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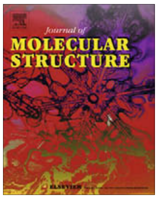

Polymorphism of cobalt(II) complex with 6-bromopicolinic acid: The influence of the solution pH value on the formation of polymorphs

Boris-Marko Kukovec, Zora Popović *

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia

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ABSTRACT

Triclinic (**1**) and monoclinic (**2**) polymorphs of cobalt(II) complex with 6-bromopicolinic acid, namely $[Co(6\text{-}Brpic)_2(H_2O)_2]\cdot 3H_2O$ were prepared and characterized by spectroscopic methods (IR), their molecular and crystal structures were determined by X-ray crystal structure analysis and their thermal stability by TGA/DTA methods. Polymorph **1** was prepared by reaction of cobalt(II) acetate tetrahydrate and 6-bromopicolinic acid in aqueous solution at pH value of 6, while **2** was obtained by the same reaction in aqueous solution at pH value of 8. The pH value was adjusted with the addition of ammonia solution. This is an example of the influence of the solution pH value on the formation of polymorphs. X-ray structural analysis revealed octahedron as a coordination polyhedron in both **1** and **2** and the same *N,O*-chelated coordination mode of 6-bromopicolinic acid. The coordination sphere of cobalt(II) ion is completed by two coordinated water molecules. The polymorphs differ in their crystal structures, which are dominated by intermolecular O–H···O hydrogen bonds and π–π stacking interactions, and in the crystal system (triclinic vs. monoclinic). The infrared spectra of **1** and **2** are very similar so the polymorphs cannot be unambiguously distinguished by IR spectroscopy. Thermal methods confirm number of co-crystallized water molecules in both polymorphs.

1. Introduction

Polymorphism, the ability of a substance to exist in more than one crystalline form [1,2], has always been relevant to the pharmaceutical industry since bioavailability and physical properties (melting point, solubility, density, conductivity, dissolution rate etc.) can be critically dependent on crystal packing. It is also the well known fact that different crystal forms of a substance can possess different properties and behave as a different material. This concept has important implications in all fields [1] of chemistry associated with manufacturing and commercialization of compounds in the form of crystalline materials (drugs, dyes, pigments, agrochemicals and food additives, explosives etc.). The crystal structures of polymorphic forms provide the valuable information on intermolecular interactions in crystals and on the influence of crystal environment on the molecular conformation. Therefore, their study is crucial to rational crystal design.

Much effort has been devoted to the design and controlled crystallization of coordination networks based on transition metal atoms and multifunctional bridging ligands due to their potential applications e.g. magnetism, electrical conductivity, molecular adsorption, heterogenous catalysis. However, the conditions that affect the formation of a particular polymorph are mostly the result of serendipity rather than a process under complete human control. Polymorphism in organic substances has been studied for some time, while the interest in the analogous behaviour of inorganic and organometallic materials has arisen more recently [3,4].

Here we report the synthesis, structural, spectroscopic and thermal characterization of two polymorphs of cobalt(II) complex with 6-bromopicolinic acid (6-BrpicH) as an example of the influence of solution pH value on the formation of particular polymorph. We performed this research, as a part of our wider research programme on polymorphism and isomerism of the late 3*d*-metal complexes with picolinic acid and its derivatives [5–10], due to the lack of data in coordination chemistry of the transition metals and 6-bromopicolinic acid as a ligand [8,10,11].

2. Experimental

2.1. Materials and physical measurements

All chemicals for the syntheses were used as received without further purification. Cobalt(II) acetate tetrahydrate was purchased from Merck, while 6-bromopicolinic acid was purchased from Aldrich.

CHN analyses were performed on Perkin–Elmer 2400 Series II CHNS analyzer in the Analytical Services Laboratories of the Ruđer Bošković Institute, Zagreb, Croatia.

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* Corresponding author. Tel.: +385 1 4606354; fax: +385 1 4606341.
E-mail address: zpopovic@chem.pmf.hr (Z. Popović).

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The IR spectra were obtained from KBr pellets in the range 4000–450 cm^{-1} with Perkin–Elmer Spectrum RXI FTIR-spectrometer.

