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# Zero-field splitting in pentacoordinate Co(II) complexes

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ABSTRACT

Pentacoordinate Co(II) complexes possessing the $\{CoN_3X_2\}$ chromophore (X = Cl, O) have been synthesized and structurally characterized. The magnetic data confirm high magnetic anisotropy expressed through the axial zero-field splitting parameter $D/hc$ = 50–70 $cm^{-1}$. These values lie between those found in tetracoordinate and hexacoordinate Co(II) complexes.



## 1. Introduction

Magnetostructural correlations are widely studied in literature since they form a basis for a relationship between structure and magnetoactivity of coordination compounds. Majority of attempts were focused to the correlation of the isotropic exchange coupling constant $J$ versus an appropriate structural parameter – an M–X–M angle or M–X bond length within the superexchange path in binuclear or polynuclear complexes [1–15]. This type of correlation can be termed the magnetostructural J-correlations since recently another type has been outlined, namely the magnetostructural D-correlations. Here the axial zero-field splitting parameter $D$ in mononuclear complexes is in a relation with the structural tetragonality.

In hexacoordinate Ni(II) complexes such a correlation is given by a straight line (in fact a pair of nearly collinear straight lines) and $D$-values vary between $D/hc$ = −8 to +8 $cm^{-1}$ [16–21]. In hexacoordinate Co(II) complexes, however, the correlation is represented by a set of parametric non-linear curves in the segment of the compressed tetragonal bipyramid [22–25]. In hexacoordinate Co(II) complexes the retrieved set of $D$-values spans the interval of $D/hc$ = +70 to +144 $cm^{-1}$ (always positive). In addition to magnetometry (temperature dependence of the magnetic susceptibility, and field dependence of the magnetization) also the FAR-IR spectra are helpful in a direct spectral determination of the $D$-parameter for centrosymmetric complexes [26–28]. In tetracoordinate Co(II) complexes a reliable data set started to be build up by combining the magnetometry, high-field/high-frequency EPR, and quantum-chemical calculations [29]. In tetracoordinate complexes possessing the $\{CoN_2X_2\}$ and/or $\{CoX_4\}$ chromophores the $D$-values are much lower and could be either negative or positive: $D/hc$ = −15 to +40 $cm^{-1}$ [29–31]. Preliminary data show that D-values are more sensitive to the angular distortions of the reference tetrahedron; in addition to the $T_d$ symmetry, $D_{2d}$, $C_{2v}$ and $C_1$ frequently occur.

A logical step forward is to investigate the pentacoordinate Co(II) complexes. However, there are more structural parameters in the play, since in addition to the radial parameters in $\{CoN_3X_2\}$ chromophores also the angular coordinates vary: the angles $\alpha$ = N–Co–N and $\beta$ = X–Co–X. The literature sources about of the magnetic parameters ($D$) in pentacoordinate Co(II) complexes are rather modest [32–35] so that the only way is to prepare a series of complexes and to investigate them by modern magnetometric hardware and magnetochemical software. A direct measurement of the energy gap by the high-frequency/high-field EPR technique meets difficulties since the estimated range of $D$-parameters (around 50 $cm^{-1}$) lies outside the capabilities of the existing hardware. Indirect EPR estimates, however, are at the disposal; they were based upon the spin lattice relaxation time as a basis for the determination of the lowest energy gap in a series of Co(II) complexes with coordination numbers 4, 5, and 6 [33].

A rational design of the zero-field parameter is a challenge of recent period. The $D$-parameter enters the formula for the barrier to spin reversal in single-molecule magnets ($\Delta = |D|S^2$) and therefore it is a first prerequisite of the magnetism at the molecular level [36]. The greater the $D$-parameter, the greater the barrier to spin

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reversal $\Delta$, and the longer the lifetime of the single-molecule magnets.

## 2. Experimental

### 2.1. General

Chemicals were purchased from Sigma–Aldrich and Merck and used as received. The solvents, *n*-hexane, $Et_2O$, EtOAc, $CH_2Cl_2$, $CH_3OH$ were used without further purification; $CH_3CN$ and $(^i pr)_2NH$ were dried by distillation over $CaH_2$.

$^1H$ and $^{13}C$ NMR spectra were recorded using FT-NMR Spectrometer (Avace III 500 MHz, Bruker) with solvent proton as an internal standard. The infrared spectra in KBr pellets in the range 4000–400 $cm^{-1}$ were acquired at room temperature using FT-IR spectrometer (Spectrum GX, Perkin Elmer). Electron spectra were measured by UV–Vis–NIR spectrophotometer (Cary 500 Scan). Mass spectra were measured by micrOTOF-QII for ESI-TOF (Bruker). Elemental analyses were carried out on a Vario MICRO cube. For thin-layer chromatography silica plates POLYGRAM SIL *G*/$UV_{254}$ and alumina plates POLYGRAM ALOX N/$UV_{254}$ were used under the ultraviolet light at 254 nm. Melting points were determined Melting Point B-540 (Büchi).

