ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 9, pp. 614–619. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © Yu.V. Kokunov, V.V. Kovalev, Yu.E. Gorbunova, S.A. Kozyukhin, 2016, published in Koordinatsionnaya Khimiya, 2016, Vol. 42, No. 9, pp. 573–578.

Reactions of 2,2'-Pyridyl with the Cadmium(II) Compounds: Synthesis, Crystal Structure, and Luminescence Properties of $[Cd(Pic)_2(H_2O)_2] \cdot H_2O$

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Received March 11, 2016

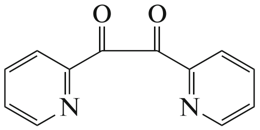
Abstract—The reactions of 2,2'-pyridyl, (2-Py)C(O)C(O)(2-Py), with the Cd(II) compounds under various conditions are studied. The medium and nature of the anions exert a decisive effect on the compositions and structures of the formed cadmium complexes. The reaction of cadmium diacetate with 2,2'-pyridyl in an aqueous-alcohol medium in air affords coordination compound $[Cd(Pic)_2(H_2O)_2] \cdot H_2O$ (**I**) (Pic^- is picolinate ion, $CO_2C_5H_4N$), and its crystal structure is determined. The crystals are monoclinic: space group $P2_1/c$, $a = 7.499(1)$, $b = 15.676(1)$, $c = 12.719(1)$ Å, $\beta = 94.79(1)°$, $V = 1490.0(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.502$ g/cm^3. The molecular packing of compound **I** is a supramolecular 3D framework consisting of discrete complexes $[Cd(Pic)_2(H_2O)_2]$ linked by hydrogen bonds O—H···O. The coordination sphere of Cd^{2+} contains two O atoms and two N atoms of the ligand and two water molecules. The coordination polyhedron of Cd^{2+} is a distorted octahedron.

Keywords: synthesis, structure, IR spectrum, photoluminescence, hydrogen bond

DOI: 10.1134/S1070328416090025

INTRODUCTION

Compound (2-Py)C(O)C(O)(2-Py) (L) with two ketone groups between the Py radicals, like $(2\text{-}Py)_2CO$ [1–6], has a specific feature: susceptibility of the CO groups to a nucleophilic attack.



For instance, H_2O or ROH in the presence of metal ions results in the decompostion of 2,2'-pyridyl to Hpic or ester of this acid followed by the formation of metal picolinates. The reactions of L with copper halides in ethanol gave the copper complex $\{Cu[PyC(O)OEt)_2]\}Cl_2$ [7]. The reaction of $MClO_4 \cdot 6H_2O$ (M = Co, Ni) with L in methanol is accompanied by the formation, for example, $\{Ni[PyC(O)CO(OH)Py]\}_2 \cdot 2H_2O$ [8]. In this case, no bond between the CO groups of ligand L is cleaved, but one of the bonds is transformed into the charged fragment $C(OH)O^-$. The structures of the cadmium coordination compounds with pyridyl-3-carboxylate and pyridyl-4-carboxylate were obtained and determined [9–12]. The compounds were synthesized by hydrothermal reactions of the cadmium salts with the corresponding pyridylcarboxylic acids at elevated temperatures and pressures. In the mentioned compounds, pyridylcarboxylates exhibit bridging functions coordinating to the Cd^{2+} ion by the N atom of the heterocycle and by the COO group. There are published data on the structures of the mixed cadmium compounds containing Pic^- and anions Cl^-, SO_4^{2-}, NCS^-, and N_3^-. In these compounds, the picolinate anions exhibit the chelate-bridging properties [13–15].

In this work we studied the reactions of 2,2'-pyridyl with compounds $Cd(CH_3CO_2)_2 \cdot 2H_2O$ and CdI_2; synthesized compounds $[Cd(Pic)_2(H_2O)_2] \cdot H_2O$ (**I**), $[CdL(CH_3CO_2)_2(H_2O)_2] \cdot 0.5CH_3CN$ (**II**), and $[CdI(Pic)] \cdot 0.25CH_3CN$ (**III**) and studied their spectra (IR and photoluminescence); and determined the crystal structure of compound **I**.

