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# Structural, spectral and magnetic properties of carboxylato cobalt(II) complexes with heterocyclic N-donor ligands: Reconstruction of magnetic parameters from electronic spectra

J. Titiš<sup>a,\*</sup>, J. Hudák<sup>a</sup>, J. Kožíšek<sup>c</sup>, A. Krutošíková<sup>a</sup>, J. Moncol<sup>'b</sup>, D. Tarabová<sup>d</sup>, R. Boča<sup>a,b</sup>

<sup>a</sup> Department of Chemistry (FPV), University of Ss. Cyril and Methodius, SK-917 01 Trnava, Slovakia

<sup>b</sup> Institute of Inorganic Chemistry (FCHPT), Slovak Technical University, SK-812 37 Bratislava, Slovakia

<sup>c</sup> Institute of Physical Chemistry and Chemical Physics (FCHPT), Slovak Technical University, SK-812 37 Bratislava, Slovakia

<sup>d</sup> Institute of Organic Chemistry, Catalysis and Petrochemistry (FCHPT), Slovak Technical University, SK-812 37 Bratislava, Slovakia

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#### ABSTRACT

Heteroleptic cobalt(II) complexes with general formula of  $[Co(N-base)_2(car)_2(H_2O)_2]$ , have been synthesized and structurally characterized; the *N*-base stands for neutral N-donor ligands: *iso*-quinoline (*iqu*), [1]benzofuro[3,2-*c*]pyridine (*bzfupy*), 1-(pyridin-3-yl)[1]benzofuro[3,2-*c*]pyridine (1-*py*-*bzfupy*) and 1-phenyl-1*H*-imidazole (*bylim*); *car* = acetato (*ac*) or benzoato (*bz*) ligands. The structure of  $[Co(iqu)_2(a-c)_2(H_2O)_2]$  **1**,  $[Co(bzfupy)_2(ac)_2(\cdot (H_2O)_2]$  **2**,  $[Co(1-py-bzfupy)_2(ac)_2(H_2O)_2]$ ·H<sub>2</sub>O **3** and  $[Co(bylim)_2(bz)_2(H_2O)_2]$ **4** complexes is formed of the  $\{CoN_2O_2O_2'\}$  chromophore. These complexes were subjected to magnetochemical investigation down to 2 K (susceptibility and magnetization measurements). They show magnetic behavior typical for the zero-field splitting systems. The axial parameter of the zero-field splitting adopts large values, D = 80-103 cm<sup>-1</sup>. We have analyzed electronic spectra of the complexes in detail with aim to extract the crystal-field parameters. These have been used for reconstruction of the magnetic parameters. The calculated axial ZFS parameters are in good agreement with the experimental values.

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## 1. Introduction

Quinoline isosters, in which the benzene ring is replaced by furan or thiophene ring (furopyridines, thienopyridines), are intensively synthesized and studied [1–3]. A few from these fused heterocycles were used as ligands in the preparation of coordination compounds with transition metals, such as Cu(II) and Ni(II). The spectral, magnetic, thermal properties, coordination chemistry and X-ray analysis of these compounds have been reported [4–6].

Recently, we outlined a novel type of magnetostructural correlations. Here, the zero-field splitting (ZFS) parameter *D* is correlated with the structural tetragonality in the series of axially distorted Ni(II) complexes [7]. In these studies, the above heterocycles have been used to prepare the thiocyanato and carboxylato nickel(II) complexes, namely with furo[3,2-*c*]pyridine, 2-methylf-uro[3,2-*c*]pyridine, 2,3-dimethylfuro[3,2-*c*]pyridine, [1]benzof-uro[3,2-*c*]pyridine and *iso*-quinoline. In the case of the thiocyanato complexes, the tetaragonality of the {NiN<sub>2</sub>N<sub>4</sub>'} chromophore varied along with the sign of the ZFS parameter *D*. The carboxylato complexes with {NiN<sub>2</sub>O<sub>2</sub>O<sub>2</sub>'} chromophore always

\* Corresponding author. E-mail addresses: jan.titis@ucm.sk, jan.titis@post.sk (J. Titiš). possess a compressed tetragonal geometry and thus the *D*-parameter clearly adopts negative values.

Some studies on structure–magnetism relationship have also been reported for cobalt(II) ion [8,9]. Cobalt(II) complexes are very attractive since its ZFS can be very large. These systems differ from the Ni(II) cases in the feature that the ground electron term in the octahedral geometry is orbitally degenerate (Fig. 1). On tetragonal compression the  ${}^{4}T_{1g}(O_{h})$  term splits into the terms  ${}^{4}A_{2g}(D_{4h}, \text{ground})$  and  ${}^{4}E_{g}(D_{4h}, \text{excited})$ ;  $E({}^{4}E_{g}) - E({}^{4}A_{2g}) = \Delta_{ax}$ . The ordering of the multiplets is:  ${}^{4}A_{2g} \rightarrow \{1\Gamma_{6} < 1\Gamma_{7}\}$  and  ${}^{4}E_{g} \rightarrow \{2\Gamma_{6} < 3\Gamma_{6} < 2\Gamma_{7} < 3\Gamma_{7}\}$  owing to which the four members of the former  ${}^{4}A_{2g}$  term can be considered within the spin-Hamiltonian formalism.

