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Supramolecular 2D Structure of $[Co(2\text{-}Me\text{-}Pyz)_2(H_2O)_4](NO_3)_2$

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Abstract—The complex $[Co(2\text{-}Me\text{-}Pyz)_2(H_2O)_4](NO_3)_2$ is synthesized and its structure is determined. The crystals are monoclinic: space group $P2_1/n$, $a = 10.685(2)$ Å, $b = 6.837(1)$, $c = 12.515(3)$ Å, $\beta = 91.84(3)°$, $V = 913.8(3)$ Å^3, $\rho_{calcd} = 1.042$ g/cm^3, $Z = 2$. The Co^{2+} ion (in the inversion center) is coordinated at the vertices of the distorted octahedron by two nitrogen atoms of methylpyrazine and four oxygen atoms of the water molecules (Co(1)–N(1) 2.180(3), average Co(1)–O(*w*) 2.079(3) Å, angles at the Co atom 87.9(1)–92.1(1)°). Supramolecular pseudometallocycles are formed in the structure through the O(*w*)–H···N(1) hydrogen bonds between the coordinated H_2O molecules and the terminal nitrogen atoms of the 2-methylpyrazine molecules. Their interaction results in the formation of supramolecular layers joined by the NO_3 groups into a three-dimensional framework.

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INTRODUCTION

Metal-containing supramolecular compounds based on transition metal ions and organic bridging ligands attract attention due to their diverse structural manifestations and potential use as functional materials [1, 2].

Coordination covalent and hydrogen bonds or other molecular interactions, as well as their combinations, are important tools for the design of such compounds with one-, two-, and three-dimensional supramolecular structures [3]. For example, a supramolecular 2D coordination polymer is formed in the compound $[Cd(Dapm)_2(CH_3CO_2)_2(H_2O)_2]$ (Dapm is diaminodiphenylmethane) [4]. In this polymer one nitrogen atom of the Dapm ligand forms a covalent bond with the Cd atom, and the second (uncoordinated) N atom is involved in hydrogen bonding with the acetate ions and the H_2O molecules of the adjacent complexes. The supramolecular three-dimensional coordination polymer is observed in the compound $[Cu(Pdc)(H_2O)_2]$ (Pdc is pyridine-3,5-dicarboxylate) [5] due to the participation of the carboxylate groups in both covalent and hydrogen bonding.

We have recently synthesized and determined the structures of two molecular complexes $\{Ni[CH_2(C_6H_4N_2)_2(NO_3)_2(H_2O)\}$ [6] and $[Ni(CH_3CO_2)_2(3,5\text{-lutidine})_2(H_2O)_2]$ [7] in which the supramolecular structure is formed due to hydrogen bonding between the coordinated H_2O molecules and uncoordinated terminal amino groups [6] or uncoordinated oxygen atoms of the acetate groups [7].

The purpose of this work is to synthesize and study the structure of the coordination cobalt(II) polymer with 2-methylpyrazine $C_5H_6N_2$ (**2-Me-Pyz**).

EXPERIMENTAL

Synthesis. Ethanolic solutions of $Co(NO_3)_2 \cdot 6H_2O$ (10 ml, 2.55 g, 8.76 mmol) and 2-methylpyrazine (10 ml, 1.65 g, 17.52 mmol) were used for the synthesis of $[Co(2\text{-}Me\text{-}Pyz)_2(H_2O)_4](NO_3)_2$ (**I**). The solutions were mixed and kept in air at room temperature for several days. Large red prismatic crystals that formed were separated from the mother liquor and dried in air. After the dried crystals were kept in air for several hours, their surface decomposed. However, the crystals were retained for a long time without changes even in a loosely closed vessel. The crystals were studied by elemental analysis, IR spectroscopy, and X-ray diffraction analysis.

Found (%):	N 18.34;	C 27.02;	H 3.80.
For $C_{10}H_{20}N_6O_{10}Co$			
anal. calcd. (%):	N 18.95;	C 27.07;	H 4.51.

IR absorption spectra were recorded on a Specord 75 IR spectrometer in a region of 400–4000 cm^{-1} (suspensions in Nujol).

X-Ray diffraction analysis. The experimental material for crystals **I** was obtained on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by a direct method and refined by least squares in the full-matrix anisotropic approximation for nonhydrogen atoms. The positions of hydrogen atoms were calculated geometrically and included into refinement by the riding model with isotropic thermal parameters held stationary. The hydrogen atoms of the water molecules were revealed from the difference Fourier synthesis. All calculations were performed using the SHELXL-97 programs.

