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A Complex of Cadmium(II) Iodide with 4-Cyanopyridine: Synthesis, Crystal Structure, and Luminescent Properties

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Abstract—The complex $[CdI_2(4\text{-}CNPy)_2]$ (**I**) was obtained by a reaction of CdI_2 with 4-cyanopyridine (4-CNPy, $C_6H_4N_2$) and structurally characterized (CIF file CCDC no. 983377). The crystals of complex **I** are monoclinic, space group $C2$, $a = 24.698(5)$ Å, $b = 4.127(1)$ Å, $c = 7.597(2)$ Å, $\beta = 96.05(1)°$, $V = 770.0(3)$ Å^3, $\rho_{calcd} = 2.477$ g/cm^3, $Z = 2$. In structure **I**, iodine atoms serve to unite complex molecules into the polymer chains $[CdI_2(4\text{-}CNPy)_2]_\infty$ along the direction [010]. The Cd(1) atom lying on a twofold axis has a slightly distorted octahedral environment made up of four bridging iodine atoms and two nitrogen atoms of two ligands 4-CNPy (Cd–I$_{av}$, 2.947(2) and Cd–N(1), 2.410(6) Å). Within each chain, cadmium atoms are spaced apart at 4.13 Å. Complex **I** exhibits photoluminescence.

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INTRODUCTION

Coordination polymers and hybrid organic–inorganic ensembles constitute a class of compounds built from metal ions and organic or inorganic bridging groups. Complexes based on d^{10}-metal centers and conjugated organic ligands usually show stable photoluminescence, are insoluble in water or common solvents, and thermally stable. The advantages provided by such crystalline hybrid polynuclear complexes include the possibility of their synthesis from certain luminescent aromatic ligands as well as their possible modification and use as precursors of functional materials.

Considerable recent interest in compounds combining a polymer of Group IIB metal halides (as an inorganic portion) and N-containing aromatic ligands (as an organic portion) is due to their promise for photoluminescence, the manufacture of sensors and materials designed to harness solar power, etc. [1, 2]. The examples cited therein include hybrid compounds based on cadmium and mercury iodides.

Several complexes of cadmium iodides with mono- and disubstituted pyridines have been synthesized to date. Depending on the composition and the substituents, these are monomeric tetrahedral structures or coordination polymers with bridging iodine atoms [3–9]. For instance, CdI_2 reacts with monosubstituted pyridines (2-methylpyridine and 3-methylpyridine) to form tetrahedral monomers, while its reactions with 3-chloropyridine, 3-bromopyridine, and 4-methylpyridine yield coordination polymers with bridging iodine atoms [7, 8].

In our further investigations of complexes of cadmium(II) iodide with monosubstituted pyridines, we obtained a complex of CdI_2 with 4-cyanopyridine. Although cyanopyridine can act as a bridging ligand, the electron-donating properties of the CN group are pronounced only slightly. That is why one could expect its monodentate coordination to the Cd^{2+} ion, only through the N atom of the pyridine ring.

In the present study, we obtained the complex $[CdI_2(4\text{-}CNPy)_2]$ (**I**) (4-CNPy is 4-cyanopyridine), determined its crystal structure, and examined its emission spectra.

EXPERIMENTAL

Cadmium(II) iodide (reagent grade) and 4-cyanopyridine (Fluka) were employed.

Synthesis of complex I. Cadmium(II) iodide (0.54 g, 1.47 mmol) and 4-cyanopyridine (0.31 g, 2.97 mmol) were separately dissolved in acetonitrile (5 mL). The resulting solutions were mixed and kept at room temperature to ensure slow evaporation of the solvent. After 8–10 h, the first, fine crystalline fraction of the reaction product was filtered off. The mother liquor was left under similar conditions until colorless prismatic crystals formed. According to elemental analysis data, complex **I** can be formulated as $[CdI_2(4\text{-}CNPy)_2]$.

For $C_{12}H_8N_4CdI_2$

anal. calcd., %:	C, 25.00;	N, 9.72;	H, 1.38.
Found, %:	C, 25.25;	N, 9.73;	H, 0.64.

