ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2020, Vol. 46, No. 6, pp. 420–429. © Pleiades Publishing, Ltd., 2020.
Russian Text © The Author(s), 2020, published in Koordinatsionnaya Khimiya, 2020, Vol. 46, No. 6, pp. 376–384.

The authors congratulate Academician I.L. Eremenko with a 70th birthday

Coordination Polymer and Monomer with the $Cd(NO_3)_2$ Fragment Containing 2-Amino-5-Bromopyridine: Synthesis, Structures, NMR Study, and Luminescence Properties

V. V. Kovalev[a, *], Yu. V. Kokunov[a], Yu. K. Voronina[a], M. A. Kiskin[a], S. G. Sakharov[a], L. D. Popov[b], and I. L. Eremenko[a, c]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *Southern Federal University, Rostov-on-Don, Russia*
[c] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
**e-mail: kovavlad@igic.ras.ru*

Received December 24, 2019; revised January 29, 2020; accepted January 31, 2020

Abstract—The reactions of $Cd(NO_3)_2 \cdot 4H_2O$ with 2-amino-5-bromopyridine (Abp) afford compounds $[Cd(NO_3)_2(Abp)(H_2O)]_n$ (**I**) and $[Cd(NO_3)_2(Abp)_2(H_2O)_2]$ (**II**). The structures of both complexes are determined by single-crystal X-ray structure analysis (CIF files CCDC nos. 1938624 (**I**) and 1959680 (**II**)). Compound **I** is a coordination 1D polymer in which two chelate-bonded NO_3^- groups act as bridges. The coordination polyhedron of the octacoordinated central cadmium atom in compound **I** consists of seven oxygen atoms (one oxygen atom of water and six atoms of the NO_3^- groups) and one nitrogen atom of Abp, being a triangular dodecahedron. Complex **II** is a mononuclear molecule in which the octahedral coordination polyhedron of Cd is formed by four oxygen atoms of two water molecules and two NO_3^- groups and two oxygen atoms of two molecules of the Abp cycle. In both complexes, the amino group of Abp is not involved in coordination with the metal. Compound **I** is studied by ^1H, ^{31}C, and ^{15}N NMR spectroscopy of a solution of the polymer complex in CD_3CN, and the most substantial difference in the chemical shifts of the bound and free Abp ligands is observed in the ^{15}N NMR spectra (37 ppm). According to the data of luminescence spectroscopy, compounds **I** and **II** exhibit an emission in a range of 430–690 nm.

Keywords: coordination polymer, molecular complex, cadmium nitrate, 2-amino-5-bromopyridine, structure, NMR, photoluminescence

DOI: 10.1134/S1070328420060032

INTRODUCTION

The synthesis and structural study of new molecular and polymeric organometallic compounds remain to be a popular area of research due to their unusual coordination architectures and a number of physicochemical properties, such as conductance, photoluminescence, and photochemical and catalytic activity, providing their potential use in diverse fields. A combination of the methods of controlling the structures of the complexes makes it possible to produce new molecular materials with the perspective application in catalysis, optics, electronic, luminescence, and biology [1, 2].

The synthesis of coordination compounds is mainly based on the self-assembling of metal ions and organic ligands in solutions. The determining factors of the reaction can be the nature of the counterions and solvent, metal–ligand ratio, reaction temperature, pH of the medium, etc. In addition, various noncovalent interactions, such as strong hydrogen bonds and weaker π–π, CH...O, *lp*...π, halogen, and other interactions, play an important role in the self-assembling processes, formation of the molecular and crystal structures of new compounds, and their stability. Depending on the electronic structure, the metal ions and organic ligands determine the functional properties of crystals of the synthesized compounds: magnetic, optical, or luminescence properties, mechanical hardness, and thermal stability. The choice of the ligand and its amount in the reaction mixture also can be a reason for the structural diversity of the reaction products, which allows a finer controlling of the properties manifested by the synthesized compounds.

As known, N-heterocycles are widely used in the synthesis of coordination discrete and polymer metal compounds. The introduction of the donor substituent (NH_2) into position 2 of the pyridine ring affects the geometric and electronic parameters of the ligand, which is manifested as a change in the structures of the compounds involving this ligand. The NH_2 group is capable of participating in hydrogen bonding and imparting stability to new structures. The introduction of two different substituents (electron donor and acceptor) imparts the nonlinear optical character to the ligand [3, 4]. Molecular materials with a low dielectric constant can be prepared on the basis of these organic compounds. In particular, the pyridine derivatives with the NH_2 group in position 2 and the halide ions or NO_2 group in position 5 are often used for these purposes. Several studies on the synthesis of the coordination compounds of Cu(I and II) and Cd(II) with 2-amino-5-nitropyridine and Cu(II), Zn(II), and Ag(I) with 2-amino-5-bromopyridine (Abp) [5–10] were carried out, and their structures and physicochemical properties were studied.

The reaction system containing cadmium(II) cations and 2-amino-5-bromopyridine was studied in this work. The variation of the Cd : L ratio made it possible to isolate two reaction products, to study their compositions and structures, and to compare the luminescence properties.