Selected characteristics of experiment and the unit cell parameters are given in Table 1. Hydrogen bonding geometry is presented in Table 2. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (no. 714 162).

RESULTS AND DISCUSSION

The IR spectrum of compound **I** exhibits an intense and broad band ν(O–H) strongly shifted to 3200 cm^{-1} due to hydrogen bonds in the complex. The spectrum also contains the bands of the ionic NO_3^- group: the very intense band at 1350 cm^{-1} including (as inflections) the ν(C=N) and ν(C=C) stretching vibrations of coordinated 2-Me-Pyz and the medium-intensity broad band (650–750 cm^{-1}).

The Co atom (in the inversion center) is coordinated at the vertices of the distorted octahedron, which are symmetrically bound by two nitrogen atoms of 2-methylpyrazine and four oxygen atoms of the water molecules (Fig. 1). The Co(1)–N(1) distance is 2.180(3) Å, the average Co(1)–O(*w*) distance is 2.079(3) Å, and the angles at the Co atom range from 87.9(1)° to 92.1(1)°. The Co–N bond lengths and average Co–O(*w*) in structure **I** are close to those found in the structures [Co(Pyz)(Terph)$(H_2O)_2$] (Co–N 2.16 and 2.19 Å, average Co–O(*w*) 2.12 Å) [8] and [Co(Bipy)(Terph)(H_2O)] (Co–N 2.11 and 2.14 Å, average Co–O(*w*) 2.12 Å) [19].

In structure **I**, the terminal nitrogen atoms of 2-methylpyrazine are involved in the O(*w*)–H···N(2) hydrogen bond with the water molecules of the adjacent complexes and are proton acceptors (Table 2). This results

Table 1. Selected crystallographic data and experimental details for structure **I**

Parameter	Value
FW	443.25
Crystal size, mm	0.45 × 0.25 × 0.20
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell parameters:	
a, Å	10.685(2)
b, Å	6.837(1)
c, Å	12.515(3)
β, deg	91.84(3)
V, Å^3	913.8(3)
Z	2
ρ_{calcd}, g/cm^3	1.611
μ_{Cu}, mm^{-1}	7.965
F(000)	458
Temperature, K	293
Radiation (λ, Å)	CuK_α (1.54178), graphite monochromator
Scan type	ω
θ range, deg	5.37–73.98
Index ranges	$0 \le h \le 13$, $-8 \le k \le 8$, $-15 \le l \le 15$
Number of reflections total/independent	3522/1773 (R_{int} = 0.0456)
Number of reflections with $I \ge 2\sigma(I)$	1437
Number of refined parameters	141
GOOF for F^2	1.274
R ($I \ge 2\sigma(I)$)	R_1 = 0.0505, wR_2 = 0.1501
R (for all data)	R_1 = 0.0643, wR_2 = 0.1643
Extinction coefficient	0.0253
Residual electron density (max/min), *e* Å^3	0.463/–0.596

Table 2. Hydrogen bonding geometry in structure **I**

Bond A–H···B	Distance, Å			Angle AHB, deg	Position of atom B
	A···B	A–H	H···B		
O(*w*1)–H(1)···O(1)	2.797(7)	0.90	1.93	160	1/2 – *x*, 1/2 + *y*, –1/2 – *z*
O(*w*1)–H(2)···O(2)	2.739(7)	0.87	1.87	171	*x*, *y*, *z*
O(*w*2)–H(3)···O(1)	2.766(7)	0.91	1.86	176	1/2 + *x*, 1/2 – *y*, 1/2 + *z*
O(*w*2)–H(4)···N(2)	2.794(7)	1.02	1.80	163	1/2 + *x*, 1/2 + *y*, 1/2 – *z*