EXPERIMENTAL

The following reagents were used: $Cd(CH_3CO_2)_2 \cdot 2H_2O$ and CdI_2 (reagent grade) and 2,2'-pyridyl (Aldrich).

Synthesis of I. Compound $Cd(CH_3CO_2)_2 \cdot 2H_2O$ (0.25 g, 0.94 mmol) was dissolved in an ethanol–water

(1 : 1) mixture (10 mL), and 2,2'-pyridyl (0.20 g, 0.94 mmol) was dissolved in ethanol (10 mL). The solutions of the reactants were mixed and kept for 24 h under the conditions of slow evaporation of the solvents. Light yellow plate-like crystals isolated from the solution were filtered off, washed with a minor amount of ethanol, and dried in air.

For $C_{12}H_{14}N_2O_7Cd$

anal. calcd., %:	N, 6.82;	C, 35.06;	H, 3.41.
Found, %:	N, 6.80;	C, 35.07;	H, 3.36.

Synthesis of II. Cadmium acetate (0.26 g, 0.97 mmol) was dissolved in ethanol (5 mL), and 2,2'-pyridyl (0.20 g, 0.94 mmol) was dissolved in acetonitrile (5 mL). The solutions were mixed and kept for several days in a weighing bottle with the not closely clasped cap. The external view of the formed crystalline phase differed substantially from that of the product of synthesis of **I** and represented large colorless spherical granules (except for a part of the surface contacting with the bottom or walls of the weighing bottle). The granules were separated from the solution by decantation, washed with acetonitrile, and dried for several days in air. The visualization of the external surface of the granules and the microscopic observation of the split sites showed that they were formed of the densely packed finely crystalline phase and were not suitable for X-ray diffraction analysis. The isolated product was insoluble in ethanol, acetonitrile, and dimethylformamide and corresponded to the composition $[Cd(2,2'\text{-pyridyl})(CH_3CO_2)_2(H_2O)_2] \cdot 0.5CH_3CN$ according to the chemical analysis data.

For $C_{12}H_{19.5}N_{2.5}O_8Cd$

anal. calcd., %:	N, 7.01;	C, 40.87;	H, 3.90.
Found, %:	N, 7.66;	C, 40.84;	H, 2.83.

The storage of the mother liquor for 24 h with a slow evaporation of the solvents resulted in the formation of plate-like crystals of compound **I**. A similar formation of the same two crystalline phases was observed in the case of the interaction of a suspension of cadmium acetate in acetonitrile with an equivalent amount of 2,2'-pyridyl with the introduction into the reaction of a minimum amount of water necessary for the dissolution of the initial cadmium salt.

Synthesis of III. Ligand L (0.25 g, 1.17 mmol) and CdI_2 (0.43 g, 1.17 mmol) were dissolved separately in acetonitrile (5 mL). The solutions were mixed, ethanol (10 mL) was added, and the solutions were kept for several hours at room temperature. As the solvents evaporated, the solution turned dark brown and a solid phase was isolated as fine needle-like crystals with inclusions of elemental iodine. The solid phase was filtered off, repeatedly dissolved in an acetonitrile–ethanol (1 : 1) mixture, filtered to separate iodine impurities, and kept in air at room temperature until the most part of solvents was removed. The formed crystals were filtered off, washed with a minor amount of acetonitrile, and dried in air. The crystals were not suitable for X-ray diffraction analysis.

For $C_{6.5}H_{4.75}IN_{1.25}O_2Cd$

anal. calcd., %:	N, 4.69;	C, 20.90;	H, 1.27.
Found, %:	N, 4.86;	C, 21.43;	H, 1.28.

The IR spectra of compound **III** and 2,2'-pyridyl were recorded on a Specord 75IR spectrometer in a range of 400–4000 cm^{-1} (KBr) using the standard procedure of trituration with Nujol.

Photoluminescence (PL) spectra were recorded at room temperature on a PerkinElmer LS-55 spectrometer (λ_{exc} = 200–800 nm, λ_{em} = 200–900 nm, instrumental resolution 0.5 nm, slit d = 8–11 nm, attachment for solid samples).

