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Cobalt(II) complexes with hydroxypyridines and halogenides

Brina Dojer [a], [*], Andrej Pevec [b], Zvonko Jagličić [c], [d], Matjaž Kristl [e]

[a] Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška cesta 160, SI-2000 Maribor, Slovenia
[b] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia
[c] Institute of Mathematics, Physics and Mechanics, Jadranska 19, SI-1000 Ljubljana, Slovenia
[d] Faculty of Civil and Geodetic Engineering, Jamova 2, SI-1000 Ljubljana, Slovenia
[e] Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia

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ABSTRACT

We have synthesized and characterized two new cobalt(II) complexes: difluoridotetrakis(3-hydroxypyridine-κ*N*)cobalt(II), $[CoF_2(C_5H_5NO)_4]$ (**1**) and hexa(2-pyridone-κ*O*)cobalt(II) tetrachloridocobaltate(II), $[Co(C_5H_5NO)_6][CoCl_4]$ (**2**). The complexes were prepared by solvothermal synthesis. A methanol solution of hydroxypyridine was added to water solution of cobalt(II) acetate dihydrate followed by a few drops of concentrated hydrofluoric or hydrochloric acid into the mixture. The crystals of the compounds **1** and **2** are stable on air. The compounds were characterized structurally by single-crystal X-ray diffraction analysis, spectrally by FT-IR spectroscopy and thermally. Thermal analysis showed that the final product of both complexes after heating to 900 °C is elemental cobalt. The interactions between building units in the crystal structures include intra- and intermolecular hydrogen bonds in both compounds and $\pi-\pi$ interactions in compound **2**.

1. Introduction

The derivatives of the 3-hydroxypyridine ligand have been studied for years as treatment for cerebrovascular and cardiovascular pathologies, diabetic and compression neuropathies, withdrawal syndromes, pulmonary tuberculosis, primary open-angle glaucoma and anxiety disorders [1,2] The biological activity derivatives of 2- and 3-hydroxypyridine were also evaluated as growth inhibitors of some parasites, like protozoan *Leishmania mexicana*[3]. There are also some compounds with hydroxypyridines and chloride ligands that possess significant antitumour activity [4,5].

Cobalt(II) coordination compounds with hydroxypyridines and halide ligands have been studied for years, mostly because of their different structural and magnetic properties.

The ligand 2-hydroxypyridine is interesting because of its different ways of coordination to the central ion. It can coordinate through nitrogen atom as a lactim (2-hydroxypyridine) ligand or through oxygen atom from the carbonyl group as a lactam (2-pyridone) ligand. The last one could be obtained because of the movement of hydrogen proton from oxygen to nitrogen (tautomery). The lactam ligand and its derivatives can also have a different coordination to the central ions. They can coordinate just through the substitute oxygen or they can be bridging ligands and can coordinate also through the ring nitrogen atom. Different coordination modes can also have a distinctive influence on molecular arrangements in the solid state as a result of different non-covalent intermolecular interactions, because the 2-pyridone ligands can act as hydrogen bond donors and acceptors, whereas 2- or 3-hydroxypyridine can act only as hydrogen bond donors [6].

In reviewing the literature, complexes with 2-pyridone compounds predominate, but also a few compounds with 2-hydroxypyridine ligands could be found [7–10].

Among a great number of structurally characterized 2-pyridone or its derivatives coordinated compounds, there is one example where cobalt is octahedrally coordinated with four 2-pyridone ligands and two water molecules [11], a few compounds where cobalt, nickel, copper and manganese are four coordinated with 2-pyridone derivatives, such as 2-hydroxy-6-chloropyridine [12,13], 2-hydroxy-5-chloropyridine [11] and 2-hydroxy-6-methylpyridine [14], and a few compounds where copper and iron complexes are six coordinated with 2-pyridone ligands [15–17].

There are also some cobalt, nickel and copper compounds with 3-hydroxypyridine which also include halides as ligands similar to our compound **1**[18–21]. The most similar is a copper compound

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[*] Corresponding author.
E-mail address: brina.dojer@um.si (B. Dojer).

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that includes two fluoride ligands [20].

Both title compounds were synthesized solvothermally from cobalt(II) acetate dihydrate, the above mentioned ligands and hydrofluoric or hydrochloric acid in a mixture of methanol and water. We decided to use the solvothermal method since we were not able to obtain any crystals suitable for X-ray analysis by the synthesis under reflux. Solvothermal synthesis is a method for the synthesis in a closed system under high pressures and temperatures, higher than the boiling point of the solvent. At these circumstances, properties of the solvents such as density, viscosity, and diffusion coefficient radically change [22]. Depending on the experimental conditions, the solvothermal system can be heterogeneous or homogeneous and in supercritical or subcritical conditions [23].

To bring new insights in the system containing cobalt ion and 2- or 3-hydroxypyridine, we have synthesized two new cobalt complexes: difluoridotetrakis(3-hydroxypyridine-κ*N*)cobalt(II), $[CoF_2(C_5H_5NO)_4]$ (**1**) and hexa(2-pyridone-κ*O*)cobalt(II) tetrachlorido cobaltate(II), $[Co(C_5H_5NO)_6][CoCl_4]$ (**2**). In continuation of our research work on cobalt coordination compounds with pyridine derivatives, aminopyridines [24,25] and pyridinecarboxamides [26], we present here structure, IR and magnetic properties of two new compounds in system cobalt - hydroxypyridines - halides.