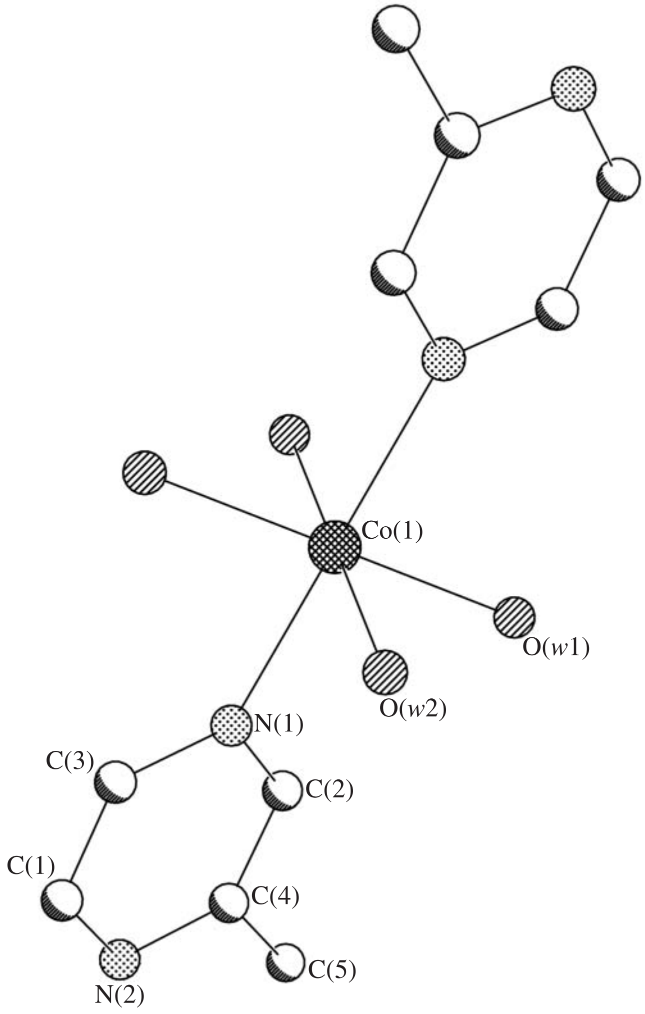

Fig. 1. Crystal structure of the Co(II) complex with 2-methylpyrazine in compound **I**.

in the formation of wave-like layers of the conjugated pseudometallocycles including four Co^{2+} ions each and pseudobridging 2-methylpyrazine ligand (Fig. 2). The uncoordinated NO_3^- anions ($Co\cdots O(NO_3) \geq 4.219$ Å) are localized in the interlayer cavities (Fig. 3), being proton acceptors in the N–H···O hydrogen bonds that join the layers into the three-dimensional framework. The planar NO_3^- groups are not almost distorted: the deviations of the N–O distances from an average value of 1.24 Å do not exceed 0.02 Å, and in the ONO angles the deviations from ideal values of 120° do not exceed 2°.

The formation of supramolecular pseudometallocycles is characteristic of bivalent metal compounds when the coordination involves water molecules along with ditopic nitrogen-containing ligands. A nonrigid supramolecular structure is formed by the involvement in weak hydrogen bonding. For example, 1D polymeric chains of supramolecular metallocycles are formed in the $Ni[CH_2(C_6H_4N_2)_2(NO_3)_2(H_2O)_2\}$ complex [6]. A layered 2D supramolecular structure is observed in compounds **I** and $[Cd(Dapm)_2(CH_3CO_2)_2(H_2O)_2]$ [4]. Note that both coordination and hydrogen bonds with the pointed effect are used in the formation of networks of two- and three-dimensional frameworks.

It can be assumed that two-dimensional layers and three-dimensional frameworks can be formed upon the substitution of the water molecules in the discrete complex cation $[Co(2\text{-}Me\text{-}Pyz)_2(H_2O)_4]^{2+}$ of compound **I** for neutral ditopic organic ligands. Complex **I** can be considered as a promising building unit for the synthesis of coordination cobalt-containing polymers with ligands of various functionality.