EXPERIMENTAL

The following reagents were used: $Cd(NO_3)_2 \cdot 4H_2O$ (reagent grade), 2-amino-5-bromopyridine (97%; Aldrich), and acetonitrile and toluene (Khimmed) used as received.

Synthesis of $[Cd(Abp)(NO_3)_2(H_2O)]_n$ (I). Weighed samples of 2-amino-5-bromopyridine (0.23 g, 1.33 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.21 g, 0.66 mmol) were separately dissolved in acetonitrile (4 mL). The solutions were poured together, stirred at 40–45°C for 10 min, filtered, and kept under the slow evaporation of the solvent at room temperature for ~36 h until the most part of the solvent was evaporated. The formed large platy crystals were decanted from the solution, washed with acetonitrile, and dissolved in an acetonitrile–toluene (1 : 1) mixture (6 mL) on heating to 40–45°C. Crystals were isolated from the solution by slow crystallization at room temperature and dried in air. According to the elemental analysis data, the crystals corresponded to the composition of compound **I**.

For $C_5H_7N_4O_7BrCd$

Anal. calcd., %	N, 13.09;	C, 14.02;	H, 1.64.
Found, %	N, 12.92;	C, 13.81;	H, 1.27.

Synthesis of $[Cd(Abp)_2(NO_3)_2(H_2O)_2]$ (II) was carried out similarly to that of compound **I**, but the primarily isolated crystals were recrystallized using acetonitrile as the solvent. The dried crystals corresponded to the composition of compound **II**.

For $C_{10}H_{14}N_6O_8Br_2Cd$

Anal. calcd., %	N, 13.60	C, 19.42	H, 2.28
Found, %	N, 13.33	C, 19.78	H, 2.79

^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer with working frequencies of 300.13 and 75.47 MHz, respectively, and with deuterium internal stabilization at room temperature (298 K). The ^1H and ^{13}C chemical shifts are presented relative to tetramethylsilane (TMS). ^{15}N NMR spectra were recorded on a Bruker AV 400 spectrometer with a working frequency of 40.54 MHz and deuterium internal stabilization at room temperature (298 K). The ^{15}N chemical shifts are presented relative to liquid NH_3. The signals in the proton and carbon resonance spectra were assigned using the 2D $^{13}C,^1H$–HMQC (heteronuclear multiple quantum correlation) experiment. The inverse 2D ^1H-1/^{15}N HMBC (heteronuclear multiple bond correlation) technique through the long-range spin-spin coupling constants ($^nJ(^1H, ^{15}N) = 10$ Hz) was used for the accumulation of the ^{15}N signals and signal assignment in the proton and nitrogen resonance spectra.

The excitation and emission spectra of the solid samples were detected at room temperature in the visible spectral range using a PerkinElmer LS-55 spectrometer.

X-ray structure analyses of the single crystals of compounds **I** and **II** were carried out on a Bruker Apex II diffractometer equipped with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [11]. An empirical absorption correction was applied for compound **I** using the SADABS program [12]. The structures were solved by a direct method and refined by least squares first in the isotropic approximation and then in the anisotropic approximation for F^2_{hkl}. The positions of the hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. All calculations were performed using the SHELXL program package [13]. The crystallographic parameters and structure refinement parameters for compounds **I** and **II** are presented in Table 1. The geometries of the polyhedra of the metal atoms were determined using the Shape 2.1 program [14–16].

The structural data for compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1938624 and 1959680, respectively).

The X-ray diffraction analyses (XRD) of the finely crystalline samples of compounds **I** and **II** were performed on a Bruker D8 Advance diffractometer

Table 1. Crystallographic parameters and structure refinement details for compounds **I** and **II**

Parameter	Value	
	I	**II**
FW	427.46	616.48
T, K	150(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	7.8517(2)	7.7061(4)
b, Å	18.5145(5)	16.5248(8)
c, Å	8.8399(2)	7.2898(5)
β, deg	111.5840(10)	96.404(2)
V, $Å^3$	1194.95(5)	922.50(9)
Z	4	2
ρ_{calc}, g cm^{-3}	2.376	2.219
μ, mm^{-1}	1.746	5.567
θ, deg	2.71–28.99	2.47–30.58
T_{min}/T_{max}	0.5706/0.7461	
Number of measured reflections	13030	12140
Number of independent reflections	3144	2814
Number of reflections with $I > 2\sigma(I)$	2939	1828
R_{int}	0.0228	0.1266
Number of refined parameters	163	134
GOOF	1.023	0.957
R_1, wR_2 ($I > 2\sigma(I)$)	0.0195, 0.0396	0.0562, 0.1136
R_1, wR_2 (all data)	0.0218, 0.0404	0.0947, 0.1136
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å ^{3}	−0.899/0.881	−1.640/0.822

(CuK_α, Ni filter, LYNXEYE detector, reflection geometry).

