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Magnetism of dinuclear benzoato cobalt(II) complexes modeled by a general bilinear exchange

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ABSTRACT

Combination of the cobalt(II) benzoate with N-heterocyclic ligands L-pyridine, 4-methylpyridine, *iso*-quinoline, furo[3,2-*c*]pyridine, 2-methylfuro[3,2-*c*]pyridine and 2,3-dimethylfuro[3,2-*c*]pyridine resulted in dinuclear complexes containing two benzoato bridging ligands (*bz*) and one aqua ligand of the composition $[(\mu_2\text{-}H_2O)(\mu_2\text{-}bz)_2\{Co(bz)(L)_2\}_2]\cdot Sol$. The cobalt(II) centers show a weak exchange interaction of an antiferromagnetic nature. The problem of non-collinear orientation of the local *D*-tensors is solved by a numerical procedure considering a general bilinear exchange. The susceptibility and magnetization data were fitted by a joint functional allowing to determine the single-ion zero-field splitting that adopts large values: D/hc of the order of 50–100 cm^{-1}.

1. Introduction

The cobalt(II) benzoates cover a wide-studied class of complexes with a variety of structural motifs. Among dinuclear complexes, one pattern is represented by structural analogs of the well-known copper(II) acetate: in $[Co_2(bz)_4L_2]$ four benzoato ligands (*bz*) adopt the role of bridges that link two metal ions (type I, see Fig. 1). In these structures the Co(II) atoms are pentacoordinate. This group is covered by $[(\mu_2\text{-}bz)_4\{Co(qu)\}_2]$ and $[(\mu_2\text{-}bz)_4\{Co(4\text{-}Me\text{-}qu)\}_2]$ where *qu* = quinoline [1–3]. A different pattern exists in complexes of the type II: they contain one aqua and two benzoato bridging ligands. Frequently, the additional benzoates serve as unidentate terminal ligands and thus in such complexes the metal ions are hexacoordinate (the coordination sphere is mostly completed by N-donor bases). Such a structural motif applies also for substituted benzoates, *n*-X-*bz* where *n* = 2, 3, and 4 [4,5]. Two benzoato bridging ligands in combination with two aqua bridges exist in complexes of the type III. As an example, the complex $[(\mu_2\text{-}H_2O)_2(\mu_2\text{-}2,6\text{-}(p\text{Tol})_2\text{-}bz)_2\{Co(2,6\text{-}(p\text{Tol})_2\text{-}bz)(py)\}_2]$ [6] is presented (*py* = pyridine). Purely aqua bridged complexes with terminal-only benzoato ligands are classified as type IV: this group is, for example, represented by $[(\mu_2\text{-}H_2O)_2\{Co(bpy)(H_2O)(4\text{-}CHO\text{-}bz)\}_2](4\text{-}CHO\text{-}bz)_2$ [7].

The present publication deals with dinuclear Co(II) complexes of the second family. We enriched this family with three novel complexes whose composition is $[(\mu_2\text{-}H_2O)(\mu_2\text{-}bz)_2\{Co(bz)(L)_2\}_2]\cdot Sol$, where Sol is an eventual solvent embodied in the crystal lattice. The neutral N-donor ligands L are furo[3,2-*c*]pyridine (*fupy*), 2-methylfuro[3,2-*c*]pyridine (*Mefupy*) and 2,3-dimethylfuro[3,2-*c*]pyridine (Me_2fupy) and *iso*-quinoline (*iqu*). For comparison we prepared two other complexes with pyridine and 4-methylpyridine (*Mepy*). Note that the complexes with this composition have already been structurally characterized [8,9]. The X-ray structure of the six prepared complexes has been determined and the powder material has been subjected to magnetochemical investigation.

2. Experimental

2.1. Synthesis

Starting materials (pyridine, 4-methylpyridine, *iso*-quinoline, $CoCl_2\cdot 6H_2O$, PhCOONa and ethanol) were purchased from commercial sources and used as received. Furopyridine, methylfuropyridine (liquid) and dimethylfuropyridine (solid) were prepared by the known procedures [10,11].