The corresponding energy gap can be attributed to the zero-field splitting:  $2D = E(1\Gamma_7) - E(1\Gamma_6) > 0$  [10]. Within this approach, the magnetic parameters obey relationships.

$$g_{x} = g_{e} - 2\lambda A^{2} \kappa_{x}^{2} / \Delta_{ax} \left({}^{4}A_{2g} \rightarrow {}^{4}E_{g}\right) > g_{e}; \ g_{z} = g_{e}$$
(1)

$$D = \lambda (g_z - g_x)/2 = \lambda^2 A^2 \kappa_x^2 / \Delta_{ax} \left({}^4A_{2g} \to {}^4E_g\right) > 0$$
<sup>(2)</sup>

$$\chi_{\rm TIP} = N_{\rm A} \mu_0 \mu_{\rm B}^2 (2/3) \left| 2A^2 \kappa_x^2 / \Delta_{\rm ax} ({}^4A_{2g} \to {}^4E_g) \right| \tag{3}$$

where  $\kappa$  is the orbital reduction factor,  $\lambda$  is the spin–orbit splitting parameter (for the Co(II) ion  $\lambda/hc = -172 \text{ cm}^{-1}$ ) and A is the



<sup>0020-1693/\$ -</sup> see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ica.2012.03.036



Fig. 1. Comparison of the low-lying energy levels for high-spin Ni(II),  $d^8$  (left) and Co(II),  $d^7$  (right) ions – not to scale.

configuration interaction mixing parameter introduced by Figgis. These parameters are considered as the molecular constants characteristic for the particular system. They can be retrieved by fitting the experimental data. However, the magnetic parameters have their origin in the electronic structure of the complex.

Several theoretical models have been proposed and a number of reviews were written, summarizing important aspects of the ZFS. Standardly, the ZFS can be modeled through the second-order perturbation theory for the spin Hamiltonian by means of the crystalfield approach [10]. In this simple model, the ZFS is directly related to the splitting of the crystal-field states due to the geometry of the complex. However, further important effects arise from covalent metal-ligand interaction. Adjustment of this purely electrostatic model to covalency effects can be carried out via the orbital reduction factors  $\kappa$  [11]. In order to forwarding beyond the spin Hamiltonian formalism, the orbital functions need be involved into the basis set and the orbital angular momentum operator considered explicitly [10]. On higher level of sophistication, it is possible to apply non-empirical methods of the quantum chemistry (correlated ab initio methods and/or variants of the density-functional method) [12,13]. These bring quantitative data about the electronic structure of the system under study. However, the calculated energy levels (and subsequently the ZFS) are outputs of the molecular composition for the given geometry and usually loose transparency in chemical terms. On the contrary, inorganic chemists are more familiar with terminology of the Racah parameter (*B* and *C*) that, in fact are parameters of the single-ion electron repulsion. These can be modified via the nephelaxeutic (cloud-expanding) effect. Moreover, electron spectra are sources about the ligand-field strengths  $(F_4)$  and the spectroscopic series is parametrized through the metal  $(k_M)$  and ligand  $(f_L)$  increments:  $\Delta_0 = k_M f_L$ . We must also emphasize, that using the crystal-field approach large number of calculations can be performed with good agreement with experimental data by means of minimal computing resources (with regards to chemical complexity of the most studied systems). Therefore, it is sometimes more helpful to investigate the zerofield splitting and other magnetic parameters resulting from the set of crystal-field parameters like *B*, *C*, *F*<sub>4</sub>(*z*), *F*<sub>4</sub>(*xy*),  $\lambda = -\xi/2S$ and  $\kappa$ .

Carboxylato Co(II) complexes with N-donor ligands, in which the equatorial positions are completed by water molecules are widely covered in the structural database (CSD). However, structures containing furopyridine rings absent. This paper deals with preparation, structural and magnetic investigation of carboxylato Co(II) complexes with *iso*-quinoline (*iqu*), [1]benzofuro[3,2-*c*]pyridine (*bzfupy*) and 1-(pyridin-3-yl)[1]benzofuro[3,2*c*]pyridine (1-*py-bzfupy*). For comparison, also the complex [Co(*bylim*)<sub>2</sub>(*bz*)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] **4** was prepared and its magnetism studied (*bylim* = 1-phenyl-1*H*-imidazole). Note that the CSD already contains a record of the *trans-bis*(acetato-*O*)-*trans*-diaqua-*transbis*(isoquinoline-*N*)-cobalt(II) (JAWJAT). For this compound, only structural data were reported [14]. Remaining three prepared complexes (**2**–**4**) are new.

#### 2. Experimental

#### 2.1. Ligands

All chemicals were of analytical grade. Two ligands (*bzfupy* and 1-*py-bzfupy*) were prepared according to the literature recipes [15].

