



Article

Zero-Field Splitting in Hexacoordinate Co(II) Complexes

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Abstract: A collection of 24 hexacoordinate Co(II) complexes was investigated by ab initio CASSCF + NEVPT2 + SOC calculations. In addition to the energies of spin–orbit multiplets (Kramers doublets, KD) their composition of the spins is also analyzed, along with the projection norm to the effective Hamiltonian. The latter served as the evaluation of the axial and rhombic zero-field splitting parameters and the g-tensor components. The fulfilment of spin-Hamiltonian (SH) formalism was assessed by critical indicators: the projection norm for the first Kramers doublet $N(KD1) > 0.7$, the lowest g-tensor component $g_1 > 1.9$, the composition of KDs from the spin states $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ with the dominating percentage $p > 70\%$, and the first transition energy at the NEVPT2 level ${}^4\Delta_1$. Just the latter quantity causes a possible divergence of the second-order perturbation theory and a failure of the spin Hamiltonian. The data set was enriched by the structural axiality D_{str} and rhombicity E_{str} , respectively, evaluated from the metal–ligand distances Co–O, Co–N and Co–Cl corrected to the mean values. The magnetic data (temperature dependence of the molar magnetic susceptibility, and the field dependence of the magnetization per formula unit) were fitted simultaneously, either to the Griffith–Figgis model working with 12 spin–orbit kets, or the SH-zero field splitting model that utilizes only four (fictitious) spin functions. The calculated data were analyzed using statistical methods such as Cluster Analysis and the Principal Component Analysis.

Keywords: cobalt(II) complexes; zero-field splitting; ab initio calculations; spin Hamiltonian; Griffith–Figgis model



Citation: Boča, R.; Rajnák, C.; Titiš, J. Zero-Field Splitting in Hexacoordinate Co(II) Complexes. *Magnetochemistry* **2023**, *9*, 100. <https://doi.org/10.3390/magnetochemistry9040100>

Academic Editor: Marius Andruh

Received: 20 February 2023

Revised: 22 March 2023

Accepted: 3 April 2023

Published: 4 April 2023



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1. Introduction

Zero-field splitting (zfs) is a phenomenon of existence of fine-structure energy levels that are further split only owing to the external magnetic field. In order to avoid confusions, one has to distinguish between the experimentally verified zfs as existing energy gap(s) and the tools used for the description of zfs based upon theoretical assumptions and approximate methods. ZFS is also a source of the magnetic anisotropy reflected in the different evolution of the magnetization components, such as the easy axis or easy plane. It is generally accepted that the magnetic anisotropy of the easy axis is the crucial factor that prevents the fast magnetic relaxation via the Orbach mechanism, and secures a slow magnetic relaxation as a prerequisite of the single molecule/ion magnetism [1,2].

ZFS can be experimentally determined by various techniques, such as (i) magnetometry, (ii) susceptometry, (iii) electron paramagnetic resonance and its variants (high-field/high-frequency electron magnetic resonance), (iv) far-infrared spectroscopy and its variants in the magnetic field (FIRMS, FDMRS), (v) magnetic circular dichroism, (vi) low-temperature calorimetry, and (vii) inelastic neutron scattering [3–13].

ZFS can be treated as an effect of the spin–orbit interaction that splits the multielectron terms—the energy states referring to an antisymmetric wave function that accounts for the interelectron repulsion (configuration interaction) and the effects of the ligands on the central atom. The active space of kets relevant to the central atom is given by all members of the electron configuration d^n that equals $\binom{10}{n} = \frac{10 \cdot 9 \cdot \dots}{1 \cdot 2 \cdot \dots n}$: 10 for d^1 and d^9 , 45 for d^2

and d^8 , 120 for d^3 and d^7 , 216 for d^4 and d^6 , and 252 for d^5 configurations. Working in such a space requires computer-aided efforts that, on the other hand, reduce transparency. However, the contemporary software based upon CASSCF + NEVPT2 + SOC calculations represents a useful tool in determining the spin–orbit multiplets using the fine-structure energy levels and the energy differences among them [14–16]. Alternate routes represent the *ab initio* *Ligand Field Theory* and the *Generalized Crystal Field Theory* [17–19].

The most common approximate concept utilized for the description of the zfs is the spin-Hamiltonian (SH) theory. This is a drastic simplification based upon reduction of the active space of kets to only a few spin functions $|S, M_S\rangle$: 2 to 6 kets for d^1 to d^9 electron configurations. For instance, for the d^7 configuration, the complete (active) space consists of 120 spin–orbit kets labelled as $|(vLS), J, M_J\rangle$ or $|\Gamma', \gamma', a'\rangle$, but the SH formalism works only with four spin kets $|S, M_S\rangle = |3/2, \pm 1/2\rangle$ and $|3/2, \pm 3/2\rangle$.

The basic assumption of the SH formalism is that the effect of the spin–orbit coupling can be treated as a small perturbation. Then, the second-order perturbation theory for non-degenerate ground multielectron term offers an explicit formula for the Λ -tensor, which serves for the calculation of the spin–spin interaction $\mathbf{D}$ -tensor, the magnetogyric-ratio $\mathbf{g}$ -tensor, the temperature-independent susceptibility $\mathbf{X}$ -tensor, and eventually the hyperfine interaction $\mathbf{A}$ -tensor [20,21]. This assumption is fulfilled when the expression $H' = \langle 0 | \hat{H}^{so} | K \rangle / (E_0 - E_K)$ is not too large, provided by a large enough denominator as the energy gap between the ground term $|0\rangle$ and excited terms $|K\rangle$. As an effect of small perturbation, the content of the original spin functions in the multiplets is high; in other words, SOC does not mix the spin states significantly. We will see later that this requirement alone often fails. Within the SH formalism, the energy gaps between spin–orbit multiplets are expressed in terms of the axial and rhombic zero-field splitting parameters. Notably, these D and E parameters are not observables introduced as eigenvalues of a quantum-mechanical operator. They serve as descriptive parameters and thus they should be handled with care.

The core of this review article is to show the limitations of the spin-Hamiltonian approach in treating the zero-field splitting for the difficult cases of hexacoordinate Co(II) and analogous Fe(I) and Ni(III) complexes.

2. Theoretical Analysis

Multielectron terms in atoms are labelled by the angular momentum quantum numbers as $|d^n: \nu, L, M_L, S, M_S\rangle$, where ν is the seniority number for repeated terms. On passage to the molecular systems belonging to a point group of symmetry G , the orbital part spans an irreducible representation Γ , its eventual component γ , and the branching index a , i.e., $|\Gamma, \gamma, a; S, M_S\rangle$; the spin part stays untouched. It is assumed that the effects of the configuration interaction are covered by the operator of the interelectron repulsion. For the irreducible representations (IRs) of the electron terms, the Mulliken notation is used, as appearing in the standard character tables of the point groups; this contains A, B, E, and T labels, with some subscripts identifying symmetry details. These definitions are compiled in Table 1.

Table 1. Involved operators and wave functions ^a.

	Free Atom/Ion		Molecule/Complex	
Operators	$\hat{H}^{ee}$	$\hat{H}^{ee} + \hat{H}^{so}$	$\hat{H}^{ee} + \hat{H}^{cf} + \hat{H}^{so}$	$\hat{H}^{ee} + \hat{H}^{cf} + \hat{H}^{so}$
Wave function	Atomic term	Atomic multiplet	Multielectron term	Spin–orbit multiplet
Notation	$ d^n: \nu, L, M_L, S, M_S\rangle$	$ (vLS), J, M_J\rangle$	$ \Gamma, \gamma, a; S, M_S\rangle$	$ \Gamma', \gamma', a'\rangle$
Irreducible representations ^b	$D^{(L)}(2L + 1):$ S, P, D, F, G, H, I	$2S + 1 D_J(2J + 1)$	${}^m A(1), {}^m B(1), {}^m E(2), {}^m T(3)$ ^b	$\Gamma_i(1, 2, 3, 4)$
-for Kramers systems	$S = 1/2, 3/2, 5/2, 7/2$	$J = L - S , \dots, L + S$	$m = 2S + 1 = 2, 4, 6, 8$	$\Gamma_i(2), \Gamma_8(4)$

^a $\hat{H}^{ee}$ —interelectron repulsion, $\hat{H}^{cf}$ —crystal-field operator, $\hat{H}^{so}$ —spin–orbit coupling. ^b Orbital degeneracy in parentheses.

The spin–orbit coupling in atoms causes a splitting of the atomic terms into a set of atomic multiplets; these are characterized by the total angular momentum quantum numbers $|\nu LS\rangle, J, M_J\rangle$. In molecules, the spin–orbit multiplets (crystal-field multiplets) are labelled according to IRs Γ' , their components γ' and branching index a' within the double point group G' : $|\Gamma', \gamma', a'\rangle$ [22]. Here, the Bethe notation (Γ_1 to Γ_8) is applied as found in character tables of the double point groups [23,24]. For Kramers systems (possessing the half-integral spin $S = 1/2, 3/2, 5/2, 7/2$), belonging to double groups with an order less than cubic, all IRs are doubly degenerate $\Gamma_i(2)$; for the cubic groups, a four-fold degenerate IR also exists: $\Gamma_8(4)$.

The spin–orbit multiplets can be considered as observables since they are eigenvalues/eigenvectors of the operator $\hat{H} = \hat{H}^{ee} + \hat{H}^{cf} + \hat{H}^{so}$. In the variation method, they result from the diagonalization of the interaction matrix $H_{IJ} = \langle I | \hat{H} | J \rangle$ where the matrix elements need to be evaluated in an appropriate basis set. The simplest approach utilizes the atomic terms as a basis set for the calculations of multiplets; other bases can be considered as a result of the unitary transformation and thus the final eigenvalues stay invariant.

Let us focus on the d^7 systems exemplified by the hexacoordinate Co(II) complexes. On symmetry descent from the octahedral geometry, the orbitally triply degenerate ground term is split ${}^4T_{1g} \rightarrow {}^4E_g \oplus {}^4A_{2g}$ (D_{4h}), and the excited term as ${}^4T_{2g} \rightarrow {}^4B_{2g} \oplus {}^4E_g$; the orbitally non-degenerate term transforms as ${}^4A_{2g} \rightarrow {}^4B_{1g}$. On further symmetry descent to the D_{2h} (isomorphous with C_{2v}), the additional splitting yields 4E_g (D_{4h}) $\rightarrow$ ${}^4B_{3g} \oplus {}^4B_{2g}$, whereas the non-degenerate term transforms as ${}^4A_{2g} \rightarrow {}^4B_{1g}$. The corresponding irreducible representations for spin–orbit multiplets, depending upon the respective double point group, are shown in Figures 1–3.

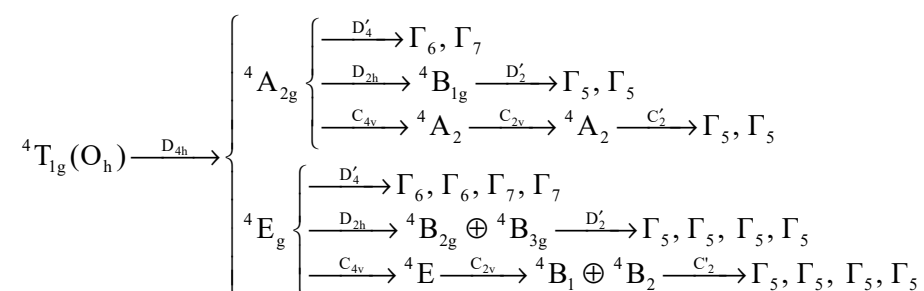


Figure 1. Development of the crystal field terms (T, A, E, B) and spin–orbit multiplets (Γ_i) under symmetry lowering for hexacoordinate Co(II) high-spin systems.

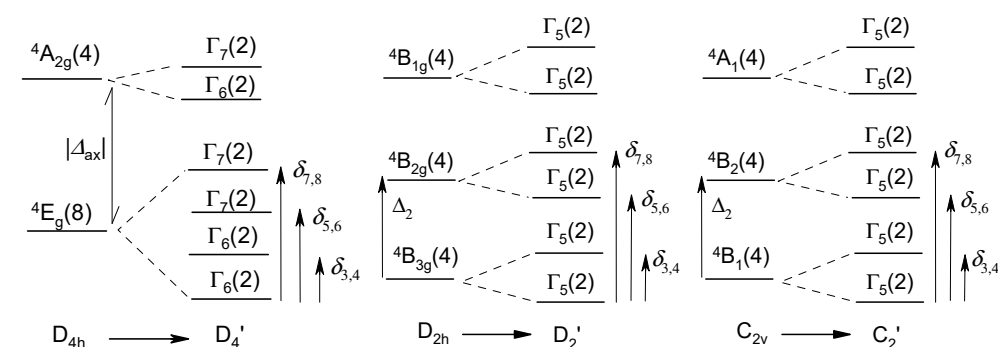


Figure 2. Scheme of 12 energy levels for elongated square bipyramid (D_{4h}), *o*-rhombic bipyramid (D_{2h}), and symmetry lower polyhedron (C_{2v}) in hexacoordinate Co(II) complexes.

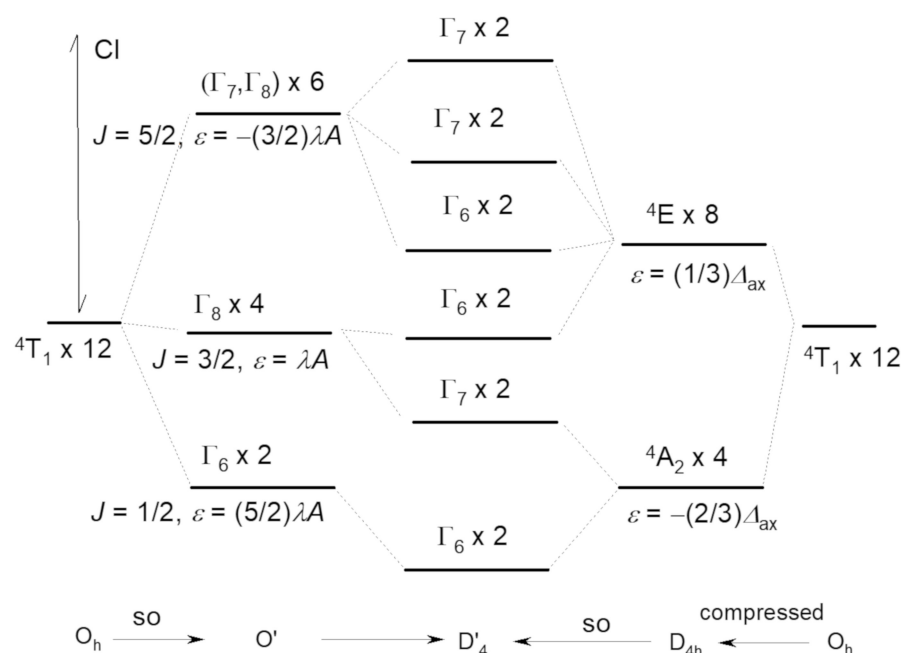


Figure 3. The relationship among the lowest terms and multiplets for d^7 systems.

There are several important consequences of the ground and the first excited electronic terms on the SH theory. When the ground multielectron term is orbitally degenerate (T_{1g} or E_g), the SH formalism cannot be applied. This is a frequent mistake: sometimes the D and E values are reported; however, they are undefined when the ground state is E_g . Note that the ground electron term for the Co(II) complexes in the geometry of an elongated tetragonal bipyramid is $4E_g$ (the above case) and the set of the spin–orbit multiplets is labelled as Γ_6 , Γ_6 , Γ_7 , and Γ_7 . The differences among these Kramers doubles, abbr. as $\delta_{1,2}$, $\delta_{3,4}$, $\delta_{5,6}$, and $\delta_{7,8}$, cannot be expressed with the help of D - and E -parameters. The splitting between the ground term $4E_g$ and the first excited $4A_{2g}$ is denoted as Δ_{ax} , and for axial elongation it is negative. Then, the asymmetry parameter $\nu = \Delta_{ax}/\lambda$ is positive, since $\lambda = -\zeta/2S < 0$ for d^7 systems.

On further symmetry descent, such as $D_{4h} \rightarrow D_{2h} \rightarrow C_{2v}$, the daughter terms B_{3g} and B_{2g} stay quasi-degenerate. Formally, the spin Hamiltonian can be applied in such a case. However, when the energy denominator in $1/(E_0 - E_K)$ is small, the second-order perturbation theory can suffer divergence, which manifests itself in overestimated D values and also in high asymmetry of the g -tensor components, sometimes unacceptable $g_i < 2$.

In the opposite distortion to the compressed tetragonal bipyramid, the ground electronic term $4A_{2g}$ (D_{4h}) produces two Kramers doubles (KDs) separated by $\delta_{3,4}$. In this case, the crystal-field splitting parameter is positive, $\Delta_{ax} > 0$, and then the asymmetry parameter $\nu < 0$. Now the spin Hamiltonian can be applied, assuming that Δ_{ax} is not too small (when the quasi degeneracy again occurs).

The impact of the lowest terms on the magnetic properties can be visualized by plotting the effective magnetic moment against the (reduced) temperature as displayed in Figure 4. The Griffith–Figgis theory working in the space of 12 spin–orbit kets $|L = 1, M_L, S = 3/2, M_S\rangle$ allows a comparison of three cases [25]. (i) The case of a perfect octahedron (rather hypothetical due to the Jahn–Teller effect), with the ground term $4T_{1g}$ for which $\nu = 0$, displays a round maximum at the μ_{eff} vs. $kT/|\lambda|$ curve. (ii) With $\nu > 10$ (the case of an elongated bipyramid), the maximum is much reduced and the high-temperature tail almost disappears for very negative Δ_{ax} ; then, the effect of the low-lying excited state $4A_{2g}$ is filtered off and the magnetic properties are dominated only by the eight members (4 KDs) originating in the $4E_g$ term. (iii) For $\nu < 10$, the ground term is orbitally non-degenerate $4A_{2g}$ and the μ_{eff} curve falls down at low temperature due to a depopulation of $\delta_{3,4}$ vs. the ground multiplet $\delta_{1,2}$. The high-temperature tail is represented by a straight line, reflecting

some temperature-independent paramagnetism. The situation is well described by the SH formalism when Δ_{ax} is not too small.

