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To the 80th anniversary of the Kurnakov Institute
of General and Inorganic Chemistry, Russian Academy of Sciences

Coordination Molecular Compounds of Cadmium(II) Iodide with Dimethylpyridines

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Abstract—The reactions of CdI_2 with dimethylpyridines (Me_2Py is C_7H_9N) afford complexes $CdI_2(2,3\text{-}Me_2Py)_2]$ (**I**), $[CdI_2(2,6\text{-}Me_2Py)$ (**II**), and $CdI_2(3,5\text{-}Me_2Py)_2$ (**III**). The structures of compounds **I** and **II** are determined. The crystals of complex **I** are orthorhombic, space group *Pbca*, $a = 7.930(1)$ Å, $b = 15.537(1)$ Å, $c = 29.943(1)$ Å, $V = 3689.1(5)$ Å^3, $\rho_{calcd} = 2.090$ g/cm^3, $Z = 8$. The crystals of complex **II** are monoclinic, space group *C*2/*c*, $a = 14.784(1)$, $b = 11.991(1)$, $c = 17.711(1)$ Å, $\beta = 90.39(1)°$, $V = 1081.1(2)$ Å^3, $\rho_{calcd} = 2.908$ g/cm^3, $Z = 4$. The structure of compound **I** is built of discrete neutral complexes $[CdI_2(2,3\text{-}Me_2Py)_2]$. The Cd polyhedron is a distorted tetrahedron (Cd–I 2.289–2.295, Cd–N 2.708–2.734 Å, angles N(I)CdN(I) 103.1°–114.8°). Polymer chains $[CdI_2(2,6\text{-}Me_2Py)]_\infty$ extended along the direction [100] are observed due to the bridging iodine atoms in structure **II**. The Cd polyhedron is a trigonal bipyramid containing iodine atoms at the axial vertices ($Cd–I_{aks}$ 3.040 Å) and two iodine atoms and the nitrogen atom of the Me_2Py ligand in the equatorial plane Me_2Py ($Cd–I_{eq}$ 2.840 Å, Cd–N 2.309 Å). The compounds in the solid state are photoluminescent.

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INTRODUCTION

Interest in hybrid inorganic–organic molecular compounds and related materials appeared recently. This interest is caused by both their unusual structure and potential application in such areas as catalysis, molecular magnets, photoluminescence, electric conductivity, sensors, materials for solar energy use, and others [1–4]. Among these hybrid inorganic–organic molecular compounds are those in which the inorganic moiety consists of IIB Group metal halides and the organic moiety is presented by N-containing ligands. These compounds can easily be modified by the replacement of the metal ion, halide ion, or N-ligand.

Structures of several compounds of cadmium diiodide with pyridine and some its derivatives (3,5-Me_2, 3,5-Cl_2, 3,5-Br_2, 3Me-, 3Cl-, 3Br-, 2,4,6-Me_3-) were synthesized to the present time, and their structures were determined [5–8]. In the most cases [5–10], compounds of CdI_2 with the stoichiometry CdI_2 : N-ligand = 1 : 2 were obtained. There is one example of the 1 : 1 compound of CdI_2 with 2,4,6-trimethylpyridine.

Discrete tetrahedral or coordination compounds with bridging iodine atoms are formed, depending on the geometric parameters and the nature of substituents in pyridine. An increase in the number of synthesized $MHal_2$ compounds (M is doubly-charged IIB Group metal) with different N-containing organic bases and the study of their structures and properties would make it possible to determine more reliably the regions of their existence and structural features of hybrid inorganic–organic molecular compounds of IIB Group metal halides.

The formation of hybrid inorganic–organic molecular compounds depends on many factors, such as the coordination preference of metal ions, geometric characteristics of organic ligands, solvents, the counterion nature, and reaction conditions.

The possibilities to synthesize hybrid compounds as coordination polymer or discrete structures by self-assembling were studied in this work. For this purpose, we synthesized coordination cadmium compounds with different pyridine derivatives, namely, $[CdI_2(2,3\text{-}Me_2Py)_2]$ (**I**), $[CdI_2(2,6\text{-}Me_2Py)]$ (**II**), and $[CdI_2(3,5\text{-}Me_2Py)_2]$ (**III**), and determined their structures. Compound **III** was synthesized using a new procedure, and its structure is similar to that presented earlier [6]. The luminescence spectra of all synthesized compounds were studied.