RESULTS AND DISCUSSION

The study of the products of the reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with Abp revealed a substantial influence of the solvent on their compositions and structures. The coordination polymer $[Cd(Abp)(NO_3)_2(H_2O)]_n$ (**I**) was synthesized using a toluene–acetonitrile (1 : 1) mixture. The mononuclear compound $[Cd(Abp)_2(NO_3)_2(H_2O)_2]$ (**II**) is formed in acetonitrile.

An analysis of the ^1H, $^{13}C\{H\}$, and ^{15}N NMR spectra of complex **I** in CD_3CN shows that some of them change appreciably upon the coordination of the organic ligand to the Cd(II) atom (Fig. 1, Table 2) as for the Ag(I) complexes with lutidines [17]. For example, the signal of the protons of the NH_2 group undergoes a downfield shift by 0.58 ppm. The lowest changes in the shifts of the CH protons (from −0.09 to 0.17 ppm) are observed in the ^1H NMR spectra. The coordination of 2-amino-5-bromopyridine results in the upfield shift of the signals of the ring protons in position 6 by 0.09 ppm only. At the same time, the maximum downfield shift is observed for the CH protons of the ring in position 3. Interestingly, the spin-spin coupling constant between the protons in positions 3 and 4 somewhat increases (by 0.2 Hz) upon the coordination of the ligand. Possibly, this is related to some increase in the electronegativity of the nitrogen atom of the pyridine ring when binding to the Cd(II) ion. This is confirmed by an increase in $^3J_{H-H}$ for positions 3 and 4 of pyridine by 0.4 Hz upon protonation [18]. The shift of the signals in the ^{13}C NMR spectrum upon complex formation is somewhat higher, namely, from −1.6 to 2.7 ppm, depending on the arrangement of the carbon nucleus. The highest downfield shift upon the coordination of the ligand is observed for the carbon atoms of the ring in positions 3 (2.7 ppm) and 4 (2.3 ppm). Almost no changes in the $^{13}C\{H\}$ NMR spectrum are observed on going to the complex with the carbon atoms in positions 2 and 5.

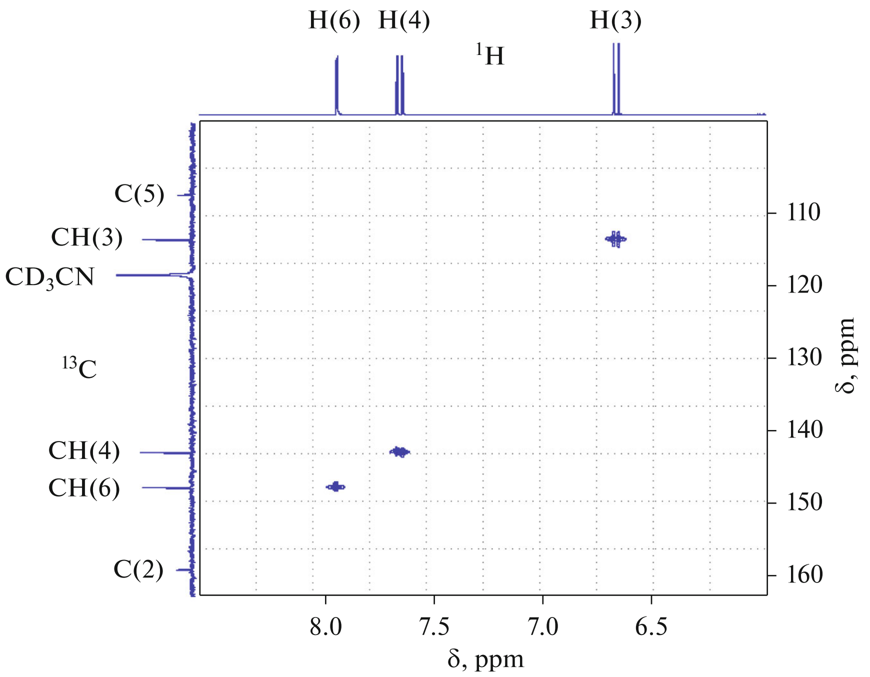


Fig. 1. 2D $^{1}H-^{13}C$ NMR spectrum (HMQC, long range) of a solution containing the 2-amino-5-bromopyridine complex with $Cd(NO_3)_2$ in CD_3CN.

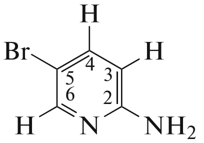
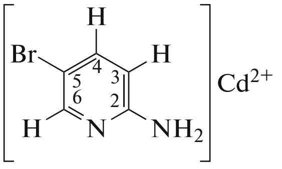
Much more considerable changes are observed in the ^{15}N NMR spectra: the signal of the coordinated nitrogen atom of the pyridine ring undergoes an upfield shift by 37 ppm compared to the corresponding signal in the spectrum of the free ligand. As in the silver complexes with lutidines, this is explained by a change in the local paramagnetic contribution upon the coordination of 2-amino-5-bromopyridine to the cadmium atom due to the lone electron pair of the nitrogen atom of the pyridine ring.

Selected bond lengths and bond angles in the structures of compounds **I** and **II** are presented in Table 3. An analysis of these values showed that they lied in the range of values standard for each type of bonds.