2. Experimental procedure

2.1. General

We prepared cobalt(II) acetate dihydrate by the already known procedure [27].

2.2. Synthesis of difluoridotetrakis(3-hydroxypyridine-κN) cobalt(II), (1)

We put the water solution of cobalt(II) acetate dihydrate (0,054 g; 0,25 mmol) to a methanolic solution of 3-hydroxypyridine (0,095 g; 1,00 mmol) and added hydrofluoric acid (22 μL; 0,50 mmol). The reaction lasted for 20 h at 393 K in a teflon lined stainless steel reactor. After filtration and slow cooling, the solution was left in the air until most of the solvent was evaporated. The red crystalline product was dried in a desiccator above KOH. Yield: 0,083 g (69,55%).

2.3. Synthesis of hexa(2-pyridone-κO)cobalt(II) tetrachloridocobaltate(II), (2)

We put the water solution of cobalt(II) acetate dihydrate (0,054 g; 0,25 mmol) to a methanolic solution of 2-hydroxypyridine (0,095 g; 1,0 mmol) and added hydrochloric acid (41 μL; 0.5 mmol). The reaction lasted for 20 h at 393 K in a teflon lined stainless steel reactor. After filtration and slow cooling, the solution was left in the air until most of the solvent was evaporated. The light red crystalline product was dried in a desiccator above KOH. Yield: 0,068 g (65,52%).

2.4. X−ray crystallography

Crystal data and refinement parameters of compounds **1** and **2** are listed in Table 1. The X−ray intensity data were collected at room temperature with Agilent SuperNova dual source with Atlas detector equipped with mirror−monochromated Mo−K_α radiation ($\lambda = 0.71073$ Å). The data were processed using CRYSALIS PRO [28]. Both structures were solved by direct methods using SIR−92 [29] (**1**) or SHELXS−97 [30] (**2**) and refined against F^2 on all data by a full−matrix least squares procedure with SHELXL−97 [30]. All non−hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon or oxygen atoms were included in the model at geometrically calculated positions and refined using a riding model. The nitrogen bonded hydrogen atoms were located in the difference map and refined with the distance restraints (DFIX) with N−H = 0.86 and with $U_{iso}(H) = 1.2U_{eq}(N)$.

2.5. Magnetic measurements

Magnetic properties of two complexes were studied between 2 K and 300 K in a magnetic field of H=1000 Oe and at a constant temperature of 5 K between H=±50 kOe with a Quantum Design MPMS-XL-5 SQUID magnetometer. The measured data in Figs. 1 and 2 are already corrected for a sample holder contribution and for a temperature independent Larmor diamagnetism of core electrons obtained from Pascal's tables [31].

2.6. IR spectroscopy

Infrared spectra were taken on a Perkin Elmer FTIR spectrometer using ATR in the range 400−4000 cm^{-1}.

3. Results and discussion

3.1. Description of the crystal structures

Selected bond lengths and angles of **1** and **2** are given in Table 2.

The compound **1** crystallizes in the orthorombic space group *Pccn*. The crystal structure consists of mononuclear molecules in which Co(II) ion is octahedrally coordinated by four 3-hydroxypyridine ligands and two fluorido anions (Fig. 1).

The 3-hydroxypyridine ligands occupy the equatorial plane (Co−N1 = 2.1667(11), Co−N2 = 2.1545(12) Å) while the two *trans* coordinated fluorine anions (Co−F1 = 2.0563(8) Å) possess shorter axial positions. In the isostructural copper coordination compound the distance Cu−F1 is longer (Cu−F1 = 2.376(1) Å), nevertheless, in other cobalt or copper compounds with coordinated chlorine ions the distances metal-chlorine (M−Cl) are much longer (M−Cl = 2.493−2.840 Å) [18–21]. The distances Co−N are similar to those in isostructural compound with chlorine ions (Co−N2 = 2.172(2), Co−N1 = 2.158(2) Å) [18]. In the compound where Co ion is octahedrally coordinated with four 3,5-dimethylpyridine and two fluoride ligands [32], the distance Co−N1 is a little bit longer than in the compound **1** (2.186(4) Å) and the distance Co−F1 is shorter (2.016(3) Å).

The fluorido ligands are acceptors of two intermolecular hydrogen bonds (Table 3) connecting mononuclear units into two-dimensional layers going parallel to the *ab* plane (Fig. 2). Details on hydrogen bond geometry are presented in Table 3. In the crystal structure of the compound **1** no significant stacking effects between aromatic rings have been observed. The dihedral angle between the opposite pyridine rings in asymmetric unit is 84.24°.

The crystal structure analysis of **2** showed that the compound crystallizes in monoclinic *C*2/*c* crystal system. The structure of the ionic compound **2** is illustrated in Fig. 3.

The structure of **2** consists of mononuclear $[Co(2\text{-hypy})_6]^{2+}$ cations and $[CoCl_4]^{2-}$ anions. As shown in Fig. 3, the cobalt(II) central ion in the cationic part of the structure lies on an inversion centre and is octahedrally coordinated with six 2-pyridone ligands. Cobalt(II) ion in anionic part is tetrahedrally coordinated with four chlorido ligands.

The distances Co ion – oxygen from pyridone ligands range from 2.0695(15) to 2.1015(14) Å which is probably due to a weak Jahn→Teller effect. Quite different distances M−O can be found in some other hexacoordinated structural motifs of 2-pyridone ligands in copper (Cu−O: 1.922(2), 1.952(2) and 2.546(2) Å [15] or