TGA/DTA measurements were performed at heating rate of 5 °C min^{-1} in the temperature range of 25–600 °C, under nitrogen flow of 10 mL min^{-1} on instrument Mettler-Toledo TGA/SDTA 851^{e}. Approximately 10 mg of sample were placed in standard aluminium crucible (40 μL).

2.2. [Co(6-Brpic)$_2$(H$_2$O)$_2$]·3H$_2$O (triclinic polymorph), (1)

An aqueous solution (15 mL) of 6-bromopicolinic acid (0.10 g, 0.50 mmol) and aqueous solution (5 mL) of cobalt(II) acetate tetrahydrate (0.06 g, 0.24 mmol) were mixed. The pH value of the resulting dark pink solution was 6. The solution was left to stand at room temperature for a month. The pink crystals were obtained and filtered off, washed with small portion of water and dried in vacuum. Yield: 0.06 g (46%). Anal. Calcd. for $C_{12}H_{16}CoBr_2N_2O_9$ (551.03): C, 26.15; H, 2.93; N, 5.09%. Found: C, 26.31; H, 3.07; N 5.18%. IR data (KBr pellet, cm^{-1}): 3324(s), 1640(vs), 1587(s), 1555(s), 1441(s), 1404(m), 1378(vs), 1247(w), 1182(w), 1157(w), 1127(m), 1081(w), 1002(w), 876(w), 848(w), 789(m), 771(m), 745(m), 661(w), 559(w), 511(w).

2.3. [Co(6-Brpic)$_2$(H$_2$O)$_2$]·3H$_2$O (monoclinic polymorph), (2)

An aqueous solution (20 mL) of 6-bromopicolinic acid (0.20 g, 1.00 mmol) and aqueous solution (5 mL) of cobalt(II) acetate tetrahydrate (0.12 g, 0.48 mmol) were mixed. The pH value of the resulting dark pink solution was adjusted to 8 by adding a few drops of concentrated ammonia solution. The solution was left to stand at room temperature for a month and then the pink crystals were filtered off, washed with small portion of water and dried in vacuum. Yield: 0.14 g (52%). Anal. Calcd. for $C_{12}H_{16}CoBr_2N_2O_9$ (551.03): C, 26.15; H, 2.93; N, 5.09%. Found: C, 26.42; H, 3.11; N, 5.11%. IR data (KBr pellet, cm^{-1}): 3337(s), 1640(vs), 1587(s), 1555(s), 1442(s), 1405(m), 1378(s), 1248(w), 1182(w), 1163(w), 1128(m), 1082(w), 1003(w), 875(w), 848(w), 789(m), 771(m), 746(m), 661(w), 560(w), 512(w).

2.4. X-ray single crystal structure determination

Suitable single crystals of **1** and **2** were selected and mounted in air onto thin glass fibres. The data collection was carried out on Oxford Diffraction Xcalibur four-circle kappa geometry diffractometer with Xcalibur Sapphire 3 CCD detector, using a graphite monochromated MoKα (λ = 0.71073 Å) radiation, and by applying the CrysAlis Software system, Version 171.32.24 at room temperature (296 K) [12]. Data reduction has been done by the same programme [12].

The X-ray diffraction data have been corrected for Lorentz-polarization factor and scaled for absorption effects by multi-scan. The structures were solved by direct methods. Refinement procedure by full-matrix least squares methods based on F^2 values against all reflections has been performed including anisotropic displacement parameters for all non-H atoms.

The positions of hydrogen atoms belonging to the carbon atoms C*sp*^{2} were geometrically optimized applying the riding model [C*sp*^{2}–H, 0.93 Å; $U_{iso}(H) = 1.2U_{eq}(C)$ for C*sp*^{2}]. Hydrogen atoms belonging to water molecules in **1** and **2** could not be found in difference Fourier maps, probably due to the lower quality of the crystal and the data collected. However, crystals of better quality could not be prepared in spite of all our attempts. Atom O17 from co-crystallized water molecule in **2** is disordered.