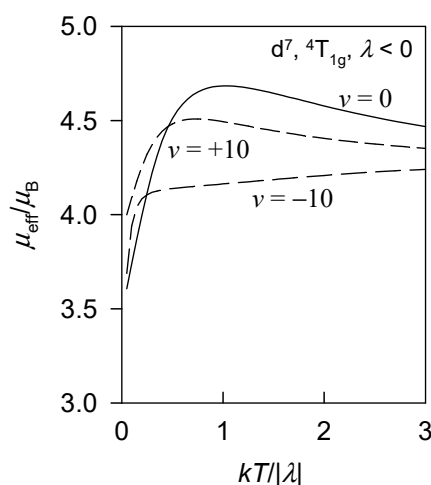


Figure 4. Temperature dependence of the effective magnetic moment for the ground $4T_{1g}$ term within the Figgis theory. Note: $v = \Delta_{ax}/\lambda$ and $\lambda = -\xi/2S < 0$ for d^7 systems.

3. Methods and Modelling

3.1. Spin Hamiltonian

Let us recapitulate the key formulae of the spin Hamiltonian appropriate to the zero-field splitting. The spin Hamiltonian contains the axial D (rhombic E) zfs parameters

$$\hat{H}^{zfs} = D(\hat{S}_z^2 - \frac{S(S+1)}{3})\hbar^{-2} + E(\hat{S}_x^2 - \hat{S}_y^2)\hbar^{-2} \quad (1)$$

and it is enriched by the Zeeman term

$$\hat{H}_{kl}^Z = \mu_B B \hbar^{-1} (g_x \hat{S}_x \sin \vartheta_k \cos \varphi_l + g_y \hat{S}_y \sin \vartheta_k \sin \varphi_l + g_z \hat{S}_z \cos \vartheta_k) \quad (2)$$

that depends on the polar angles $\{\vartheta_k, \varphi_l\}$ distributed uniformly over a sphere in order to mimic a powder average correctly. There are also higher-order zfs parameters expressed with the help of the Stevens operators [21]. Depending upon the situation, a reduced set of parameters is often utilized (D, g_z, g_x). Additionally, only the Cartesian components are often considered: $x\{\pi/2, 0\}$, $y\{\pi/2, \pi/2\}$, $z\{0, 0\}$. The diagonalization of the Hamiltonian matrix $\langle I | \hat{H}^{zfs} + \hat{H}_{kl}^Z(B_m) | J \rangle$ yields energy levels (two KDs for d^7 systems) $\varepsilon_{kl}(B_m)$ that depend upon discrete (at least three) values of the magnetic field. They enter the partition function $Z_{kl}(B_m, T)$ from which the magnetization $M_{kl}(B, T)$ and magnetic susceptibility $\chi_{kl}(B, T)$ are evaluated via the first and second (numerical) derivatives with respect to the magnetic field. In addition to this universal method, there are also some simpler procedures; for instance, based upon the van Vleck equation for magnetic susceptibility. The powder average is a simple arithmetic average of the grid-dependent M_{kl} and χ_{kl} .

Technically, it is too ambitious to obtain reliable values of the E -parameter from the magnetic data taken above 2 K (usual range). Therefore, E as a rule is neglected. Then, the grids of the magnetic field can be limited to only a few points (e.g., 11) distributed uniformly over the half of the meridian with $\varphi = 0$.

The magnetic anisotropy can be visualized in the 2D graphs as the separate curves $M_z(B)$ and $M_{xy}(B)$. More informative are 3D graphs, as shown in Figure 5, where the value of $D > 0$ leads to the easy plane and $D < 0$ to easy-axis magnetism.

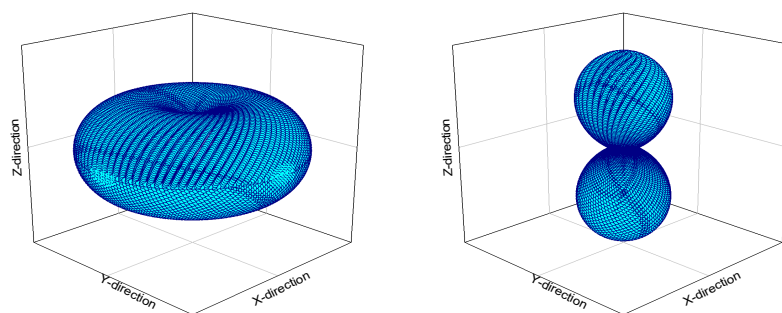


Figure 5. The 3D model of magnetization $M(x,y,z)$ within the zfs model at $T = 2.0$ K and $B = 1.0$ T. Left—for $D = +20$ cm $^{-1}$ (easy-plane magnetism); right—for $D = -20$ cm $^{-1}$ (easy-axis magnetism).

The experimental set of DC magnetic data (temperature dependence of the molar magnetic susceptibility χ at $B_0 < 0.5$ T, and field dependence of the magnetization per formula unit M_1 at $T_0 < 5$ K) has been fitted simultaneously by minimizing the error functional $F(\chi, M) \rightarrow \min$. Several forms of the error functional have been applied; for instance, $F = w_1 \cdot E(\chi) + (1 - w_1) \cdot E(M)$, $F = E(\chi) \times E(M)$, and $F = w_1 \cdot C(\chi) + (1 - w_1) \cdot C(M)$, where the relative error $E(P)$ and the “city-block” factor $C(P)$ for individual observable $P = \chi$ or M are

$$E(P) = \frac{1}{N} \sum_i \left| \frac{P_i^{\text{obs}} - P_i^{\text{calc}}}{P_i^{\text{obs}}} \right| \quad (3)$$

$$C(P) = \frac{1}{N} \frac{\sum_i |P_i^{\text{obs}} - P_i^{\text{calc}}|}{\sum_i P_i^{\text{obs}}} \quad (4)$$

In order to balance the dominating low-temperature susceptibility data against the high-temperature tail, the product $P_i = \chi_i \cdot T_i$ or the effective magnetic moment $P_i = \mu(\text{eff})_i$ were also used.

3.2. Griffith–Figgis Model

The GF model is based upon the Hamiltonian working in the space of twelve spin–orbit kets $|L = 1, M_L, S, M_S\rangle$ [25,26].

$$\hat{H}^{\text{GF}} = \underbrace{(-\lambda^{\text{sf}} A \kappa)(\vec{L}_p \cdot \vec{S}) \hbar^{-2}}_{\text{spin-orbit coupling}} + \underbrace{\mu_B \vec{B} \cdot (g_e \vec{S} + g_L \vec{L}_p) \hbar^{-1}}_{\text{spin and orbital Zeeman terms}} + \underbrace{\Delta_{\text{ax}}(\hat{L}_z^2 - \vec{L}^2/3) \hbar^{-2}}_{\text{axial distortion}} + \underbrace{\Delta_{\text{rh}}(\hat{L}_x^2 - \hat{L}_y^2) \hbar^{-2}}_{\text{rhombic distortion}} \quad (5)$$

where $A\lambda$ —spin–orbit splitting parameter modified by the Figgis CI factor A (3/2 for the weak crystal field), Δ_{ax} (Δ_{rh})—axial (rhombic) crystal-field splitting energy, $g_L = -A\kappa$ effective orbital magnetogyric factor (negative owing to the T-p isomorphism), κ —orbital reduction factor accounting to some degree of covalency. This formula has been extended by considering the asymmetry of the Zeeman term

$$\begin{aligned} \hat{H}_{kl}^{\text{GF}} = & -A\kappa\lambda(\vec{L}_p \cdot \vec{S}) \hbar^{-2} + [\Delta_{\text{ax}}(\hat{L}_{p,z}^2 - \vec{L}_p^2/3) + \Delta_{\text{rh}}(\hat{L}_{p,x}^2 - \hat{L}_{p,y}^2)] \hbar^{-2} \\ & + \mu_B B g_e (\cos \vartheta_k \hat{S}_z + \sin \vartheta_k \cos \varphi_l \hat{S}_x + \sin \vartheta_k \sin \varphi_l \hat{S}_y) \hbar^{-1} \\ & - \mu_B B (A\kappa_z \cos \vartheta_k \hat{L}_{p,z} + A\kappa_x \sin \vartheta_k \cos \varphi_l \hat{L}_{p,x} + A\kappa_y \sin \vartheta_k \sin \varphi_l \hat{L}_{p,y}) \hbar^{-1} \end{aligned} \quad (6)$$

where k, l define positions of the grids distributed uniformly over the polar angles $\{\vartheta_k, \varphi_l\}$. In practice, $k = 11$ distributed along half of the meridian secures the correct powder average for the sample with an axial character. Formally, the above Hamiltonian is isomorphous

to the exchange-coupled dimer, possessing the axial zero-field splitting adapted for the powder average. The energy levels obtained by the diagonalization are treated as above. This form allows a reproduction not only of the magnetic susceptibility but also the field dependence of magnetization.

The magnetic anisotropy for either $\Delta_{ax} < 0$ (easy axis) or $\Delta_{ax} > 0$ (easy plane) is essentially the same as obtained by the SH-zfs model. However, the key parameter has a completely different physical origin: in the SH-zfs model, it is the anisotropy of the fictitious spin angular momentum $[D(\hat{S}_z^2 - \vec{S}^2/3) + E(\hat{S}_x^2 - \hat{S}_y^2)]$; in the GF model, it is the anisotropy of the orbital angular momentum $[\Delta_{ax}(\hat{L}_{p,z}^2 - \vec{L}_p^2/3) + \Delta_{rh}(\hat{L}_{p,x}^2 - \hat{L}_{p,y}^2)]$. It can be concluded that the negative axial crystal-field splitting parameter causes the easy-axis magnetization (Figure 6).

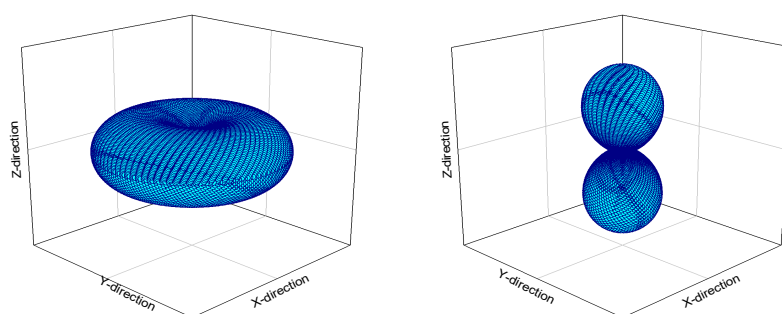


Figure 6. The 3D model of magnetization $M(x,y,z)$ within the Griffith model at $T = 2.0$ K, $B = 1.0$ T, $\lambda = -170$ cm $^{-1}$ and $g_L = -1.5$. Left—for $\Delta_{ax} = +500$ cm $^{-1}$ (easy plane); right—for $\Delta_{ax} = -500$ cm $^{-1}$ (easy axis).

The general procedure for evaluating the magnetic susceptibility and magnetization has been employed in order to model the temperature dependence of the effective magnetic moment and the field dependence of the magnetization for realistic parameters of the FG model relevant to Co(II) complexes (Figure 7). With $\Delta_{ax} = \pm 500$ cm $^{-1}$, the susceptibility and magnetization curves are almost the same; some differences are seen at the effective magnetic moment. For $\Delta_{ax} = \pm 1000$ cm $^{-1}$, the differences in the magnetization become visible; the μ_{eff} for $\Delta_{ax} = +1000$ cm $^{-1}$ rises according to the straight line, which reflects the presence of the excited state manifesting itself in the temperature-independent paramagnetism. For $\Delta_{ax} = \pm 3000$ cm $^{-1}$, the differences are substantial in magnetization, susceptibility, and effective magnetic moment. For $\Delta_{ax} = +3000$ cm $^{-1}$, the effect of the excited state is filtered off and the system behaves like a typical zfs system.

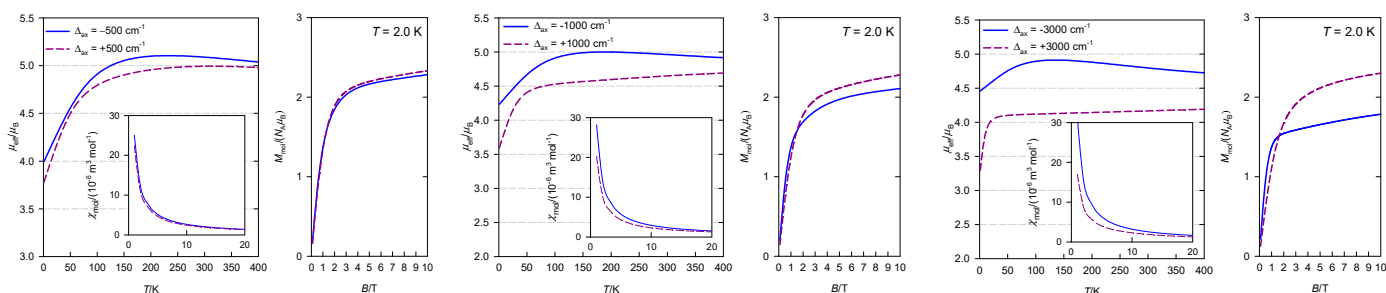


Figure 7. Modelling of the magnetic functions using various Δ_{ax} in the GF model; $\lambda = -170$ cm $^{-1}$, $g_L = -1.5$. Left—temperature dependence of the effective magnetic moment (inset—molar magnetic susceptibility); right—magnetization per formula unit.

3.3. Ab Initio Calculations

The only input for this kind of first-principle calculations is the molecular geometry (atomic coordinates) and the associated basis set. As the basis set, the Gaussian type

functions are exclusively used with large enough angular momentum (for example, f- and g-functions for d-orbitals).

In the CASSCF (Complete Active Space Self Consistent Field) method, which is beyond the Hartree–Fock approximation, the coefficients of the linear combination of atomic orbitals (LCAO MO) and the coefficients of the configuration interaction (CI) are evaluated by the variation method. In this version of the multi-configuration method, the electrons in the active space (N, M) have variable occupations unlike those in the inactive space [27]. For transition metal complexes, the complete active space contains N d-electrons in M d-orbitals (10 spinorbitals). For a given CAS, the average energy of all states is minimized, whereas each state is weighted equally (SA-CASSCF). This version of the multi-configuration method accounts partly for the correlation energy (static correlation).

Dynamic electron correlation energy is calculated from excited configuration state functions (CSF) in which electrons are excited into empty orbitals. These CSF $|\tilde{\Phi}_K\rangle$ are used in a linear combination [28–30].

$$|\tilde{\Psi}_I\rangle = \sum_{K \in \text{CAS}} C_{KI} |\Phi_K\rangle + \sum_{K \in \text{CAS}} T_{KI} |\tilde{\Phi}_K\rangle \quad (7)$$

where the expansion coefficients (C and T) can be determined by application of the perturbation theory, such as second-order N -electron valence perturbation theory (NEVPT2). This method provides a second-order correction ΔE_I^{PT2} of the total CAS energy for each state. It is a good reference for the interpretation of excitation energies in the electronic d-d spectra.

Magnetic parameters are calculated through the quasi-degenerate perturbation theory, within which the spin–orbit coupling (SOC) operator is diagonalized over the manifold of all CAS states corrected by the NEVPT2 [31]

$$H_{II}^{\text{QDPT}} = \delta_{II} (E_{I,\text{CAS}} + \Delta E_I^{\text{PT2}}) + \langle \Psi_{I,\text{CAS}}^{SM} | \hat{H}_{\text{SOC}} + \dots | \Psi_{I,\text{CAS}}^{S'M'} \rangle \quad (8)$$

The SOC operator has the Breit–Pauli form in which the spin–orbit mean-field (SOMF) approximation is used [32]

$$\hat{H}_{\text{SOC}}^{\text{SOMF}} = \sum_i \hat{z}_i^{\text{SOMF}} \hat{s}_i \quad (9)$$

where $\hat{z}_i^{\text{SOMF}}$ is an appropriately defined effective one-electron operator.

Application of the partitioning technique and/or quasi-degenerate perturbation theory yields the matrix elements of the effective Hamiltonian spanned by the spin manifold of the orbitally non-degenerate ground electronic state as follows

$$H_{MM'}^{\text{eff}} = E_0 \delta_{MM'} + \langle \Psi_0^{SM} | \hat{H}_1 | \Psi_0^{SM'} \rangle - \sum_{IS''M''} \Delta_I^{-1} \langle \Psi_0^{SM} | \hat{H}_1 | \Psi_I^{S''M''} \rangle \cdot \langle \Psi_I^{S''M''} | \hat{H}_1 | \Psi_0^{SM'} \rangle \quad (10)$$

with the denominator defined by excitation energies $\Delta_I^{-1} = (E_I - E_0)^{-1}$. Then, the D -tensor and g -tensor components arising from the spin–orbit coupling are obtained using closed formulae.

An alternate way of calculating magnetic parameters (used here) is provided by the effective Hamiltonian theory [33,34]. This method is based on the construction of a model Hamiltonian which is projected into the complete space of the CAS Hamiltonian $\hat{H}^{\text{rel}}$ in the sense of des Cloizeaux definition of the effective Hamiltonian

$$\hat{H}_C^{\text{eff}} = \sum_k |\tilde{\Psi}_k^C\rangle E_k \langle \tilde{\Psi}_k^C| \quad (11)$$

Here, the effective Hamiltonian reproduces the energy levels of the CAS Hamiltonian E_k and the wavefunctions of the states projected to the model space $\tilde{\Psi}_k$. Using a singular value decomposition procedure, the elements of D - and g -tensor are extracted [35]. In case

of the low norm of the projections ($N \ll 1$), the trial model Hamiltonian is inapplicable to the given system.

All calculations were conducted using the ORCA package [14,15,36] in the experimental geometry of Co(II) complexes (neutral or charged). As a basis set, ZORA-def2-SV(P) was used for non-metal atoms, and ZORA-def2-TZVPP for the Co(II) center.

3.4. Generalized Crystal-Field Theory

This method (GCFT) works in the basis set of atomic terms characterized by the angular momentum quantum numbers $|I\rangle = |d^n : \nu, L, M_L, S, M_S\rangle$. The space covers 120 kets for a d^7 system like in the CAS method. By applying the irreducible tensor algebra, the matrix elements of the interaction operators are evaluated: the interelectron repulsion $\hat{H}^{ee}$, crystal field $\hat{H}^{cf}$, spin-orbit coupling $\hat{H}^{so}$, Zeeman orbital, and Zeeman spin interactions [18,19,37]. The parameters dependent upon the radial functions are expressed by the Racah B and C parameters for the interelectron repulsion, and the crystal-field poles $F_2(L)$ and $F_4(L)$ for individual ligands L , respectively. The angular parts of the matrix elements are integrated using coefficients of fractional parentage and vector coupling coefficients (3j- and 6j-symbols). The positions of ligands involve the spherical harmonic functions owing to which the matrix elements are complex. The spin-orbit interaction is characterized by the spin-orbit coupling constant ζ_{Co} . The diagonalization of the matrix $\langle J | \hat{H}^{ee}(B, C) + \hat{H}^{cf}(F_2, F_4) + \hat{H}^{so}(\zeta) | I \rangle$ yields the crystal-field multiplets $|K\rangle = |(d^n \nu LS); \Gamma'_a, \gamma'_a, a'\rangle$, where we used labelling of the irreducible representations (IRs) and their components $\{\Gamma'_a, \gamma'_a, a'\}$ within the double point group of symmetry.