Detailed characterization (elemental analysis, IR and NMR spectra) of the prepared ligands can be found elsewhere [16]. Here, we will describe only the synthesis. The starting 1-benzofuran-2-carbaldehyde (**a**) was subjected to the Doebner condensation resulting in the corresponding acid (**b**) (Fig. 2). The acylazide was prepared by treatment of (**b**) with ethyl chloroformate and sodium azide in one-pot reaction and then was transformed by thermal cyclization in Dowtherm with tributylamine to [1]benzofuro[3,2-c]pyridin-1(2H)-one (**c**). Refluxing of (**c**) with phosphorus oxychloride gave chloro-derivative (**d**), which by the reduction yielded [1]benzofuro[3,2-c]pyridine (**e**).

The ligand 1-(pyridin-3-yl)[1]benzofuro[3,2-*c*]pyridine (1-py-bzfupy) (**f**) was prepared in moderate yield from 1-chloro[1]benzofuro[3,2-*c*]pyridine (**d**) and pyridine-3-boronic acid (Py-3-B(OH)<sub>2</sub>) by Suzuki coupling reaction in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst in dichloromethane (Fig. 2).

Other ligands were purchased from commercial sources and were used as received.

#### 2.2. Preparation of the complexes

The starting materials (CoCl<sub>2</sub>·6H<sub>2</sub>O, potassium acetate and potassium benzoate) were purchased from commercial sources. Cobalt(II) acetate, as well as the cobalt(II) benzoate, was synthesized by adding potassium acetate/benzoate to a cobalt(II) chloride ethanol solution.

The four complexes  $[Co(iqu)_2(ac)_2(H_2O)_2]$  **1**,  $[Co(bzfupy)_2(ac)_2(H_2O)_2]$  **2**,  $[Co(1-py-bzfupy)_2(ac)_2(H_2O)_2]$ ·H<sub>2</sub>O **3** and  $[Co(by-lim)_2(bz)_2(H_2O)_2]$  **4** were prepared from cobalt(II) acetate/benzoate. Into the ethanol solution of cobalt(II) acetate/benzoate a stoichiometric amount of ligand was added and stirred for half hour at 60 °C. After few days the pink solid complexes were collected. Single crystals were grown from the ethanol solution. The composition of the obtained complexes was confirmed by elemental analysis. X-ray structure analysis was performed for all compounds. *Anal.* Calc. for (**1**)  $C_{22}H_{24}N_2COO_6$ : C, 56.10; H, 5.13; N, 5.94. Found: C, 55.80; H, 5.14; N, 5.99%. *Anal.* Calc. for (**2**)  $C_{26}H_{24}N_2COO_8$ : C, 56.63; H, 4.39; N, 5.08. Found: C, 56.62; H, 4.48; N, 5.10%. *Anal.* Calc. for (**3**)  $C_{36}H_{32}N_4COO_9$ : C, 59.76; H, 4.46; N, 7.74. Found: C, 58.05; H, 4.57; N, 7.57%. *Anal.* Calc. for (**4**)  $C_{34}H_{34}N_4COO_6$ : C, 62.48; H, 5.24; N, 8.57. Found: C, 62.80; H, 5.74; N, 8.11%.

#### 2.3. Analytical methods and equipment

Elemental C–H–N analysis was carried out with a commercial analyzer (Carlo Erba, 1108). Electronic spectra were measured in



Fig. 2. Preparation of the [1]benzofuro[3,2-c]pyridine (e) and the 1-(pyridin-3-yl)[1]benzofuro[3,2-c]pyridine (f).

Nujol mull (Specord 200, Analytical Jena) in the range 9000–  $50\,000\,\mathrm{cm^{-1}}$ .

Single-crystal X-ray diffraction experiments have been performed using Gemini R CCD apparatus (Oxford Diffraction). Data reduction and analytical absorption [17] corrections were performed by CRYSALISPRO package [18]. The structures were solved by direct methods using SIR-97 [19] or SHELXS-97 [20] and refined by the full-matrix least-squares procedure with SHELXL-97.

Magnetic susceptibility and magnetization measurements were done using a SQUID magnetometer (Quantum Design, MPMS-XL7) between 2 and 300 K at B = 0.1 T. The magnetization data until B = 7 T were taken at T = 2.0 K. Raw susceptibility data were corrected for underlying diamagnetism using the set of Pascal constants. The effective magnetic moment has been calculated as usual:  $\mu_{\text{eff}}/\mu_{\text{B}} = 798(\chi'T)^{1/2}$  when SI units are employed.

#### 3. Computational

Calculations based on the crystal-field theory were done using the TERMS package [21]. The matrix elements of the relevant operators (electron repulsion  $\hat{V}_{ee}$ , crystal-field  $\hat{V}_{cf}$ , spin–orbit  $\hat{H}_{so}$ ) were evaluated in the basis set of free-atom terms using the full battle of the irreducible tensor operators approach [22,23]. There is no need to pass from the free-atom terms to the crystal-field terms as such a process is the only unitary transformation that leaves the eigenvalues invariant. The key role in the above calculations plays the unit tensor operators that are expressed with the help of the genealogic coefficients (coefficients of the fractional parentage) and the 6*j*-symbols of composition of angular momenta. Having these reduced matrix elements of the spherical tensor operators determined, the calculation proceeds with the help of the Wigner-Eckart theorem where the reduced matrix element is multiplied by a proper 3*j*-symbol (the integral of angular momentum functions).

