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Coordination Polymer of Cadmium(II) Iodide with Tetramethylpyrazine

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Abstract—Compound [$CdI_2(Me_4Pyz)$] is synthesized by the reaction of CdI_2 with tetramethylpyrazine (Me_4Pyz, $C_8H_{12}N_2$), and its structure is determined (CIF file CCDC 1538646). The crystals are monoclinic, space group $C2/c$, a = 14.732(3), b = 11.084(2), c = 7.792(2) Å, β = 95.27(3)°, V = 1267.0(4) Å, ρ_{calcd} = 2.634 g/cm^3, Z = 4. Polymer chains $[CdI_2(Me_4Pyz)]_\infty$ extended along the direction [001] are formed in the structure of the complex due to the bridging iodine atoms. The coordination polyhedron of the Cd^{2+} ion is a trigonal bipyramid with four bridging iodine atoms and one nitrogen atom of the organic ligand lying in the equatorial plane along with two iodine atoms. The distance between the cadmium atoms in the chain is 4.155 Å.

Keywords: cadmium iodide, coordination polymer, structure

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INTRODUCTION

Many published works on coordination polymers, metal-organic frameworks, and inorganic–organic hybrid materials are available. However, the family of polymers with halide bridges remains insufficiently studied. Nevertheless, several reviews on the topic were published recently [1, 2], where the syntheses of the compounds and their structures and properties were considered, in particular, for the neutral halide-bridged polymers of bivalent metals with organic donor ligands. These compounds can find use as electroconducting polymers and magnetic materials in nonlinear optics and luminescence.

The nature of metal ions, counterions, and ligands are the main factors determining the structure, properties, and dimensionality of coordination polymer compounds. Halides of Zn(II) and Cd(II) are used most frequently for studying the halide-bridged compounds. The Cd^{2+} ion can coordinate both soft and hard ligands. Such hard bases as Cl^-, Br^-, and I^- located in the internal sphere of the complexes can modify stereochemistry of the obtained compounds. It is known that the Cd^{2+} ion can change the coordination geometry from tetrahedron to trigonal bipyramid or square pyramid to octahedron. A change in the steric and electronic properties of organic molecules, such as heterocyclic N-ligands in the composition of the compound considered, makes it possible to affect the structures of coordination polymers.

Several works are known that are related to the synthesis and study of the structures and properties of the cadmium halide compounds with N-ligands. The data on compounds [$CdHal_2L_2$] (L is pyridine, 2-methylpyridine, or quinoxaline) and [$CdHal_2L^1$] (L^1 is 2,4,6-trimethylpyridine) are presented [3]. The results of studying compounds [$CdHal_2(3,5\text{-}R_2Py)_2$] (R is Hal or CH_3) are given [4]. We synthesized and studied several compounds based on cadmium iodide: [CdI_2(2-Am-4-MePy)] [5], [$CdI_2(Me_2Py)$] [6], [$CdI_2(4\text{-}CNPy)_2$] [7], [$CdI_2(4\text{-}MePy)_2$], and [$CdI_2(4\text{-}MeQuin)_2$] [8]. Pyrazine (Pyz), its substituted analogs, and 1,3-bipyridylpropane (Bpp) act mainly as bidentate bridging ligands favoring the formation of polymer compounds with various structures. For the coordination of pyrazine and its analogs, the structures of the polymers are assumed to depend on the geometric parameters of the bridging ligands, i.e., the size, number, and orientation of substituents [9]. In compound [$CdI_2(Bpp)$] [10], the I^- ions are terminal and Bpp is the bridging ligand. In compounds [$CdI_2(4,4'\text{-}Bipy)$] [11] and [$CdI_2(Pyz)$] [12], the iodide ions and N atoms of the organic ligand Pyz perform the bridging functions. Compound $[CdI_2(Quinox)_2H_2O]$ (quinoxaline is an analog of pyrazine) has a discrete structure with terminal N-ligands [13].

Continuing our studies of the hybrid inorganic–organic coordination compounds, in this work we present the results of the synthesis and structural investigation of coordination polymer $[CdI_2(Me_4Pyz)]$ (**I**).