X-ray diffraction analysis. An 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 all non-hydrogen atoms (SHELX-97) [16]. Positions of hydrogen atoms were calculated geometrically and included into refinement by the riding model. The hydrogen atoms of the water molecules were found from the difference Fourier synthesis. The unit cell parameters and selected experimental characteristics are presented in Table 1. The geometric parameters of hydrogen bonds are given in Table 2.

The full crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC 1454072; http://www.ccdc.cam.ac.uk/deposit/).

RESULTS AND DISCUSSION

Structure **I** contains discrete complexes $[Cd(Pic)_2(H_2O)_2]$ (Fig. 1). The Cd^{2+} ion is octahedrally coordinated by two N atoms of the pyridine rings of the independent Pic ligands (Cd(1)N(1) 2.338(8) and Cd(1)N(2) 2.313(8) Å), two O atoms of the carboxylate group (Cd(1)–O(2) 2.276(7), Cd(1)–O(4) 2.304(7) Å), and two O(H_2O) atoms (Cd(1)Ow(1) 2.306(8), Cd(1)–Ow(2) 2.283(7) Å). The nitrogen atoms occupy the axial positions of the octahedron (angle N(1)Cd(1)N(2) 154.1(3)°), and two O atoms of the carboxylate groups of Pic and two O atoms of the Ow(H_2O) molecules are arranged in the equatorial plane (angles O(4)Cd(1)O(1w) 160.2(3)°, O(2)Cd(1)O(2w) 150.2(3)°, O(2)Cd(1)O(4) 99.4(3)°, O(2)Cd(1)O(1w) 82.5(3)°, O(2)Cd(1)N(1) 72.1(3)°, O(4)Cd(1)N(2) 71.5(3)°, O(4)Cd(1)O(2w) 102.8(3)°, O(1w)Cd(1)O(2w) 83.3°). Note that the H_2O molecules occupy the *cis* positions. Complexes $[Cd(Pic)_2(H_2O)_2]$ are joined by

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

Parameter	Value
FW	410.65
Color, habitus	Colorless, block
Crystal size, mm	0.30 × 0.20 × 0.15
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell parameters:	
a, Å	7.499(1)
b, Å	15.676(1)
c, Å	12.719(1)
β, deg	94.79(1)
V, Å^3	1490.0(2)
Z; ρ_{calcd}, g/cm^3	4; 1.831
μ_{Mo}, mm^{-1}	1.502
F(000)	816
Temperature, K	293
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
Completeness to θ = 30.01°, %	99.1
θ Range, deg	2.07–30.01
Index range	$-1 \leqslant h \leqslant 10$, $-1 \leqslant k \leqslant 22$, $-17 \leqslant l \leqslant 17$
Total number of reflections/independent	5574/4325 (R_{int} = 0.0813)
Number of reflections with $I \geqslant 2\sigma(I)$	1536
Number of refined parameters	199
GOOF for F^2	1.100
R ($I \geqslant 2\sigma(I)$)	R_1 = 0.0463, wR_2 = 0.1218
R (all data)	R_1 = 0.2467, wR_2 = 0.2245
Residual electron density (max/min), e/Å^3	2.279/–2.224

Table 2. Geometric parameters of hydrogen bonds in the structure

D–H···A	Distance, Å D···A	D–H	H···A	Angle DHA, deg	Coordinates of A atom
O(1*w*)–H(1)···O(3*w*)	2.766(8)	0.93	1.85	170	x, y, z
O(1*w*)–H(2)···O(4)	2.765(8)	0.93	2.08	130	$x, -y + 3/2, z + 1/2$
O(2*w*)–H(3)···O(3*w*)	3.143(9)	0.83	2.41	148	$x - 1, y, z$
O(2*w*)–H(4)···O(3)	2.674(8)	0.87	1.81	180	$x, -y + 3/2, z + 1/2$
O(3*w*)–H(5)···O(4)	3.527(9)	1.17	2.40	160	$x + 1, -y + 3/2, z + 1/2$
O(3*w*)–H(6)···O(1)	2.976(8)	0.99	2.21	133	$x, -y + 3/2, z + 1/2$
O(3*w*)–H(6)···O(2)	3.477(8)	0.99	2.54	158	$x, -y + 3/2, z + 1/2$

hydrogen bonds O–H···O including O–H donors of both coordinated and out-of-sphere water molecules (Table 2). The supramolecular 3D structure is formed due to the indicated interactions (Fig. 2). The π–π-stacking interaction occurs along the [100] direction between two pairs of the centrosymmetric pyridine rings of Pic. The interaction is characterized by the horizontal shift of the aromatic group, the distance