Having the set of spectral parameters on input (*B*, *C*,  $\xi$ , *F*<sub>4</sub>(*R*) and eventually  $\kappa_x$ ,  $\kappa_y$ ,  $\kappa_z$ ) the magnetic parameters, preferentially the axial zero-field splitting, can be calculated in TERMS by two methods. First, the spin Hamiltonian formalism is taken into account; here, the matrix elements of the orbital angular momentum operator  $\hat{L}$  in basis of the atomic terms are transformed to the basis set of crystal-field terms using the matrix that diagonalizes the  $\hat{H} = \hat{V}_{ee} + \hat{V}_{cf}$  operator

$$\mathbf{L}_{cf} = \mathbf{C}^{\dagger} \mathbf{L}_{at} \mathbf{C} \tag{4}$$

Then the Lambda tensor (a, b = x, y, z) is constructed as

$$\Lambda_{ab} = \sum_{i} [L_a \cdot L_b] / E_i - E_0 \tag{5}$$

This enters the formulae for the magnetic parameters within the spin Hamiltonian formalism (Eqs. (1-3)). Second method works beyond the spin Hamiltonian where the zero-field energy levels – the crystal-field multiplets result from the diagonalization of the effective Hamiltonian  $\hat{H} = \hat{V}_{ee} + \hat{V}_{cf} + \hat{H}_{so}$ . At this level of sophistication the zero-field splitting is read off from the energies of the lowest multiplets,  $2D = \Gamma_7 - \Gamma_6$ . Energy levels are optionally labeled according to irreducible representations of the given double group.

Density functional calculations reported in this paper have been obtained with the ORCA electronic structure program system [24]. Unrestricted Kohn-Sham (UKS) formalism was applied for the solution of the SCF equations without geometry optimization (crystallographic coordinates of the complexes were used). Two different calculations have been performed: (i) determination of composition of the relevant molecular orbitals (MOs) for all studied complexes; (ii) calculation of the ZFS for complex 4. In the first calculation, the local density approximation (LDA) was applied with the Vosko-Wilk-Nusair (VWN) parameterization [25]. The all atoms basis set was triple- $\zeta$  quality with one set of polarization functions (TZVP) [26]. Tight SCF convergence criteria were applied. The resulting UKS orbitals were transformed to natural orbitals (UNOs) and subjected to Löwdin population analysis. For calculation of the ZFS the hybrid B3LYP exchange-correlation functional [27] was used with combination of the TZVP basis set and the spin-orbit mean field (SOMF) representation of the spin-orbit coupling operator as described in reference manual [24].

#### 4. Results and discussion

#### 4.1. Molecular and crystal structure

Crystal data for compounds **1** through **4** are collected in Table 1. The molecular structure (ORTEP) is viewed in Supplementary material Figs. S1–S4.

The structure of all complexes consist of  $[Co(N-base)_2(car)_2-(H_2O)_2]$  monomeric units in which the central Co(II) atom has a distorted octahedral configuration (Fig. 3). The coordination sphere of the Co(II) atom is, therefore, defined by two aqua ligands (*w*), two carboxylato ligands (*c*) and two neutral N-donor base ligands. Two oxygen atoms from water molecules and two oxygen atoms from carboxylato groups form the equatorial plane and two nitrogen atoms from the heterocycles are situated in the axial sites,  $\{CoN_2O_2O_2'\}$ . The metal-ligand distance intervals are: Co-O<sup>c</sup> 2.079–2.140, Co-O<sup>w</sup> 2.107–2.121 and Co-N 2.135–2.188 Å (see Table 2). Complete set of important bond distances and bond angles for **1–4** can be found in Supplementary material.

In our previous works we systematically introduced a parameterization of the tetragonal distortion in mononuclear complexes. The definition is simple and clear,  $D_{\text{str}} = R_{\text{ax}} - R_{\text{eq}}$ . However, in case of the heteroleptic complexes we need be careful since we are dealing with the heterogeneous donor set. The distortion parameter for such complexes is redefined as

Table 1		
Summary of X	K-ray crystallographic	data

Compound	1	2	3	4
Formula weight (g mol <sup>-1</sup> )	471.367	551.409	723.592	653.589
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P1	P121/c1	C12/c1	P121/c1
Cell parameters				
a (Å)	8.3670(17)	12.277(4)	27.8882(10)	15.9585(3)
b (Å)	13.294(3)	7.836(6)	17.0215(18)	5.5747(1)
c (Å)	19.513(4)	12.724(7)	7.5121(3)	17.0424(4)
α (°)	90	90	90	90
β(°)	90	93.94(2)	95.425(3)	95.868(2)
γ(°)	89.97(3)	90	90	90
V (Å <sup>3</sup> )	2170.4(8)	1221.2(12)	3550.0(4)	1508.20(6)
Ζ	4	2	4	4
Density, $D_{calc}$ (g cm <sup>-3</sup> )	.345	1.500	1.350	1.661
Absorption coefficient (mm)	0.814	0.757	0.542	1.174
F(000)	908	570	1492	772
Reflections collected	10355	1985	3307	2595
Data/restrains/parameters	15800/3/1117	2486/0/175	4610/1/239	3456/0/214
$R_1[F^2 > 2\sigma(F^2)]$	0.0376	0.0314	0.0446	0.0325
$wR_2(F^2)$	0.1195	0.0934	0.1590	0.0850
CCDC Deposit No.	831600	831602	831601	831599
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**Fig. 3.** Scheme of the Co(II) monomeric units; *iqu* = *iso*-quinoline, *bzfupy* = [1]benzofuro[3,2-*c*]pyridine, 1-*py*-*bzfupy* = 1-(pyridin-3-yl)[1]benzofuro[3,2-*c*]pyridine and *bylim* = 1-phenyl-1*H*-imidazole.