The magnetic measurements were conducted using a SQUID apparatus (MPMS-XL7, Quantum Design) in the RSO mode of detection. About 20 mg of the sample was encapsulated in a gelatin-made sample holder. The susceptibility taken at $B = 0.1$ T has been corrected for the underlying diamagnetism and converted to the effective magnetic moment. The magnetization has been measured at two temperatures: $T = 2.0$ and $T = 4.6$ K.

### 2.2. Synthesis

The ligand 4′-iodo-2′,6′-dipyrazolyl-pyridine (**L$^1$**) was synthesized following reported procedures [37–41].

The ligand 4′-dodecynyl-2′,6′-dipyrazolyl pyridine (**L$^2$**) was prepared as follows. In a 100 $cm^3$ two necked round bottom flask, a freshly distilled $(i\text{-}pr)_2NH$ (50 $cm^3$) was deoxygenated under the Ar flux for 1 h. **L$^1$** (0.674 g, 2 mmol), 10% of $Pd^0(PPh_3)_4$ and CuI (0.038 g, 0.2 mmol) were suspended in an Ar-gas bubbled solution of $(^i pr)_2NH$ and stirred for 1 h. 1-Dodecyne (0.665 g, 4 mmol) was added and the mixture was stirred for 3 days at RT. The solvent was removed using a rotary evaporator. The solid residue was at first column chromatographed on alumina with EtOAc/*n*-Hex (1:20, $R_f = 0.50$) as an eluent. The combined slightly yellowish solutions yielded upon evaporation and dried in vacuum to 0.35 g of a white powder (0.93 mmol, 46.6%). *Anal.* Calc. $C_{23}H_{29}N_5$: C, 73.57, H, 7.78; N, 18.65. Found: C, 73.59; H, 7.63; N, 18.59%. Melting point 53–55 °C. $^1H$ NMR [500 MHz, $CDCl_3$, 25 °C, $\delta$/ppm]: 8.53 (d, 2H), 7.83 (s, 2H), 7.75 (t, 2H), 6.49 (dd, 2H), 2.45 (t, 2H), 1.61 (m, 2H), 1.44 (m, 2H), 1.29 (m, 12H), 0.87 (t, 3H). $^{13}C$ NMR [125 MHz, $CDCl_3$, 25 °C, $\delta$/ppm]: 150.10, 142.43, 137.73, 127.09, 111.69, 108.02, 97.46, 78.32, 31.92, 29.16, 22.70, 19.52, 14.13. UV–Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}\,cm^{-1}$) = 251 (61204), 322 (16213). FT-IR (KBr): $\nu/cm^{-1}$ = 3114, 3094, 2914, 2850, 2244, 1783, 1738, 1615, 1555, 1523, 1468, 1398, 1266, 1210, 1115, 1053, 1039, 959, 938, 856, 794, 757.

Single crystals for X-ray diffraction were grown from $CH_3OH$. Formula $C_{23}H_{29}N_5$; $M = 375.51$; $T = 180(2)$ K; crystal system: monoclinic; crystal size/mm = 0.25 × 0.07 × 0.05; space group: $P2(1)/c$; $a = 5.395(3)$ Å; $b = 20.0348(10)$ Å; $c = 19.9239(12)$ Å; $\alpha = 90°$, $\beta = 94.245(53)°$, $\gamma = 90°$, $V = 2147.6(2)$ Å$^3$; $Z = 4$; $\rho_{calc} = 1.161$ g $cm^{-3}$, $\mu$(Mo K$\alpha$) = 0.71073 $mm^{-1}$; reflections measured: 4056, $F(000) = 808$, goodness-of-fit on $F^2 = 0.881$, final *R* indices [$I > 2\sigma(I)$]: $R1 = 0.0482$; $wR_2 = 0.1005$, *R* indices (all data): $R_1 = 0.1041$, $wR_2 = 0.1163$, extinction coefficient = 0.0193(17).

