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Pseudopolymorphism in nickel(II) complexes with 6-bromopicolinic acid. Synthesis, structural and thermal studies

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ABSTRACT

Nickel(II) complexes of 6-bromopicolinic acid, namely $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot 3H_2O$ (**1**) and $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot H_2O$ (**2**) 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. Compound **1** was prepared by reaction of nickel(II) nitrate and 6-bromopicolinic acid in aqueous solution at pH value of 8, while **2** was obtained by spontaneous recrystallization of **1** in its mother liquor during few months. These complexes are an example of pseudopolymorphs which differ in number of co-crystallized water molecules but both crystallize in the same crystal system (triclinic). 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 nickel(II) ion is completed by two coordinated water molecules. These pseudopolymorphs differ in their crystal structures which are dominated by intermolecular O–H···O hydrogen bonds and π–π stacking interactions in both cases. The infrared spectra of **1** and **2** are very similar so these pseudopolymorphs cannot be unambiguously distinguished by IR spectroscopy. Thermal methods confirm number of co-crystallized water molecules in both pseudopolymorphs.

1. Introduction

Polymorphism and crystal growth are among the most intensively researched area of present times because of the tremendous basic and commercial interest in pharmaceutical solids and new materials. The primary process of crystallization, governed predominantly by intermolecular interactions, remains intractable even for small organic molecules due to the complexity with which molecules interact with each other [1,2].

Moreover, conversions between different polymorphs i.e. crystal forms are possible and often take place. Among many possibilities for conversion depending on variables like temperature or pressure, there are several more specific ones such as a conversion of metastable form into a thermodynamically more stable one through very slow kinetics, conversion of unsolvated form into various solvates or co-crystalline forms, conversion of anhydrous form into hydrates or a conversion of solvate into another one with different degree of solvation etc.

In this paper, we report two pseudopolymorphs of nickel(II) complex with 6-bromopicolinic acid, namely $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot 3H_2O$ (**1**) and $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot H_2O$ (**2**) as an example of transformation of one crystal form into another with different degree of hydration. The possibility of formation of pseudopolymorphs should be considered in the presence of solvent. Although transformation of **1** into **2** on prolonged standing of reaction mixture is not surprising, it could not be anticipated.

As a part of our wider research programme on polymorphism or isomerism of the late 3*d*-metal complexes with picolinic acid and its derivatives [3–7] we undertook this research, partially because of a lack of data in coordination chemistry of the transition metals and 6-bromopicolinic acid as a ligand. Until now, only ruthenium(II) [8] and copper(II) [6] complexes with 6-bromopicolinic acid have been prepared and structurally characterized.

2. Experimental

2.1. Materials and physical measurements

All chemicals for the syntheses were used as received without further purification. Nickel(II) nitrate hexahydrate was purchased from Kemika, Croatia, 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.

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

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TGA/DTA measurements were performed at heating rate of 10 °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. cis-diaquabis(6-bromopyridine-2-carboxylato-N,O)nickel(II) trihydrate, $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot 3H_2O$, (**1**)*

A solution of 6-bromopicolinic acid (0.05 g, 0.25 mmol) in 10 mL of water was added to a solution of nickel(II) nitrate hexahydrate (0.04 g, 0.14 mmol) in 5 mL of water. The pH value of the resulting green solution was adjusted to 8 by adding a few drops of concentrated ammonia solution and then left to stand at room temperature for 3 weeks. The light green crystals were obtained and filtered off, washed with small portion of water and dried in vacuum. Yield: 0.04 g (50%). Anal. Calcd. for $C_{12}H_{16}NiBr_2N_2O_9$ (550.79): C, 26.17; H, 2.93; N, 5.09%. Found: C, 26.21; H, 3.11; N 5.19%. IR data (KBr pellet, cm^{-1}): 3344(m), 1643(s), 1586(s), 1555(s), 1441(m), 1404(m), 1377(s), 1248(w), 1159(w), 1128(m), 1083(w), 1003(w), 766(m), 746(m).

*2.3. cis-diaquabis(6-bromopyridine-2-carboxylato-N,O)nickel(II) monohydrate, $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot H_2O$, (**2**)*

A solution of 6-bromopicolinic acid (0.10 g, 0.50 mmol) in 15 mL of water was added to a solution of nickel(II) nitrate hexahydrate (0.07 g, 0.24 mmol) in 5 mL of water. The pH value of the resulting green solution was adjusted to 8 by adding a few drops of concentrated ammonia solution. The solution was left to stand at room temperature for 1 week and then the light green crystals of **1** were formed. The crystals of **1** were left to stand in mother liquor at room temperature for 2 months, resulting with the formation of dark green crystals of **2**. These crystals were filtered off, washed with small portion of water and dried in vacuum. Yield: 0.10 g (83%). Anal. Calcd. for $C_{12}H_{12}NiBr_2N_2O_7$ (514.75): C, 28.00; H, 2.35; N, 5.44%. Found: C, 28.14; H, 2.41; N 5.46%. IR data (KBr pellet, cm^{-1}): 3400(m), 1641(s), 1584(s), 1554(s), 1441(m), 1375(s), 1248(w), 1161(m), 1127(m), 1085(w), 1004(w), 779(m), 771(m), 742(m).