Selected crystallographic parameters and the data collection and refinement statistics for structure **I**

Parameter	Value
M	574.42
Crystal dimensions, mm	0.35 × 0.20 × 0.10
Crystal system; space group	Monoclinic; $C2$
Unit cell parameters:	
a, Å	24.698(5)
b, Å	4.127(1)
c, Å	7.597(2)
β, deg	96.05(3)
V, Å^3	770.0(3)
Z	2
ρ_{calcd}, g/cm^3	2.477
μ_{Mo}, mm^{-1}	5.418
$F(000)$	524
T, K	293
Radiation (λ, Å)	MoK_α (1.54178), graphite monochromator
Scan mode	ω
θ scan range, deg	2.70–27.97
Ranges of h, k, and l indices	$-1 \le h \le 32$, $-1 \le k \le 5$, $-10 \le l \le 9$
Number of measured/unique reflections (R_{int})	1356/1270 (0.0207)
Number of reflections with $I \ge 2\sigma(I)$	1111
Absorption correction/T_{min} and T_{max}	Empirical/0.09823 and 0.28367
Number of parameters refined	88
GOOF on F^2	1.458
R, $I \ge 2\sigma(I)$	$R_1 = 0.0563$, $wR_2 = 0.1546$
R, for all reflections	$R_1 = 0.0630$, $wR_2 = 0.1600$
Molar absorption coefficient	0.017(2)
Residual electron density (max/min), e/Å^3	4.493/–3.682

When the same starting reagents were used in an equimolar ratio, their reaction yielded crystals of the complex CdI_2(4-CNPy) (**II**).

For $C_6H_4N_2CdI_2$			
anal. calcd., %:	C, 5.93;	N, 15.25;	H, 0.84.
Found, %:	C, 15.68;	N, 5.90;	H, 0.51.

Unfortunately, single crystals of complex **II** suitable for X-ray diffraction experiment were not obtained.

X-ray diffraction study. Experimental reflection intensity data for single crystals of complex **I** were collected on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by the direct methods (SHELXS-97) [10] and refined by the least-squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [11]. The hydrogen atoms were located geometrically and refined using a riding model with fixed isotropic thermal parameters.

Selected crystallographic parameters and the data collection and refinement statistics for structure **I** are summarized in table.

Comprehensive structural data have been deposited with the Cambridge Crystallographic Data Collection (no. 983377; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Photoluminescence spectra were recorded at room temperature on a PerkinElmer LS-55 spectrometer (λ_{ex} = 200–800 nm, λ_{em} = 200–700 nm, resolution 0.5 nm, fluorescence mode) with an attachment for solid-state measurements.

RESULTS AND DISCUSSION

In structure **I**, iodine atoms act as bridging ligands to form polymer chains $[CdI_2(4\text{-}CNPy)_2]_\infty$ along the direction [010]. The Cd(1) atom lying on a twofold axis has an octahedral environment made up of four bridging iodine atoms and two nitrogen atoms of two ligands 4-CNPy. The octahedron is slightly distorted (Cd–I, 2.946(2) and 2.948(2) Å; Cd(1)–N(1), 2.410(6) Å; the angles N(I)CdN(I) are less than 1° off the idealized octahedral angles) (Fig. 1). The rings NC_5 of two ligands CNPy are planar (±0.05 Å) and slightly non-coplanar with each other: the dihedral angle between their planes is 13.7°. A fragment of the crystal packing of complex **I** is shown in Fig. 2. Within each chain, adjacent cadmium atoms are spaced apart at 4.13 Å. Similar Cd···Cd distances have been found in the chain structures $[CdI_2(2,6\text{-}Me_2Py)]$ [7] 4.17 Å, $[Cd(\mu\text{-}I_2)(3,5\text{-}Cl_2Py)_2]$ and $[Cd(\mu\text{-}I)(3,5\text{-}Br_2Py)_2]$ [8] 4.14 Å, $[CdI_2(4\text{-}MePy)_2]$ 4.33 Å [9].

The emission spectra of the ligand 4-cyanopyridine and complex **I** ($\lambda_{ex} = 255$ nm) at room temperature are shown in Fig. 3. Both the spectral patterns are complicated, being superpositions of several characteristic bands. The most intense bands appear at 424 and 480 nm; their positions and intensities are virtually insensitive to excitation frequency variations. When the excitation frequency is decreased, the emission bands of the ligand with $\lambda < 400$ nm become less intense. At $\lambda_{ex} = 360$ nm, the ligand emits only at $\lambda > 420$ nm; i.e., the emission spectra of the ligand and complex **I** become nearly identical. This suggests that the emission of complex **I** is due to charge transfer within the ligand.