The evaluation of the spin-Hamiltonian parameters represents an approximation based upon the construction of the Λ -tensor by means of the second-order perturbation theory

$$\Lambda_{ab} = \hbar^{-2} \sum_{J \neq 0} \langle 0 | \hat{L}_a | J \rangle \langle J | \hat{L}_b | 0 \rangle / (E_J - E_0) \quad (12)$$

where the summation runs over all excited terms $|J\rangle$. The Λ -tensor is used in the definition of the $\mathbf{D}$ -tensor $D'_{ab} = -\lambda^2 \Lambda_{ab}$. In the traceless form

$$D_{ab} = D'_{ab} - \delta_{ab}(D'_{xx} + D'_{yy} + D'_{zz})/3 \quad (13)$$

the axial and rhombic zero-field splitting parameters are expressed as

$$D = (-D'_{xx} - D'_{yy} + 2D'_{zz})/2 \quad (14)$$

$$E = (D'_{xx} - D'_{yy})/2 \quad (15)$$

In the GCFT calculations, the key role plays an appropriate choice of the crystal field poles $F_4(L)$ and eventually $F_2(L)$ for individual ligands. This method is suitable for the modelling of SH parameters over a wide range of geometries and crystal-field strengths.

4. Results and Discussion

4.1. Geometry of Complexes

The complexes under study have the shape of an elongated or compressed tetragonal bipyramid with some *o*-rhombic component in the equatorial plane (Table 2). Distances on the *trans*-ordinate were averaged and further processed as follows. Assuming that the highest eccentricity lies along the *z*-axis, the structural distortion parameters are defined as

$$D_{\text{str}} = (d_i - \bar{d}_i)_z - [(d_i - \bar{d}_i)_x + (d_i - \bar{d}_i)_y]/2 \quad (16)$$

$$E_{\text{str}} = [(d_i - \bar{d}_i)_x - (d_i - \bar{d}_i)_y]/2 \quad (17)$$

where $\bar{d}_i$ is the mean distance for a given bond ($i = \text{N, O, Cl}$). These have been taken from compounds containing the $[\text{Co}(\text{NH}_3)_6]^{2+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CoCl}_6]^{4-}$ complex units, giving rise to $\bar{d}(\text{Co} - \text{N}) = 2.185 \text{ \AA}$, $\bar{d}(\text{Co} - \text{O}) = 2.085 \text{ \AA}$, and $\bar{d}(\text{Co} - \text{Cl}) = 2.475 \text{ \AA}$ [38]. This procedure is effective for complexes with a heterogeneous donor set with different averaged metal–ligand distances. Sometimes it is not clear which distances should be selected as axial, and which as equatorial. Hereafter, a constraint is utilized: $E_{\text{str}}/|D_{\text{str}}| < 1/3$. (Analogous constraints are used for axial and rhombic zero-field splitting parameters in SH theory.) Some of the studied complexes possess the form of a pincer-type: there are severe deviations of four donor atoms from the equatorial plane due to the rigidity of the organic ligand. Therefore, the values of D_{str}^* need to be handled with care.

In some cases, the compound contains two crystallographic independent complex units. The ab initio calculations were performed for each of them. Some compounds contain identical or similar structural units. In the series $[\text{Co}(\text{dppm}^{\text{O,O}})_3][\text{Co}(\text{NCS})_4]$ (**J**), $[\text{Co}(\text{dppm}^{\text{O,O}})_3][\text{CoBr}_4]$ (**K**) and $[\text{Co}(\text{dppm}^{\text{O,O}})_3][\text{CoI}_4]$ (**L**) with the chromophores $\{\text{CoO}_2\text{O}'_2\text{O}''_2\}$, the values of D_{str} vary as -1.65 , -1.45 , and $+2.15 \text{ pm}$; $[\text{Co}(\text{dppm}^{\text{O,O}})_3][\text{CoCl}_4]$ (**U**) has a different symmetry of the chromophore $\{\text{CoO}_3\text{O}'_3\}$. The complex $[\text{Co}(\text{pydm})_2](\text{dmbz})_2$ (**O**) is analogous to $[\text{Co}(\text{pydm})_2](\text{mdmbz})_2$ (**P**), but differing in $D_{\text{str}} = -20.1$ and -17.9 pm . Finally, $[\text{Co}(\text{bzpy})_4\text{Cl}_2]$ (**F**) contains two crystallographic different units with $D_{\text{str}} = +7.05$ and -3.5 pm .

4.2. Elongated Tetragonal Bipyramid

Some hexacoordinate Co(II) complexes possess the geometry of the chromophore close to the elongated tetragonal bipyramid with eventual small *o*-rhombic component. Their structural parameter (axiality) is $D_{\text{str}} > 0$. In such a case, it is expected that the temperature dependence of the effective magnetic moment passes through a round maximum (which not necessarily is visible until room temperature). The effective magnetic moment exceeds $\mu_{\text{eff}} > 5 \mu_{\text{B}}$ and the magnetization per formula unit saturates close to $M_1 = M_{\text{mol}}/(N_{\text{A}}\mu_{\text{B}}) \sim 3$. In some cases, the magnetic data have been refitted by a more appropriate model than published previously. Note that the magnetization data can suffer of some orientation effect in higher fields especially when the rso- or vsm-mode of detection is used in the modern SQUID apparatus. Then, the detected magnetization data could be a bit higher than calculated by the fitting procedure which equally weights the susceptibility data taken in small DC field. The free parameters also cover some temperature-independent (para)magnetism χ_{TIM} that influences the high-temperature tail of the magnetic susceptibility, and the molecular field correction zj effective at the lowest temperatures (not listed here).

The key results of the ab initio calculations and fitted magnetic data (susceptibility and magnetization) are presented in Table 2. Certain calculations were redone with respect to the published data in order to keep the same basis set. The success of the spin-Hamiltonian theory is classified as either 5—fulfilled, 4—acceptable, 3—questionable, 2—problematic, or 1—invalid. However, such a classification is rather subjective; a more objective classification is the quantitative evaluation of the spin Hamiltonian according to the score S_1 , introduced as follows:

$$S_1 = N(\text{KD1}) \cdot g_1 \cdot [E(\text{KD3}) - E(\text{KD2})] \cdot \Delta_1 / 10,000 \quad (18)$$

Table 2. Elongated tetragonal bipyramid, $D_{\text{str}} > +3$ pm.

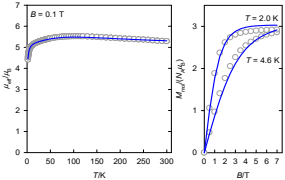
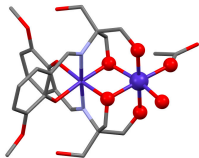
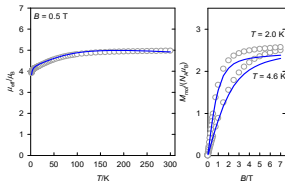
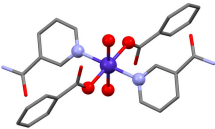
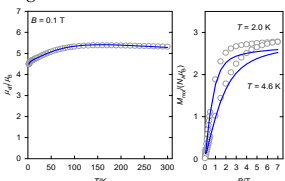
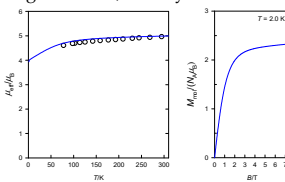
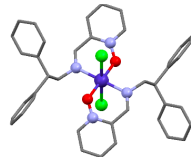
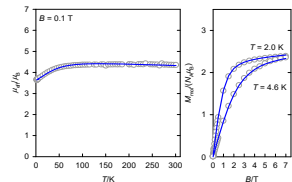
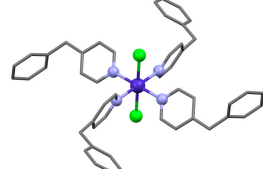
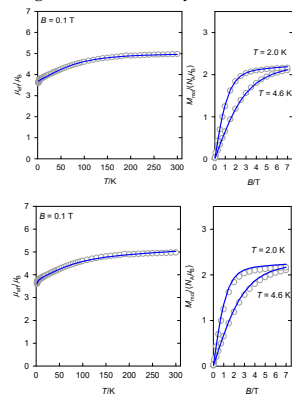
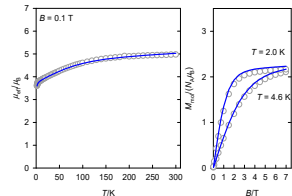
A, $[\text{Co}(\text{H}_2\text{O})_6]^{2+} (\text{OHnc}^-)_2, [\text{CoH}_{12}\text{O}_6]^{2+} 2(\text{C}_6\text{H}_4\text{NO}_3)^-$		CAS Theory: Spin–Orbit Multiplets			
CCDC FONQUV, 295 K, $R_{\text{gt}} = 0.054$ [39,40]	$[\text{CoO}_4\text{O}'_2]$ Co–O' 2.113 Å Co–O 2.042 Å $D_{\text{str}} = +7.1$ pm $E_{\text{str}} = 0$	KD1, 0.61 ^a $\delta_{1,2} = 0$ $41 \cdot \pm 1/2 \rangle +$ $57 \cdot \pm 3/2 \rangle$	KD2, 0.78 $\delta_{3,4} = 209$ $58 \cdot \pm 1/2 \rangle +$ $40 \cdot \pm 3/2 \rangle$	KD3 $\delta_{5,6} = 526$ $55 \cdot \pm 1/2 \rangle +$ $42 \cdot \pm 3/2 \rangle$	KD4 $\delta_{7,8} = 814$ $42 \cdot \pm 1/2 \rangle + 57 \cdot \pm$ $3/2 \rangle$
 Magnetic data, SMR–n.a. 		SH theory: score $S_1 = 7$, $S_2 = 4$, classification 1–invalid			
GF model $\lambda_{\text{eff}} = -188 \text{ cm}^{-1}$ $g_L = -1.10$ $\Delta_{\text{ax}} = -112 \text{ cm}^{-1}$		$^4\Delta_0 = 0$ $^4\Delta_1 = 199$ $^4\Delta_2 = 2468$	$D = -100.9$ $D_1 = -119.9$ $D_2 = +10.5$	$E/D = 0.16$ $E_1 = -0.01$ $E_2 = -10.8$	$g_1 = 1.762g_2 = 1.906g_3 =$ $3.104g_{\text{iso}} = 2.258$
B, $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{L}^1\text{H}_2)_2(\text{H}_2\text{O})(\text{ac})] \cdot (\text{H}_2\text{O})_3, [\text{C}_{26}\text{H}_{35}\text{Co}_2\text{N}_2\text{O}_{13}] 3(\text{H}_2\text{O})$		CAS Theory: Spin–Orbit Multiplets			
CCDC 1440294, 100 K, $R_{\text{gt}} = 0.039$ [41]	$[\text{CoO}_4\text{O}'_2]$ Co–O' 2.150 Å Co–O 2.061 Å $D_{\text{str}} = +8.9$ pm $E_{\text{str}} = 0$	KD1, 0.71 $\delta_{1,2} = 0$ $56 \cdot \pm 1/2 \rangle +$ $43 \cdot \pm 3/2 \rangle$	KD2, 0.88 $\delta_{3,4} = 220$ $38 \cdot \pm 1/2 \rangle +$ $58 \cdot \pm 3/2 \rangle$	KD3 $\delta_{5,6} = 736$ $36 \cdot \pm 1/2 \rangle +$ $62 \cdot \pm 3/2 \rangle$	KD4 $\delta_{7,8} = 1006$ $64 \cdot \pm 1/2 \rangle + 34 \cdot \pm$ $3/2 \rangle$
 Magnetic data, SMR–yes 		SH theory: $S_1 = 30$, $S_2 = 17$, classification 3–questionable			
GF model $\lambda_{\text{eff}} = -198 \text{ cm}^{-1}$ $g_{Lz} = -1.64$ $g_{Lx} = -1.11$ $\Delta_{\text{ax}} = -774 \text{ cm}^{-1}$		$^4\Delta_0 = 0$ $^4\Delta_1 = 444$ $^4\Delta_2 = 1516$	$D = -100.9$ $D_1 = -114.8$ $D_2 = +20.0$	$E/D = 0.25$ $E_1 = -0.01$ $E_2 = -20.0$	$g_1 = 1.842g_2 = 2.293g_3 =$ $3.102g_{\text{iso}} = 2.412$
C, <i>trans</i> - $[\text{Co}(\text{bz})_2(\text{H}_2\text{O})_2(\text{nca})_2], [\text{C}_{26}\text{H}_{26}\text{CoN}_4\text{O}_8]$		CAS Theory: Spin–Orbit Multiplets			
CCDC 804191, 293 K, $R_{\text{gt}} = 0.038$ [42]	$[\text{CoO}_2\text{O}'_2\text{N}_2]$ Co–N 2.147 Å Co–O 2.084 Å Co–O' 2.143 Å $D_{\text{str}} = +7.75$ pm $E_{\text{str}} = 1.85$ pm	KD1, 0.58 $\delta_{1,2} = 0$ $65 \cdot \pm 1/2 \rangle +$ $34 \cdot \pm 3/2 \rangle$	KD2, 0.73 $\delta_{3,4} = 256$ $31 \cdot \pm 1/2 \rangle +$ $67 \cdot \pm 3/2 \rangle$	KD3 $\delta_{5,6} = 525$ $31 \cdot \pm 1/2 \rangle +$ $67 \cdot \pm 3/2 \rangle$	KD4 $\delta_{7,8} = 850$ $72 \cdot \pm 1/2 \rangle + 27 \cdot \pm$ $3/2 \rangle$
 Magnetic data, SMR–n.a. 		SH theory: score $S_1 = 3$, $S_2 = 2$, classification 1–invalid			
GF model $\lambda_{\text{eff}} = -172 \text{ cm}^{-1}$ $g_{Lz} = -2.06$ $g_{Lx} = -1.50$ $\Delta_{\text{ax}} = -739 \text{ cm}^{-1}$		$^4\Delta_0 = 0$ $^4\Delta_1 = 117$ $^4\Delta_2 = 1138$	$D = -113.3$ $D_1 = -131.0$ $D_2 = +26.9$	$E/D = 0.31$ $E_1 = -0.08$ $E_2 = -27.0$	$g_1 = 1.507g_2 = 2.042g_3 =$ $3.160g_{\text{iso}} = 2.237$
D, $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2], [\text{C}_{10}\text{H}_{18}\text{CoO}_6]$		CAS Theory: Spin–Orbit Multiplets			
CCDC 1842364, 100 K, $R_{\text{gt}} = 0.024$ [43]	$[\text{CoO}_2\text{O}'_2\text{O}_w]$ Co–O 2.040 Å Co–O' 2.034 Å Co–O _w 2.157 Å $D_{\text{str}} = +12.0$ pm $E_{\text{str}} = 0.30$ pm	KD1, 0.81 $\delta_{1,2} = 0$ $53 \cdot \pm 1/2 \rangle +$ $45 \cdot \pm 3/2 \rangle$	KD2, 0.93 $\delta_{3,4} = 155$ $46 \cdot \pm 1/2 \rangle +$ $52 \cdot \pm 3/2 \rangle$	KD3 $\delta_{5,6} = 915$ $56 \cdot \pm 1/2 \rangle +$ $40 \cdot \pm 3/2 \rangle$	KD4 $\delta_{7,8} = 1153$ $40 \cdot \pm 1/2 \rangle + 57 \cdot \pm$ $3/2 \rangle$
 Magnetic data, SMR–yes 		SH theory: $S_1 = 91$, $S_2 = 48$, classification 5–fulfilled			
SH-zfs model from ab initio calculations		$^4\Delta_0 = 0$ $^4\Delta_1 = 763$ $^4\Delta_2 = 1398$	$D = +72.0$ $D_1 = +39.7$ $D_2 = +22.7$	$E/D = 0.23$ $E_1 = -39.6$ $E_2 = -22.8$	$g_1 = 1.943g_2 = 2.462g_3 =$ $2.804g_{\text{iso}} = 2.403$

Table 2. Cont.