Preparation of complex ***1*** *=* $[(\mu_2\text{-}H_2O)(\mu_2\text{-}PhCOO)_2\{Co(PhCOO\text{-}\kappa^1\text{-}O)(py)_2\}_2]\cdot 0.5(PhCOOH)\cdot 1.5(MePh)$*:* Natrium benzoate (2 mmol) and cobalt(II) chloride (1 mmol) were finely ground in mortar and heated at 100 °C for 10 min. The solid mixture was cooled to the room temperature and toluene (10 cm^3) was added. Heterogeneous mixture was stirred at the room temperature for 5 min. followed by the addition of pyridine (2 mmol). The blue liquid turned to pink. The insoluble solid precipitate was filtered and the filtrate was left for 2 days for

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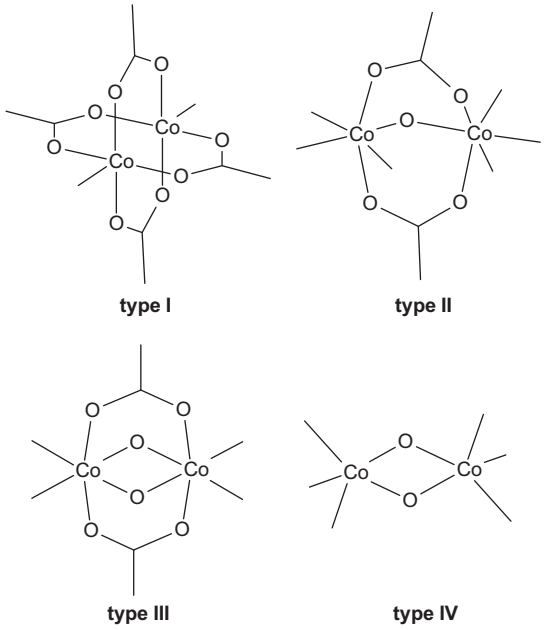

Fig. 1. Structural types of dinuclear cobalt(II) benzoates.

a spontaneous evaporation. The pink crystals were separated on Büchner funnel and washed with ethanol.

Preparation of complex ***3*** *= [(μ_2-H_2O)(μ_2-PhCOO)$_2${Co(PhCOO-κ^1-O)(iqu)$_2$}$_2$]·(iqu):* A solution of natrium benzoate (2 mmol) in ethanol/water (10 cm^3) was added dropwise with stirring at 50 °C to a solution of cobalt(II) chloride (1 mmol) in water (5 cm^3). The solution was stirred for 2 h at laboratory temperature. Ethanol solution of the *iso*-quinoline (10 cm^3) was added dropwise to this suspension. The clear red solution was stirred for 1 h at 60 °C and then cooled to the room temperature. The filtrate was left for 2 days for a spontaneous evaporation. The pink crystals were separated on Büchner funnel and washed with ethanol.

Preparation of complexes ***2*** *= [(μ_2-H_2O)(μ_2-PhCOO)$_2${Co(PhCOO-κ^1-O)(Mepy)$_2$}$_2$],* ***4*** *= [(μ_2-H_2O)(μ_2-PhCOO)$_2${Co(PhCOO-κ^1-O)(fupy)$_2$}$_2$],* ***5*** *= [(μ_2-H_2O)(μ_2-PhCOO)$_2${Co(PhCOO-κ^1 O)(Mefupy)$_2$}$_2$] and* ***6*** *= [(μ_2-H_2O)(μ_2-PhCOO)$_2${Co(PhCOO-κ^1-O)(Me$_2$fupy)$_2$}$_2$]:* A suspension of L in 10 cm^3 of ethanol was combined with a mixture of PhCOONa and $CoCl_2{\cdot}6H_2O$ in 10 cm^3 of ethanol/water (the molar ratio L:PhCOONa:$CoCl_2 6H_2O$ = 2:2:1). After stirring for 1 h at 60 °C the insoluble solid precipitate was filtrated. The filtrate was left for 2 days for a spontaneous evaporation. The dark violet crystals were separated on Büchner funnel and washed with ethanol.

Anal. Calc. for **1**, $C_{62}H_{57}Co_2N_4O_{10}$, *M* = 1135.98: C, 64.6; H, 5.07; N, 4.86. Found: C, 64.5; H, 4.98; N, 4.74%. *Anal.* Calc. for **2**, $C_{52}H_{50}Co_2N_4O_9$, *M* = 992.82: C, 62.9; H, 5.08; N, 5.64. Found: C, 61.0; H, 4.97; N, 5.32%. *Anal.* Calc. for **3**, $C_{73}H_{57}Co_2N_5O_9$, *M* = 1266.10: C, 69.2; H, 4.54; N, 5.53. Found: C, 68.7; H, 4.62; N, 6.36%. *Anal.* Calc. for **4**, $C_{56}H_{42}Co_2N_4O_{13}$, *M* = 1096.80: C, 61.3; H, 3.86; N, 5.11. Found: C, 60.5; H, 3.91; N, 4.96%. *Anal.* Calc. for **5**, $C_{60}H_{50}Co_2N_4O_{13}$, *M* = 1152.90: C, 62.5; H, 4.37; N, 4.86. Found: C, 62.6; H, 5.37; N, 5.15%. IR (KBr, cm^{-1}): $\nu_{as}(CO_2^-)$ = 1598, $\nu_s(CO_2^-)$ = 1380, δ(py) = 686. *Anal.* Calc. for **6**, $C_{64}H_{58}Co_2N_4O_{13}$, *M* = 1209.00: C, 63.6; H, 4.84; N, 4.63. Found: C, 62.8; H, 5.59; N, 4.62%. IR (KBr, cm^{-1}): $\nu_{as}(CO_2^-)$ = 1604, $\nu_s(CO_2^-)$ = 1386, δ(py) = 686.