EXPERIMENTAL

Synthesis. Cadmium iodide CdI_2 (reagent grade) and 2,6-, 2,3-, and 3,5-dimethylpyridines (2,6-Me_2Py, 2,3-Me_2Py, and 3,5-Me_2 Py) (Aldrich) were used.

To synthesize compound **I**, weighed samples of CdI_2 (1.39 g, 3.79 mmol) and 2,3-Me_2Py (0.41 g, 3.79 mmol) were separately dissolved in an acetonitrile–ethanol (1 : 1) mixture (5 mL). Both solutions were heated to ~30°C and mixed. A finely crystalline precipitate that formed was filtered off. The filtrate was kept for 12 h, the first portion of crystals was separated by filtration, and prismatic crystals suitable for X-ray diffraction analysis were obtained from the remaining solution.

For $C_{14}H_{18}N_2I_2Cd$

anal. calcd, %:	C, 28.94;	N, 4.82;	H, 3.10.
Found, %:	C, 28.94;	N, 5.12;	H, 3.65.

To synthesize compound **II**, weighed samples of CdI_2 (1.10 g, 3.00 mmol) and 2,6-Me_2Py (0.32 g, 3.00 mmol) were separately dissolved in acetonitrile (5 mL), the solutions were mixed, and a finely crystalline precipitate was filtered off. The obtained precipitate was heated in ethanol (10 mL) with stirring at ~40–50°C for 15 min, and the undissolved solid phase was filtered off. Prismatic crystals were isolated from the filtrate by slow crystallization and then dried in air.

For $C_7H_9NI_2Cd$

anal. calcd, %:	C, 17.75;	N, 2.96;	H, 1.90.
Found, %:	C, 18.17;	N, 3.11;	H, 2.72.

Compound **III** was synthesized similarly to compound **II** in an acetonitrile medium but with a twofold excess of an organic ligand. Mixing of solutions of CdI_2 (0.71 g, 1.94 mmol) and 3,5-Me_2Py (0.42 g, 3.88 mmol) immediately resulted in the isolation of well formed prismatic crystals.

For $C_{14}H_{18}N_2I_2Cd$

anal. calcd, %:	C, 28.94;	N, 4.82;	H, 3.10.
Found, %:	C, 29.70;	N, 5.37;	H, 3.65.

All obtained crystals are colorless and stable in air.

X-ray diffraction analysis. An experimental material for the crystals of compounds **I** and **II** was obtained on an Enraf-Nonius CAD-4 automated diffractometer. The structures were solved by a direct method (SHELXS-97) [11] and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [12]. Positions of hydrogen atoms were calculated geometrically and refined by the riding model with fixed isotropic temperature parameters. The main crystallographic data and experimental characteristics for structures **I** and **II** are presented in Table 1. The full crystallographic data were deposited with the Cambridge Crystallographic Data Centre (941965 (**I**) and 941966 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

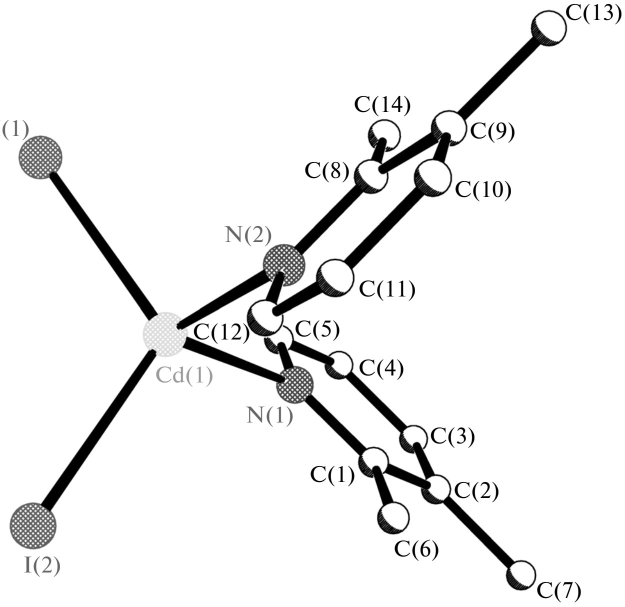

Fig. 1. Mononuclear tetrahedral complex $[CdI_2(2,3\text{-}Me_2Py)_2]$ in structure **I**.