E, [CoL ² ₂ Cl ₂].3.5H ₂ O, [C ₄₀ H ₃₆ Cl ₂ CoN ₄ O ₂].3.5H ₂ O		CAS Theory: Spin–Orbit Multiplets							
	CCDC 796703, 150 K, R _{gt} = 0.045 [44]	{CoN ₂ O ₂ Cl ₂ }							
		Co–N 2.081 Å Co–O 2.034 Å Co–Cl 2.492 Å D _{str} = +9.45 pm E _{str} = 2.65 pm E _{str} /D _{str} = 0.28	KD1, 0.91 δ _{1,2} = 0 88· ± 1/2> + 9· ± 3/2>	KD2, 0.96 δ _{3,4} = 94 8· ± 1/2> + 89· ± 3/2>	KD3 δ _{5,6} = 1238 11· ± 1/2> + 86· ± 3/2>	KD4 δ _{7,8} = 1441 87· ± 1/2> +9· ± 3/2>			
Magnetic data, SMR–n.a.		SH theory: S ₁ = 257, S ₂ = 226, classification 5–fulfilled							
		SH-zfs model D = 75.1 cm ^{−1} E = 4.8 cm ^{−1} g _z = 2 g _x = 2.51 g _y = 2.36				$\begin{matrix} {}^4\Delta_0 = 0 \\ {}^4\Delta_1 = 1217 \\ {}^4\Delta_2 = 2039 \end{matrix}$	$\begin{matrix} D = +43.3 \\ D_1 = +21.5 \\ D_2 = +13.9 \end{matrix}$	$\begin{matrix} E/D = 0.24 \\ E_1 = +13.6 \\ E_2 = -3.8 \end{matrix}$	$\begin{matrix} g_1 = 2.032g_2 = 2.341g_3 = \\ 2.566g_{\text{iso}} = 2.313 \end{matrix}$
Fa, [Co(bzpy) ₄ Cl ₂], [C ₄₈ H ₄₄ Cl ₂ CoN ₄]		CAS Theory: Spin–Orbit Multiplets							
	CCDC 1497488, 120 K, R _{gt} = 0.027 [45]	{CoN ₄ Cl ₂ }							
		Unit A Co–Cl 2.443 Å Co–N 2.235 Å Co–N 2.176 Å D _{str} = +7.05 pm E _{str} = 1.15 pm	KD1, 0.69 δ _{1,2} = 0 69· ± 1/2> + 29· ± 3/2>	KD2, 0.89 δ _{3,4} = 179 24· ± 1/2> + 73· ± 3/2>	KD3 δ _{5,6} = 633 36· ± 1/2> + 62· ± 3/2>	KD4 δ _{7,8} = 911 73· ± 1/2> +24· ± 3/2>			
Magnetic data, SMR–yes		SH theory: S ₁ = 27, S ₂ = 19, classification 3–questionable							
		GF model/11 λ _{eff} = −175 cm ^{−1} g _{Lz} = −1.02 g _{Lx} = −1.28 Δ _{ax} = −424 cm ^{−1}				$\begin{matrix} {}^4\Delta_0 = 0 \\ {}^4\Delta_1 = 448 \\ {}^4\Delta_2 = 993 \end{matrix}$	$\begin{matrix} D = +87.6 \\ D_1 = +43.2 \\ D_2 = +31.6 \end{matrix}$	$\begin{matrix} E/D = 0.13 \\ E_1 = +43.1 \\ E_2 = -31.4 \end{matrix}$	$\begin{matrix} g_1 = 1.948g_2 = 2.498g_3 = \\ 2.779g_{\text{iso}} = 2.408 \end{matrix}$
		SH-zfs model D = +106 cm ^{−1} g _x = 2.53 g _z = 2							
Fb, [Co(bzpy) ₄ Cl ₂], [C ₄₈ H ₄₄ Cl ₂ CoN ₄]		CAS Theory: Spin–Orbit Multiplets							
Structure as above for Fa		{CoN ₄ Cl ₂ }							
		Unit B Co–Cl 2.433 Å Co–N 2.187 Å Co–N 2.169 Å D _{str} = −3.5 pm E _{str} = 0.9 pm E/ D = 0.26	KD1, 0.49 δ _{1,2} = 0 54· ± 1/2> + 44· ± 3/2>	KD2, 0.68 δ _{3,4} = 252 47· ± 1/2> + 51· ± 3/2>	KD3 δ _{5,6} = 455 34· ± 1/2> + 65· ± 3/2>	KD4 δ _{7,8} = 787 66· ± 1/2> +33· ± 3/2>			
Magnetic data as above for Fa		SH theory: score S ₁ = 2, S ₂ = 1, classification 1–invalid							
		$\begin{matrix} {}^4\Delta_0 = 0 \\ {}^4\Delta_1 = 130 \\ {}^4\Delta_2 = 804 \end{matrix}$	$\begin{matrix} D = +120.9 \\ D_1 = +56.2 \\ D_2 = +34.8 \end{matrix}$	$\begin{matrix} E/D = 0.17 \\ E_1 = +56.2 \\ E_2 = -34.7 \end{matrix}$	$\begin{matrix} g_1 = 1.604g_2 = 2.163g_3 = \\ 2.942g_{\text{iso}} = 2.237 \end{matrix}$				

^a Explanation: $| \pm 1/2 \rangle$ means a cumulative percentage of the spin contributions in the given spin–orbit multiplet arising from the lowest roots referring to the block of the spin multiplicity $m = 4$ (sum of contributions $> 1\%$); ${}^m\Delta_i$ —transition energies between terms at NEVPT2 level; δ —spin–orbit multiplets; D_i (E_i)—contributions to the D (E) parameter from the lowest excitations; all energy data in cm^{-1} . For cations and the solvent containing species, the calculations run for atoms in square brackets in the chemical formula moiety. Critical data—*Italic*.

The set of critical parameters involves the norm of the projected state for the first Kramers doublet $N(\text{KD1})$, the smallest g -tensor component g_1 , the separation of the two subsets of KDs [$E(\text{KD3}) - E(\text{KD2})$], and the first transition energy at the NEVPT2 level ${}^4\Delta_1$ (scaled to smaller numbers). Values of $S_1 > 50$ refer to class 5—fulfilled; $S_1 < 10$ span class 1—invalid. Limiting value for the fulfillment is $S_1 = 0.7 \times 1.9 \times 600 \times 600/10,000 = 48$.

The above parameter can be extended by considering the mixing of the spin states: $S_2 = S_1 \times P/100$ where P —percentage of the greater portion of spins $| \pm 1/2 \rangle$ or $| \pm 3/2 \rangle$ in the first KD (ideally $p > 70$).

The simplest complex containing the hexa-aqua ligands is $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{OHnic})^-_2$ (**A**). The complex cation adopts the geometry of an elongated tetragonal bipyramid with a considerable axiality and zero rhombicity, $D_{\text{str}} = +7.1$ pm and $E_{\text{str}} = 0$. The orbitally degenerate ground term $^4T_{1g}(\text{O}_h)$ causes the Jahn–Teller effect, leading to the symmetry descent, and consequently to the splitting of the ground mother term. The energies of the daughter terms lie at $\{0, 199, 2468\} \text{ cm}^{-1}$, which is consistent with the ground term 4E_g and the excited $^4A_{2g}$ ($\Delta_2 = 2468 \text{ cm}^{-1}$). Small splitting of the ground term $\{0, 199\} \text{ cm}^{-1}$ is caused by “innocent” hydrogen atoms that disturb the ideal D_{4h} symmetry (the ground state is orbitally quasi-degenerate). As valuable results, comparable with experiments, serve the energies of Kramers doublets $\delta\{0, 209, 526, 814\} \text{ cm}^{-1}$, the transitions among them can be identified, for instance, by the FAR-infrared spectra. Rather unexpected is the fact that the compositions of these KDs contain almost equal contributions from $| \pm 1/2 \rangle$ and $| \pm 3/2 \rangle$ spins. This means that the spin–orbit coupling seriously mixes the states of the different spin projections, or in other words, $\hat{H}^{\text{so}}$ cannot be considered as a small perturbation. Therefore, all “products” of the spin Hamiltonian can be false. Indeed, $g_1 = 1.76 \ll 2$, $D = -101 \text{ cm}^{-1}$ are artefacts and this conclusion is also supported by the small norm of the projected state $N(\text{KD1}) = 0.61 \ll 1$. The attempts to fit the magnetic data with the GF model were successful: the round maximum at the effective magnetic moment was perfectly reproduced with $\lambda_{\text{eff}} = A\kappa\lambda = -188 \text{ cm}^{-1}$, $g_L = -1.10$, and $\Delta_{\text{ax}} = -112 \text{ cm}^{-1}$.

The complex $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{L}^1\text{H}_2)_2(\text{H}_2\text{O})(\text{ac})] \cdot (\text{H}_2\text{O})_3$ (**B**) contains the homogeneous donor set $\{\text{CoO}_4\text{O}'_2\}$ with averaged distances $\text{Co}-\text{O}_{\text{eq}} = 2.061$ and $\text{Co}-\text{O}_{\text{ax}} = 2.150 \text{ \AA}$ owing to which $D_{\text{str}} = +8.9$ pm. The energies of KDs are $\delta\{0, 220, (736, 1006)\} \text{ cm}^{-1}$, and they are better separated owing to higher $\Delta_2 = 1516 \text{ cm}^{-1}$. The secondary splitting of 4E_g term is $\Delta_1 = 444 \text{ cm}^{-1}$ so that the orbital degeneracy is partly removed. However, there are critical indicators warning that the spin-Hamiltonian theory is questionable in the present case: $N(\text{KD1}) = 0.71$, $g_1 = 1.84$, and severe mixing of the spin states with the principal contribution < 0.7 ; $D = -101 \text{ cm}^{-1}$. GF Hamiltonian was used in fitting the magnetic data with $\Delta_{\text{ax}} < 0$ resulting in $\lambda_{\text{eff}} = -198 \text{ cm}^{-1}$, $g_{Lz} = -1.64$, $g_{Lx} = -1.11$, and $\Delta_{\text{ax}} = -774 \text{ cm}^{-1}$.

The complex *trans*- $[\text{Co}(\text{bz})_2(\text{H}_2\text{O})_2(\text{nca})_2]$ (**C**), after the corrections to the heterogeneous donor set $\{\text{CoO}_2\text{O}_{w2}\text{N}_2\}$, possesses $D_{\text{str}} = +7.75$; its room-temperature effective magnetic moment reaches $\mu_{\text{eff}} \sim 5 \mu_B$ and the magnetization saturates close to $M_1 \sim 3$. These features are typical for systems with the ground electronic term 4E_g for which the spin-Hamiltonian formalism could fail. The energies of KDs are not well separated into two subsets of KDs $\delta\{0, 256, 525, 850\} \text{ cm}^{-1}$. The critical indicators are: $N(\text{KD1}) = 0.58$, $g_1 = 1.51$, $^4\Delta_1 = 117 \text{ cm}^{-1}$ (almost degenerate ground state), and a boundary mixing of the spin states; $D = -113 \text{ cm}^{-1}$ could be an artefact. The fitting of magnetic data based upon the GF Hamiltonian gave $\lambda_{\text{eff}} = -172 \text{ cm}^{-1}$, $g_{Lz} = -2.06$, $g_{Lx} = -1.50$, and $\Delta_{\text{ax}} = -739 \text{ cm}^{-1}$.

In the complex $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$ (**D**) with the chromophore $\{\text{CoO}_4\text{O}_{w2}\}$, the longest distance is $\text{Co}-\text{O}_w = 2.157 \text{ \AA}$ gave $D_{\text{str}} = +12.0$ pm. The energies of KDs are $\delta\{0, 155, (915, 1153)\} \text{ cm}^{-1}$ and they form two well separated sub-sets. Additionally, the energy of the first electronic transition $^4\Delta_1 = 763 \text{ cm}^{-1}$ suggests that the ground state is well separated from the excited counterpart. Therefore, the spin-Hamiltonian formalism could work, which is also supported by the critical indicators $N(\text{KD1}) = 0.81$ and $g_1 = 1.943$, yielding the score $S1 = 91$. The calculated $D = +73 \text{ cm}^{-1}$ and $E/D = 0.23$ yield an estimate of the energy gap $G_{3,4} = 2(D^2 + 3E^2)^{1/2} = 2|D|[1 + 3(E/D)^2]^{1/2} = 155 \text{ cm}^{-1}$ that equals the energy of the KD2 $\delta_{3,4} = 155 \text{ cm}^{-1}$. The calculated magnetic susceptibility passes through the experimental points and the magnetization per formula unit amounts to $M_{\text{mol}}/(N_A\mu_B) = 2.35$ at $B = 7.0$ T.

The complex $[\text{CoL}^2_2\text{Cl}_2]$ with the $\{\text{CoO}_2\text{N}_2\text{Cl}_2\}$ chromophore (**E**), after correction to the heterogeneity of the donor set, displays $D_{\text{str}} = +9.45$ pm with large rhombicity $E_{\text{str}} = 2.65$ pm ($E_{\text{str}}/D_{\text{str}} = 0.28$) close to the critical value of 0.33 when the sign of the D_{str} is uncertain. The alternate structural parameters are $D_{\text{str}} = -8.7$, $E_{\text{str}} = 3.4$ pm, and

$E_{\text{str}}/D_{\text{str}} = 0.39$. The ab initio calculations confirm that the SH theory for this system is appropriate since $N(\text{KD1}) = 0.91$, $g_1 = 2.03$, ${}^4\Delta_1 = 1217 \text{ cm}^{-1}$, and a weak mixing of spin states exists: $D = +43 \text{ cm}^{-1}$. The estimated energy gap $G_{3,4} = 2(D^2 + 3E^2)^{1/2} = 94 \text{ cm}^{-1}$ matches perfectly the energy of the KD2 $\delta_{3,4} = 94 \text{ cm}^{-1}$. The magnetic data were fitted with the SH-zfs model using $D = 75$, ${}^\circ E = 4.8 \text{ cm}^{-1}$, and $g\{2.51, 2.36, 2.0\}$.

The compound $[\text{Co}(\text{bzpy})_4\text{Cl}_2]$ contains two crystallographic independent molecular complexes with different axiality $D_{\text{str}} = +7.05$ and -3.5 pm, respectively. The unit **Fa** possesses two well-separated subsets of KDs $\delta\{(0, 179), (633, 911)\} \text{ cm}^{-1}$. The first transition energy ${}^4\Delta_1 = 448 \text{ cm}^{-1}$ indicates that the orbital degeneracy is partly removed. Critical indicators classify the SH as acceptable and calculated $D = 88 \text{ cm}^{-1}$ as reasonable. The unit **Fb** displays different properties: not separated groups of KDs $\delta\{0, 252, 455, 787\} \text{ cm}^{-1}$, $N(\text{KD1}) = 0.49$, orbital degeneracy ${}^4\Delta_1 = 130 \text{ cm}^{-1}$, and subnormal $g_1 = 1.60$ that approves classification of SH as invalid. Though the ab initio calculations were performed for individual units separately, the magnetic data reflect some average of their response. The GF model gave $\lambda_{\text{eff}} = -175 \text{ cm}^{-1}$, $g_{Lz} = -1.02$, $g_{Lx} = -1.28$, and $\Delta_{\text{ax}} = -424 \text{ cm}^{-1}$, whereas the SH-zfs model yields $D = +106 \text{ cm}^{-1}$ and $g_x = 2.53$.

4.3. Nearly Octahedral Systems

Since the distance-corrected values $\bar{d}(\text{Co-O})$ and $\bar{d}(\text{Co-N})$ can vary [46], complexes with small negative or small positive D_{str} were included in this group. The results of ab initio calculations and magnetic data fitted either with the GF or SH-zfs model are presented in Table 3.

The compound $[\text{Co}(\text{hfac})_2(\text{etpy})_2]$ contains two independent crystallographic units, and thus ab initio calculations were performed for both of them. The unit **Ga** shows four KDs at $\delta\{0, 237, 461, 804\} \text{ cm}^{-1}$ with a serious mixing of spin states. The critical indicators show that the SH theory is invalid: $N(\text{KD1}) = 0.50$; $g_1 = 1.66$ (subnormal), ${}^4\Delta_1 = 109 \text{ cm}^{-1}$ (quasi degeneracy). The unit **Gb** possesses a better separation of the two subgroups of KDs $\delta\{(0, 196), (568, 873)\} \text{ cm}^{-1}$ owing to increased transition energy ${}^4\Delta_1 = 359 \text{ cm}^{-1}$. The critical indicators are $N(\text{KD1}) = 0.64$; $g_1 = 1.93$ (SH is still problematic). Both complexes have small negative $D_{\text{str}} = -2.00$ and -2.45 pm, which prefer the application of the GF model for the magnetic data fitting with $\lambda_{\text{eff}} = -159 \text{ cm}^{-1}$, $g_{Lz} = -1.96$, $g_{Lx} = -1.79$, and $\Delta_{\text{ax}} = -771 \text{ cm}^{-1}$.

Table 3. Nearly octahedral systems, $|D_{\text{str}}| < 2.5$ pm.

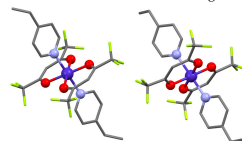
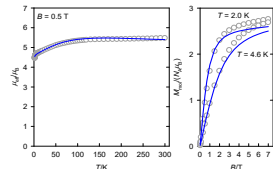
Ga, [Co(hfac) ₂ (etpy) ₂], [C ₂₄ H ₂₀ CoF ₁₂ N ₂ O ₄]		CAS Theory: Spin–Orbit Multiplets				
CCDC 2223471, 100 K, R _{gt} = 0.050		A: {CoO ₄ N ₂ } Co–N 2.132 Å Co–O 2.056 Å Co–O 2.048 Å D _{str} = –2.0 pm E _{str} = 0.4 pm	KD1, 0.50 δ _{1,2} = 0 49· ± 1/2> + 50· ± 3/2>	KD2, 0.73 δ _{3,4} = 237 50· ± 1/2> + 49· ± 3/2>	KD3 δ _{5,6} = 461 52· ± 1/2> + 46· ± 3/2>	KD4 δ _{7,8} = 804 46· ± 1/2> + 52· ± 3/2>
 Magnetic data, SMR–yes 		GF model λ _{eff} = –159 cm ^{–1} g _{Lz} = –1.96 g _{Lx} = –1.79 Δ _{ax} = –771 cm ^{–1}	SH theory: S ₁ = 2, S ₂ = 1, classification 1–invalid			
			⁴ Δ ₀ = 0 ⁴ Δ ₁ = 109 ⁴ Δ ₂ = 785	D = +112 D ₁ = +59.8 D ₂ = +33.4	E/D = 0.20 E ₁ = 58.8 E ₂ = –33.4	g ₁ = 1.661 g ₂ = 2.043 g ₃ = 2.932 g _{iso} = 2.212
Gb, [Co(hfac) ₂ (etpy) ₂], [C ₂₄ H ₂₀ CoF ₁₂ N ₂ O ₄]		CAS Theory: Spin–Orbit Multiplets				
Magnetic data as above		B: {CoO ₄ N ₂ } Co–N = 2.151 Å Co–O 2.040 Å Co–O 2.058 Å D _{str} = –1.45 pm E _{str} = 0.35 pm	KD1, 0.64 δ _{1,2} = 0 37· ± 1/2> + 63· ± 3/2>	KD2, 0.87 δ _{3,4} = 196 45· ± 1/2> + 55· ± 3/2>	KD3 δ _{5,6} = 568 55· ± 1/2> + 45· ± 3/2>	KD4 δ _{7,8} = 873 40· ± 1/2> + 60· ± 3/2>
			SH theory: S ₁ = 16, S ₂ = 10, classification 2–problematic			
			⁴ Δ ₀ = 0 ⁴ Δ ₁ = 359 ⁴ Δ ₂ = 901	D = +94 D ₁ = +47.9 D ₂ = +29.7	E/D = 0.18 E ₁ = –47.9 E ₂ = 29.7	g ₁ = 1.931 g ₂ = 2.351 g ₃ = 2.808 g _{iso} = 2.364

Table 3. Cont.