Preparation of the complex [$CoCl_2L^1$], **1**. In a 100 $cm^3$ two necked round bottom flask a solution of **L$^1$** (100 mg, 0.30 mmol) and $CoCl_2{\cdot}6H_2O$ (70.57 mg, 0.30 mmol) in $CH_3CN$ (40 $cm^3$) was heated at 80 °C for overnight under Ar flow. The reaction mixture was cooled down to room temperature. Blue block-shaped crystals were grown from diffusing the $Et_2O$ into the $CH_3CN$ solution of the complex under Ar at room temperature in several days. Yield 103.1 mg (0.22 mmol, 74.44%). *Anal.* Calc. $C_{11}H_8Cl_2CoIN_5{\cdot}0.45H_2O$: C, 27.81; H, 1.89, N 14.74. Found: C, 27.75; H, 1.78; N, 14.74%. $\theta_f$ = 394–396 °C. ESI-TOF MS ($CH_3CN$): $m/z = 430.86$ $[M]^+$. UV/VIS (Nujol): $\nu_{max}/10^3\,cm^{-1}$ (absorbance) = 15.649 (0.247), 17.483 (0.201), 24.445 (0.600), 30.121 (1.078). FT-IR (KBr): $\nu/cm^{-1}$ = 3340, 3207, 3108, 3096, 1602, 1561, 1519, 1496, 1453, 1414, 1390, 1335, 1271, 1216, 1205, 1173, 1136, 1078, 1050, 962, 923, 910, 861, 834, 788, 766, 745, 642, 601, 539.

Preparation of the complex [$CoCl_2L^2$], **2**. In a 100 $cm^3$ two necked round bottom flask a solution of **L$^2$** (100 mg, 0.27 mmol) and $CoCl_2{\cdot}6H_2O$ (63.36 mg, 0.27 mmol) in $CH_3CN$ (40 $cm^3$) was heated at 80 °C for overnight under Ar flow. The reaction mixture was cooled down to room temperature. This compound was synthesized as described for **1**. Blue needle-shaped crystals were grown by evaporation of $CH_3CN$ solution of the complex at the room temperature in several days. Yield 110 mg (0.218 mmol, 81.45 %). *Anal.* Calc. $C_{23}H_{29}CoCl_2N_5{\cdot}0.3H_2O$: C, 54.09; H, 5.84 N, 13.71. Found: C, 53.99; H, 5.73; N, 13.67%. Melting point 276–278 °C. ESI-TOF MS ($CH_3CN$): $m/z = 469.11$ [M]. UV–Vis (Nujol): $\nu_{max}/10^3\,cm^{-1}$ (absorbance) = 16.313 (0.172), 30.030 (0.977). FT-IR (KBr): $\nu/cm^{-1}$ = 3107, 2922, 2852, 2218, 1618, 1553, 1525, 1495, 1453, 1402, 1399, 1266, 1225, 1171, 1049, 965, 901, 853, 791, 761, 629, 587, 480.

### 2.3. X-ray structure determination

Single crystal X-ray data were collected on a STOE IPDS II diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Structure solution and refinement against $F^2$ were carried out using SHELXS and SHELXL software [42]. Refinement was performed with anisotropic temperature factors for all non-hydrogen

**Table 1**
Crystal data for compounds **1** and **2**.

| | Complex **1** | Complex **2** |
|---|---|---|
| Empirical formula | $C_{11}H_8Cl_2CoIN_5$ | $C_{27}H_{35}Cl_2CoN_7$ |
| Formula weight (g $mol^{-1}$) | 466.95 | 587.45 |
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2(1)/c$ | $Pbca$ |
| $T$ (K) | 180(2) | 180(2) |
| Crystal size (mm) | 0.21 × 0.12 × 0.11 | 0.24 × 0.09 × 0.01 |
| $Z$ | 4 | 8 |
| a (Å) | 10.5357(8) | 15.3677(5) |
| $b$ (Å) | 8.1978(7) | 14.5418(6) |
| $c$ (Å) | 17.1482(11) | 26.9215(10) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 97.523(5) | 90 |
| $\gamma$ (° | 90 | 90 |
| $V$ (Å$^3$) | 1468.33(19) | 6016.3(4) |
| Calculated density $D_{calc}$ (g $cm^{-3}$) | 2.112 | 1.297 |
| Absorption coefficient ($mm^{-1}$) | 3.630 | 0.0776 |
| Reflections collected/ unique ($R_{int}$) | 5182/2421 [R(int) = 0.0422] | 19388/5626 [R(int) = 0.0677] |
| Final *R* indices | $R_1 = 0.0304$, $wR_2 = 0.0661$ | $R_1 = 0.0402$, $wR_2 = 0.1065$ |
| *R* indices (all data) | $R_1 = 0.0465$, $wR_2 = 0.0699$ | $R_1 = 0.0614$, $wR_2 = 0.1226$ |