 Table 2

 Selected structural parameters for the Co(II) complexes.

Complex	<i>d</i> <sub>z</sub> (Co–N) (Å)	<i>d<sub>xy</sub></i> (Co–O) (Å)	D <sub>str</sub> (pm)	$E_{\rm str}({\rm pm})$
1	2.175	2.121 <i>w</i> , 2.085 <i>c</i>	-2.80	1.80
2	2.188	2.107w, 2.085c	-0.80	1.10
3	2.171	2.109w, 2.079c	-2.30	1.50
4	2.135	2.115w, 2.140c	-9.25	1.25

$$D_{\text{str}} = \Delta_z - (\Delta_x + \Delta_y)/2 \tag{6}$$

where

$$\Delta_a = (d_a^i - \bar{d}^i) \tag{7}$$

where a = x, y, z is a shift relative to the mean distance  $\bar{d}^i$  for a given bond (i = N, O). For the N- and O-donor ligands these values have been taken from complexes containing the  $[Co(NH_3)_6]^{2+}$  and  $[Co(H_2O)_6]^{2+}$  units, respectively, giving rise to  $\bar{d}^N = 2.185$  Å and  $\bar{d}^0 = 2.085$  Å [28]. For the rhombic structural distortion the relationship  $E_{str} = (\Delta_x - \Delta_y)/2$  is valid. We also assume the validity of the condition  $|E_{str}/D_{str}| \le 1/3$  which is, however, sometimes difficult to satisfy for the heteroleptic complexes. Note that for the complex **4** the above inequality is obeyed,  $|E_{str}/D_{str}| = 0.14$ ; for the remaining ones  $|E_{str}/D_{str}| = 0.64 - 1.37$ . For complexes **1**–**3** the  $\Delta$ (Co–N) and  $\Delta$ (Co–O<sup>c</sup>) shifts are small while the  $\Delta$ (Co–O<sup>w</sup>) are much larger. This suggests a need to identify the Co–O<sup>w</sup> bond as axially positioned. However, in terms of the ligand-field strengths it follows: Co– $N > \{Co-O^w, Co-O^c\}$ . Therefore, the Co–N bond as axially positioned seems to be the better choice and thus we prefer to consider small axial distortion with large rhombic contribution for these complexes.

The system of hydrogen bonds for the Co(II) complexes is shown in Fig. 4. The intermolecular  $O^w-H\cdots O^c$  hydrogen bonds for **1** and **2** [ $H\cdots O^c$  = 1.905 and 1.884 Å;  $O^w-H\cdots O^c$  = 165° and 162°] are formed through aqua-ligand OH groups to uncoordinated acetato-ligand *O*-atoms from neighbor-lying molecule, and they are situated in the equatorial plane. In the crystal structure of the complex **2**, the furan ring *O*-atoms are not involved into the hydrogen bonds; consequently only a two-dimensional network is formed. Also the intramolecular  $O^w-H\cdots O^c$  hydrogen bonds are present in these structures [ $H\cdots O^c = 1.876$  and 1.842 Å;  $O^w H\cdots O^c = 172°$  and 167°]. An analogous system of hydrogen bonds can be found in compound **4**. Its geometric characteristics are: [ $H\cdots O^c = 2.069$  Å and  $O^w-H\cdots O^c = 168°$ ] for intermolecular contacts, and [ $H\cdots O^c = 1.824$  Å and  $O^w-H\cdots O^c = 167°$ ] for intramolecular contacts.

The registered intermolecular contacts for the complex **3** are  $O^{W*}$ -H... $O^{c}$  [H... $O^{c}$  = 2.085 Å and  $O^{W*}$ -H... $O^{c}$  = 176°] (*w*\* denotes the uncoordinated water molecules) and Ow-H...N [H...N = 2.238 Å and Ow-H...N = 177°]. They are formed by OH groups of the uncoordinated water molecules connected with a free acetato-ligand *O*-atoms in the equatorial plane. The N-atoms of the benzo[4,5]furo[3,2-*c*]pyridine fragments are connected with the aqua-ligand OH groups, thus a complex three-dimensional network is formed. There are also present the intramolecular OW-H... $O^{c}$  = 1.879 Å and OW-H... $O^{c}$  = 170°].