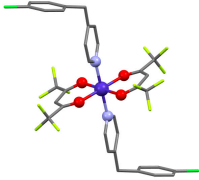
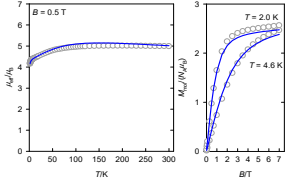
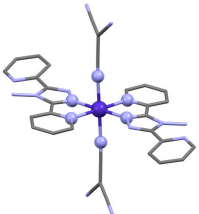
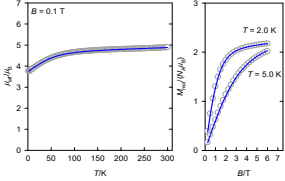
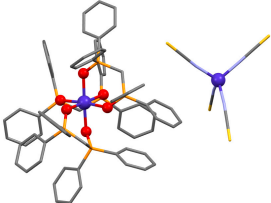
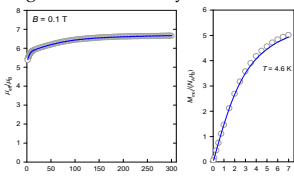
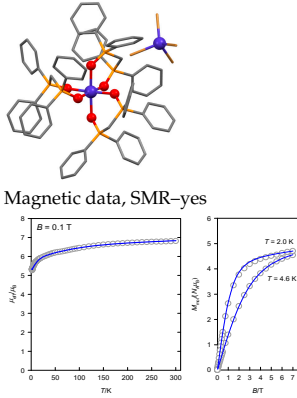
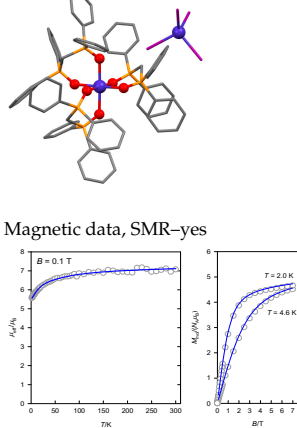
H, [Co(hfac) ₂ (bzpyCl) ₂], [C ₃₄ H ₂₂ Cl ₂ CoF ₁₂ N ₂ O ₄]		CAS Theory: Spin–Orbit Multiplets			
CCDC 2223472, 100 K, $R_{\text{gt}} = 0.036$	[CoO ₄ N ₂]* Co–N 2.137 Å Co–O 2.061 Å Co–O 2.062 Å $D_{\text{str}} = -2.45$ pm $E_{\text{str}} = 0.05$ pm	KD1, 0.58 $\delta_{1,2} = 0$ $24 \cdot \pm 1/2 > +$ $74 \cdot \pm 3/2 >$	KD2, 0.83 $\delta_{3,4} = 188$ $78 \cdot \pm 1/2 > +$ $20 \cdot \pm 3/2 >$	KD3 $\delta_{5,6} = 582$ $79 \cdot \pm 1/2 > +$ $20 \cdot \pm 3/2 >$	KD4 $\delta_{7,8} = 883$ $6 \cdot \pm 1/2 > +$ $90 \cdot \pm 3/2 >$
 Magnetic data, SMR–yes 		SH theory: $S_1 = 17$, $S_2 = 13$, classification 2–problematic			
GF model $\lambda_{\text{eff}} = -170$ cm ^{−1} $g_{Lz} = -1.83$ $g_{Lx} = -1.11$ $\Delta_{\text{ax}} = -643$ cm ^{−1}		$^4\Delta_0 = 0$ $^4\Delta_1 = 392$ $^4\Delta_2 = 905$	$D = +91$ $D_1 = +45.9$ $D_2 = +29.6$	$E/D = 0.16$ $E_1 = 45.7$ $E_2 = -29.0$	$g_1 = 1.954$ $g_2 = 2.372$ $g_3 = 2.781$ $g_{\text{iso}} = 2.369$
I, [Co(abpt) ₂ (tcm) ₂], [C ₃₂ H ₂₀ CoN ₁₈]		CAS Theory: Spin–Orbit Multiplets			
CCDC 997721, 173 K, $R_{\text{gt}} = 0.036$ [47]	[CoN ₄ N' ₂]* Co–N' 2.133 Å Co–N 2.109 Å Co–N 2.125 Å $D_{\text{str}} = -2.0$ pm $E_{\text{str}} = 0.4$ pm	KD1, 0.86 $\delta_{1,2} = 0$ $20 \cdot \pm 1/2 > +$ $79 \cdot \pm 3/2 >$	KD2, 0.96 $\delta_{3,4} = 131$ $76 \cdot \pm 1/2 > +$ $17 \cdot \pm 3/2 >$	KD3 $\delta_{5,6} = 862$ $85 \cdot \pm 1/2 > +$ $13 \cdot \pm 3/2 >$	KD4 $\delta_{7,8} = 1066$ $5 \cdot \pm 1/2 > +$ $92 \cdot \pm 3/2 >$
 Magnetic data, SMR–yes [47] 		SH theory: $S_1 = 115$, $S_2 = 91$, classification 5–fulfilled			
SH-zfs model $D = +55$ cm ^{−1} $E = 14.6$ cm ^{−1} $g_x = 2.53$ $g_z = 2$		$^4\Delta_0 = 0$ $^4\Delta_1 = 900$ $^4\Delta_2 = 1878$	$D = +50.3$ $D_1 = +28.5$ $D_2 = +17.6$	$E/D = 0.29$ $E_1 = +28.5$ $E_2 = -17.6$	$g_1 = 2.037$ $g_2 = 2.333$ $g_3 = 2.636$ $g_{\text{iso}} = 2.335$
J, [Co(dppm ^{O,O}) ₃][Co(NCS) ₄], [C ₇₅ H ₆₆ CoO ₆ P ₆] ²⁺ Co(NCS) ₄ ^{2−}		CAS Theory: Spin–Orbit Multiplets			
CCDC 1526142, 100 K, $R_{\text{gt}} = 0.041$ [48]	[CoO ₂ O' ₂ O'' ₂] Co–O 2.094 Å Co–O' 2.089 Å Co–O'' 2.074 Å $D_{\text{str}} = -1.65$ pm $E_{\text{str}} = 0.35$ pm	KD1, 0.61 $\delta_{1,2} = 0$ $51 \cdot \pm 1/2 > +$ $48 \cdot \pm 3/2 >$	KD2, 0.86 $\delta_{3,4} = 211$ $47 \cdot \pm 1/2 > +$ $51 \cdot \pm 3/2 >$	KD3 $\delta_{5,6} = 562$ $47 \cdot \pm 1/2 > +$ $51 \cdot \pm 3/2 >$	KD4 $\delta_{7,8} = 966$ $57 \cdot \pm 1/2 > +$ $41 \cdot \pm 3/2 >$
 Magnetic data, SMR–yes 		SH theory: $S_1 = 21$, $S_2 = 11$, classification 2–problematic			
SH-zfs model $D = +93$ cm ^{−1} $g_x = 2.76$ $g_z = 2$		$^4\Delta_0 = 0$ $^4\Delta_1 = 445$ $^4\Delta_2 = 539$	$D = +105.5$ $D_1 = +46.3$ $D_2 = +42.0$	$E/D = 0.03$ $E_1 = +45.7$ $E_2 = -41.9$	$g_1 = 1.972$ $g_2 = 2.592$ $g_3 = 2.688$ $g_{\text{iso}} = 2.417$

Table 3. Cont.

K, [Co(dppm ^{O,O}) ₃][CoBr ₄], [C ₇₅ H ₆₆ CoO ₆ P ₆] ²⁺ CoBr ₄ ^{2−}		CAS Theory: Spin–Orbit Multiplets			
CCDC 1526141, 100 K, $R_{\text{gt}} = 0.044$ [49]	{CoO ₂ O'':O'' ₂ } Co–O 2.109 Å Co–O' 2.102 Å Co–O'' 2.091 Å $D_{\text{str}} = -1.45$ pm $E_{\text{str}} = 0.35$ pm	KD1, 0.61 $\delta_{1,2} = 0$ $51 \cdot \pm 1/2 \rangle +$ $47 \cdot \pm 3/2 \rangle$	KD2, 0.86 $\delta_{3,4} = 211$ $46 \cdot \pm 1/2 \rangle +$ $53 \cdot \pm 3/2 \rangle$	KD3 $\delta_{5,6} = 562$ $47 \cdot \pm 1/2 \rangle +$ $52 \cdot \pm 3/2 \rangle$	KD4 $\delta_{7,8} = 966$ $59 \cdot \pm 1/2 \rangle +$ $39 \cdot \pm 3/2 \rangle$
		SH theory: $S_1 = 19$, $S_2 = 10$, classification 2–problematic			
SH-zfs model $D = +122$ cm ^{−1} $g_x = 2.68$ $g_z = 2$		${}^4\Delta_0 = 0$ ${}^4\Delta_1 = 445$ ${}^4\Delta_2 = 539$	$D = +105.5$ $D_1 = +46.3$ $D_2 = +42.53$	$E/D = 0.03$ $E_1 = +45.7$ $E_2 = -41.9$	$g_1 = 1.972$ $g_2 = 2.592$ $g_3 = 2.688$ $g_{\text{iso}} = 2.417$
L, [Co(dppm ^{O,O}) ₃][CoI ₄], [C ₇₅ H ₆₆ CoO ₆ P ₆] ²⁺ CoI ₄ ^{2−}		CAS Theory: Spin–Orbit Multiplets			
CCDC 1526143, 100 K, $R_{\text{gt}} = 0.028$ [48]	{CoO ₂ O'':O'' ₂ } Co–O 2.092 Å Co–O' 2.076 Å Co–O'' 2.065 Å $D_{\text{str}} = +2.15$ pm $E_{\text{str}} = 0.55$ pm	KD1, 0.57 $\delta_{1,2} = 0$ $45 \cdot \pm 1/2 \rangle +$ $54 \cdot \pm 3/2 \rangle$	KD2, 0.80 $\delta_{3,4} = 223$ $56 \cdot \pm 1/2 \rangle +$ $41 \cdot \pm 3/2 \rangle$	KD3 $\delta_{5,6} = 508$ $49 \cdot \pm 1/2 \rangle +$ $49 \cdot \pm 3/2 \rangle$	KD4 $\delta_{7,8} = 874$ $49 \cdot \pm 1/2 \rangle +$ $48 \cdot \pm 3/2 \rangle$
		SH theory: $S_1 = 8$, $S_2 = 4$, classification 1–invalid			
SH-zfs model $D = +99$ cm ^{−1} $g_x = 2.70$ $g_z = 2$		${}^4\Delta_0 = 0$ ${}^4\Delta_1 = 258$ ${}^4\Delta_2 = 732$	$D = +107.9$ $D_1 = +54.6$ $D_2 = +34.1$	$E/D = 0.15$ $E_1 = +54.6$ $E_2 = -34.1$	$g_1 = 1.860$ $g_2 = 2.319$ $g_3 = 2.868$ $g_{\text{iso}} = 2.349$

An analogous complex [Co(hfac)₂(bzpyCl)₂] (**H**) shows $D_{\text{str}} = -2.45$ pm with well-separated subgroups of KDs $\delta\{(0, 188), (582, 883)\}$ cm^{−1}. The set of indicators is still critical: $N(\text{KD1}) = 0.58$; $g_1 = 1.95$, ${}^4\Delta_1 = 392$ cm^{−1} (degeneracy is partly lifted), and the mixing of spin states is rather weak. The SH formalism is problematic; $D = +91$ cm^{−1}. The GF model for the magnetic data fitting gave $\lambda_{\text{eff}} = -170$ cm^{−1}, $g_{Lz} = -1.83$, $g_{Lx} = -1.11$, and $\Delta_{\text{ax}} = -643$ cm^{−1}.

The molecular complex [Co(abpt)₂(tcm)₂] (**I**) displays small $D_{\text{str}} = -2.0$ pm. All critical indicators confirm that the SH formalism is fulfilled: $\delta\{(0, 131), (862, 1066)\}$ cm^{−1}, $N(\text{KD1}) = 0.86$; $g_1 = 2.04$, ${}^4\Delta_1 = 900$ cm^{−1} (orbital degeneracy lifted), weak mixing of spin states. Then, the evaluated $D = +50$ cm^{−1} can be considered as a valid parameter. The composition of the ground KD1 is $\{20 \cdot | \pm 1/2 \rangle + 79 \cdot | \pm 3/2 \rangle\}$ with dominating contributions of $| \pm 3/2 \rangle$; for $D > 0$, just $| \pm 1/2 \rangle$ is expected as a dominating component of the ground multiplet Γ_6 . Perhaps large rhombicity $E/D = 0.29$ causes this feature.

Three complexes of the type [Co(dppm^{O,O})₃][CoX₄], X = NCS[−], Br[−] and I[−] possess the same cationic complex (with 154 atoms) with small axiality $D_{\text{str}} = -1.65$, -1.45 , and $+2.15$ pm, respectively. (The fourth member with X = Cl[−] has a different geometry of the chromophore {CoO₃O'':O''₂}). The presence of the complex anions was not involved in calculations; however, the experimental data reflect their effect on the increased values of the effective magnetic moment and magnetization.

The complex cation in [Co(dppm^{O,O})₃][Co(NCS)₄] (**J**) possesses $\delta\{(0, 211), (562, 966)\}$ cm^{−1}, $g_1 = 1.97$, ${}^4\Delta_1 = 445$ cm^{−1} (degeneracy partly lifted), but a serious mixing of spin states. Therefore, it is classified as SH–problematic; $D(\text{O}_h) = +105$ cm^{−1}. Note that the solid-state magnetic data

were fitted assuming the presence of both nearly octahedral and nearly tetrahedral units with $D(O_h) = 91$, $D(T_d) = -5.0 \text{ cm}^{-1}$.

The complex cation in $[\text{Co}(\text{dppm}^{\text{O},\text{O}})_3][\text{CoBr}_4]$ (**K**) behaves analogously to its NCS analogue: $\delta\{(0, 211), (562, 966)\} \text{ cm}^{-1}$, $g_1 = 1.97$, ${}^4\Delta_1 = 445 \text{ cm}^{-1}$ (degeneracy partly lifted), $N(\text{KD1}) = 0.61$ and a serious mixing of spin states; $D(O_h) = +105 \text{ cm}^{-1}$. The SH is classified as problematic and the fitting of magnetic data gave $D(O_h) = +122$ and $D(T_d) = +15 \text{ cm}^{-1}$.

The complex $[\text{Co}(\text{dppm}^{\text{O},\text{O}})_3][\text{CoI}_4]$ (**L**) with $\delta\{(0, 223), (508, 874)\} \text{ cm}^{-1}$ shows different critical parameters: ${}^4\Delta_1 = 258 \text{ cm}^{-1}$ (near degeneracy), subnormal $g_1 = 1.86$ and again a strong mixing of spin states. The SH is classified as invalid; calculated $D(O_h) = +107 \text{ cm}^{-1}$ and fitted $D(O_h) = +99$ and $D(T_d) = +19 \text{ cm}^{-1}$.

In summary, the ab initio calculations for nearly octahedral Co(II) complexes predicted $D > 0$ when the spin Hamiltonian was appropriate and matching the magnetic data fitting.

4.4. Compressed Tetragonal Bipyramid

This numerous group involves complexes with a considerable negative axiality of $D_{\text{str}} \ll 3$ (Table 4). In general, the magnetic data for them can be fitted with the SH-zfs model which assumes $g_z = 2$, $g_x \gg 2$, $D \gg 0$. Alternatively, the GF model can also be used with $\Delta_{\text{ax}} > 0$.

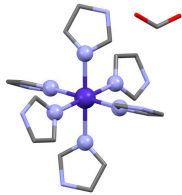
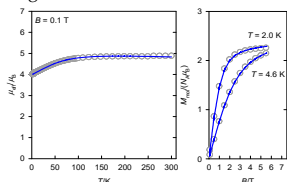
The compound $[\text{Co}(\text{bzpy})_4(\text{NCS})_2]$ contains two crystallographic independent molecular complexes with $D_{\text{str}} = -11.75$ and -11.05 pm , respectively. The electronic properties of them are similar: two subgroups of KDs $\delta\{(0, 187), (646, 965)\} \text{ cm}^{-1}$, ${}^4\Delta_1 = 473 \text{ cm}^{-1}$ and $g_1 = 1.93$. Therefore, the SH is classified as questionable; $D = +89 \text{ cm}^{-1}$ for **Na** (and similar for **Nb**). The magnetic data fitting using the SH model gave $D = +95 \text{ cm}^{-1}$ and $g_x = 2.52$.

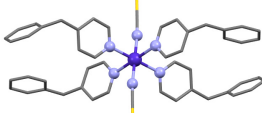
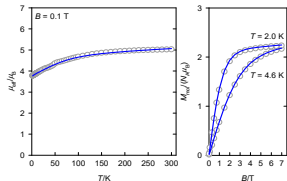
The cationic complex of $[\text{Co}(\text{pydm})_2](\text{dnbz})_2$ (**O**) contains the pincer-type ligands pydm which, owing to a rigidity, do not coordinate on the axes of the equatorial plane, so that the values of $D_{\text{str}}^* = -20.15 \text{ pm}$ need be considered with care. Two sub-set of KDs are well separated $\delta\{(0, 188), (864, 1099)\} \text{ cm}^{-1}$ owing to increased ${}^4\Delta_1 = 614 \text{ cm}^{-1}$. The critical parameters indicate that the SH might be fulfilled: $N(\text{KD1}) = 0.71$, $g_1 = 1.98$, weak mixing of spin states. The only disturbance is the negative value of $D = -92 \text{ cm}^{-1}$, since positive value is expected for the compressed tetragonal bipyramid. This point will be explained later using the GCFT calculations.

An analogous compound contains the same cationic complex $[\text{Co}(\text{pydm})_2](\text{mdnbz})_2$ (**P**) with the same pincer ligand but slightly modified counter anion; $D_{\text{str}}^* = -17.9 \text{ pm}$. Again, two groups of KDs are well separated $\delta\{(0, 145), (870, 1099)\} \text{ cm}^{-1}$ and the first transition energy is ${}^4\Delta_1 = 708 \text{ cm}^{-1}$. However, $N(\text{KD1}) = 0.68$ and increased mixing of the spin states cause the classification of the SH—close to fulfilled. Again, negative $D = -69 \text{ cm}^{-1}$ was calculated for this system. With this data, the energy gap $G_{3,4} = 145 \text{ cm}^{-1}$ matches the energy of the first excited KD, $\delta_{3,4} = 145 \text{ cm}^{-1}$. The magnetic data were fitted almost perfectly using the SH-zfs model with $D = -50 \text{ cm}^{-1}$.

