



Magnetism, IR and Raman spectra of a tetracoordinate and hexacoordinate Co(II) complexes derived from aminopyrimidine



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ABSTRACT

Two mononuclear Co(II) complexes of the $[\text{CoCl}_2\text{L}_2]$ and $[\text{CoCl}_2\text{L}_4]$ family, with L being a heterocyclic N-donor ligand – 2-aminopyrimidine were prepared and subjected to magnetochemical investigation. Temperature dependence of the magnetic susceptibility and the field dependence of magnetization have been analyzed simultaneously in terms of the spin Hamiltonian formalism. The magnetic parameters obtained by a fitting procedure show a considerable magnetic anisotropy measured by the g -factor difference and the zero-field splitting parameter $2D$, which splits the ground ${}^4\text{B}_1(\text{D}_{2d})$ term and/or ${}^4\text{A}_{1g}(\text{D}_{4h})$ term. The temperature dependence of the Far-IR spectra for the centrosymmetric hexacoordinate complex shows variable-temperature absorption peaks which yield the value of the zero-field energy gap $\Delta_{\text{IR}} = 455 \text{ cm}^{-1}$. Raman spectra, *ab initio* and DFT calculations assist in an accurate assignment of the absorption peaks.

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1. Introduction

Magnetism of high-spin cobalt(II) complexes is rather rich in its manifestations [1]. The ground electronic term in the octahedral geometry ${}^4\text{T}_{1g}$ is orbitally degenerate and thus it is subjected to the Jahn-Teller effect. Consequently a slight displacement along the e_g or t_{2g} mode stabilizes the distorted geometry. Nevertheless the homoleptic complexes of the $[\text{CoL}_6]$ type can be treated by applying the Griffith magnetic Hamiltonian that utilizes the T-p isomorphism [2]. An improvement of the model through the Figgis approach leads to a more realistic description of the system when the ground $\text{T}_{1g}(\text{F})$ term is in a configuration interaction with the excited $\text{T}_{1g}(\text{P})$ term [3]. More pronounced distortions due to the inequivalence of ligands can be modeled by the symmetry descent model of Figgis et al. [4] where the energetic parameters referring to tetragonal and/or orthorhombic distortions assist.

On tetragonal elongation and under the effect of the spin-orbit coupling the 12-membered manifold of the ${}^4\text{T}_{1g}$ term is split into six Kramers doublets labeled as $1\Gamma_6$, $2\Gamma_6$, $1\Gamma_7$, $2\Gamma_7$, $3\Gamma_6$, $3\Gamma_7$ multiplets; this order of levels excludes an application of the spin-Hamiltonian formalism which assumes $1\Gamma_6$ and $1\Gamma_7$ as the lowest levels [5]. On the contrary, on tetragonal compression one gets the following order of multiplets $1\Gamma_6$, $1\Gamma_7$, $2\Gamma_6$, $3\Gamma_6$, $2\Gamma_7$, $3\Gamma_7$ (Fig. 1), so that the two lowest of them can be treated with the help of the spin Hamiltonian

$$\hat{H}_{kl} = D \left[\hat{S}_z^2 - S(S+1)/3 \right] \hbar^{-2} + E \left[\hat{S}_x^2 - \hat{S}_y^2 \right] \hbar^{-2} + \hat{H}_{kl}^Z \quad (1)$$

where D is the axial zero-field splitting (ZFS) parameter, E – rhombic ZFS parameter, and the last contribution is the spin Zeeman term. When the magnetic field is not aligned with the principal axes of the D -tensor (like in the powder material), the Zeeman term should be considered in the form

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

Then averaging over grids distributed uniformly at a sphere need be applied [6]. Actually, the distribution of grid points (ϑ_k , φ_l) is done as in the SOPHE (EPR) program via triangles: at the equator there are 20 knots, above it 19, then 18, etc., in total $20 \times 21/2 = 210$ points. This guarantees a uniform distribution of knots.

The spin-Hamiltonian formalism brings insight into the nature of the magnetic parameters for a hexacoordinate d^7 system through the formulae [5,6]

$$g_x = g_e - 2\lambda A^2 \kappa_x^2 / \Delta_{\text{ax}} ({}^4\text{A}_{2g} \rightarrow {}^4\text{E}_g) > g_e; g_z = g_e \quad (3)$$

$$D = \lambda (g_z - g_x) / 2 = \lambda^2 A^2 \kappa_x^2 / \Delta_{\text{ax}} ({}^4\text{A}_{2g} \rightarrow {}^4\text{E}_g) > 0 \quad (4)$$

$$\chi_{\text{TIP}} = N_A \mu_0 \mu_B^2 (2/3) \left[2A^2 \kappa_x^2 / \Delta_{\text{ax}} ({}^4\text{A}_{2g} \rightarrow {}^4\text{E}_g) \right] \quad (5)$$

where κ is the orbital reduction factor, λ is the spin-orbit splitting parameter (for the Co(II) ion $\lambda/hc = -172 \text{ cm}^{-1}$) and A is the Figgis CI-mixing parameter. In these formulae the excitation energies $\Delta_{\text{ax}} ({}^4\text{A}_{2g} \rightarrow {}^4\text{E}_g)$ occur which, on approaching the octahedral