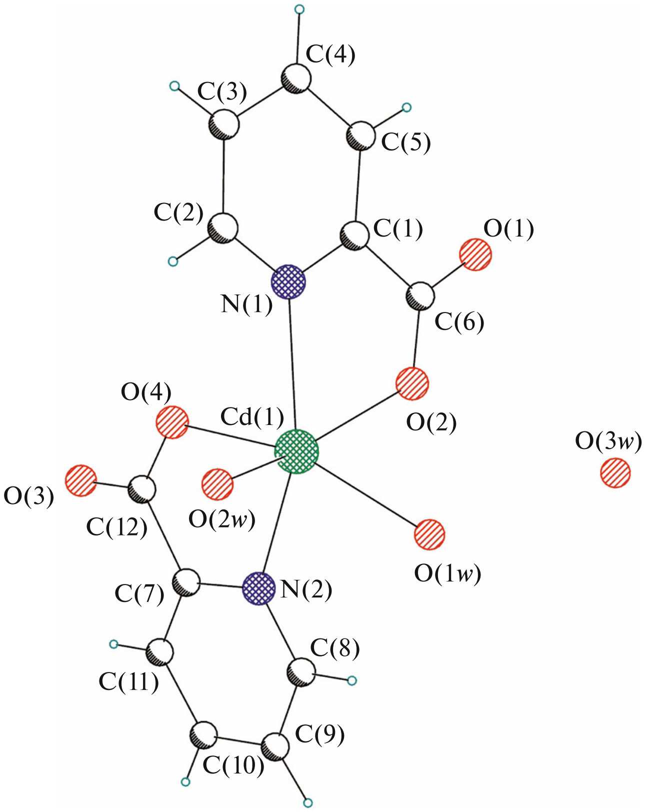


Fig. 1. Coordination environment of the Cd^{2+} ions in **I**.

between which is 3.35 and 3.71 Å for N(1)···N(1*) and N(2)···N(2*), respectively (Fig. 2). The angle between the normal to the plane of the rings and the vector between their centers corresponds to the horizontal shift of the aromatic groups and is equal to 20° and 15°, respectively.

Both independent ligands Pic are planar (±0.01 Å) and are added through the chelate mode to the cadmium ion (the dihedral angle between their planes is 102.4°). This mode of Pic addition induces a significant distortion of the octahedron. As shown above, the OCdN angles in the chelate rings are smallest.

The analysis of the structures of the studied complex **I**, $[Cd(Pic)_2(Tu)_2] \cdot 0.5H_2O$ (**Ia**) [17], and known diaquadi(picolinates) $[Zn(Pic)_2(H_2O)_2] \cdot 2H_2O$ (**Ib**) [18], $[Mn(Pic)_2(H_2O)_2] \cdot H_2O$ (**Ic**) [19], and $[Mn(Pic)_2(H_2O)_2]$ (**Id**) [20] shows that the indicated compounds contain discrete octahedral complexes $[M(Pic)_2(H_2O)_2]$ (M = Cd, Zn, Mn) with different mutual arrangements of the ligands and different contents of out-of-sphere water. In hydrate complexes **I**, **Ib**, and **Ic**, the N atoms of the Pic ligands are arranged in the *trans* position to each other (angles NMN 154.1(3)°, 157.78(8)°, and 180° for **I**, **Ic**, and **Ib**, respectively) in the axial vertices of the octahedron. Note that in complex **Ib** the Zn atom is localized at the inversion center and is coordinated by two crystallographically equivalent ligands, inducing an insignificant distortion of the Zn tetrahedron unlike **I** and **Ic**, where Pic are independent ligands.