The complex $[\text{Co}(\text{iz})_6](\text{fm})_2$ (**M**) with the homogeneous ligand sphere contains the $\{\text{CoN}_6\}$ chromophore that can be classified as a compressed tetragonal bipyramid with considerable, but negative axiality and small rhombicity: $D_{\text{str}} = -6.10$ and $E_{\text{str}} = 0.71 \text{ pm}$. The energies of the spin-orbit multiplets $\delta\{0, 256, 450, 836\} \text{ cm}^{-1}$ are quite similar to the complex $[\text{Co}(\text{H}_2\text{O})_6](\text{OHnc})_2$ (**A**). There is a set of critical indicators warning that the spin-Hamiltonian theory fails: $N(\text{KD1}) = 0.46$, ${}^4\Delta_1 = 35 \text{ cm}^{-1}$ (orbital degeneracy), $g_1 = 1.30$, $g_2 = 1.83$ (subnormal values), and severe mixing of the spin states; $D = +124 \text{ cm}^{-1}$. Nevertheless, the magnetic data were fitted with the SH-zfs model with parameters $D = +69 \text{ cm}^{-1}$ and $g_x = 2.75$.

Table 4. Compressed tetragonal bipyramid, $D_{\text{str}} < -3$ pm.

M [Co(iz)₆]²⁺(fm[−])₂, [C₁₈H₂₄CoN₁₂]²⁺ 2(CHO₂)[−]		CAS Theory: Spin–Orbit Multiplets			
CCDC 624939, 296 K, R _{gt} = 0.034 [39,50]	[CoN ₄ N'₂] Co–N' 2.211 Å Co–N 2.197 Å Co–N' 2.143 Å D _{str} = −6.10 pm E _{str} = 0.71 pm	KD1, 0.46 δ _{1,2} = 0 60· ± 1/2> + 38· ± 3/2>	KD2, 0.54 δ _{3,4} = 256 34· ± 1/2> + 64· ± 3/2>	KD3 δ _{5,6} = 450 35· ± 1/2> + 64· ± 3/2>	KD4 δ _{7,8} = 836 72· ± 1/2> + 26· ± 3/2>
					
Magnetic data, SMR–n.a.		SH theory: S ₁ = 0.4, S ₂ = 0.2, classification 1–invalid			
	SH-zfs model D = +69.2 cm ^{−1} g _x = 2.75 g _z = 2	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 35 ⁴ Δ ₂ = 591	D = +124.0 D ₁ = +62.4 D ₂ = +39.0	E/D = 0.15 E ₁ = +61.9 E ₂ = −37.0	g ₁ = 1.302 g ₂ = 1.829 g ₃ = 2.974 g _{iso} = 2.035

Na, [Co(bzpy)₄(NCS)₂], [C₅₀H₄₄CoN₆S₂]		CAS Theory: Spin–Orbit Multiplets			
CCDC 1497489, 120 K, R _{gt} = 0.036 [45]	[CoN ₄ N'₂] Unit A Co–N' 2.086 Å Co–N 2.217 Å Co–N 2.180 Å D _{str} = −11.7 pm E _{str} = 1.35 pm	KD1, 0.68 δ _{1,2} = 0 79· ± 1/2> + 21· ± 3/2>	KD2, 0.88 δ _{3,4} = 187 13· ± 1/2> + 85· ± 3/2>	KD3 δ _{5,6} = 646 33· ± 1/2> + 67· ± 3/2>	KD4 δ _{7,8} = 965 78· ± 1/2> + 20· ± 3/2>
					
Magnetic data, SMR–yes		SH theory: S ₁ = 28, S ₂ = 22, classification 3–questionable			
	SH-zfs model D = +90.5 cm ^{−1} g _x = 2.52 g _z = 2	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 473 ⁴ Δ ₂ = 838	D = +88.9 D ₁ = +47.2 D ₂ = +30.7	E/D = 0.17 E ₁ = +47.0 E ₂ = −30.4	g ₁ = 1.932 g ₂ = 2.446 g ₃ = 2.823 g _{iso} = 2.400

Nb, [Co(bzpy)₄(NCS)₂], [C₅₀H₄₄CoN₆S₂]		CAS Theory: Spin–Orbit Multiplets			
	Unit B Co–N' 2.094 Å Co–N 2.213 Å Co–N 2.196 Å D _{str} = −11.0 pm E _{str} = 0.85 pm	KD1, 0.67 δ _{1,2} = 0 79· ± 1/2> + 21· ± 3/2>	KD2, 0.88 δ _{3,4} = 189 12· ± 1/2> + 85· ± 3/2>	KD3 δ _{5,6} = 638 33· ± 1/2> + 66· ± 3/2>	KD4 δ _{7,8} = 975 80· ± 1/2> + 18· ± 3/2>
Magnetic data as above		SH theory: S ₁ = 28, S ₂ = 22, classification 3–questionable			
		⁴ Δ ₀ = 0 ⁴ Δ ₁ = 481 ⁴ Δ ₂ = 776	D = +91.7 D ₁ = +47.0 D ₂ = +32.1	E/D = 0.15 E ₁ = +46.6 E ₂ = −31.6	g ₁ = 1.938 g ₂ = 2.466 g ₃ = 2.806 g _{iso} = 2.403

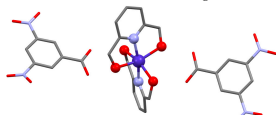
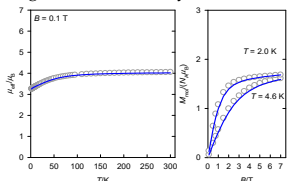
O, [Co(pydm)₂]²⁺(dnbz)[−], [C₁₄H₁₈CoN₂O₄]²⁺ 2(C₇H₃N₂O₆)[−] pincer type		CAS Theory: Spin–Orbit Multiplets			
CCDC 1533249, 100 K, R _{gt} = 0.037 [51]	[CoO ₄ N ₂] Co–N 2.039 Å Co–O 2.110 Å Co–O 2.171 Å D _{str} * = −20.15 E _{str} * = 3.05	KD1, 0.71 δ _{1,2} = 0 22· ± 1/2> + 75· ± 3/2>	KD2, 0.89 δ _{3,4} = 188 75· ± 1/2> + 21 ± 3/2>	KD3 δ _{5,6} = 864 59· ± 1/2> + 36· ± 3/2>	KD4 δ _{7,8} = 1099 37· ± 1/2> + 61· ± 3/2>
					
Magnetic data, SMR–yes		SH theory: S ₁ = 58, S ₂ = 44, classification 5–fulfilled			
	SH-zfs model D = −62 cm ^{−1} g _z = 2.13 g _x = 2	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 615 ⁴ Δ ₂ = 2199	D = −91.8 D ₁ = −103.0 D ₂ = +8.9	E/D = 0.13 E ₁ = −0.3 E ₂ = −11.4	g ₁ = 1.983 g ₂ = 2.169 g ₃ = 3.058 g _{iso} = 2.403

Table 4. Cont.

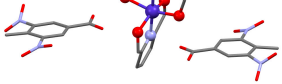
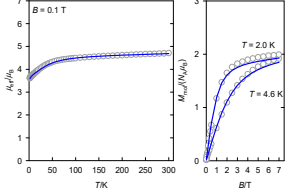
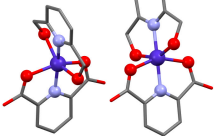
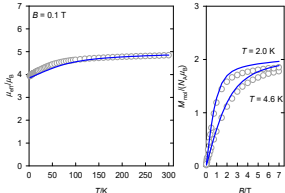
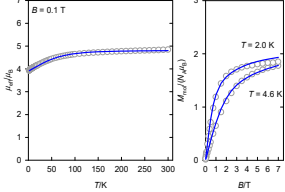
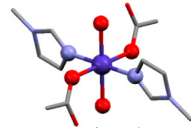
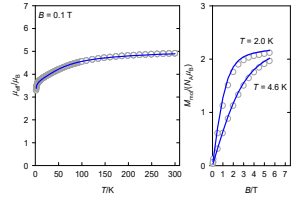
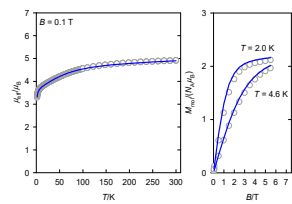
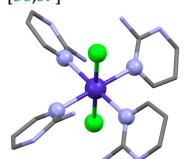
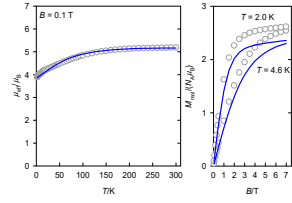
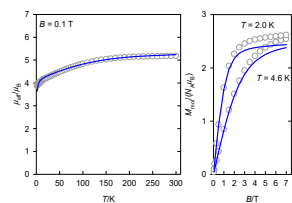
P, [Co(pydm) ₂] ²⁺ (dmnbz) [−] ₂ , [C ₁₄ H ₁₈ CoN ₂ O ₄] ²⁺ ·2(C ₈ H ₅ N ₂ O ₆) [−] ; <i>pincer</i> type		CAS Theory: Spin–Orbit Multiplets			
 CCDC 1945478, 100 K, R_{gt} = 0.042 [52]	{CoO ₄ N ₂ } Co–N 2.038 Å Co–O 2.120 Å Co–O 2.114 Å D _{str} * = −17.9 pm E _{str} * = 0.30 pm	KD1, 0.68 δ _{1,2} = 0 40· ± 1/2> + 57· ± 3/2>	KD2, 0.88 δ _{3,4} = 145 57· ± 1/2> + 38· ± 3/2>	KD3 δ _{5,6} = 870 63· ± 1/2> + 35· ± 3/2>	KD4 δ _{7,8} = 1099 32· ± 1/2> + 65· ± 3/2>
	Magnetic data, SMR–yes 	SH theory: S ₁ = 72, S ₂ = 41, classification 5–fulfilled			
	SH-zfs model D = −50.0 cm ^{−1} g _z = 2.30 g _x = 2	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 708 ⁴ Δ ₂ = 1831	D = −69.0 D ₁ = −86.9 D ₂ = +11.7	E/D = 0.19 E ₁ = −0.02 E ₂ = −11.8	g ₁ = 2.047 g ₂ = 2.213 g ₃ = 2.878 g _{iso} = 2.379
Qa, [Co(pydca)(dmpy)], [C ₁₄ H ₁₂ CoN ₂ O ₆]; <i>pincer</i> type		CAS Theory: Spin–Orbit Multiplets			
 [Co(pydca)(dmpy)]·0.5 H₂O CCDC 1585697, 100 K, R_{gt} = 0.041 [53]	A: {CoO ₄ N ₂ } Co–N 2.031 Å Co–O 2.152 Å Co–O 2.163 Å D _{str} * = −22.6 pm E _{str} * = 0.55 pm	KD1, 0.78 δ _{1,2} = 0 64· ± 1/2> + 34· ± 3/2>	KD2, 0.93 δ _{3,4} = 162 37· ± 1/2> + 61· ± 3/2>	KD3 δ _{5,6} = 813 20· ± 1/2> + 77· ± 3/2>	KD4 δ _{7,8} = 1046 77· ± 1/2> + 21· ± 3/2>
	Magnetic data, SMR–yes 	SH theory: S ₁ = 62, S ₂ = 40, classification 5–fulfilled			
	SH-zfs model D = −89.5 cm ^{−1} g _x = 2.42 g _z = 2.50	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 614 ⁴ Δ ₂ = 2228	D = −77.2 D ₁ = −93.6 D ₂ = +11.0	E/D = 0.18 E ₁ = −0.01 E ₂ = −11.4	g ₁ = 1.992 g ₂ = 2.226 g ₃ = 2.945 g _{iso} = 2.388
	GF model λ _{eff} = −141 cm ^{−1} g _L = −1.13 Δ _{ax} = −811 cm ^{−1}				
Qb, [Co(pydca)(dmpy)], [C ₁₄ H ₁₂ CoN ₂ O ₆]; <i>pincer</i>		CAS Theory: Spin–Orbit Multiplets			
B: {CoO ₄ N ₂ } Co–N 2.028 Å Co–O 2.133 Å Co–O 2.176 Å D _{str} * = −22.6 pm E _{str} * = 2.15 pm	Magnetic data as above	KD1, 0.82 δ _{1,2} = 0 8· ± 1/2> + 90· ± 3/2>	KD2, 0.95 δ _{3,4} = 147 90· ± 1/2> + 7· ± 3/2>	KD3 δ _{5,6} = 968 83· ± 1/2> + 12· ± 3/2>	KD4 δ _{7,8} = 1179 14· ± 1/2> + 85· ± 3/2>
		SH theory: S ₁ = 107, S ₂ = 96, classification 5–fulfilled			
		⁴ Δ ₀ = 0 ⁴ Δ ₁ = 786 ⁴ Δ ₂ = 2692	D = −97.1 D ₁ = −112.0 D ₂ = +9.6	E/D = 0.10 E ₁ = −0.08 E ₂ = −6.9	g ₁ = 2.022 g ₂ = 2.112 g ₃ = 2.898 g _{iso} = 2.377

Table 4. Cont.

R, [Co(ac) ₂ (H ₂ O) ₂ (MeIm) ₂], [C ₁₂ H ₂₂ CoN ₄ O ₆]		CAS Theory: Spin–Orbit Multiplets				
CCDC 618142, 100 K, R _{gt} = 0.033 [54,55]		{CoO ₂ O'₂N ₂ }	KD1, 0.84	KD2, 0.93	KD3	KD4
		Co–N 2.127 Å	δ _{1,2} = 0	δ _{3,4} = 156	δ _{5,6} = 1030	δ _{7,8} = 1230
		Co–O' 2.122 Å	41· ± 1/2> +	58· ± 1/2> +	54· ± 1/2> +	41· ± 1/2> +
		Co–O _w 2.170 Å	57· ± 3/2>	40· ± 3/2>	44· ± 3/2>	57· ± 3/2>
		D _{str} = −11.9 pm				
		E _{str} = 2.4 pm	SH theory: S ₁ = 123, S ₂ = 70, classification–5 <i>fulfilled</i>			
Magnetic data, SMR–yes		GF model				
		λ _{eff} = −217 cm ^{−1}	⁴ Δ ₀ = 0	D = +75.1	E/D = 0.16	g ₁ = 1.910
		g _{Lz} = −1.23	⁴ Δ ₁ = 878	D ₁ = +35.0	E ₁ = +35.0	g ₂ = 2.508
		g _{Lx} = −1.37	⁴ Δ ₂ = 1593	D ₂ = +23.2	E ₂ = −23.0	g ₃ = 2.764
		Δ _{ax} = +568 cm ^{−1}				g _{iso} = 2.394
		SH-zfs model				
		D = +82 cm ^{−1}				
		g _x = 2.54				
		g _z = 2				

S, [Co(ampyd) ₂ Cl ₂], [C ₁₆ H ₂₀ Cl ₂ CoN ₁₂]		CAS Theory: Spin–Orbit Multiplets				
CCDC SEQFUQ, 293 K, R _{gt} = 0.023 [56,57]		{CoN ₄ Cl ₂ }	KD1, 0.50	KD2, 0.63	KD3	KD4
		Co–Cl 2.450 Å	δ _{1,2} = 0	δ _{3,4} = 262	δ _{5,6} = 461	δ _{7,8} = 800
		Co–N 2.233 Å	54· ± 1/2> +	41· ± 1/2> +	50· ± 1/2> +	53· ± 1/2> +
		Co–N 2.233 Å	45· ± 3/2>	57· ± 3/2>	49· ± 3/2>	46· ± 3/2>
		D _{str} = −7.03 pm				
		E _{str} = 0	SH theory: S ₁ = 1, S ₂ = 0.6, classification 1– <i>invalid</i>			
Magnetic data, SMR–n.a.		GF model				
		λ _{eff} = −181 cm ^{−1}	⁴ Δ ₀ = 0	D = +121	E/D = 0.23	g ₁ = 1.434
		g _{Lz} = −1.5	⁴ Δ ₁ = 77	D ₁ = +60.9	E ₁ = +60.9	g ₂ = 1.900
		g _{Lx} = −1.3	⁴ Δ ₂ = 869	D ₂ = +30.9	E ₂ = −30.9	g ₃ = 3.066
		Δ _{ax} = +377 cm ^{−1}				g _{iso} = 2.133
		SH-zfs model				
		D = +146 cm ^{−1}				
		g _x = 2.91				
		g _z = 2				

* denotes the “pincer”-type complexes possessing deviations from the equatorial plane.

The compound [Co(pydc)(dmpy)]·0.5H₂O contains two crystallographic independent units, both with negative axiality $D_{\text{str}} = -22.65$ pm. The site **Qa** possesses well-separated subgroups of KDs $\delta\{(0, 162), (813, 1046)\}$ and $^4\Delta_1 = 614$ cm^{−1}. The critical indicators signalize that the SH is fulfilled: $N(\text{KD1}) = 0.78$, $g_1 = 1.99$; only the mixing of the spin states is stronger. The unit **Qb** exhibits similar characteristics with $D = -97$ cm^{−1} in comparison with $D = -77$ cm^{−1} for **Qa**. The fitting of the magnetic data with the SH-zfs model gave $D = -89$ cm^{−1}, $g_z = 2.50$, and $g_x = 2.42$.

The complex [Co(ac)₂(H₂O)₂(MeIm)₂] (**R**) possesses $D_{\text{str}} = -11.9$ pm and the ab initio data confirm a separation of the two subsets of KDs $\delta\{(0, 156), (1030, 1230)\}$ cm^{−1} owing to large $^4\Delta_1 = 878$ cm^{−1}. The critical indicators show that the SH is fulfilled: $N(\text{KD1}) = 0.84$ and $g_1 = 1.91$. With expectations, $D = +75$ cm^{−1} is positive for compressed tetragonal

bipyramid. There is a serious mixing of spin states. The same quality of the magnetic data fits was obtained using the GF model ($\lambda_{\text{eff}} = -217 \text{ cm}^{-1}$, $g_{Lz} = -1.23$, $g_{Lx} = -1.37$, $\Delta_{\text{ax}} = +568 \text{ cm}^{-1}$) and/or the SH-zfs model ($D = +82 \text{ cm}^{-1}$, $g_x = 2.54$).