The coordination polyhedron of the octacoordinated central cadmium atom Cd(1) (CdO_7N) in the structure of compound **I** is a triangular dodecahedron (D_{2d}, $S_Q(P) = 4.703$) consisting of three bidentate nitro groups and monodentate ligands Abp and water (Fig. 2). The oxygen atoms of the axial nitro groups (O(41a) and O(42)) are maximally remote from the cadmium atom. These oxygen atoms are bridging in the polymeric structure of the studied compound. This arrangement of the bridging groups leads to the ribbon-like structure of the whole polymer chain at which the cadmium atoms lie in the same plane and the atoms of the nitro groups only insignificantly shift from this plane. The pyrimidine cycle is unfolded by 45.35° relative to this plane, and the N(1) nitrogen atom lies directly on the plane. The plane formed by the oxygen atom of the water molecule and free nitro group is nearly perpendicular to the base plane of the polymeric structure (the angle between the planes is 81.05°). This geometric structure and several centers of hydrogen bonding result in the situation where the polymeric ribbons are bonded to each other by O–H...O hydrogen bonds from one side and by N–H...O hydrogen bonds from another side (Figs. 3a, 3b; Table 4). In addition, the crystal structure of the studied compound is additionally stabilized by the CH...O interactions, π...π interactions between the pyridine cycles (the distance between the centers of the interacting cycles is 4.3912(14) Å, the angle between the planes is 0.00(11)°, and the distance from the center of one cycle to the plane of another cycle is 3.3553(9) Å), and Br...O interactions involving the oxygen atom of water (the Br...O distance is 3.4070(50) Å, and the C–Br...O angle is 148.71(7)°).

Complex **II** is a mononuclear molecule in which the Cd(1) atom is arranged in the inversion center. The coordination polyhedron CdO_4N_2 corresponds to an octahedron (O_h, $S_Q(P) = 2.150$) and is formed by four oxygen atom of two water molecules and two NO_3 groups and two nitrogen atoms of two Abp molecules (Fig. 4, selected bond lengths and angles are presented in Table 3). The same ligands are arranged in the *trans* position relative to each other. Hydrogen bonds are formed between the nitrogen atom of the NH_2 group and the oxygen atom of the water molecule and between the hydrogen atoms of the water molecule and the oxygen atoms of the NO_3 group (Fig. 4a,

Table 2. Parameters of the NMR spectra of solutions of 2-amino-5-bromopyridine and its complex with $Cd(NO_3)_2$ in CD_3CN

Compound	Atoms and groups	^1H NMR, ppm (relative to TMS)		^{13}C NMR, ppm (relative to TMS)		^{15}N NMR, ppm (relative to NH_3(liq))	
	2-C			159.3			
	5-C			107.6			
	3-CH	6.48		110.9			
	4-CH	7.51		140.6			
	6-CH	8.03		149.3			
	NH_2	5.05					
	1-N					274	
	^3J (3,4)	8.8 Hz					
	^3J (3,6)	0.7 Hz					
	^3J (4,6)	2.6 Hz					
			Δδ*		Δδ		Δδ
	2-C			159.0	–0.3		
	5-C			107.4	–0.2		
	3-CH	6.65	0.17	113.6	2.7		
	4-CH	7.65	0.14	142.9	2.3		
	6-CH	7.94	–0.09	147.7	–1.6		
	NH_2	5.63	0.58				
	1-N					237	–37
			Δν**				
	^3J (3,4)	9.0 Hz	0.2 Hz				
	^3J (3,6)	0.7 Hz	0.0 Hz				
	^3J (4,6)	2.5 Hz	–0.1 Hz				

* Δδ = δ (complex) – δ (ligand), ppm; ** Δν = $^3J_{H-H}$ (complex) – $^3J_{H-H}$ (ligand), Hz.

Table 4). In the crystal, the molecules of the complex form a supramolecular layer parallel to the *ac* plane due to hydrogen bonds between the water molecules and oxygen atoms of the NO_3 groups (Fig. 4b, Table 4). The crystal structure of the studied compound is additionally stabilized by the NH...Br and CH...O interactions, which favor the binding of the layers into a three-dimensional network (Table 4).

Since the structure of the ligand plays one of the key structure forming roles in the properties of the complex, in particular, with the Cd(II) ions, we examined the structure of Abp in both the organic compounds and complexes of some *d* metals. An analysis of the CCDC data revealed 22 structures of 2-amino-5-bromopyridine in which aminopyridine is not bound to the metal atom and eight structures in which aminopyridine acts as a ligand. A comparison of the bond lengths inside the pyridine cycle showed that the formation of the complexes resulted in some increase in the C–N(H_2) and C(N)–C(Br) bond lengths (corresponding to C(2)–N(2) and C(5)–C(6) in the structure of compound **I** and C(1)–N(3) and