#### 4.2. Electronic spectra and crystal-field parameters

The electronic spectra of **1** through **4** are essentially similar (Fig. 5). In the range of 9000–27000 cm<sup>-1</sup> they exhibit a number d–d transitions which are followed by an intense charge transfer band. The first visible transition is a broad band at ca 9500 cm<sup>-1</sup>. The second, more intense d–d peak appears at ca 20000 cm<sup>-1</sup>. Since the structure of the complexes is derived from an octahedron, the interpretation of the spectra could be done in the O<sub>h</sub> group of symmetry in the first approximation. The estimate for



Fig. 4. Coordination mode of ligands and system of hydrogen bonds in the Co(II) complexes (only asymmetric units are shown).



**Fig. 5.** Electronic d-d spectra for the studied Co(II) complexes taken in the Nujol mull; the band assignments were made from a Lorentzian analysis in  $D_{4h}$  point group (left). Energy levels for  $d^7$  system in near-octahedral environments (right).

the crystal-field strength for octahedral complexes is  $Dq(O_h) = (1/6)F_4(R)$ , where the typical  $F_4$  value for  $Co^{II}$ –N/O systems is ca 6500 cm<sup>-1</sup>. Therefore, the first transition  $\Delta_1 = 8Dq$  lies in the NIR region and it has not been detected by the used hardware. For

the second spin-allowed transition the estimated value is  $\Delta_{2}$  = 18Dq  $\sim$  19500 cm  $^{-1}.$ 

For a more detailed analysis (in  $D_{4h}$  symmetry), a Lorentzian deconvolution of the spectra has been applied first. The Co(II) ion

in tetragonal symmetry is expected to have six spin-allowed transitions, but the recorded spectra apparently have only two to three major components. It is evident from the previous discussion that the lowest transitions,  ${}^{4}A_{2g} \rightarrow {}^{4}E_{g}({}^{4}T_{1g})$  and  ${}^{4}A_{2g} \rightarrow {}^{4}E_{g}({}^{4}T_{2g})$ , are located in the region of  $<9000 \text{ cm}^{-1}$ , thus we focused on the four highest one. We fitted the spectra (without the energy level calculations) roughly with three Lorentzian primitives first, then two minor components were added to reproduce the more suitable shapes. The deconvoluted spectra for 1-4 are shown in Supplementary material (Fig. S6). The next step was the band assignment and determination of the crystal-field parameters. Here, we fitted the spectra by means of the generalized crystal-field theory using the obtained Lorentzian function characteristics (position, halfwide, height) as fixed input parameters. The optimized set of input parameters was  $\{F_4(xy), F_4(z), B\}$ , the Racah C parameter was constrained as C = 4/3B.

The optimum set of the crystal-field parameters is collected in Table 3. There are also shown the calculated values of the lowest transition,  ${}^{4}A_{2g} \rightarrow {}^{4}E_{g}({}^{4}T_{1g}) = \Delta_{ax}$ , (axial splitting parameter) which is a measure of the crystal-field tetragonality. The band assignments (see Fig. 5) have been done according of the calculated energy levels. In the used software, the levels (crystal-field terms) are classified under the characters of the irreducible representations of the respective point group resulting from the matrix transformation

$$\mathbf{R_{cf}} = \mathbf{C}^{\dagger} \mathbf{R} \mathbf{C} \tag{8}$$

where **R** is matrix representation of the symmetry operator  $\hat{R}(\alpha, \beta, \gamma)$  in  $|L, M_L\rangle$  basis and **C** are eigenvectors of the crystal-field matrix.

We can conclude: (i) three spin-allowed transitions have been identified in the measured spectra at ~9500, 19000 and 21000 cm<sup>-1</sup>; (ii) the transition  ${}^{4}A_{2g} \rightarrow {}^{4}A_{2g}[{}^{4}T_{1g}({}^{4}P)]$  is not resolved since it is only few wavenumbers above the  ${}^{4}A_{2g} \rightarrow {}^{4}E_{g}[{}^{4}T_{1g}({}^{4}P)]$  band; (iii) at ~15000 and 25000 cm<sup>-1</sup> a spin-forbidden transitions occur, it is expected that the enhanced intensities are consequence of the "borrowing" mechanism [29].

#### 4.3. Magnetic data and magnetic parameters

Magnetic data of the Co(II) complexes are consistent with the zero-field splitting (Fig. 6). On cooling the effective magnetic moment stays almost constant at its room temperature  $\mu_{\rm eff} \approx 5.0 \ \mu_{\rm B}$  until 150–100 K when it gradually decreases to a value of  $\mu_{\rm eff} \approx 3.5$ –4.0  $\mu_{\rm B}$  at T = 2 K. The magnetization at T = 2.0 K saturates to the value of  $M_{\rm mol}/N_A\mu_B \approx 2.0$ –2.5.

The low-temperature susceptibility data are dominated by the lower Kramers doublet  $M_{\rm S} = \pm 1/2$  and the limiting value is  $\mu_{\rm eff}({\rm LT}) = [g_z^2/4 + 2g_x^2]^{1/2} \mu_{\rm B}$  irrespective of *D*. With  $g_z = 2.0$  and typical  $g_x = 2.7$  one gets  $\mu_{\rm eff}({\rm LT}) = 3.95 \mu_{\rm B}$ . Lower values observed at the  $T \sim 2$  K are attributed to the presence of intermolecular interactions described by the molecular field correction. The high-temperature limit is  $\mu_{\rm eff}({\rm HT}) = [(g_z^2 + 2g_x^2)(5/4)]^{1/2} \mu_{\rm B}$  which with the above typical values yields 4.23  $\mu_{\rm B}$  again irrespective of *D*.