The coordinated water molecules in the considered structures are oriented in the octahedral coordination mode in the *cis* positions (angles OMO 83.3°, 97.35(8)°, and 84.48° in **I**, **Ic**, and **Id**, respectively) and in the *trans* position in **Ib** (angle OZnO 180°). Anhydrous compound **Id** includes a strongly distorted octahedron in which both the N atoms of the ligands and the O atoms of the water molecules are in the *cis* positions (angles NMnN 94.51(8)° and OMnO 84.48(9)°).

In the indicated structures, the metal complexes are joined by hydrogen bonds O–H···O of two types involving coordinated and out-of-sphere water. These interactions result in the formation of supramolecular layers along the diagonal [101] plane. Note that the layers joined into a supramolecular 3D framework are formed in structure **I** due to the participation of the out-of-sphere molecule, being both proton donor and acceptor in hydrogen bonding.

The IR spectrum of compound **I** in a range of 1600–1500 cm^{-1}, characteristic of the ν(C=N) and ν(C=C) stretching vibrations of the heterocycle and ν_{as}(COO) antisymmetric vibrations of the carboxylate group, exhibits a group of intense bands with the most discernible maxima at 1607, 1580, and 1550 cm^{-1} and an intense band ν_s(COO) of the Pic anion at 1370 cm^{-1}. It is substantial that the formation of this dianion during the synthesis of compound **I** is consistent with the absence in the IR spectrum of the band of the carbonyl group, which is observed in the spectrum of the free ligand at ~1690 cm^{-1}. In the case of compound **II**, an intense band appears in the spectrum at 1638 cm^{-1} along with the intense absorbance in a range of 1600–1500 cm^{-1}. This new band can be assigned to the ν(C=O) band of ligand L shifted to the low-frequency range because of the participation of the C=O groups in binding with the central metal ion. The ν_s(COO) band in the spectrum of **II** is noticeably shifted to the low-frequency range (1350 cm^{-1}) compared to the same band in the spectrum of **I**, indicating that the compound contains other anion (acetate). The spectrum of **I** in the range of ν(O–H) stretching vibrations of water contains several broad bands at 3550, 3197, and 3035 cm^{-1} due to different states of the H_2O molecules and their participation in hydrogen bonding. In the spectrum of **II**, the absorbance in this range appears as one broad line without pronounced maxima.

The Pl spectrum of compound **I** is shown in Fig. 3. As can be seen from Fig. 3, the studied coordination compound has a bright emission band with a maximum at 620 nm corresponding to the red spectral range. A band at 440 nm is detected in the Pl spectrum