Table 3. Selected bond lengths (Å) and bond angles (deg) in compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Cd(1)–N(1)	2.2570(16)	O(32)Cd(1)O(43)	76.37(6)
Cd(1)–O(1)	2.2663(14)	N(1)Cd(1)O(31)	89.75(6)
Cd(1)–O(31)	2.5149(16)	O(1)Cd(1)O(31)	149.13(5)
Cd(1)–O(32)	2.4126(19)	O(41)Cd(1)O(31)	75.66(5)
Cd(1)–O(41)	2.3830(13)	O(32)Cd(1)O(31)	51.55(5)
Cd(1)–O(42)	2.5930(14)	O(43)Cd(1)O(31)	113.61(5)
Cd(1)–O(41*A*)	2.5436(13)	N(1)Cd(1)O(41)	84.76(5)
Cd(1)–O(43)	2.4538(16)	O(1)Cd(1)O(41)	87.55(5)
N(2)–C(2)	1.347(3)	O(41)Cd(1)O(41)	128.909(15)
C(5)–C(6)	1.365(3)	O(32)Cd(1)O(41)	72.45(5)
		II	
Cd(1)–N(2)	2.319(4)	N(2)–C(5)	1.355(6)
Cd(1)–O(3)	2.474(6)	N(3)–C(1)	1.347(7)
Cd(1)–O(1*w*)	2.365(4)	C(2)–C(3)	1.365(8)
N(2)–C(1)	1.348(6)		
Angle	ω, deg	Angle	ω, deg
		I	
N(1)Cd(1)O(1)	93.10(5)	O(43)Cd(1)O(41)	51.39(4)
N(1)Cd(1)O(41)	146.05(5)	O(31)Cd(1)O(41)	123.32(5)
O(1)Cd(1)O(41)	85.18(5)	N(1)Cd(1)O(42)	95.06(5)
N(1)Cd(1)O(32)	93.14(7)	O(1)Cd(1)O(42)	77.46(5)
O(1)Cd(1)O(32)	158.39(5)	O(41)Cd(1)O(42)	51.41(4)
O(41)Cd(1)O(32)	100.83(6)	O(32)Cd(1)O(42)	122.50(5)
N(1)Cd(1)O(43)	136.13(5)	O(43)Cd(1)O(42)	126.73(5)
O(1)Cd(1)O(43)	84.83(5)	O(31)Cd(1)O(42)	71.66(5)
O(41)Cd(1)O(43)	77.59(4)	O(41)Cd(1)O(42)	164.98(5)
		II	
N(2)Cd(1)O(1*w*)	89.50(14)	O(1*w*)Cd(1)O(3)	70.35(15)
N(2)Cd(1)O(3)	87.49(14)		

C(2)–C(3); in the nonmetallic compounds, the bond lengths lie in ranges of 1.313–1.346 and 1.335–1.366 Å, and those in the complexes lie in ranges of 1.334–1.373 and 1.353–1.377 Å, respectively). The M...N bond length is determined by the metal nature.

Three coordination modes of the NO_3 groups are observed: monodentate, symmetric bidentate, and asymmetric bidentate [19]. The differences in the distances metal–oxygen atoms of NO_3^- determine the coordination mode. The monodentate coordination mode is observed for the difference higher than 0.6 Å, the symmetric bidentate mode is observed for the difference lower than 0.3 Å, and the asymmetric bidentate mode takes place in the case of intermediate values of the difference. The NO_3 groups in the presented structures of compound **I** are symmetric bidentate, whereas they are monodentate in the structure of compound **II**. In addition, one of the NO_3 groups in compound **I** exhibits the bridging tridentate properties coordinating to different cadmium ions due to three

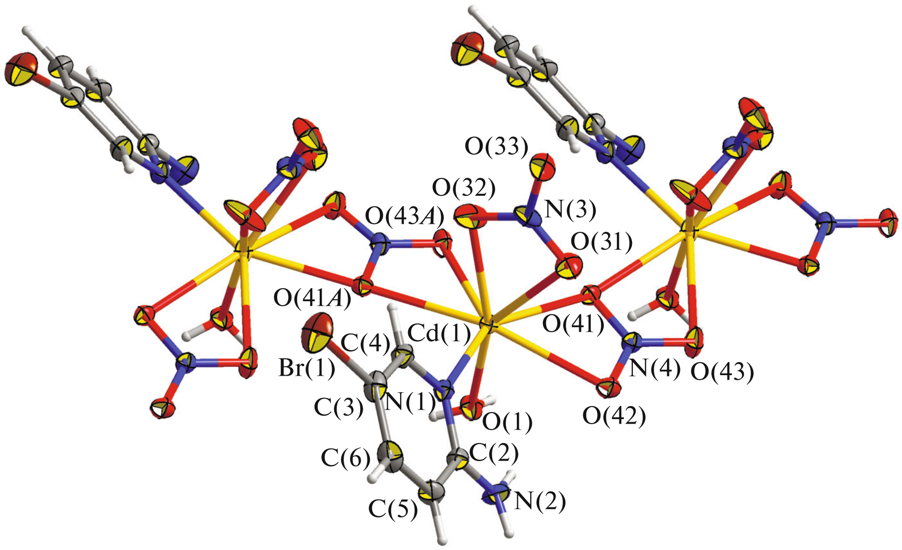


Fig. 2. Fragment of the polymer chain of compound **I**.