Table 3					
Crystal-field parameters	for	the stud	lied	complexes.	

Complex	$\Delta_{\rm ax}~({\rm cm}^{-1})$	<i>B</i> (cm <sup>-1</sup> )	$F_4(z)$ (cm <sup>-1</sup> )	$F_4(xy)$ (cm <sup>-1</sup> )
1	632	876	6720	5261
2	459	845	6383	5325
3	593	901	6646	5273
4	743	914	6869	5147
4	743	914	6869	5147

Magnetic parameters were determined using a fitting procedure where the energy levels results from a full-matrix diagonalization of the spin Hamiltonian,

$$\hat{H}^{S} = \hbar^{-2} \left[ D \left( \hat{S}_{z}^{2} - \hat{S}^{2} / 3 \right) + E \left( \hat{S}_{x}^{2} - \hat{S}_{y}^{2} \right) \right] + \hbar^{-1} \mu_{\mathrm{B}} (\vec{B} \cdot \overline{\overline{g}} \cdot \vec{S})$$
(9)

which is a good approximation for this case since a sufficiently strong tetragonality lifts the members of the  ${}^{4}E_{g}$  term outside the thermal accessibility ( $\Delta_{ax} > |\lambda|$ ). Otherwise, the Griffith/Figgis approach should be considered. Furthermore, a molecular-field correction is essential in reproducing the low-temperature susceptibility data for *T* < 10 K [8]; thus the calculation has been improved by the correction

$$\chi_{\rm corr} = \frac{\chi}{1 - (zj/N_{\rm A}\mu_0\mu_{\rm B}^2)\cdot\chi} + \alpha \tag{10}$$

where the parameter zj includes the isotropic exchange interaction j with the number of nearest neighbors z;  $\alpha$  compensates uncertainties in determining the underlying diamagnetism and it accounts to the temperature-independent paramagnetism;  $\chi$  is the net molar magnetic susceptibility. The susceptibility data-set ( $\chi$  versus T at B = 0.1 T) as well as the magnetization data-set (M versus B at T = 2.0 K) have been treated simultaneously. They were used in constructing a common functional to be optimized by the same set of magnetic parameters:  $g_x$ ,  $g_y$ , D, E, zj and  $\alpha$ . The z-component of the *g*-factor ( $g_z$ ) has been fixed to 2.0 (for details see Ref. [10]). The optimum set of the magnetic parameters is listed in Table 4.

Experimental determination of the ZFS is not a trivial problem. In any case, theoretical calculations can help in the analysis of experimental data and verification of results. We have calculated the magnetic parameters by crystal-field theory methods as described in Section 3. For this purpose, a set of spectral parameters were extracted from electronic spectra. Orbital reduction factors ( $\kappa_x = \kappa_y = \kappa_{xy}$  and  $\kappa_z$  in D<sub>4h</sub>) are also in play since covalency effects in real metal complexes cannot be ignored. One can approximately set  $\kappa = 0.7$ –0.8 for general studies, however, in this case we need to consider the reduction factors more carefully (magnetic properties of complexes are quite sensitive on it). For  $\hat{L}_z$  no contribution to ZFS is found, thus only in-plane covalency ( $\kappa_{xy}$ ) is significant for the Co(II) ion [10].

Conventionally  $\kappa = 1 - (c^{L})^{2}$ , where the  $c^{L}$  coefficient determines the amount of ligand character that is mixed into the metal *d*-derived orbitals [30]. To estimate the  $\kappa_{xy}$  factors, DFT characterization of the relevant  $\sigma d$ -p and  $\pi d$ -p MOs (mainly  $d_{x^2-y^2}$  and  $d_{xy}$ derived) has been performed for all studied complexes. Results are summarized in Table 5: larger averaged O-character of the in-plane bonds has been found for 1 and 3 (12% and 13%, respectively); for **2** and **4** the O-contribution is less, 7–10%. We assumed that these quantities are approximately equal to  $100(c^{L})^{2}$ ; subsequently the orbital reduction factors were evaluated. Final set of the magnetic parameters is shown in Table 6. As can bee seen in Fig. 7, the CFTM provides somewhat better results for D-parameter than the SH formalism (slope of the correlation line is close to unity for CFTM). In general, however, it can be concluded that the calculated magnetic parameters are consistent with experimental data.

For comparison, the B3LYP/TZVP coupled-perturbed (CP) method has been used for the calculation of the ZFS for complex **4**. This complex has been chosen since its negative tetragonality is the most distinctive within the series ( $D_{str} = -9.25$  pm,  $|E_{str}/D_{str}| < 1/$ 3). In this advanced method, the ZFS is defined as [31]

$$D = D_{\rm ss} + D_{\rm soc}^{\rm S,S} + D_{\rm soc}^{\rm S,S+1} + D_{\rm soc}^{\rm S,S-1} \tag{11}$$

The  $D_{ss}$  part that accounts for the spin–spin coupling contribution to the ZFS has been treated with the "UNO" option. This allows the calculation of the spin–spin coupling term with a restricted



Fig. 6. Magnetic data for the Co(II) complexes. Temperature dependence of the effective magnetic moment at *B* = 0.1 T and field dependence of the magnetization at *T* = 2.0 K. Empty circles - experimental, lines - fitted.