The IR spectra of coordination compounds **I–III** were recorded on a NEXUS spectrometer (Nicolet) in the range from 550 to 4000 cm^{-1} using the attenuated total internal reflectance method (the procedure of sample deposition on a diamond crystal).

Photoluminescence was measured on an LS55 spectrometer (PerkinElmer) in the range from 200 to 900 nm at room temperature (resolution 0.5 nm, slit width from 3 to 10 nm). An attachment for measuring luminescence of solids and a quartz cell for measuring luminescence of liquids were used.

RESULTS AND DISCUSSION

In the IR spectra of compounds **I–III**, the bands ν(C=N) and ν(C=C) and the intense bands of antisymmetric bending vibrations of the CH_3 group of the organic ligand are observed at 1593, 1469, and 1452 cm^{-1} (**I**); 1604, 1463, and 1437 cm^{-1} (**II**); and 1597, 1458, and 1432 cm^{-1} (**III**) [13]. The IR spectra of the compounds differ substantially in the region 700–800 cm^{-1}, where the characteristic bands of out-of-plane bending vibrations of the unsubstituted protons of the ring appear. The spectrum of compound **I** exhibits three bands at 793, 745, and 719 cm^{-1}, that of compound **II** contains only one band at 787 cm^{-1}, and the spectrum of compound **III** exhibits two bands of the same intensity at 756 and 699 cm^{-1}.

Table 1. Crystallographic data and the main experimental characteristics for structures **I** and **II**

Complex	**I**	**II**
M	580.50	473.35
Crystal size, mm	0.40 × 0.33 × 0.30	0.45 × 0.18 × 0.15
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C*2/*c*
Cell parameters:		
a, Å	7.930(1)	14.784(1)
b, Å	15.537(1)	11.991(1)
c, Å	29.943(1)	17.711(1)
β, deg	90	90.39(1)
V, Å^3	3689.1(5)	1081.1(2)
Z; ρ_{calcd}, g/cm^3	8; 2.090	4; 2.908
μ_{Mo}, mm^{-1}	4.522	7.676
F(000)	2120	848
Temperature, K	293	
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator	
Scan mode	ω	ω/θ
θ Range, deg	2.62–26.97	2.50–27.97
Index ranges	$-10 \le h \le 1$, $-19 \le k \le 19$, $-38 \le l \le 1$	$-18 \le h \le 18$, $-13 \le k \le 13$, $-1 \le l \le 10$
Total number of reflections	9257	3081
Reflections with $I \ge 2\sigma(I)$	3973 (R_{int} = 0.0428)	1304 (R_{int} = 0.0349)
Number of refined parameters	173	53
Goodness-of-fit for F^2	0.912	0.766
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0402$, $wR_2 = 0.1054$	$R_1 = 0.0294$, $wR_2 = 0.0825$
R [all data]	$R_1 = 0.0913$, $wR_2 = 0.1349$	$R_1 = 0.0446$, $wR_2 = 0.0954$
Extinction coefficient	0.0039(3)	0.0023(3)
Residual electron density (max/min), e/Å^3	0.968/–0.792	1.964/–1.053