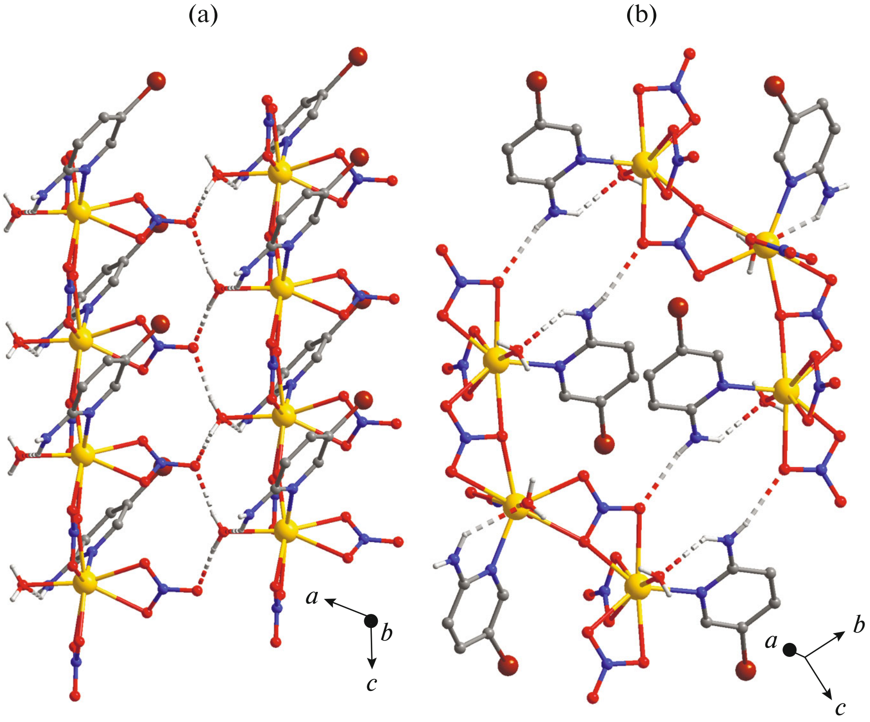


Fig. 3. Hydrogen bonds (a) O–H...O and (b) N–H...O in the crystal of compound **I**.

oxygen atoms of NO_3^- forming the polymeric structure. Interestingly, this NO_3 group is attached to the metal ions via the bidentate chelate mode.

The structural wholeness and phase purity of the finely crystalline samples of compounds **I** and **II** formed as the major reaction products were confirmed by the XRD method (Fig. 5).

The excitation and emission spectra of the synthesized compounds **I** and **II** and neutral ligand Abp were studied (Fig. 6). Pyridine and its derivatives, as well as the simple cadmium compounds, for example, halides, exhibit no luminescence properties. However, upon excitation all coordination cadmium compounds containing the pyridine ligands exhibit an intense fluorescence at the frequency corresponding

Table 4. Parameters of hydrogen bonds in the crystals of compounds **I** and **II**

D–H...A	Distance, Å			Angle D–H...A, deg	Symmetry element of atom A ($^{\#}$)
	D–H	H...A	D...A		
			I		
O(1)–H(11)...O(33$^{\#}$)	0.75	2.04	2.774(2)	168	$x - 1, y, z$
O(1)–H(12)...O(33$^{\#}$)	0.82	1.99	2.800(2)	171	$x - 1, -y + 3/2, z - 1/2$
N(2)–H(21)...O(1)	0.91	2.32	3.079(2)	141	
N(2)–H(21)...O(42)	0.91	2.51	3.136(2)	127	
N(2)–H(22)...O(42$^{\#}$)	0.80	2.23	3.007(2)	166	$-x, -y + 1, -z$
C(4)–H(4*A*)...O(32)	0.95	2.57	3.236(3)	128	
C(6)–H(6*A*)...O(31)	0.95	2.49	3.371(3)	155	$-x + 1, -y + 1, -z + 1$
			II		
O(2)...O(1*w*)			2.881(6)		
N(3)–H(3*A*)...O(1*w*)	0.90	2.15	2.953(7)	119	
O(1*w*)...O(1$^{\#}$)			3.223(6)		$x, y, z - 1$
O(1*w*)...O(2$^{\#}$)			2.909(8)		$x, y, z - 1$
O(1*w*)...O(1$^{\#}$)			2.896(6)		$-x, 1 - y, 1 - z$
C(3)–H(3C)...O(2$^{\#}$)	0.93	2.53	3.341(6)	145	
C(5)–H(5C)...O(3$^{\#}$)	0.93	2.49	3.130(7)	126	$-x + 1, -y + 1, -z + 1$
N(3)–H(3*B*)...Br(1$^{\#}$)	0.90	2.98	3.527(5)	121	$x - 1, -y + 1/2, z - 1/2$

to the absorption band of the ligand [20, 21]. Compounds **I** (λ_{exc} = 390 nm) and **II** (λ_{exc} = 405 nm) exhibit an emission in a range of 430–690 nm, whereas ligand Abp (λ_{exc} = 236 nm) emits in a range of 350–540 nm; i.e., upon the coordination to the metal ion, the luminescence of Abp shifts to the long-wavelength spectral range. According to the literature data, the luminescence properties of the cadmium and zinc compounds are induced by the intraligand π–π^* transitions of the aromatic fragments of the organic molecules. The photoluminescence behavior is associated with the local environment of the metal ion and the ligand–metal ratio [22, 23]. In spite of the same nature of the N and O atoms in the coordination spheres of cadmium, a slight difference in the spectra of compounds **I** and **II** can be related, most likely, to different coordination numbers of the metal ion (coordination number 8 and 6 in compounds **I** and **II**, respectively).