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 by applying the CrysAlis Software system, Version 171.32.24 at room temperature (296 K) [9]. Data reduction has been applied by the same programme [9].

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 Csp^2 were geometrically optimized applying the riding model [Csp^2–H, 0.93 Å; $U_{iso}(H) = 1.2U_{eq}(C)$ for Csp^2]. Hydrogen atoms belonging to water molecules in **1** 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. Atoms O16 and O17 from co-crystallized water molecules in **1** are disordered. Hydrogen atoms belonging to water molecules in **2** were found in difference Fourier maps, the distance between them and the corresponding water oxygen atoms was restrained to the average value of 0.82(3) Å using SHELXL-97 DFIX instruction. The isotropic $U_{iso}(H)$ value was fixed at the same time [$U_{iso}(H) = 1.2U_{eq}(O)$].

Table 1

Crystal data and details of the structure determination for $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot 3H_2O$ (**1**) and $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot H_2O$ (**2**).

Compound	**1**	**2**
Formula	$C_{12}H_6NiBr_2N_2O_9$	$C_{12}H_{12}NiBr_2N_2O_7$
M_r	540.68	514.73
Colour and habit	Green, prism	Green, block
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Crystal dimensions (mm^3)	0.80 × 0.18 × 0.16	0.59 × 0.48 × 0.32
Unit cell parameters:		
a (Å)	8.9359(3)	8.0378(2)
b (Å)	13.8752(9)	11.2015(3)
c (Å)	16.1480(11)	19.8394(5)
α (°)	72.401(6)	74.148(2)
β (°)	78.756(4)	79.170(2)
γ (°)	80.779(4)	71.703(3)
V (Å^3)	1860.79(19)	1621.21(8)
Radiation, MoKα (Å)	0.71073	0.71073
Z	4	4
D_{calc}($g\ cm^{-3}$)	1.966	2.109
μ (mm^{-1})	5.385	6.164
θ range for data collection (°)	3.88–25.00	3.93–27.00
h, k, l range	−10:10; −16:16, −19:19	−10:10; −14:14, −25:25
Scan type	ω	ω
No. measured reflections	33140	35760
No. independent reflections (R_{int})	6517 (0.2339)	7028 (0.0424)
No. observed reflections, $I \geq 2\sigma(I)$	4754	5043
No. refined parameters	488	470
R[a], wR[b] [$I \geq 2\sigma(I)$]	0.0683, 0.1293	0.0398, 0.1029
R, wR [all data]	0.1138, 0.1444	0.0638, 0.1089
g_1, g_2 in w[c]	0.0535, 0.1738	0.0669, 0
Goodness of fit on F^2, S[d]	1.112	1.048
Max., min. electron density (e Å^{-3})	1.677, −1.125	1.398, −1.090
Maximum Δ/σ	0.001	0.001
Range of transmission factors min., max.	0.330, 0.420	0.035, 0.135
Extinction coefficient	–	0.0125(6)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $wR = [\sum(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

[c] $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[d] $S = \sum[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

Calculations were performed with SHELXS-97 [10], SHELXL-97 [10] and PLATON [11]. The molecular graphics were done with ORTEP-3 [12] and MERCURY (Version 1.4.2) [13].

Crystal data and details of the structure determination for **1** and **2** are given in Table 1.

3. Results and discussion

3.1. Preparation of complexes

Complex $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot 3H_2O$ (**1**) was prepared by reaction of nickel(II) nitrate hexahydrate and 6-bromopicolinic acid in aqueous solution in the presence of ammonia, at a pH value of at least 8. Complex **1** cannot be prepared in acidic aqueous solutions (without the addition of base e.g. ammonia).

Pseudopolymorph $[Ni(6\text{-}Brpic)_2(H_2O)_2]\cdot H_2O$ (**2**) was obtained by spontaneous recrystallization of **1** in its mother liquor during 2 months. Two crystal water molecules are lost during this process, leading to the formation of another pseudopolymorph, which crystallizes in a same crystal system with different number of co-crystallized water molecules (*vide infra*). Compound **1** appears as light green prisms, it is not air-stable and decomposes in air due to the release of co-crystallized water molecules. Compound **2** is air-stable and appears as dark green blocks. Both compounds are soluble in water, ethanol and in solvents with donor properties (*N,N*-dimethylformamide, dimethylsulfoxide, pyridine and 4-picoline).