Structure **I** includes mononuclear tetrahedral complexes [$CdI_2(2,3\text{-}Me_2Py)_2$]. The cadmium atom is coordinated by two nitrogen atoms of crystallographically nonequivalent ligands 2,3-Me_2Py and two independent iodine atoms (Fig. 1) (Cd–I_{av} 2.721, Cd–N_{av} 2.292 Å, angles at the Cd atom 103.1°–114.8°). The tetrahedron is noticeably distorted, the NCdN angles between the nitrogen atoms of the 2,3-dimethylpyridine ligands are minimum (103.1°), and the maximum value of the ICdI angle is 114.8°. The effect of 3,5-Me_2Py ligand contraction at the central metal atom is also observed in the mononuclear tetrahedral complexes [$CdI_2(3,5\text{-}Me_2Py)_2$] (**III**), [$ZnCl_2(3,5\text{-}Me_2Py)_2$] (**IV**), where the corresponding angles vary from 96.1° (**III**) to 107.4° (**IV**). The same mononuclear complex is observed in the [[$ZnBr_2(3,5\text{-}Me_2Py)_2$] structure (**V**) [7]. The authors observed short intermolecular interactions of ~3 Å in structures **III** and **IV** and considered them as nonclassical hydrogen bonds C–H···Hal with CHHal angles of 144°–165°. No hydrogen bonds are observed in complex **I**, and the distances from the methyl groups to the iodine atoms (C···I) exceed 4 Å.

The 1D coordination polymer is observed in structure **II**. The Cd polyhedron is a trigonal bipyramid containing iodine atoms in the axial vertices (Cd–I_{ax} 3.0399(5) Å × 2, angle ICdI 175.12(2)°) and two iodine atoms and the nitrogen atom of the ligand in the equatorial plane (Cd–I_{eq} 2.8402(5) Å × 2, Cd–N 2.309(5) Å, angles $NCdI_{eq}$126.82(1)° × 2 and $I_{eq}CdI_{eq}$ 126.82(1)°) (Fig. 2). The Cd and N atoms of the ligand (2,6-Me_2Py) lie on the 2-fold axis. The Cd polyhedra are joined into infinite chains [$CdI_2(2,6\text{-}Me_2Py)]_\infty$ extended along the direction [100] due to the bridging iodine atoms (Fig. 3). The Cd···Cd distance in the chain (4.17 Å) is consistent with the distances (4.14 Å) in the [$Cd(\mu\text{-}I_2)(3,5\text{-}Cl_2Py)_2$] and [$Cd(\mu\text{-}I_2)(3,5\text{-}Br_2Py]$ structures [7].

The photoluminescence spectrum of ligand L (3,5-Me_2Py is liquid) as a broad band is shown in Fig. 4. The emission spectrum of crystalline compound **I** is presented in Fig. 5. The shapes of the spectra for com-

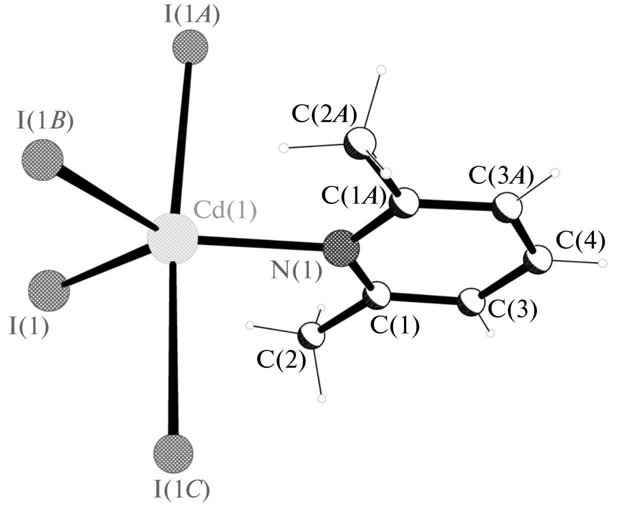

Fig. 2. Coordination mode of the Cd atom in structure **II**.

