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Molecular and Polymeric Cadmium Nitrate Complexes with Bridging 3-Aminoquinoline: Synthesis, Structures, and Luminescence Properties

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Abstract—The reaction of $Cd(NO_3)_2{\cdot}4H_2O$ with 3-aminoquinoline (3-Aq) affords the molecular and polymeric complexes $[Cd(NO_3)_2(H_2O)(3\text{-Aq})]{\cdot}2MeCN$ (**I**) and $\{[Cd(NO_3)_2(3\text{-Aq})_2]{\cdot}MeCN\}_n$ (**II**), respectively, depending on the ratio of the reagents and composition of the medium. Compounds **I** and **II** are studied by elemental analysis, X-ray structure analysis (CIF files CCDC nos. 2015059 (**I**) and 2015060 (**II**)), X-ray diffraction analysis, and luminescence investigation. In both cases, the environment of the cadmium atom is a pentagonal bipyramid. The 3-Aq molecules of dimer **I** are bridging ligands, and the monodentate mode of binding with Cd(II) along with the indicated function is observed in the polymer. Hydrogen bonds between the H atoms of the NH_2 group and the N atom of the solvate MeCN molecule and the O atom of the NO_3 group result in the formation of a three-dimensional supramolecular network, which is additionally strengthened by intermolecular stacking interactions between the aromatic fragments of 3-Aq of the adjacent molecules. Both compounds luminesce in the red spectral range. As compared to the spectrum of free 3-Aq, the shift of the emission bands of dimer **I** and polymer **II** in this range is 93 and 38 nm, respectively.

Keywords: cadmium nitrate, 3-aminoquinoline, dimer, polymer, structure, luminescence

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INTRODUCTION

The synthesis of new coordination polymers evokes increased interest in the recent years. The main tasks in this field are the production of compounds with fruitful physical properties and construction of structure–properties relationships. The topology of the complexes depends, to a high extent, on the coordination behavior of the metal ions, the nature of the counterions, and the electronic and geometric parameters of the ligands. Therefore, the cadmium ion is of special interest, since its coordination numbers vary from 4 to 8. When choosing the organic ligand, the main attention is given to the N- and N,O-donor heterocyclic compounds, in particular, the pyridine derivatives, which is due to the stability of the formed compounds and a high probability of ligand-centered luminescence to occur.

Quinoline and its derivatives are often used for the synthesis of compounds with luminescence properties [1–3]. 3-Aminoquinoline (3-Aq) is capable of binding metal ions by both N-donor functional groups (N atoms of the heterocycle and amino group). Two joined aromatic cycles can participate in the formation of π–π-stacking interactions. The rich π system of quinoline provides conditions for the appearance of luminescence properties of coordination compounds involving quinoline. Weak noncovalent interactions (π–π stacking and hydrogen bonds) substantially affect the structure formation, solubility, thermal behavior, and electronic and optical properties of the compound. The presence of the NH_2 group and π system in the complexes with 3-Aq provides prerequisites for the formation of intermolecular interactions in crystals imparting the nonlinear optical properties to the latter.

Cadmium(II) complexes evoke increased interest because of the ability of cadmium to simultaneously form bonds with various donors exhibiting diverse coordination modes. The data on the cadmium compounds with 3-Aq are restricted by the work describing the synthesis and structure of the $[CdI_2(3\text{-Aq})_2]$ complex with the tetrahedral coordination of the cadmium ion with the 3-Aq molecules bound via the monodentate mode [4]. The $[ZnCl_2(3\text{-Aq})_2]{\cdot}H_2O$ complex has a similar structure [5]. In both cases, 3-Aq is coordinated via the heterocyclic nitrogen atom. Much more information is available for the compounds of 3-aminopyridine (3-Ampy) with cadmium ions in which 3-Ampy exhibits both the monodentate and bidentate-bridging functions coordinating to the Cd^{2+} ion by both nitrogen atoms. The character of 3-Ampy addition depends on the composition of the compound, the coordination sphere of the metal ion, and the 3-Ampy to Cd ratio in the reaction mixture.

In some coordination polymers, a change in the binding ligand to metal ratio is accompanied by a change in its dimensionality [6]. We have previously shown for the coordination polymeric compounds of cadmium nitrate with 2-amino-5-bromopyridine (Abp) [7] that a change in the Abp to Cd ratio resulted in an increase in the dimensionality of the reaction product from the binuclear complex to 1D coordination polymer.

In order to obtain more information about the synthesis and structures of the cadmium compounds with 3-Aq and to determine the factors affecting the coordination mode, we synthesized the dimeric and polymeric compounds of cadmium nitrate with 3-Aq with various metal to ligand ratios, determined their compositions and structures, and studied the luminescence spectra.

EXPERIMENTAL

The following reagents were used as received: $Cd(NO_3)_2{\cdot}4H_2O$ (reagent grade), 3-aminoquinoline (97%, Aldrich), and acetonitrile and methanol (Khimmed).

Synthesis of $[Cd(NO_3)_2(H_2O)(3\text{-Aq})]{\cdot}2MeCN$ (I). Weighed samples of $Cd(NO_3)_2{\cdot}4H_2O$ (0.68 g, 2.22 mmol) and 3-Aq (0.32 g, 2.22 mmol) were separately dissolved in 10 and 8 mL of MeCN, respectively. The solutions were mixed, heated to 30–35°C, and filtered after cooling to room temperature. The obtained filtrate was kept for 2 h under the conditions of slow crystallization of the reaction product, and the formed prismatic crystals were separated by the decantation of the liquid phase and dried in air. According to the elemental analysis data, the crystals corresponded to the composition of compound **I**.