Calculations were performed with SHELXS-97 [13], SHELXL-97 [13] and PLATON [14]. The molecular graphics were done with ORTEP-3 [15] and MERCURY (Version 1.4.2) [16]. Crystal data and details of the structure determination for **1** and **2** are given in Table 1.

3. Results and discussion

3.1. Crystal structures of 1 and 2

There are two crystallographically independent molecules of complex in the asymmetric unit of polymorphs **1** and **2**. The asymmetric unit of **1** and **2** also contains six co-crystallized water molecules, respectively. ORTEP-3 view of the molecular structure of polymorph **1** is depicted in Fig. 1, while molecular structure of polymorph **2** is not shown due to the great similarity with the structure of **1**. The crystal structures of polymorphs **1** and **2** are shown in Figs. 2a and 2b, respectively. Some selected interatomic bond distances and angles are listed in Table 2.

The cobalt(II) ion in the molecular structures of **1** and **2** is coordinated by two *N*,*O*-bidentate 6-bromopyridine-2-carboxylate ligands (bound through pyridine *N* atom and carboxylate *O* atom) which are approximately perpendicular to each other and form five-membered chelate rings. Furthermore, the coordination sphere of cobalt(II) ion is completed by two water molecules in *cis* position (Fig. 1). The coordination polyhedron around cobalt(II) ion in both polymorphs is a distorted octahedron. The angles between water molecules have the values of 95.1(1)° for one crystallographically independent molecule in **1** (angle O6–Co1–O5) and of 94.7(1)° for the other crystallographically independent molecule in **1** (angle O11–Co2–O12). The analogous values for **2** are 94.3(3)° for angle O6–Co1–O5 and 96.1(2)° for angle O11–Co2–O12. Polymorphs **1** and **2** appear as *cis* instead of *trans* isomers (similar as the analogous pseudopolymorphs of nickel(II) complex with 6-bromopicolinic acid [10]) probably due to the steric effects caused by the bromine substituent in the pyridine ring at position-6. The same effect of the methyl substituent was observed for the analogous pseudopolymorphs of *cis* cobalt(II) [9,17] and nickel(II) [7] complexes with 6-methylpicolinic acid. Other related octahedral cobalt(II) complexes with picolinic [18,19], 3-hydroxypicolinic [20,21] and 6-hydroxypicolinic acid [22] appear as the expected *trans* isomers. The *trans* disposition of donor atoms are far more abundant in the literature than the *cis* one for this type of complexes.

The bond distances and angles in **1** and **2** are quite similar, as expected for polymorphs (Table 2). The bond distances Co–N and Co–O (*N* and *O* atoms are from 6-bromopicolinic acid) in **1** and **2** are in accordance with the values reported in the literature for similar complexes e.g. cobalt(II) complexes with picolinic [18,19], 3-hydroxypicolinic [20,21], 6-hydroxypicolinic [22] and 6-methylpicolinic [9,17] acid. Triclinic polymorph **1** is isostructural with the analogous nickel(II) complex with 6-bromopicolinic acid [10].

The values for bond angles indicate severe distortion from the ideal octahedral geometry (Table 2). This distortion is specially observed in the bite angles O1–Co1–N1 with values of 77.4(2)° for **1** and 76.3(3)° for **2**, O3–Co1–N2 with values of 77.0(1)° for **1** and 78.5(3)° for **2**, O7–Co2–N3 with values of 77.9(1)° for **1** and 76.9(3)° for **2** and O9–Co2–N4 with values of 77.7(1)° for **1** and 77.5(3)° for **2**. The bite angles are rather small due to the chelate ring formation (Table 2).

The crystal packing is similar for **1** and **2** and dominated by numerous hydrogen bonds of the O–H···O type (Figs. 2a and 2b). The hydrogen atoms which belong to coordinated and co-crystallized water molecules could not be found in difference Fourier maps. Therefore, the intermolecular O···O contacts shorter than 3 Å are the indication of the present hydrogen bonds.

Two molecules of cobalt(II) complex in **1** are linked into centrosymmetric dimers which are further connected into an infinite chain in [1 0 0] direction by hydrogen bonds. Such chains are