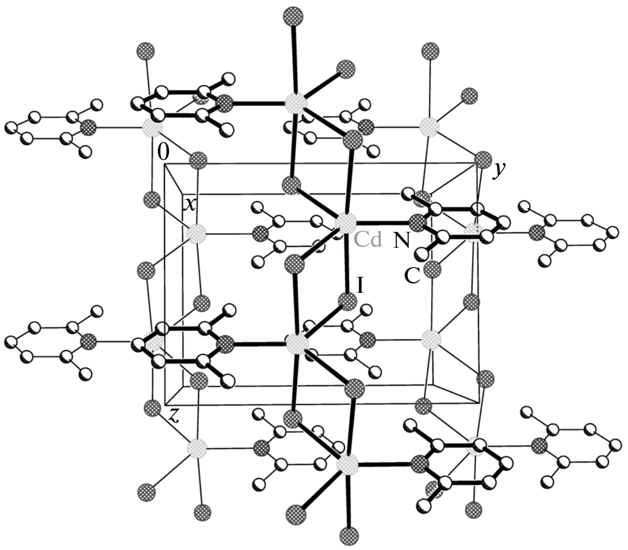

Fig. 3. General view of structure **II**. The 1D polymer chains $[CdI_2(2,6\text{-}Me_2Py)]_\infty$ along the direction [100] are marked by bold.

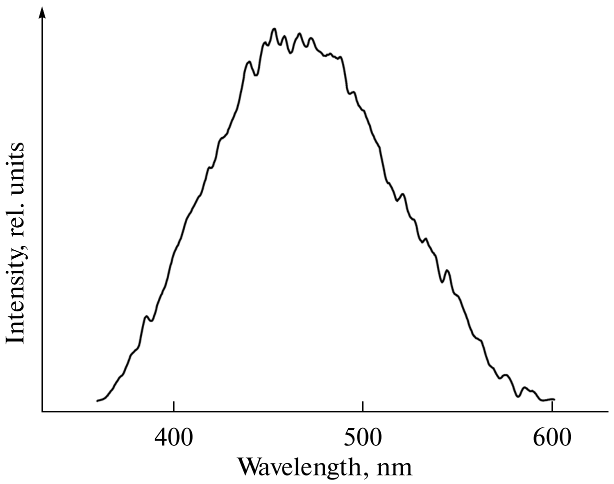

Fig. 4. Photoluminescence spectrum of the 3,5-Me_2Py ligand (λ_{exc} = 220 nm).

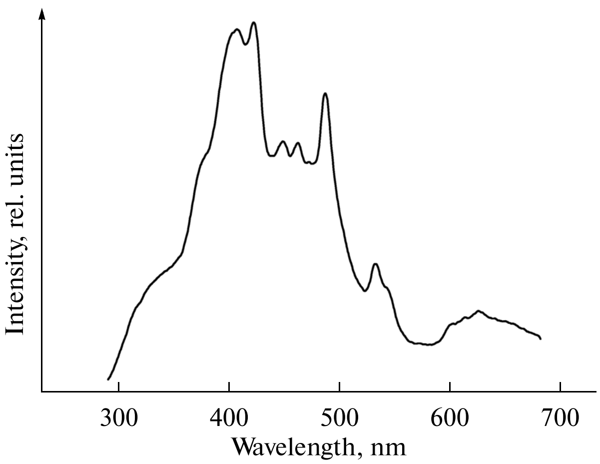

Fig. 5. Photoluminescence spectrum of compound $[CdI_2(2,3\text{-}Me_2Py)_2]$ (λ_{exc} = 255 nm).

pounds **II** and **III** are similar to that of the spectrum in Fig. 5. As can be seen from Figs. 4 and 5, the experimental spectra represent superpositions of several peaks in the wavelength region from 336 to 633 nm. Therefore, the spectra were approximated using the OriginPro 8.0 program ($R^2 \geq 0.998$), which made it possible to pick up the peaks of major intensity (Table 2).

An analysis of the obtained data shows that the spectra of all studied compounds contain bands characteristic of 3,5-Me_2Py (Table 2), and the coincidence is fairly exact for the most intense bands at 450 and 485 nm. This assumes that one of possible energy transfer mechanisms for these compounds is the intraligand charge transfer (so-called LLCT transition). The spectra of all three compounds also exhibit three groups of bands at ~340, 423, and 465 nm, which are not typical of the free ligand, a low-intensity bands at 370 nm for compounds **II** and **III**, and a weak band at ~630 nm for compound **I**. Compound $[CdI_2(4,4'\text{-}Bipy)]_n$ was shown [14] to have a strong emission at 425 nm, which was related to the intraligand energy transfer in this compound. At the same time, it is known that unalloyed crystals of CdI_2 at room temperature manifest almost no luminescence and intense emission bands are observed at lowered temperatures (lower than 100 K) or in crystals activated by such impurities as Bi, Br, and Pb [15–17]. It was shown that