The complex *trans*-[Co(ampyd)₂Cl₂] (**S**) possesses $D_{\text{str}} = -7.03$ and the critical indicators warn that the SH fails: $N(\text{KD1}) = 0.50$, subnormal $g_1 = 1.43$, and $g_2 = 1.90$, very small transition energy ${}^4\Delta_1 = 76.6 \text{ cm}^{-1}$ which causes the two subgroups of KDs to not be separated $\delta\{0, 262, 461, 800\} \text{ cm}^{-1}$. Then, the calculated $D = +121 \text{ cm}^{-1}$ is false and the magnetic data fitting is not satisfactory when the SH is used. The GF model gave acceptable fit with $\lambda_{\text{eff}} = -181 \text{ cm}^{-1}$, $g_{Lz} = -1.5$, $g_{Lx} = -1.3$, and $\Delta_{\text{ax}} = +377 \text{ cm}^{-1}$.

4.5. Miscellaneous Geometry

This section involves data for complexes that do not span the above three classes: the structural axiality D_{str} is either undefined or oddly defined (Table 5). It shows a versatility of the magnetic behavior of hexacoordinate Co(II) complexes.

Table 5. Miscellaneous geometry.

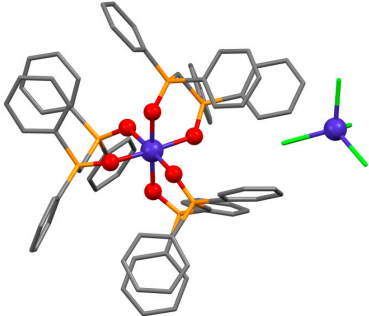
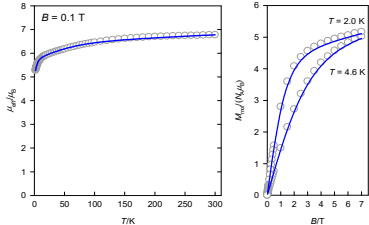
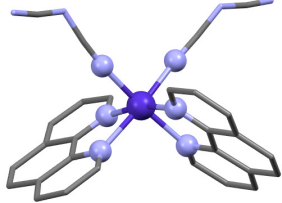
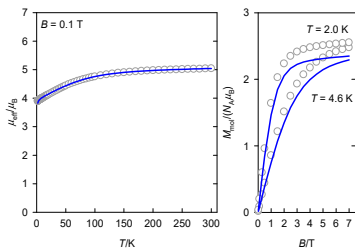
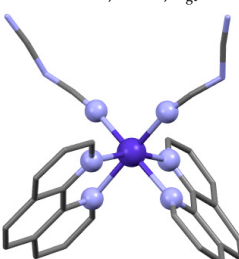
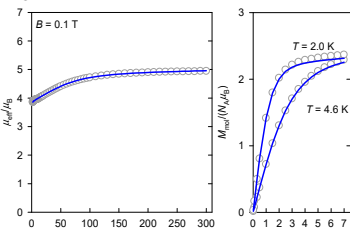
T, [Co(dppm ^{O,O}) ₃] ²⁺ ·CoCl ₄ ^{2−} , [C ₇₅ H ₆₆ CoO ₆ P ₆] ²⁺ CoCl ₄ ^{2−}		CAS Theory: Spin–Orbit Multiplets			
	CCDC 296003, 100 K, $R_{\text{gt}} = 0.066$ [48]	{CoO ₃ O' ₃ }	KD1, 0.40 $\delta_{1,2} = 0$ $50 \cdot \pm 1/2 > +$ $49 \cdot \pm 3/2 >$	KD2, 0.72 $\delta_{3,4} = 317$ $49 \cdot \pm 1/2 > +$ $49 \cdot \pm 3/2 >$	KD3 $\delta_{5,6} = 389$ $49 \cdot \pm 1/2 > +$ $50 \cdot \pm 3/2 >$
		Co–O 2.112 Å Co–O' 2.074 Å			KD4 $\delta_{7,8} = 925$ $48 \cdot \pm 1/2 > +$ $50 \cdot \pm 3/2 >$
Magnetic data, SMR–yes 		SH theory: $S_1 = 0.7$, $S_2 = 0.4$, classification 1–invalid			
SH-zfs model $D = +77 \text{ cm}^{-1}$ $g_x = 2.55$ $g_z = 2$			${}^4\Delta_0 = 0$ ${}^4\Delta_1 = 142$ ${}^4\Delta_2 = 142$	$D = +158.3$ $D_1 = +59.1$ $D_2 = +59.1$	$E/D = 0.00$ $E_1 = +59.1$ $E_2 = -59.1$
					$g_1 = 1.781$ $g_2 = 2.505$ $g_3 = 2.505$ $g_{\text{iso}} = 2.263$
Ua, <i>cis</i> -[Co(phen) ₂ (dca) ₂], [C ₂₈ H ₁₆ CoN ₁₀] α-polymorph		CAS Theory: Spin–Orbit Multiplets			
	CCDC 997503, 193 K, $R_{\text{gt}} = 0.029$ [58]	{CoN ₄ N' ₂ }	KD1, 0.54 $\delta_{1,2} = 0$ $19 \cdot \pm 1/2 > +$ $79 \cdot \pm 3/2 >$	KD2, 0.65 $\delta_{3,4} = 243$ $82 \cdot \pm 1/2 > +$ $17 \cdot \pm 3/2 >$	KD3 $\delta_{5,6} = 495$ $82 \cdot \pm 1/2 > +$ $15 \cdot \pm 3/2 >$
		Co–N 2.153 Å Co–N' _{dca} 2.076 Å			KD4 $\delta_{7,8} = 838$ $8 \cdot \pm 1/2 > +$ $90 \cdot \pm 3/2 >$
Magnetic data, SMR–n.a. 		SH theory: $S_1 = 2$, $S_2 = 2$, classification 1–invalid			
SH-zfs model $D = +91 \text{ cm}^{-1}$ $g_x = 2.66$ $g_z = 2$			${}^4\Delta_0 = 0$ ${}^4\Delta_1 = 110$ ${}^4\Delta_2 = 961$	$D = 108.2$ $D_1 = 63.7$ $D_2 = 27.3$	$E/D = 0.30$ $E_1 = 63.7$ $E_2 = -27.2$
					$g_1 = 1.487$ $g_2 = 1.956$ $g_3 = 3.085$ $g_{\text{iso}} = 2.176$

Table 5. Cont.

Ub, <i>cis</i> -[Co(phen) ₂ (dca) ₂], [C ₂₈ H ₁₆ CoN ₁₀] β-polymorph		CAS Theory: Spin–Orbit Multiplets				
CCDC 997504, 293 K, <i>R</i> _{gt} = 0.040 [58]		{CoN ₄ N'₂}	KD1, 0.76	KD2, 0.91	KD3	KD4
		Co–N 2.153 Å	δ _{1,2} = 0	δ _{3,4} = 168	δ _{5,6} = 737	δ _{7,8} = 1029
		Co–N' dca 2.071 Å	51· ± 1/2> +	46· ± 1/2> +	52· ± 1/2> +	47· ± 1/2> +
			48· ± 3/2>	51· ± 3/2>	46· ± 3/2>	50· ± 3/2>
Magnetic data, SMR–n.a.		SH theory: <i>S</i> ₁ = 51, <i>S</i> ₂ = 26, classification 5–fulfilled				
		SH-zfs model <i>D</i> = +85 cm ^{−1} <i>g</i> _{<i>x</i>} = 2.60 <i>g</i> _{<i>z</i>} = 2	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 618 ⁴ Δ ₂ = 1041	<i>D</i> = 81.2 <i>D</i> ₁ = 40.3 <i>D</i> ₂ = 25.7	<i>E</i> / <i>D</i> = 0.16 <i>E</i> ₁ = 40.1 <i>E</i> ₂ = −25.7	<i>g</i> ₁ = 1.923 <i>g</i> ₂ = 2.460 <i>g</i> ₃ = 2.768 <i>g</i> _{iso} = 2.383

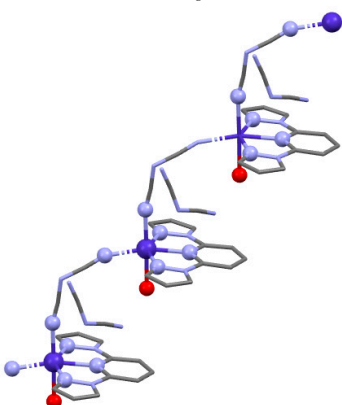
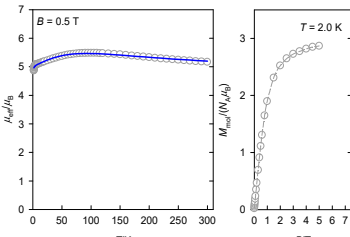
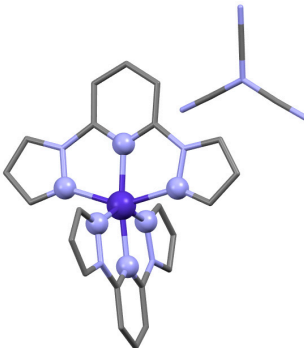
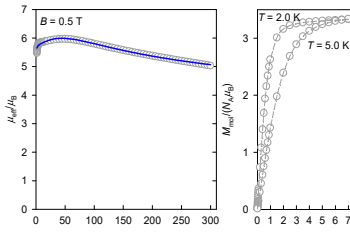
V, [μ-(dca)Co(pypz)(H ₂ O)] dca ^a					
CCDC 1973544, 295 K, <i>R</i> _{gt} = 0.033 [59]					
					
		{CoN ₃ N'₂O}			
		Co–N 2.155 Å Co–N' 2.076 Å Co–O 2.134 Å			
Magnetic data, SMR–yes					
		GF model λ _{eff} = −131 cm ^{−1} <i>g</i> _L = −2.00 Δ _{ax} = −2000 cm ^{−1}			

Table 5. Cont.

W, [Co(pypz) ₂] ²⁺ (tcm) [−] ₂ , [C ₂₂ H ₁₈ CoN ₁₀] ²⁺ ·2(C ₃ N ₄) [−] ^a		CAS Theory: Spin–Orbit Multiplets				
	CCDC 1973546, 295 K, R _{gt} = 0.037 [59]	{CoN ₄ N'₂}	KD1, 0.74	KD2, 0.91	KD3	KD4
		Co–N' 2.082 Å Co–N 2.164 Å Co–N 2.164 Å D _{str} * = −8.2 pm E _{str} = 0	δ _{1,2} = 0 14· ± 1/2> + 85· ± 3/2>	δ _{3,4} = 159 85· ± 1/2> + 11· ± 3/2>	δ _{5,6} = 717 88· ± 1/2> + 11· ± 3/2>	δ _{7,8} = 1003 3· ± 1/2> + 95· ± 3/2>
Magnetic data, SMR–yes		SH theory: S ₁ = 47, S ₂ = 40, classification 4–acceptable				
		GF model λ _{eff} = −87 cm ^{−1} g _L = −2.77 Δ _{ax} = −4000 cm ^{−1}	⁴ Δ ₀ = 0 ⁴ Δ ₁ = 571 ⁴ Δ ₂ = 1179	D = +72.2 D ₁ = +43.4 D ₂ = +21.0	E/D = 0.26 E ₁ = +43.6 E ₂ = −21.0	g ₁ = 1.990 g ₂ = 2.349 g ₃ = 2.818 g _{iso} = 2.384

^a No ab initio calculations for the chain complex.

The complex [Co(dppm^{O,O})₃][CoCl₄] (**T**) spans the series [Co(dppm^{O,O})₃][CoX₄], but unlike the NCS[−], Br[−], and I[−] members, it displays different geometry of the {CoO₃O₃'} chromophore so that axiality D_{str} is not defined in this case. The critical indicators warn that the SH is not fulfilled, since g₁ = 1.78, ⁴Δ₁ = 150.6, and ⁴Δ₂ = 150.9 cm^{−1}, strong mixing of spin states are demonstrated, and not separated subsets of KDs δ{0, 314, 393, 926} cm^{−1}. Therefore, the calculated D = +157 cm^{−1} could be false. However, the magnetic data were satisfactorily fitted with D = +77 cm^{−1}.

The complex *cis*-[Co(phen)₂(dca)₂] exists as two polymorphs (**Ua**, **Ub**) and again does not fulfil the definition of axiality D_{str}. According to the critical indicators for **Ua**, the SH is classified as invalid: N(KD1) = 0.54, g₁ = 1.49, very low transition energy ⁴Δ₁ = 110 cm^{−1}, and the two subsets of KDs not separated δ{0, 243, 495, 838} cm^{−1}. The calculated value of D = +108 cm^{−1} seems to be overestimated. The magnetic data were fitted with D = 91 cm^{−1} and g_x = 2.66; however, the fit was not satisfactory for the magnetization data. For the polymorph **Ub**, the situation was completely different with a high score of S₁ = 51 (mainly due to the high first transition energy ⁴Δ₁ = 618 cm^{−1}) that allows a classification of the SH as fulfilled. At the same time, both the susceptibility and magnetization data were fitted excellently using D = 85 cm^{−1} and g_x = 2.60.

The complex cation in [Co(pypz)₂](tcm)₂ (**V**) possesses the considerable axiality D_{str} = −8.2, E_{str} = 0. However, the deviations of four N-donor atoms from the equatorial plane are not negligible owing to the rigid geometry of the pincer-type ligand. The energies of KDs are split into two well-separated subsets δ{(0, 159), (717, 1003)} cm^{−1}, owing to the removal of the orbital degeneracy, ⁴Δ₁ = 571 cm^{−1}. The critical indicators confirm that the SH is fulfilled: N(KD1) = 0.74, g₁ = 1.99, weak mixing of spin states; the value of D = +72 cm^{−1} is fully acceptable. However, the calculations were performed for a free complex cation abstracting from the environment. The environment alone plays a critical role, since the tcm[−] ligands link several cationic units into a complex network which shows features of the exchange interaction of a ferromagnetic nature. The magnetic susceptibility passes through a maximum that is typical for tetragonal systems with positive axiality, and at the same time the magnetization per formula unit exceeds a value of M₁ > 3. The

magnetic data cannot be fitted by a reliable set of parameters using both GF and SH-zfs models for a single magnetic center.

The complex $[\mu\text{-(dca)Co(pypz)(H}_2\text{O)}]$ dca (**W**) has structure of a 1D chain decorated by free dca[−] ions. The ab initio calculations were not performed; the magnetic data were fitted with the GF model.

5. Statistical Analysis

The calculated ab initio data were used to form a worksheet for modern statistical analysis [60]. The Cluster Analysis divides the observables according to the “distance” into four or five groups; for codes, see Figure 8.

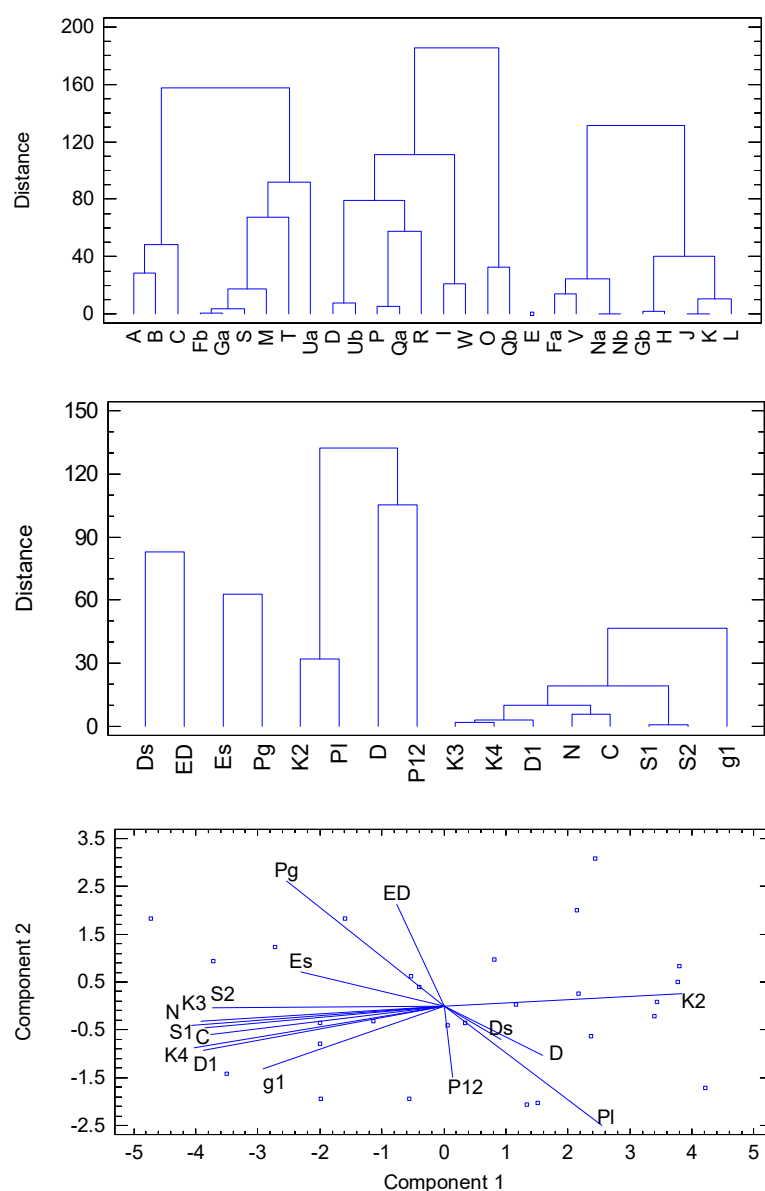


Figure 8. Results of the statistical analysis. Top and center—cluster analysis, Wards method, squared Euclidean distance. Bottom—biplot of principal component analysis. Codes: K2, K3, K4—energies of Kramers doublets; D1—transition energy ${}^4\Delta_1$; g1—the lowest g-factor; N—projection norm $N(KD1)$; Pg (P1)—greater (lower) portion of spins in multiplets of KD1; P12—portion of $\pm 1/2$ spins in multiplets of KD1; S1 and S2—score of SH; C—classification factor of SH (1 = invalid, 5 = fulfilled); D—axial zero-field splitting parameter; ED—ratio E/D ; Ds—axiality D_{str} ; Es—rhombicity E_{str} .

Complementary information brings the biplot of the Principal Component Analysis: (i) with decreasing D_1 , the energy of K2 increases and simultaneously the energies of K3 and K4 decrease; (ii) at the same time, the critical indicators g_1 and N decrease, thus showing a failure of the spin-Hamiltonian formalism; (iii) D correlates with D_s ; and (iv) C anticorrelates with D (with increasing calculated D , the classification factor C decreases from 5 to 1).