2.2. Physical measurements

Elemental analysis was carried out on FlashEA 1112, Thermo-Finnigan. IR spectra were measured in KBr pellets (Magna FTIR 750, Nicolet) in the 4000–400 cm^{-1} region. Electron spectra were measured in Nujol mull (Specord 200, Analytical Jena) in the range 9000–50 000 cm^{-1}.

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 and 4.6 K, respectively. Raw susceptibility data were corrected for underlying diamagnetism using an estimate χ_{dia} [10^{-12} m^3 mol^{-1}] = $-5M$ [g mol^{-1}]. The effective magnetic moment has been calculated as usual: $\mu_{eff}/\mu_B = 798(\chi' T)^{1/2}$ when SI units are employed.

Data collection and cell refinement of **1**–**6** were carried out using a κ-axis diffractometer Gemini R CCD (Oxford Diffraction) with graphite monochromated Mo Kα radiation. The diffraction intensities were corrected for Lorentz and polarization factors.

2.3. Details of refinement

The structures were solved by direct methods using SIR-97 [12] or SHELXS-97 [13] and refined by the full-matrix least-squares procedure with SHELXL-97 [13]. The analytical corrections [14] were made by using CRYSALIS-RED [15]. Geometrical analyses were performed with SHELXL-97. Crystal data and conditions of data collection and refinement are reported in Table 1.

Discrete substitution disorder of one benzoic acid molecule [O1S,O2S,C1S–C7S] (solid lines) and one toluene molecule [C1B,C3B,C5B,C7B–C10B] (dashed lines) of **1** is observed (Fig. 2). The second toluene molecule is disordered in two discrete positions represented by carbon atoms [C11A–C17A] (solid lines) and [C11B–C17B] (dashed lines). The disordered benzoic acid and toluene molecules are restrained using SADI and EADP commands of SHELXL-97 program.

Discrete positional disorder of the uncoordinated *iso*-quinoline molecule of **3** is observed. The uncoordinated *iso*-quinoline molecule lies around a 2-fold rotation axis and its two carbon atoms [C43,C44] are localized exactly in special positions. A non-crystallographic mirror plane perpendicular to the 2-fold rotation axis is also observed in the disordered *iso*-quinoline molecule. The two couples of alternative atoms N3/C40 and C41/N4 are localized in 2- or 3-positions of *iso*-quinoline molecule, respectively, with occupancy factors 0.25 for N atoms and 0.75 for C atoms. The alternate couple of atoms N3/C40 and C41/N4 are modeled using EXYZ and EADP commands of SHELXL-97 program.

Three benzoato ligands of **4** are disordered occupying two statistical positions, represented by atoms [C2A–C7A]/[C2B–C7B]; [C36A–C41A]/[C36B–C41B]; and [C43A–C48A]/[C43B–C48B] with site occupancy factors of 0.67/0.33; 0.53/0.47; and 0.79/0.21, respectively. The disordered benzene groups are constrained using AFIX66/AFIX65 commands, and restrained using SADI and EADP commands of SHELXL-97.

3. Results and discussion

3.1. Molecular and crystal structure

The molecular structures of complexes **1**–**6** are similar one to another, but the complexes crystallize in different crystal systems. A complete complex molecule in the independent part of unit cell is observed in the crystal structures **1** and **4** (Figs. 2 and 5). These complexes crystallize in the monoclinic system with the space group $P2_1/c$. Two independent complex molecules are observed in the crystal structure of **2** (Fig. 3), which crystallizes in the monoclinic system and the space group $P2_1$. On the other hand, only halves of complex molecules of **3** (Fig. 4), and isostructural **5** and **6** (Figs. 6 and 7) are localized in the independent part of the unit cell. The complex **3** crystallizes in the orthorhombic system with