Table 2. Position of emission peaks for compounds **I–III** and ligand 3,5-Me_2Py

Compound	Position of emission peaks, nm								
Ligand			411		447		485	531	
I	343		409	424	449	464	487	527	633
II	343	371	406	423	450	465	485	540	
III	336	372	404	423	450	466	488	548	

emission bands were observed either in the UV region at 360–380 nm (Br, Pb), or on the green spectral range at 510 nm (Bi), depending on the type of an impurity. Thus, it can be assumed that the emission bands in the UV and violet spectra ranges are caused by the interligand transfer of a portion of energy to the iodine ions playing the role of bridges in compounds CdI_2L_2.

The synthesis and structure determination of one of the first compounds of CdI_2 with pyridine were described [5]: this is the clathrate complex $[CdI_2(Py)_4] \cdot 2Py$ in which the Cd^{2+} ion had the octahedral environment of two iodine atoms and four nitrogen atoms of pyridine. The Cd(II) compounds with different halides and some pyridine derivatives were synthesized. The coordination compounds $[CdCl_2(Py)_2]$ and $[CdBr_2(Py)_2]$ form polymer chains due to the bridging halide ions with the octahedral environment of Cd (4Hal and 2N). In turn, $[CdI_2(Py)_2]$ is a monomeric tetrahedral complex [7]. The appearance of different substituents in different positions of the heterocycle in a pyridine molecule noticeably affects the structures of the compounds. The coordination compounds $[CdHal_2(3\text{-}Br(Cl)Py)_2]$, $[CdCl_2(3\text{-}MePy)_2]$, and $[CdBr_2(3\text{-}MePy)_2]$ [7] include 1D coordination polymers with Hal molecules and the octahedral environment of Cd. On the contrary, $[CdI_2(3\text{-}MePy)_2]$ is a monomeric tetrahedral complex.

The data on the structures of the coordination compounds of cadmium halide with disubstituted pyridine molecules are presented [6]. Atoms Cl and Br and the CH_3 group were used as substituents. Compounds $[CdCl_2(3,5\text{-}Cl_2(Br_2)(Me_2)Py)_2]$, $[CdBr_2(3,5\text{-}Cl_2(Br_2)(Me_2)Py)_2]$, and $[CdI_2(3,5\text{-}Cl_2(Br_2)Py)_2]$ are 1D coordination polymers with bridging halides and the octahedral environment of Cd(II). The organic ligands occupy the apical position in the octahedron. However, compound **III** is not polymer but a discrete tetrahedral complex.

Newly synthesized coordination compounds of cadmium iodide with disubstituted pyridine molecules **I** and **II** differ in structure. Compound **I** is a mononuclear tetrahedral complex as $[CdI_2(Py)_2]$ and $[CdI_2(3\text{-}MePy)_2]$, whereas compound **II** is a 1D polymer with the 5-coordinated Cd^{2+} ion with a shape of a trigonal bipyramid. Cadmium compounds $[CdI_2(2,4,6\text{-}Me_3)Py)]$ and $[CdBr_2(Quin)]$ (Quin is quinoline) have the same structure [8]. Interestingly, the mercury(II) compound $[HgBr_2(3,5\text{-}Cl_2)Py)_2]$ [18] contains the metal atom with the coordination number 5, but the N-ligand occupies the apical position in the distorted tetragonal pyramid with the bridging Br atoms in the plane.

Thus, it can be assumed that the inorganic–organic hybrid compounds of IIB Group metal halides at the ratio $MHal_2$: N-ligand = 1 : 1 include polymer structures with the bridging halides and coordination number of the metal equal to 5. Discrete tetrahedral complexes and polymers with the octahedral environment of the metal ion and with halide bridges can be formed at the ratio $MHal_2$: N-ligand = 1 : 2.

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