B.3 Results and discussion



(5)[Co(dapbhH_2)-$(SCN)_2$].$3H_2O$



(6)[Co(dapbh)$(H_2O)_2$]

Figure 5B.1: Optimized geometries of [Co(dapbhH_2)-$(SCN)_2$].$3H_2O$ **(5)** and [Co(dapbh)$(H_2O)_2$]**(6)** complexes.

Table 5B.1: DFT calculated spin-orbit and spin-spin contributions to total D-tensor values of **(5)** and **(6)**

Sl. No.	**Complexes**	**Total D-tensor (Experimental) (in cm^{-1})**	**Total D-tensor (Theoretical) (in cm^{-1})**	**D_{SOC} (in cm^{-1})**	**D_{SS} (in cm^{-1})**
(5)	[Co(dapbhH$_2$)-(SCN)$_2$].3H$_2$O	15.9	14.663	12.353	2.320
(6)	[Co(dapbh)(H$_2$O)$_2$]	13.1	12.486	10.251	2.235

Table 5B.2: Decomposed excitations (in cm^{-1}) contributing towards spin-orbit coupling D_{SOC} calculated by DFT.

Sl. No.	**Complexes**	**D_{SOC}**	**α→α (SOMO→VMO)**	**β→β (DOMO→SOMO)**	**α→β* (SOMO→SOMO)**	**β→β (DOMO→SOMO)**
(5)	[Co(dapbhH$_2$)-(SCN)$_2$].3H$_2$O	12.353	0.039	9.132	3.228	-0.047
(6)	[Co(dapbh)(H$_2$O)$_2$]	10.251	1.196	5.981	4.203	-1.128

Table 5B.1 shows the comparison of experimental and the theoretically calculated D-tensors of both the complexes alongwith the contribution of spin-orbit coupling and spin-spin interaction towards the total D-tensor. Table 5B.2 shows the contribution of the decomposed excitations towards the spin-orbit coupling part of D-tensor, D_{SOC}. The most dominant contribution towards the total D-tensor comes from the spin-orbit interaction while the spin-spin part is negligible. The mixing between the ground quartet state and the excited quartet and doublet electronic levels contribute towards the spin-orbit perturbation. The spin-orbit contribution terms are addition of the decomposed excitations happening among VMO, SOMO and DOMO. These excitations of the electrons can be classified as: α→α, β→β, α→β and β→ α. The α→α is the excitation of a spin-up electron from a SOMO to a VMO that leads to the state of same spin S as of ground state; β→β is the excitation of a spin-down electron from SOMO to DOMO and this too results in same spin S as of ground state. Thirdly, α→β is a spin-flip excitation that leads to states of $\acute{S} = S - 1$. And the last β→ α is also a spin-flip excitation from a DOMO to VMO and this leads to $\acute{S} = S + 1$. From the calculated decomposed excitations we can see that the highest contribution towards the total D-tensor comes from DOMO to SOMO that too giving rise to a same spin S as that of the ground state. These excitations can be categorized as charge-transfer contributions from ligand-field point of view. The excitation from SOMO→VMO is indicative of isolated closed-shell singlet and the contribution to D_{SOC} is insignificant. Contribution from SOMO to SOMO is not required to be evaluated even if the magnitude is worthy because there is same spatial distributions and orbital energies between spin α and β.

The D-tensor calculated by theoretical means is smaller as compared to the experimentally observed values. It is known that the large positive D-tensor value in pentagonal bipyramidal Co(II) complexes [25] is due to the mixing of spin-orbit coupling of the ground quartet state with three excited states where two states are quartet and the other being a doublet. When an electron is promoted from d_{xz} or d_{yz} orbital to the d_{z^2} orbital, then this electronic configuration corresponds to a quartet excited state with highest contribution to D-tensor. With subsequent plotting of a better σ-donor apical ligand into the coordination environmentthe energy of the d_{z^2} orbital increases. This reduces the spin-orbit interaction between the ground quartet state and the excited quartet electronic levels. Therefore, when a better σ-donor apical ligand in complex (**5)** [Co(dapbhH$_2$)-(SCN)$_2$].3H$_2$O is employed, the second-order perturbation in spin orbit coupling is reduced that consequently reduces the positive D-tensor value. Besides this explanation, there is another reason which attributes to the positive D-tensor values in these two complexes is the mixing of the ground quartet state with the excited doublet state. The excited doublet state represents an electronic state that is either obtained by excitation of an electron from d_{xy} to the $d_{x^2-y^2}$ orbital or vice-versa. In presence of a symmetric equatorial field the energy gap between d_{xy} and $d_{x^2-y^2}$ orbitals is reduced. Since in complex (**6)** [Co(dapbh)(H$_2$O)$_2$] the apical ligands are poor σ-donor, the spin-orbit mixing of the ground quartet state with the excited quartet level is present. But both the anionic charges gets conjugated since the ligand in complex (**6)** [Co(dapbh)(H$_2$O)$_2$] is dianionic in nature. Since the metal-donor atom bond length is not much longer, hence the energy of the excited doublet state is higher. Unlike in the neutral dapbhH_2, where the equatorial coordination geometry is less symmetric, in the dapbh ligand the equatorial plane is structurally symmetric. On account of this symmetry factor there is spin-orbit coupling of ground quartet level with excited doublet level and this gives rise to positive D-tensor. This explains that how the second-order perturbation of spin-orbit coupling can alter the magnetic anisotropy by altering the coordination environment. In case of complex (**5)** the better σ-donating ability of the apical ligand decreases the positive magnitude of the D-tensor while in complex (**6)** the symmetrical equatorial ligand in the pentadentate form helps to reduce the positive contribution towards the total D-tensor.

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