The emission spectra of Zn and Cd complexes with N-containing heteroaromatic ligands usually show blue shifts. The emission spectrum of complex **I** is virtually identical with that of the free ligand. Small red shifts have been reported for the spectra of complexes of Zn and Cd halides compared to the spectra of the corresponding free organic ligands [12–14]. One can believe that the luminescence of complex **I** is due to the iodine → N-ligand charge transfer.

As noted above, 4-cyanopyridine is coordinated to CdI_2 in a monodentate fashion through the N atom of the pyridine ring. A similar coordination has been reported for the silver ion in $[Ag(CNpy)_2(Hpta)]$ [15]. However, in some other silver complexes, CNPy acts as a bridging ligand to form coordination polymers [16, 17].

It is known that the cadmium ion can have different coordination numbers and can coordinate both soft and hard bases. By varying the steric and electronic properties of organic (specifically, heterocyclic N-donating) ligands, one can modulate the structures and sizes of the complexes.

Analysis of the results obtained and available literature data on the structures of complexes of cadmium iodides with monosubstituted pyridines showed that the position of substituents in the pyridine (involving a change in the geometry and electronic properties) is most often crucial for the structural (monomeric or polymeric) motif of the complex. For instance, $[CdI_2(2\text{-}MePy)_2]$ [4] and $[CdI_2(3\text{-}MePy)_2]$ [8] are discrete tetrahedral structures, while $[CdI_2(4\text{-}MePy)_2]$ [9] and structure **I** we studied here are polymers with bridging iodine atoms.

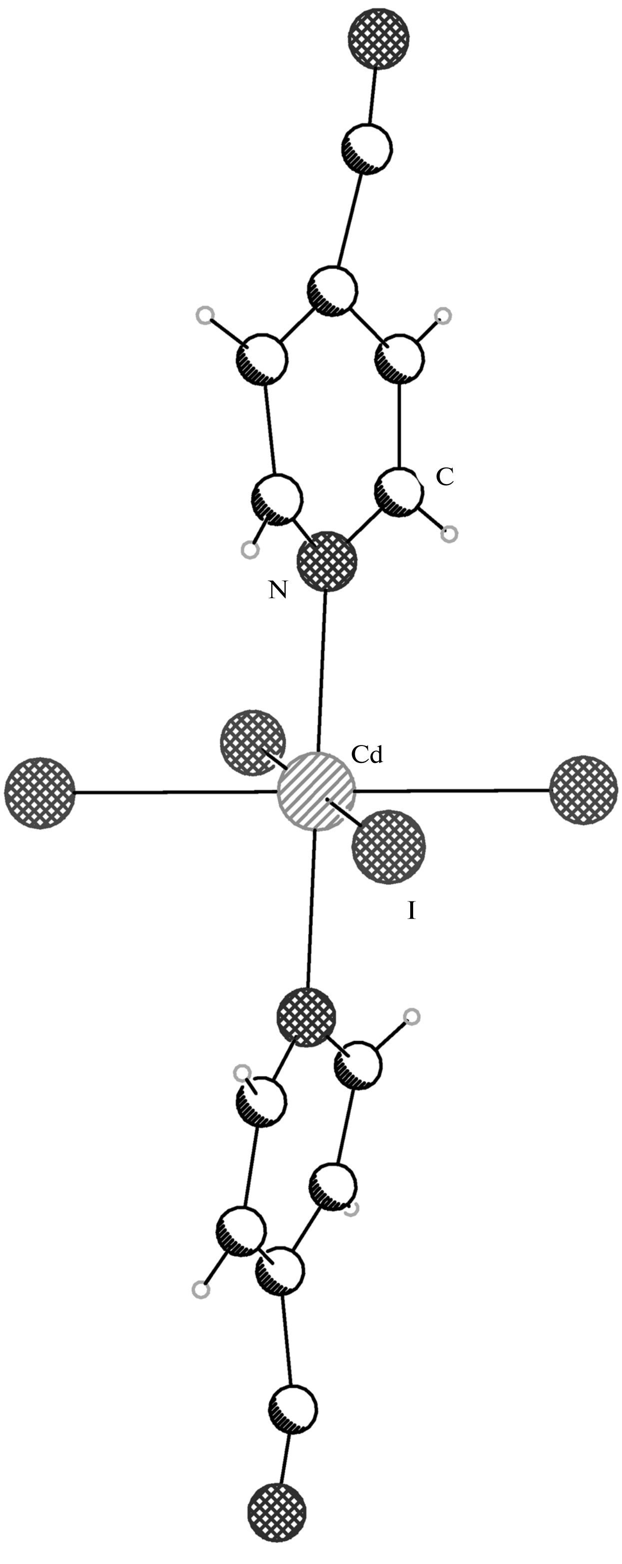

Fig. 1. Coordination entity of the Cd^{2+} ion in structure **I** [001].