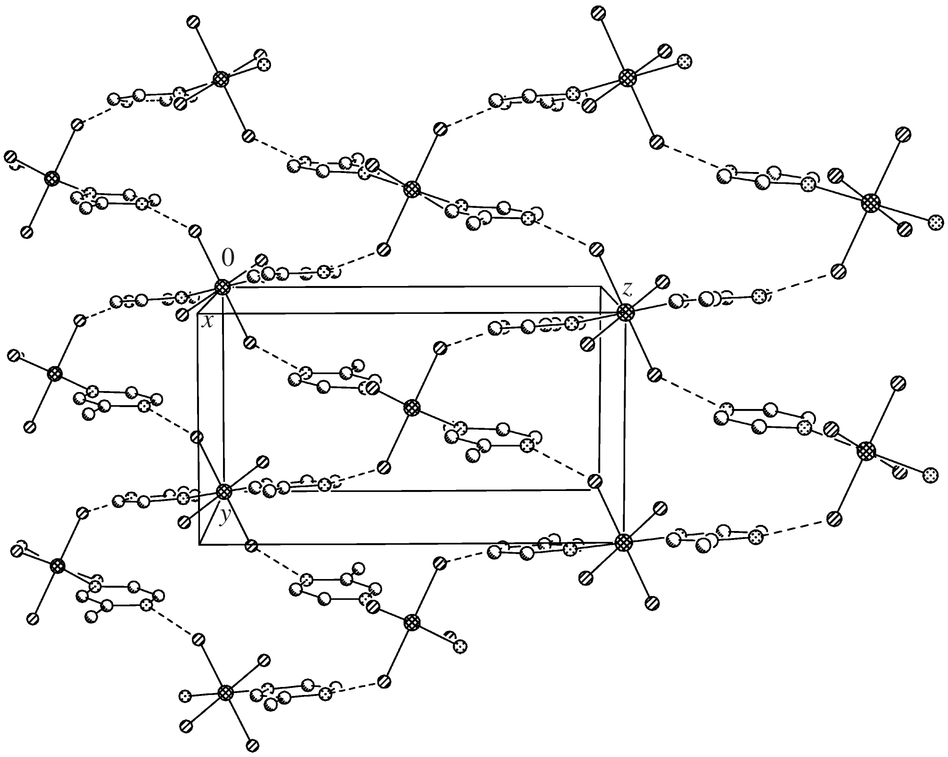

Fig. 2. Fragment of structure **I**: the layer of the conjugated supramolecular cycles.

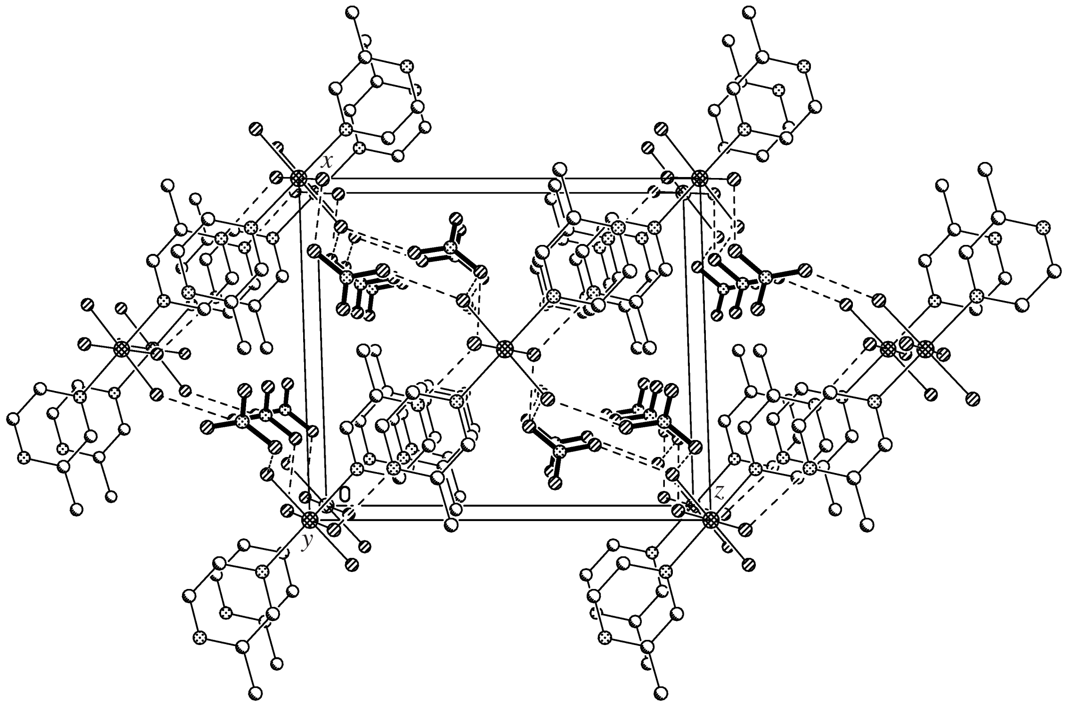

Fig. 3. General view of structure **I** along the direction [010].

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