EXPERIMENTAL

Synthesis. The starting reagents in the synthesis of compound **I** were CdI_2 (reagent grade) and 2,3,5,6-tetramethylpyrazine (Aldrich) taken in a ratio of 1 : 1. Weighed samples of CdI_2 (0.97 g, 2.64 mmol) and Me_4Pyz (0.36 g, 2.64 mmol) were dissolved separately in acetonitrile (5 mL). The solutions were mixed and, after filtration, kept for several hours under the conditions of the slow evaporation of the solvent. Prismatic crystals that formed were separated from the mother liquor, washed with a minor amount of acetonitrile, and dried in air. According to the elemental analysis data, the crystals corresponded to the composition $[CdI_2(Me_4Pyz)]$.

For $C_8H_{12}N_2I_2Cd$

Anal. calcd., %	N, 5.57;	C, 19.12;	H, 2.40.
Found, %	N, 5.74;	C, 18.54;	H, 2.14.

It is important that the reaction in a more polar solvent (ethanol) results in the formation of a polycrystalline solid phase only on the walls of the flask during evaporation. The crystals were formed in a solution only upon an almost complete removal of the solvent. After the crystals were treated with acetonitrile, the compound was isolated with the analytical data nearly the same as those for compound **I**.

X-ray diffraction analysis. The experimental material for the crystals of compound **I** was obtained on an Enraf-Nonius CAD-4 automated diffractometer (MoK_α radiation, $\lambda = 0.71073$, graphite monochromator). The structure was solved by a direct method (SHELXS-97) [14] and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [15]. The positions of hydrogen atoms were calculated geometrically and included into the refinement by the riding model. Selected crystallographic data and experimental characteristics for the structure of compound **I** are presented in the Table 1.

The full crystallographic data for the structure were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1538646; http://www.ccdc. cam.ac.uk/deposit/).

RESULTS AND DISCUSSION

Polymer chains $[CdI_2(Me_4Pyz)]_\infty$ are formed in the structure of compound **I** due to the bridging iodine atoms (Fig. 1). The pyrazine rings are oriented to opposite directions relative to the Cd atoms, and the C_8N_2 rings are planar (±0.04 Å). The distance between the adjacent Cd atoms in the chain is 4.15 Å. Similar Cd···Cd distances were observed in some polymer compounds of cadmium iodides [10].

The Cd(1) atom in compound **I** localized at the 2-fold axis is coordinated by four bridging iodine atoms and the N atom of the Me_4Pyz ligand. The coordination polyhedron of the Cd^{2+} ion is a trigonal bipyramid, whose axial vertices are occupied by the I(2*A*) and I(2*C*) atoms (Cd–I(2*A*), I(2*C*) 3.0295(10) Å; angle I(2*A*)Cd(1)I(2*C*) 169.52(3)° (Fig. 2). The I(2), I(2*B*), and N(1) atoms of the Me_4Pyz ligand are arranged in the equatorial plane of the bipyramid. The Cd(1)–I(2) and Cd(1)–I(2*B*) distances are 2.8259(8), and the Cd(1)–N(1) distance is 2.344(7) Å. The angles are as follows: N(1)Cd(1)I(2), N(1)Cd(1)I(2*B*) 127.54(2)°, I(2)Cd(1)I(2*B*) 104.91(4)°. The $[CdI_2(Me_4Pyz)]_\infty$ chains are extended along the direction [001] and alternate along the axis *y* at an interval of 1/2*b* (Fig. 3).

As shown above, the tetrahedral or octahedral coordination mode of Cd^{2+} ions takes place in the most part of compounds with the formation of discrete or mainly polymer chains. Compound **I** studied by us, $CdI_2(2,4,6\text{-}Me_3Py)$ [3], $CdI_2(2,6\text{-}Me_2Py)$ [6], and $CdCl_2(PhMe_2P)$ [16] have polymer structures due to the bridging halide ions, and the coordination polymer of Cd^{2+} is a trigonal bipyramid.

Probably, the formation of pentacoordinated cadmium compounds is related to the size and steric factors of halide ions and added organic ligands and also to the stoichiometry $CdHal_2$: L. The data obtained for the structure of compound **I** confirm our earlier conclusions [7].