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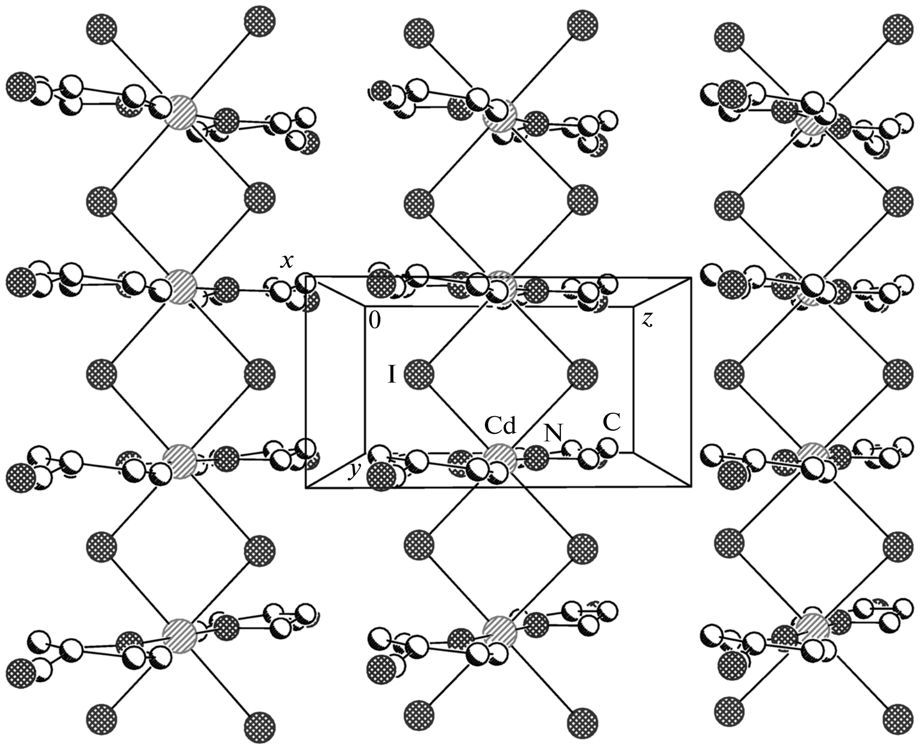

Fig. 2. Fragment of the crystal packing of the structure [$CdI_2(4\text{-}NCPy)_2$] along the direction [001].

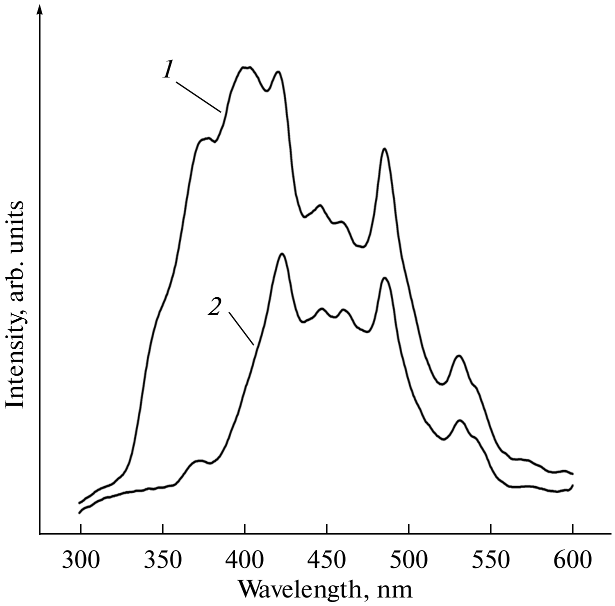

Fig. 3. Emission spectra of (*1*) 4-cyanopyridine and (*2*) complex **I** (λ_{ex} = 255 nm) at room temperature.

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