Table 4	1
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Magnetic parameters for the Co(II) complexes extracted from SQUID data.

Complex	g <sub>x</sub>	$g_y$	D/hc <sup>a</sup>	E/hc <sup>a</sup>	zj/hc <sup>a</sup>	$\alpha^{\mathbf{b}}$
1	2.587	2.689	85.96	3.01	-0.01	2.04
2	2.613	2.801	103.10	6.03	-0.14	0.23
3	2.607	2.758	87.59	2.84	-0.01	-6.49
4	2.435	2.520	79.99	0.55	-0.09	19.43

<sup>a</sup> In cm<sup>-1</sup>.

 $^{\rm b}~{\rm In}~10^{-9}\,{\rm m}^3\,{\rm mol}^{-1}.$  R-factor (%): (1) 0.49, (2) 0.54, (3) 0.83, (4) 0.68.

Table 5								
Population	analysis of	the Co-O	bonds	and es	stimated	orbital	reduction	factors.

	1	2	3	4
$d_{x^2-y^2}^{a}$	91.2/6.6	85.4/8.3	74.8/17.0	83.3/9.1
$d_{xy}^{a}$	78.6/16.5	86.1/7.4	82.4/9.2	81.1/11.9
κ <sub>xy</sub>	0.88	0.93	0.87	0.90

<sup>a</sup> Cobalt/oxo character (%) of the MOs obtained from Löwdin population analysis.

spin density obtained from the unrestricted natural orbitals. To calculate the spin-orbit coupling contribution to ZFS, four types of excitations are considered: (i) DOMO  $\rightarrow$  SOMO ( $\beta \rightarrow \beta$ ), (ii) SOMO  $\rightarrow$  VMO ( $\alpha \rightarrow \alpha$ ), (iii) SOMO  $\rightarrow$  SOMO ( $\alpha \rightarrow \beta$ ) and (iv) DOMO  $\rightarrow$  VMO ( $\beta \rightarrow \alpha$ ), where the abbreviations stand for doubly occupied, singly occupied and virtual MOs.

The results are summarized in Table 7. As can be seen, the calculated D-parameter is approximately 10-fold smaller than the

Table 6	
Reconstructed magnetic parameters $(D_{4h})$ .	

Complex	g <sub>xy</sub>	$\alpha^{\text{TIP}}$	D <sup>SH</sup>	$D^*$
1	2.907	11.51	77.63	84.59
2	3.443	18.34	123.70	109.7
3	2.965	12.25	82.64	88.36
4	2.828	10.50	70.83	78.01

 $D^{SH}$  – spin Hamiltonian formalism.  $D^*$  – crystal-field theory of multiplets (CFTM),  $D^* = (\Gamma_7 - \Gamma_6)/2.$ 



Fig. 7. Correlation between theoretical and experimental D-values for complexes 1-4 as predicted from two different crystal-field theory methods.

Table 7DFT-CP modeling of the ZFS for complex 4.

ZFS parameters ( $cm^{-1}$ )	
D <sub>soc</sub> part	
$\alpha \rightarrow \alpha$	0.21
$\beta \rightarrow \beta$	2.34
$\alpha \rightarrow \beta$	3.95
$\beta \rightarrow \alpha$	-0.11
D <sub>ss</sub> part	
Coulomb	1.53
Exchange	0.17
D	8.07
E/D	0.09

experimental value. Many works shows that the small *D*-values of the manganese and iron complexes (<5 cm<sup>-1</sup>) are well reproduced by the DFT-CP approach [32,33]. However, it appears that for systems with large ZFS this method has limited use.

#### 5. Conclusions

Four sixcoordinate cobalt(II) complexes of the  $[Co(L^N)_2(car)_2 (H_2O)_2]$  type have been prepared and structurally characterized. Their chromophores  $\{CoN_2O_2O_2'\}$  exhibit distortions from the octahedral pattern that refer to the  $D_{4h}$  symmetry  $(D_{str})$  in first approximation. In complexes **1–3** large rhombic contribution is present. The analysis of magnetic data shows that the *D*-values in the complexes under study adopt values between 80 and 103 cm<sup>-1</sup>.

The crystal-field theory analysis of the electronic spectra provided assignments for characteristic absorption bands in the visible region. Obtained spectral (crystal-field) parameters coupled with the estimated orbital reduction factors were used for reconstruction of the magnetic parameters. The results are in good agreement with available experimental data. Parallel calculation of the ZFS was performed with the DFT model for complex **4**. Comparison of the individual results supports the use of crystal-field theory methods for modeling the magnetic parameters in this class of compounds.

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#### Appendix A. Supplementary material

CCDC 831600, 831602, 831601 and 831599 contain the supplementary crystallographic data for **1** through **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.03.036.

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