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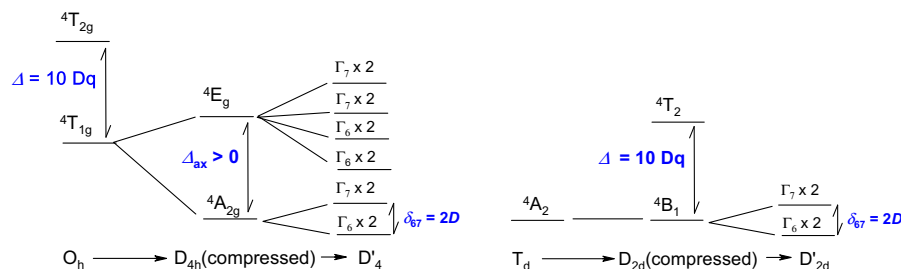


Fig. 1. Comparison of low-lying energy levels for high-spin Co(II): hexacoordinated compressed bipyramid D_{4h} – left, tetracoordinated bisphenoid D_{2d} – right.

geometry, vanish and thus the formulae diverge. The largest g -factor anisotropy $g_z - g_x$, and the largest zero-field splitting parameter $D > 0$ are predicted in the vicinity of the octahedral geometry. The recent analysis of magnetic data (susceptibility and magnetization) show that in hexacoordinate Co(II) complexes the D -parameter is as high as $D/hc = 90\text{--}110\text{ cm}^{-1}$ [7,8]. This range was confirmed also by the variable-temperature Far-IR spectroscopy [9]. An attempt to correlate the magnetochemical D -parameter vs the geometrical tetragonality parameter (a search for so called magnetostructural D -correlation) was successful; however the correlation is highly non-linear and proceeds according to parametric curves [10]. This is in strong contrast to the magnetostructural D -correlation outlined previously for a series of Ni(II) complexes [11]. The magnetic anisotropy interrelates to the zero-field splitting – an energy gap between a pair of the lowest Kramers doublets $|S, M_S\rangle$ so that $\Delta = E(|3/2, \pm 3/2\rangle) - E(|3/2, \pm 1/2\rangle) = 2D$ holds true.

In tetracoordinate Co(II) complexes referring to a regular tetrahedron the ground electronic state (the crystal-field term) is 4A_2 and $D = 0$ (exactly). The ground term is well separated from the first excited terms: the excitation energy to the 4T_2 term is about $10Dq(T_d) = 5000\text{ cm}^{-1}$. On distortion to a flattened or elongated bisphenoid of the D_{2d} symmetry the ground state is 4B_1 ; the D -values become non-zero (negative or positive) and they span the typical range of $|D/hc| = -15$ to $+11\text{ cm}^{-1}$ [12–14], though also higher D -values were reported [15].

A reliable determination and understanding of how to tune the zero-field splitting parameter D is a key factor for a rational synthesis of single molecule magnets, including those belonging to mononuclear Co(II) complexes [16,17].

Two Co(II) complexes of the $[\text{CoCl}_2\text{L}_2]$ and $[\text{CoCl}_2\text{L}_4]$ type with L – 2-aminopyrimidine have been studied in this communication. Electronic spectra and magnetic data were investigated and compared. The determination of the zero-field splitting parameter in **2** is not only based on the analysis of magnetic data but also by direct spectroscopic analysis using Far-IR spectra. Such an independent check of the magnetometric data by a spectroscopic technique is of great importance especially for Co(II) complexes where the powder susceptibility data is insensitive to the sign and value of the D -parameter. In the present case D cannot be determined by high-field/high-frequency EPR because of very high D -value for the quasi-octahedral Co(II).

2. Experimental

2.1. Synthesis

Compound **1**, $[\text{CoCl}_2(\text{L})_2]$, has been prepared according to the following recipe. A solution of 0.39 g (0.42 mmol) of L (L = 2-aminopyrimidine; 2-amino-1,3-diazabenzene) in 15 cm^3 methanol was slowly added to the solution of 0.50 g (0.21 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 cm^3 methanol under intense stirring (the molar ratio L: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} = 2:1$). The mixture was stirred at room temperature. After 1 h dark-blue crystals formed and were separated on Büchner

funnel. Anal. Calc. for **1**, $\text{C}_8\text{H}_{10}\text{N}_6\text{CoCl}_2$, $M = 320.04$: C, 30.0; H, 3.15; N, 26.3. Found: C, 30.3; H, 3.20; N, 27.0%.