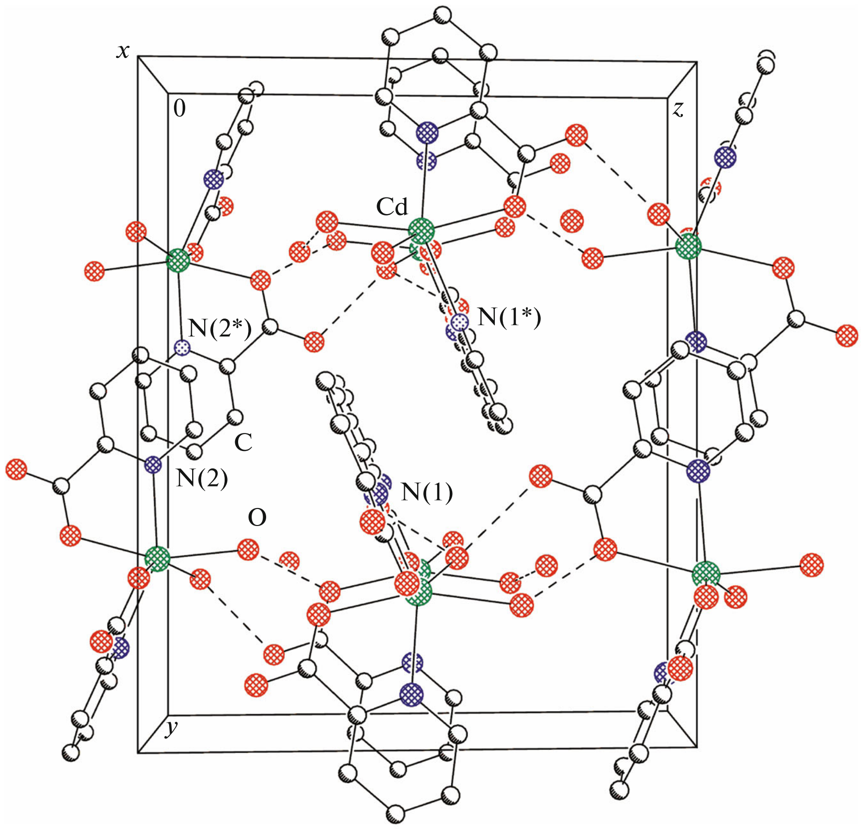


Fig. 2. Molecular packing of structure **I** along the direction [100].

of compound [Cd(Pic)(Cl)] [13] in which the coordination sphere of Cd contains the carboxylate group of the adjacent picolinate and bridging Cl atoms along with the chelate picolinate anion. It is most likely that in compound **I** the internal coordination sphere is more rigid, which results in a decrease in energy losses to nonradiative intraligand π–π* transitions and a decrease in the energy gap between the π and π* molecular orbitals of the ligand [21].

The oxidation of I^- to the elemental state occurs along with the transformation of ligand L into the Pic^- anion in the course of the reaction of CdI_2 with 2,2'-pyridyl in an alcohol–acetonitrile mixture. The isolated complex $[CdI(Pic)] \cdot 0.25CH_3CN$ (**III**) is a Cd(II) compound with mixed anions. In the known and structurally studied cadmium compound $[Cd_2Cl_2(Pic)_2(PicH)_2] \cdot C_2H_5OH$ [18], the bridging Cl atoms and H_2O molecules in **I** are in the *cis* positions. The chelate Pic and PicH cycles are almost perpendicular to each other (angle OCdO 87.5°). This means that all the same atoms of the ligands occupy the *cis* positions to each other [18]. Similar mixed-ligand cadmium picolinates with other acid anions are polymer formations in which the Cl^-, SO_4^{2-}, NCS^-, and N_3^- anions exhibit bridging functions, and picolinate anions are chelate-bridging [13–15]. Therefore, it can be assumed that in complex **III** the I^- and Pic^- anions are linked with Cd(II) in a similar way, and the compound has a polymer structure.

Note that the behavior of 2,2'-pyridyl in the reactions with the cadmium and zinc salts undoubtedly

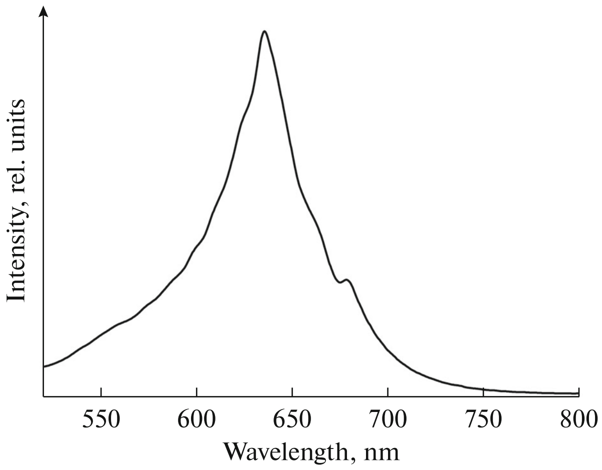


Fig. 3. Photoluminescence spectrum of $[Cd(Pic)_2(H_2O)_2] \cdot H_2O$ ($\lambda_{exc} = 470$ nm).

requires more detailed investigation. Nevertheless, the data presented show that the use of this N- and O-containing ligand is interesing, because the ligand substantially affects the variety of the obtained reaction products, taking into account its possible participation in redox processes.

ACKNOWLEDGMENTS

The luminescence spectra were measured using the equipment of the Center for Cooperative Use at the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

This work was supported by the Presidium of the Russian Academy of Sciences (program for basic research “Scientific Foundations for the Preparation of New Functional Materials”).

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Translated by E. Yablonskaya