Thus, new coordination polymer $[Cd(Abp)(NO_3)_2(H_2O)]_n$ (**I**) and monomer $[Cd(NO_3)_2(Abp)_2(H_2O)_2]$ (**II**) are presented. The structures of both compounds were determined by single-crystal X-ray structure analysis and characterized by chemical analysis, XRD, and photoluminescence properties. Compound **I** in a CD_3CN solution was additionally characterized by the NMR method. The environment of the cadmium(II) ion (coordination number 8) in compound **I** is a triangular dodecahedron. In compound **II**, Cd has an octahedral environment. The polymer structure in compound **II** is determined by the bridging nitrate groups. The NMR study of compound **I** in a CD_3CN solution showed that the highest changes were observed in the ^{15}N NMR spectra of coordinated 2-amino-5-bromopyridine. The emission bands in the luminescence spectra of compounds **I** and **II** lie in a range of 430–690 nm.

ACKNOWLEDGMENTS

The compounds were synthesized and studied in the framework of the state task of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences) in the sphere of basic research. The single-crystal X-ray structure analysis, XRD, luminescence studies, and elemental analysis were carried out using the equipment of the Center for Collective Use “Physical Methods of Investigation” at the Kurnakov Institute of General and Inor-

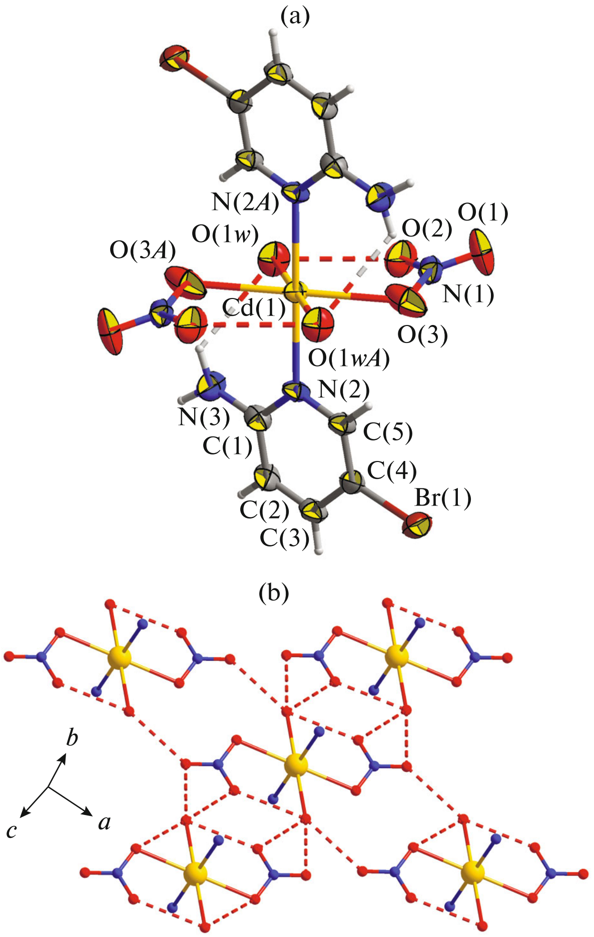


Fig. 4. (a) Molecular structure of compound **II** (intramolecular hydrogen bonds are shown by dashed lines, ellipsoids of 50% probability) and (b) the fragment of the supramolecular layer in the crystal of compound **II** formed by the hydrogen bonds $O(H_2O)...O(NO_3)$ (hydrogen atoms and 2-NH_2-5-Br-pyridine molecules are omitted).

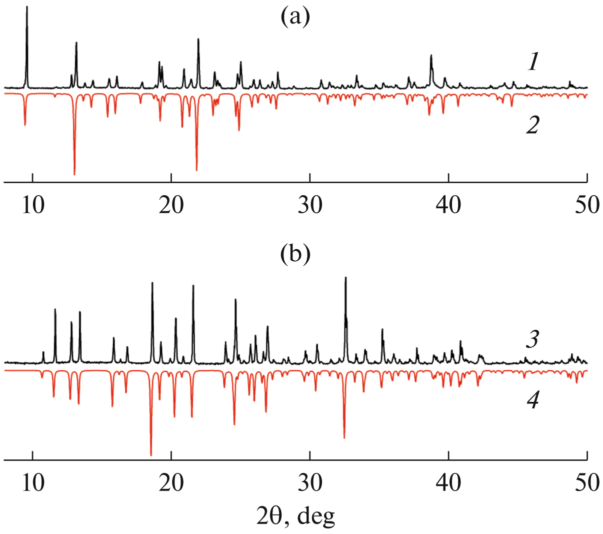


Fig. 5. Powder XRD patterns for the samples of compounds (a, *1*) **I** and (b, *3*) **II** and those theoretically calculated using the X-ray structure data (a, curve *2* and b, curve *4*, respectively).