The classification score of the spin Hamiltonian (between 1 to 5) correlates with the first transition energy ${}^4\Delta_1$ (Figure 9). For $\Delta_1 < 300 \text{ cm}^{-1}$, the SH data are barely reliable (class 1) because of the quasi-degeneracy. For $\Delta_1 > 600 \text{ cm}^{-1}$, the SH data are highly reliable (class 4 or 5). A numerical correlation including the correlation coefficient is presented in Figure 10.

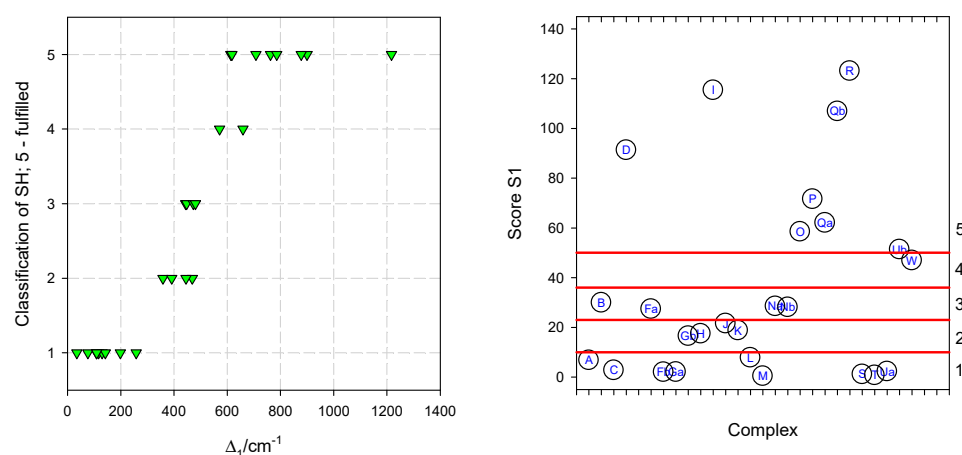


Figure 9. Classification of the spin Hamiltonian by qualitative score: 5—fulfilled, 4—acceptable, 3—questionable, 2—problematic, 1—invalid. $S_1 = N(KD1) \times g_1 \times [E(KD3) - E(KD2)] \times \Delta_1 / 10,000$ for individual complexes. Limiting value $S_1 = 0.7 \times 1.9 \times 600 \times 600 / 10,000 \sim 50$. Values $S_1 > 50$ refer to the class 5—fulfilled; $S_1 < 10$ span the class 1—invalid.

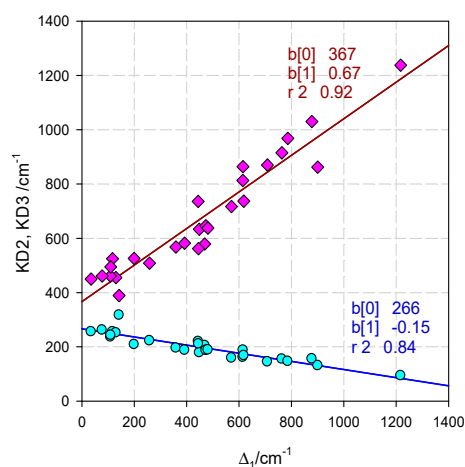


Figure 10. Correlations among ab initio calculated parameters: $KD2(KD3) = b_0 + b_1 \cdot \Delta_1$. The greater the first transition energy Δ_1 : (i) the lower the energy of the second Kramers doublet ($KD2 \sim 2D$); (ii) the greater the energy of $KD3$. For $\Delta_1 < 300 \text{ cm}^{-1}$, the SH data are barely reliable because of the quasi-degeneracy ($C = 1$). For $\Delta_1 > 600 \text{ cm}^{-1}$, the SH data are highly reliable ($C = 5$).

The sign of the axial zero-field splitting parameter D attracts great attention, mainly in the light of the D-U paradigm, according to which the barrier to spin reversal U for the Orbach process of slow magnetic relaxation fulfills the relationship $U = |D|(S^2 - 1/4)$ for Kramers systems [1]. A deeper analysis of experimental data shows: (i) slow magnetic

relaxation exists also in systems with D —positive, negligible, or in systems where D is undefined ($S = 1/2$); (ii) quantitatively, the above paradigm is not true, at least for the hexacoordinate Co(II) complexes. In the cases of hexacoordinate Co(II) complexes when the SH is fulfilled (D_{4h} , D_{2h} symmetry of the chromophore), $D > 0$ generally holds true. Ab initio calculations can indicate some $D < 0$; however, in the cases when HS fails ($D_{str} \gg 0$).

There is an exception for complexes containing the pincer-type ligands when the donor set occupies sites outside the axes of the equatorial plane. This point has already been modelled by using GCFT calculations, as depicted in Figure 11 [51].

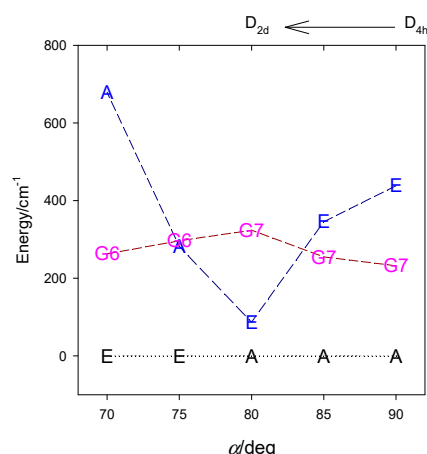


Figure 11. Calculated energies of the crystal field terms (A, E) and multiplets (G6, G7) on angular distortion of square bipyramid D_{4h} to D_{2d} via angle α bisecting O–Co–O. Expt.: $2\alpha = \text{O2-Co1-O1} = 151.88$ and $\text{O4-Co1-O3} = 154.16$ deg for the complex $\text{Co}(\text{pydca})(\text{dmpy})$ (O) with the pincer-type ligands.

The GCFT allows a wide-range modelling of the energies of spin–orbit multiplets (KDs) $\delta_{i,i+1}$ and SH parameters (D , g_z , g_x , χ_{TIP}) depending upon the strength of the crystal field poles $F_4(\text{ax})$ and $F_4(\text{eq})$; the results are presented in Figure 12. For the elongated tetragonal bipyramid, the D -values are undefined, since the ground term is orbitally degenerate 4E_g and the two lowest multiplets span the irreducible representations Γ_6 and Γ_6 .

A majority of hexacoordinate Co(II) complexes investigated in this work were tested for a slow magnetic relaxation (SMR), and all of the tested cases confirm the presence of SMR. The existence of SMR is independent of the geometry—whether the complex belongs to the elongated or compressed tetragonal bipyramid, the nearly octahedral, or miscellaneous geometry. The contemporary state of the art is as follows (Figure 13). (i) A more careful data selection at low frequencies of the oscillating AC magnetic field reveals the second (LF) and eventually third (IF) relaxation channel in addition to the high-frequency (HF) one. These channels are strongly dependent upon the applied DC field. (ii) The low-frequency relaxation channel attenuates on heating more progressively than the HF one. (iii) The temperature ranges, in which the maximum (maxima) on the out-of-phase susceptibility is visible, are often limited to $T < 6$ K. (iv) The analysis of the relaxation data according to the Arrhenius-like equation $\tau = \tau_0 \exp(U/k_B T)$ is appropriate only for the Orbach relaxation process. Using a few high-temperature data, the evaluation of the extrapolated relaxation time (for infinite temperature) τ_0 , and the barrier to spin reversal U is often possible; however, it can yield incorrect values when the slow relaxation at the highest edge of the data taking is not attenuated. The collection of $\{D, U, \tau_0\}$ data is of little value when the relaxation proceeds according to the alternate mechanisms such as Raman, phonon bottleneck, and direct relaxation mechanisms. (v) The plot $\ln \tau$ vs. $\ln T$ brings information about the temperature coefficient in the above mechanisms proceeding via eqn. $\tau^{-1} = CT^m$: $m \sim 1$ for the direct process, $m \sim 2$ for the phonon bottleneck process, or $m = 5\text{--}9$ for the Raman process. The Orbach process requires $m > 9$, which, as a rule, is not the case. Data in Figure 13 confirm that the HF relaxation mode at elevated temperatures proceeds via the Raman mechanism with the temperature coefficient $m = 5.9$; at low temperature,

a reciprocating thermal behavior applies, $m = -0.64$ when on cooling the relaxation time decreases [61,62].

axial strengthening – axial weakening

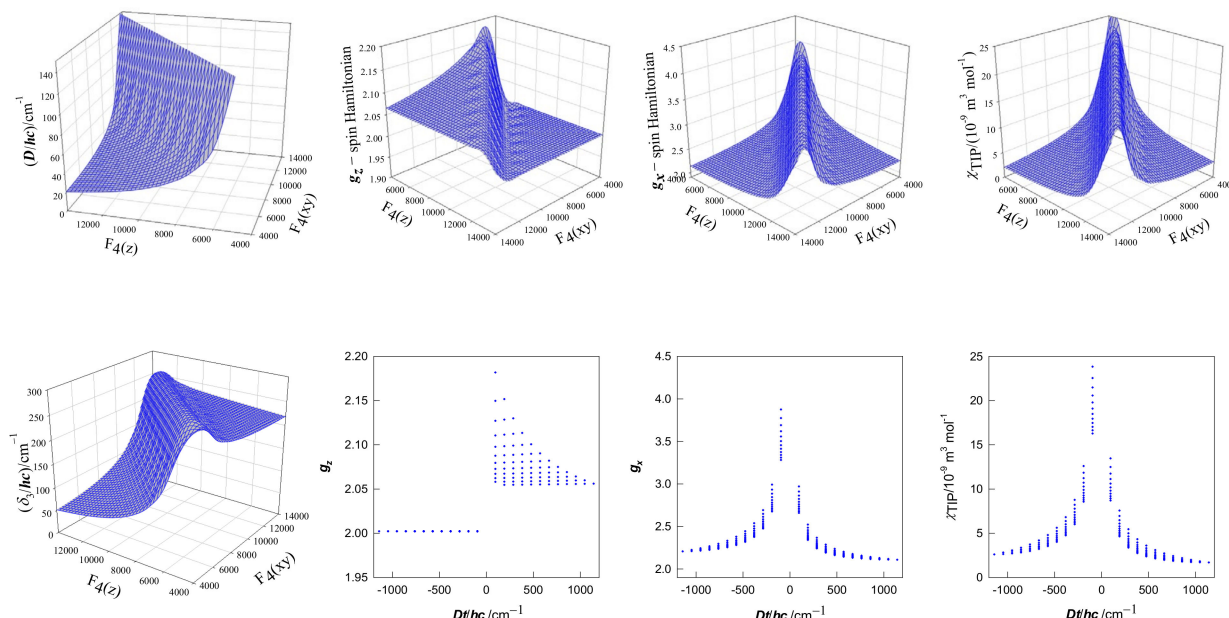


Figure 12. Three-dimensional diagram of D vs. $F_4(z)$ - $F_4(xy)$ calculated by GCFT for hexacoordinate Co(II) complexes. $\delta_3 = E_3(\Gamma_7) - E_1(\Gamma_6)$ for compressed form ($\sim 2D$); $\delta_3 = E_3(\Gamma_6) - E_1(\Gamma_6)$ for elongated form not matching the spin Hamiltonian. Manifold co-ordinate points for g_z , g_x and χ_{TIP} refer to different $10Dq$.

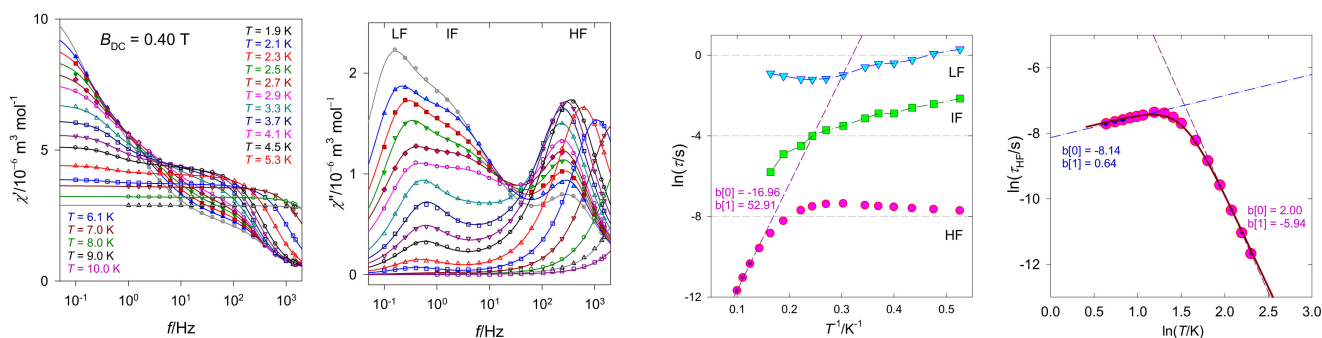


Figure 13. AC susceptibility data for $[\text{Co}(\text{pydc})(\text{dmpy})] \cdot 0.5\text{H}_2\text{O}$. Left: frequency dependence of AC susceptibility at various temperatures and applied field $B_{DC} = 0.4$ T showing three relaxation channels; solid lines—fitted with the three-set Debye model. Right: dependences of the relaxation time and their fit to the exponential Arrhenius-like equation $\ln \tau = b_0 + b_1 T^{-1}$ and power equation $\ln \tau = b_0 + b_1 \ln T$ [53].

The final critical remark is addressed to the spin-Hamiltonian formalism that considers the existence of only two KDs separated by $2D$. If this gap, for instance, is only $G = 100 \text{ cm}^{-1}$ (144 K), then the Boltzmann population of KD2 at $T = 10 \text{ K}$ is $P_{3,4} = 2 \times (5.6 \times 10^{-7})$, i.e., negligible. This discriminates the Orbach relaxation mechanism and related U and τ_0 as unrealistic parameters. In the light of these findings, the value of the collection of the published data on D and their relationship to U in hexacoordinate Co(II) complexes is questionable [63]. There are several original and review articles about the impact of the zero-field splitting on the DC and AC magnetic properties of hexacoordinate Co(II) complexes; some of them are accompanied by ab initio calculations; however, a deeper validity assessment of the spin-Hamiltonian formalism is missing [64–70].

6. Conclusions

The hexacoordinate Co(II) complexes can be classified into four groups according to their structural axiality (tetragonality) D_{str} : (i) complexes with large positive values referring to the elongated tetragonal bipyramid (with some *o*-rhomobicity); (ii) nearly octahedral complexes with small $|D_{\text{str}}|$; (iii) complexes with large negative D_{str} referring to the compressed tetragonal bipyramid; and (iv) complexes with miscellaneous geometry. The first type possesses the ground electronic terms orbitally (nearly) degenerate 4E_g (with corresponding daughter terms on symmetry lowering). The spin Hamiltonian, as a rule, fails, and thus the magnetic data need to be fitted by employing the extended Griffith–Figgis model working in the space of 12 spin–orbit kets. The GF theory is an intermediate step between the spin Hamiltonian recognizing only 4 (fictitious) spin kets and the complete active space of 120 kets generated by the d^7 configuration.

The activation of the spin-Hamiltonian formalism in the first-principle calculations yields the D -parameters that could be false. Typically, $D > 0$ holds true for hexacoordinate Co(II) complexes with the exception of those with pincer-type ligands. The perfect fulfilment of the spin-Hamiltonian formalism is rather rare; some critical indicators allow a classification as 5—fulfilled, 4—acceptable, 3—questionable, 2—problematic, and 1—invalid. Of 24 compounds containing 28 hexacoordinate complexes studied by *ab initio* method, only 10 span the categories 5 and 4, and 9 the category 1. The failure of the SH manifests itself in low first transition energy ${}^4\Delta_1 < 300 \text{ cm}^{-1}$, low projection norm $N(\text{KD1}) < 0.7$, subnormal value of the lowest g -factor $g_1 < 1.9$, and large mixing of the spin components into multiplets with the highest portion $p < 70\%$. In such a case, the second-order perturbation theory tends to diverge and the calculated D parameters are overestimated. The statistical methods (Cluster Analysis, Principal Component Analysis) bring information which parameters mutually correlate.

The D values obtained by fitting the magnetic data are risky to accept without deep theoretical analysis. The first energy gap given by the energy of the second Kramers doublet $G = \delta_{3,4}$ can be reconstructed by assuming $G = 2|D|$, or $G = 2(D^2 + 3E^2)^{1/2}$. Thus, the successful fit itself is not a guarantee that the spin-Hamiltonian formalism is fulfilled for the given case. The main obstacle lies in the fact that for hexacoordinate Co(II) complexes, six Kramers doublets result from the ground electronic term ${}^4T_{1g}$; four of them can be close in energy while the spin-Hamiltonian formalism recognizes only two of them.

Author Contributions: All authors contributed equally. All authors have read and agreed to the published version of the manuscript.

Funding: Slovak grant agencies (APVV 19-0087 and VEGA 1/0086/21) are acknowledged for the financial support.

Data Availability Statement: Magnetic data are available from the corresponding author by requirement.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

abpt	4-amino-3,5-bis(2-pyridyl)-1,2,4-triazol
ac	acetato(1-) ligand
ampyd	2-aminopyrimidine
bz	benzoato(1-) ligand
bzpy	4-benzylpyridine
bzpyCl	4-(4-Chlorobenzyl)pyridine
dca	dicyanamide(1-)
dmphen	2,9-dimethyl-1,10-phenanthroline
dnbz	3,5-dinitrobenzoato(1-)
dppm ^{O,O}	bis-(diphenylphosphanoxido)methane
etpy	4-ethylpyridine

fm	formiate(1-) ion
hfac	hexafluoroacetylacetonato(1-)
im, iz	1H-imidazole
L ¹ H ₂	2-[[2-(hydroxy-3-methoxyphenyl)-methylene]amino}-2-(hydroxymethyl)-1,3-propanediol
L ²	2-[(2,2-diphenylethylimino)methyl]pyridine-1-oxide
mdnbz	3,5-dinitrobenzoato(1-)
MeIm	N-methylimidazole
OHnic	6-hydroxynicotinate
pydca	pyridine-2,6-dicarboxylato(1-)
pydm, dmpy	2,6-pyridinedimethanol
pypz	2,6-bis(pyrazol-1-yl)pyridine
tcm	tricyanomethanide(1-)
w	aqua ligand

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