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Table 1. Crystallographic data and selected experimental characteristics for the structure of compound **I**

Parameter	Value
FW	502.40
Color, habitus	Colorless, block
Crystal size, mm	0.18 × 0.15 × 0.10
Crystal system, space group	Monoclinic, $C2/c$
Cell parameters:	
a, Å	14.732(3)
b, Å	11.084(2)
c, Å	7.792(2)
β, deg	95.27(3)
V, Å^3	1267.0(4)
Z	4
ρ_{calcd}, g/cm^3	2.634
μ_{Mo}, mm^{-1}	6.560
F(000)	912
T, K	293(2)
Scan mode	ω
Range θ, deg	2.30–29.96
Index ranges	$-20 \leq h \leq 20$, $-15 \leq k \leq 1$, $-1 \leq l \leq 10$
Total number of reflections/independent (R_{int})	2418/1847 (0.0556)
Completeness to θ = 29.96°, %	100.0
Number of reflections with $I \geq 2\sigma(I)$	1160
Absorption correction	Semiempirical, by equivalents
(T_{min}/T_{max})	0.3847/0.5599
Number of refined parameters	62
GOOF for F^2	1.001
R ($I \geq 2\sigma(I)$)	$R_1 = 0.0453$, $wR_2 = 0.1079$
R (all data)	$R_1 = 0.0960$, $wR_2 = 0.1249$
Extinction coefficient	0.0059(5)
Residual electron density (max/min), e Å^{-3}	2.331/–2.186

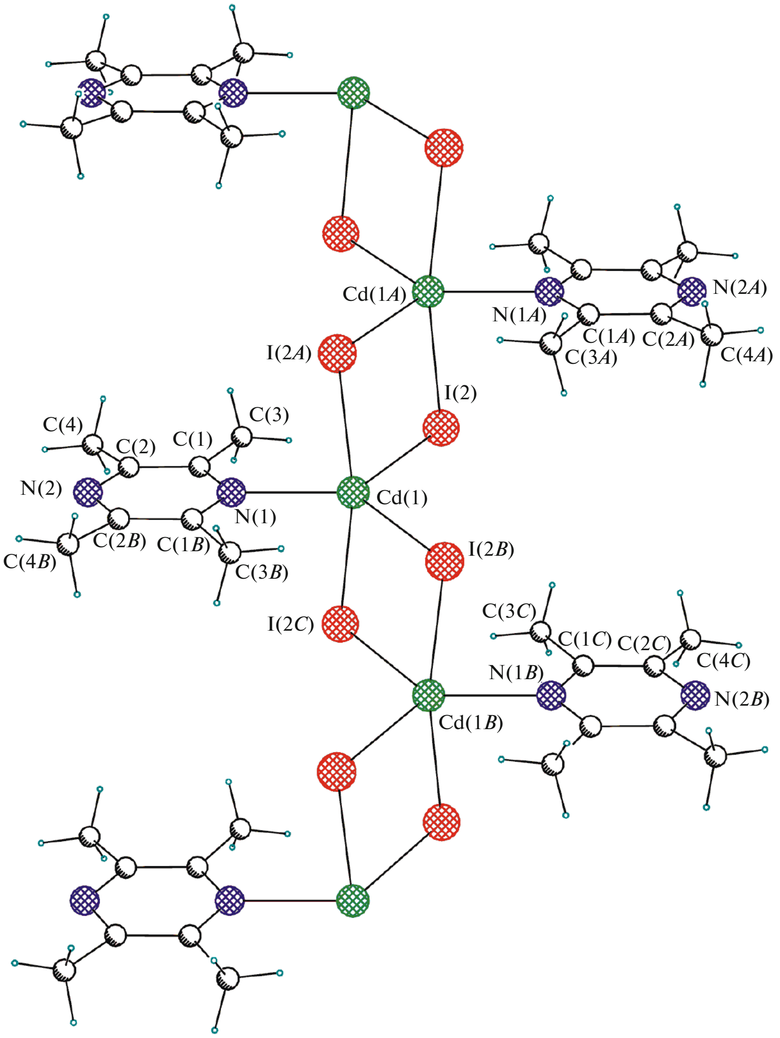

Fig. 1. Fragment of the structure of compound **I**: polymer chain $[CdI_2(Me_4Pyz)]_\infty$.