Compound **2**, $[\text{CoCl}_2(\text{L})_4]$, has been prepared as follows. A solution of 0.39 g (0.42 mmol) of L in 15 cm^3 methanol was slowly added to a solution of 0.50 g (0.21 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 cm^3 methanol under stirring at $60\text{ }^\circ\text{C}$ for 1 h (the molar ratio L: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} = 2:1$). The solution was filtered off. The filtrate was left for 4 days for spontaneous evaporation at room temperature. Dark-pink crystals formed and were separated. Anal. Calc. for **2**, $\text{C}_{16}\text{H}_{20}\text{N}_{12}\text{CoCl}_2$, $M = 510.24$: C, 37.3; H, 3.95; N, 32.9. Found: C, 37.4; H, 4.10; N, 33.0%.

Crystal data for **1**, literature source [18], CCDC code SEQFIE, hereafter polymorph- α ; space group $C2/c$, $a = 11.277$, $b = 6.595$, $c = 16.569\text{ \AA}$, $\alpha = 90$, $\beta = 92.27$, $\gamma = 90$, $V = 1231.27\text{ \AA}^3$, $Z = 4$, $\rho = 1.727\text{ g cm}^{-3}$; $R = 0.0285$. Metal-ligand distances: Co–N 2.037, 2.037, and Co–Cl 2.237, 2.237 \AA ; bond angles N–Co–N = 110.72 and Cl–Co–Cl = 116.54.

Structure redetermination for **1**, actually investigated sample [14], hereafter polymorph- β ; space group $C2/c$, $a = 10.6381(3)$, $b = 13.2780(4)$, $c = 8.8554(2)$, $\alpha = 90$, $\beta = 97.658(3)$, $\gamma = 90^\circ$, $V = 1239.69(6)\text{ \AA}^3$, $Z = 4$, $\rho = 1.715\text{ g cm}^{-3}$; $R = 0.0182$. Metal-ligand distances: Co–N 2.0408(10), 2.0408(10), and Co–Cl 2.2427(3), 2.2427(3) \AA ; bond angles N–Co–N = 114.47(6) and Cl–Co–Cl = 110.42(2) deg.

Crystal data for **2**, literature source [18], CCDC code SEQFUQ; space group $C2/c$, $a = 7.678$, $b = 18.722$, $c = 15.042\text{ \AA}$, $\alpha = 90$, $\beta = 99.67$, $\gamma = 90^\circ$, $V = 2131.41\text{ \AA}^3$, $Z = 4$, $\rho = 1.590\text{ g cm}^{-3}$; $R = 0.0264$. Metal-ligand distances: Co–N 2.221, 2.221, 2.232, 2.232, and Co–Cl 2.455, 2.455 \AA .

Structure redetermination for **2**, actually investigated sample; space group $C2/c$, $a = 7.700(5)$, $b = 18.730(5)$, $c = 15.130(5)$, $\alpha = 90$, $\beta = 99.860(5)$, $\gamma = 90^\circ$, $V = 2149.8(17)\text{ \AA}^3$, $Z = 4$, $\rho = 1.577\text{ g cm}^{-3}$; $R = 0.0280$. Metal-ligand distances: Co–N 2.2279(14), 2.2279(14), 2.2394(14), 2.2394(14), and Co–Cl 2.4503(13), 2.4503(13) \AA . Bond angles: Cl–Co–Cl = 179.19(2), $trans\text{-N-Co-N} = 177.23(5)$ and 177.23(5) deg.

2.2. Physical measurements

Elemental analysis was carried out on FlashEA 1112 (ThermoFinnigan). A powder diffractogram has been scanned (Almelo, Philips) using the Co-anode, $\lambda = 1.78892\text{ \AA}$. IR spectra were measured (Magna FTIR 750, Nicolet) in KBr pellets in the $400\text{--}4000\text{ cm}^{-1}$ region and in polyethylene pellets in the $50\text{--}600\text{ cm}^{-1}$ region. Raman spectra have been taken with DXR SmartRaman spectrometer (Thermo Scientific) using laser 532 nm. Electronic spectra were measured in Nujol mull (Specord 200, Analytical Jena) in the range $9000\text{--}50000\text{ cm}^{-1}$. Magnetic data was taken with a SQUID magnetometer (MPMS-XL7, Quantum Design) using the RSO mode of detection. The susceptibility data was scanned in the temperature range 2–300 K at the applied field of $B = 0.1\text{ T}$. The magnetization has been measured at $T = 2.0$ and 4.6 K. Raw data was corrected for the underlying diamagnetism using estimate of $\chi_{\text{dia}}/(10^{-12}\text{ m}^3\text{ mol}^{-1}) = -5M[\text{g mol}^{-1}]$.

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