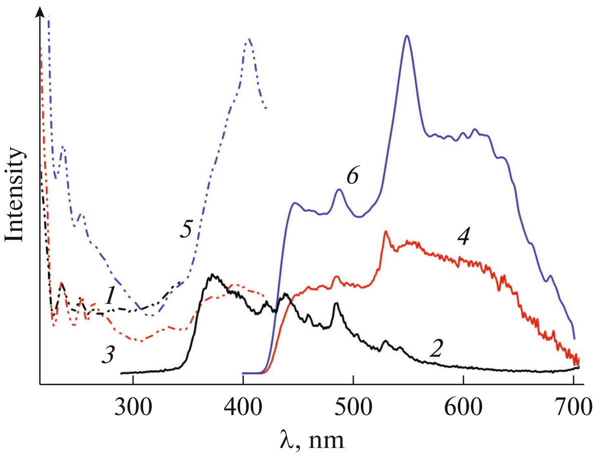


Fig. 6. Excitation (λ_{em} = 372 (*1*), 480 (*3*), and 550 nm (*5*)) and emission (λ_{exc} = 236 (*2*), 390 (*4*), and 405 nm (*6*)) spectra for the solid samples of 2-NH_2-5-Br-pyridine, **I**, and **II**, respectively, at room temperature.

ganic Chemistry (Russian Academy of Sciences) in the sphere of basic research.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Ho, C.-L. and Wong, W.-Y., *Coord. Chem. Rev.*, 2011, vol. 255, p. 2469.
2. Leong, W.L. and Vittal, J.J., *Chem. Rev.*, 2011, vol. 111, p. 688.
3. Koshima, H., Hamada, M., Yagi, I., and Uosaki, K., *Cryst. Growth. Des.*, 2001, vol. 1, p. 467.
4. Tomaru, S., Matsumoto, S., Kurihara, T., et al., *Appl. Phys. Lett.*, 1991, vol. 58, p. 2583.
5. Luque, A., Sertucha, J., Lesama, L., et al., *J. Chem. Soc., Dalton Trans.*, 1997, p. 847.
6. Mojdekaulous, S., Khalaji, A.D., and Xu, D., *Jpn. Soc. Analyt. Chem.*, 2007, vol. 23, p. x189.
7. Zhou, W.-W., Zhao, W., Wei, B., et al., *Inorg. Chim. Acta*, 2012, vol. 386, p. 17.
8. Futriani, Hausongnern, K., Leesakul, N., et al., *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2013, vol. 69, p. m302.
9. Zhou, W.-W., Zhao, W., Zhao, X., et al., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 2013, vol. 43, p. 1171.
10. Seth, S.K., *CrystEngComm*, 2013, vol. 15, p. 1772.
11. *SMART (control) and SAINT (integration) Software. Version 5.0*, Madison: Bruker AXS, Inc., 1997.
12. Krause, L., Herbst-Irmer, R., Sheldrick, G.M., and Stalke, D., *J. Appl. Crystallogr.*, 2015, vol. 48, p. 3.
13. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.

14. Cirera, J., Alemany, P., and Alvarez, S., *Chem.-Eur. J.*, 2004, vol. 10, p. 190.
15. Casanova, D., Llunell, M., Alemany, P., and Alvarez, S., *Chem.-Eur. J.*, 2005, vol. 11, p. 1479.
16. Avnir, D., Llunell, M., and Pinsky, M., *New J. Chem.*, 2002, vol. 26, p. 996.
17. Sakharov, S.G., Kovalev, V.V., Gorbunova, Yu.E., and Kokunov, Yu.V., *Russ. J. Coord. Chem.*, 2013, vol. 39, p. 187. https://doi.org/10.1134/S1070328413020061
18. *Tables of Spectral Data for Structue Determination of Organic Compounds*, Berlin: Springer, 1983, p. H275.
19. Kleywegt, J.G.J., Weismeijer, W.G.R., Van Driel, G.J., et al., *J. Chem. Soc., Dalton Trans.*, 1985, p. 2171.
20. Chattopadhyay, T., Banerjee, A., Banu, K.S., et al., *Polyhedron*, 2008, vol. 27, p. 2452.
21. Neumann, T., Germann, L.S., Mandrakovski, I., et al., *Z. Anorg. Allg. Chem.*, 2017, vol. 643, p. 1904.
22. Fu, Z.-Y., Wu, X.-T., Dai, J.-C., et al., *Eur. J. Inorg. Chem.*, 2002, p. 2730.
23. Nather, C., Jess, I., Germann, L.S., et al., *Eur. J. Inorg.Chem.*, 2017, p. 1245.

Translated by E. Yablonskaya