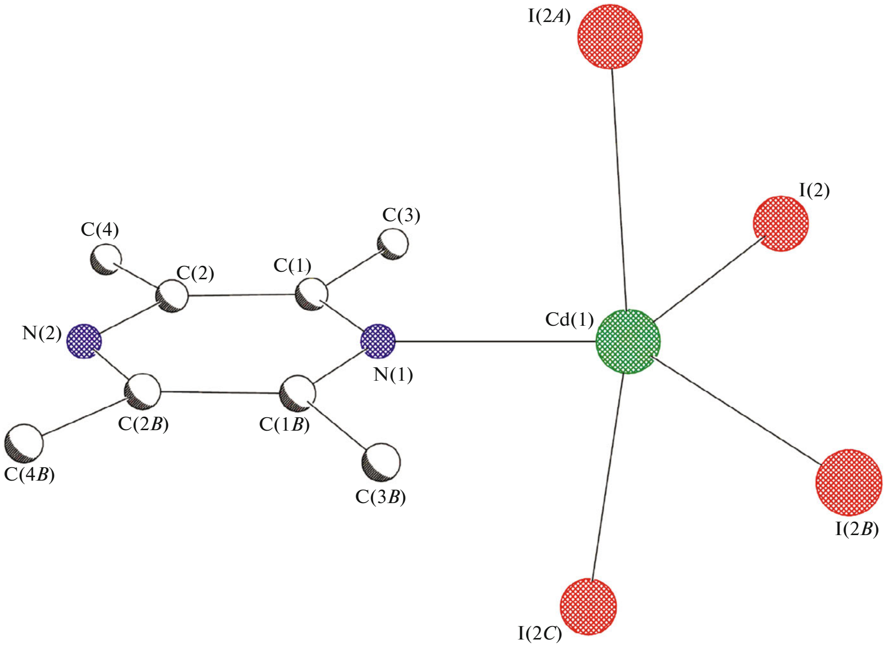

Fig. 2. Coordination environment of the Cd^{2+} ion.

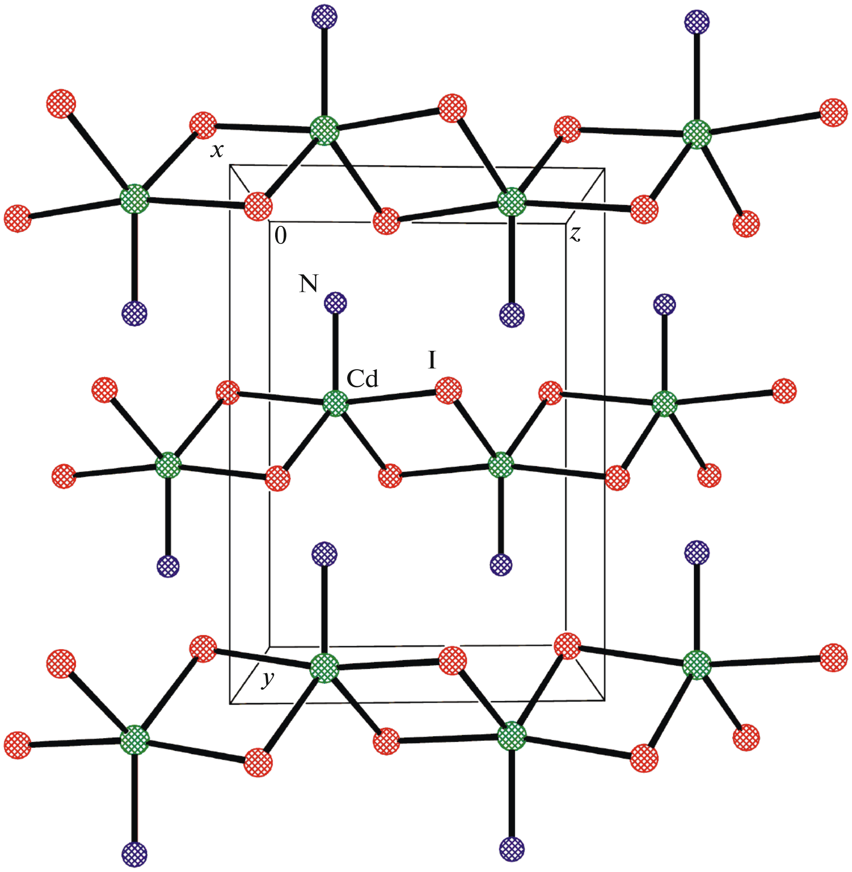

Fig. 3. General view of the structure of compound **I** along the direction [100].

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