For $C_{11}H_{13}N_5O_7Cd$

Anal. calcd., %	N, 15.92	C, 30.02	H, 2.95
Found, %	N, 15.25	C, 30.07	H, 3.07

Synthesis of $\{[Cd(NO_3)_2(3\text{-Aq})_2]{\cdot}MeCN\}_n$ (II). The reaction of cadmium nitrate with 3-Aq taken in a twofold excess and the isolation of the reaction product were carried out similarly to the procedures for compound **I**, but a mixture of acetonitrile with methanol in a volume ratio of 3 : 1 was used as the solvent. After the end of the reaction, the solution was filtered, and the filtrate was kept for 3 days under the conditions of slow solvent removal. According to the elemental analysis data, the isolated crystals corresponded to the composition of complex **II**.

For $C_{20}H_{19}N_7O_6Cd$

Anal. calcd., %	N, 17.28	C, 42.32	H, 3.37
Found, %	N, 17.28	C, 42.35	H, 3.90

X-ray structure analyses of single crystals of compounds **I** and **II** were carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [8]. A semiempirical absorption correction was applied [9]. The structure was solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined in the riding model. The calculations were performed using the SHELX-2014/2018 program package [10]. The crystallographic parameters and structure refinement details for compounds **I** and **II** are presented in Table 1. Selected bond lengths and angles are given in Table 2.

The full set of X-ray diffraction data was deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2015059 (**I**) and 2015060 (**II**); http://www.ccdc.cam.ac.uk/data_request/cif).

X-ray diffraction analyses of finely crystalline samples of compounds **I** and **II** were carried out on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector, reflection geometry).

The excitation and emission spectra of the solid samples were recorded on a Perkin-Elmer LS-55 spectrometer at room temperature in the visible spectral range.

RESULTS AND DISCUSSION

Compound **I** crystallizes in the form of a solvate with two MeCN molecules in the triclinic space group $P\bar{1}$, and the inversion center lies between two cadmium atoms bound into a binuclear molecule by two bridging 3-Aq molecules (Fig. 1a). Each cadmium atom builds up its environment (CdN_2O_5) to a pentagonal bipyramid by the coordination of two chelate NO_3^- anions and water molecules (Table 2). The equatorial positions are occupied by the O atoms of the NO_3 groups and the pyridinic N atom of the 3-Aq molecule. Hydrogen bonds are formed between the H atoms of the NH_2 group and the N atom of the solvate MeCN molecules and the O atom of the NO_3 group of the adjacent molecule of the complex (Table 2). The coordinated molecule forms two

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

Parameter	Value	
	I	**II**
Empirical formula	$C_{22}H_{26}N_{10}O_{14}Cd_2$	$C_{20}H_{19}N_7O_6Cd$
FW	879.33	565.82
T, K	150(2)	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Crystal size, mm	0.24 × 0.20 × 0.18	0.40 × 0.34 × 0.28
Color	Colorless	Colorless
a, Å	8.3365(2)	6.5810(12)
b, Å	10.4583(3)	9.2749(18)
c, Å	10.4888(3)	17.932(6)
α, deg	111.0900(10)	80.779(11)
β, deg	94.8920(10)	89.001(9)
γ, deg	112.9110(10)	87.983(10)
V, Å^3	758.41(4)	1079.6(4)
Z	1	2
ρ_{calc}, g/cm^3	1.925	1.741
μ, mm^{-1}	1.487	1.066
F(000)	436	568
Range of data collection over θ, deg	2.34–28.99	2.66–30.56
Ranges of reflection indices	$-11 \le h \le 11$, $-14 \le k \le 14$, $-14 \le l \le 14$	$-8 \le h \le 9$, $-13 \le k \le 11$, $-25 \le l \le 25$
T_{min}/T_{max}	0.410/0.494	0.608/0.746
Number of measured reflections	9191	12664
Number of independent reflections	4062	6536
Number of reflections with $I > 2\sigma(I)$	3158	6101
R_{int}	0.0214	0.0217
Number of refinement parameters	234	324
GOOF	0.996	1.080
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0220$ $wR_2 = 0.0490$	$R_1 = 0.0317$ $wR_2 = 0.0728$
R factors for all reflections	$R_1 = 0.0245$ $wR_2 = 0.0499$	$R_1 = 0.0355$ $wR_2 = 0.0744$
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	−0.531/0.475	−1.179/1.099

Table 2. Selected bond lengths (Å), angles (deg), and hydrogen bond parameters in compounds **I** and **II***

I		**II**	
Bond	*d*, Å	Bond	*d*, Å
Cd(1)–O(4)	2.2771(14)	Cd(1)–O(1)	2.466(2)
Cd(1)–O(21)	2.3969(13)	Cd(1)–O(2)	2.510(2)
Cd(1)–O(22)	2.5439(14)	Cd(1)–O(4)	2.3552(17)
Cd(1)–O(31)	2.3765(14)	Cd(1)–O(5)	2.5026(18)
Cd(1)–O(32)	2.4525(14)	Cd(1)–N(1)	2.3426(17)
Cd(1)–N(1)	2.3240(15)	Cd(1)–N(2)[a]	2.3818(19)
Cd(1)–N(4)[a]	2.3877(16)	Cd(1)–N(4)	2.419(2)
Angle	ω, deg	Angle	ω, deg
O(4)Cd(1)N(1)	108.73(5)	N(1)Cd(1)O(4)	140.91(6)
O(4)Cd(1)O(31)	89.10(5)	N(1)Cd(1)N(2)[a]	92.80(6)
N(1)Cd(1)O(31)	127.63(5)	O(4)Cd(1)N(2)[a]	89.27(6)
O(4)Cd(1)N(4)[a]	160.95(6)	N(1)Cd(1)N(4)	89.71(7)
N(1)Cd(1)N(4)[a]	88.52(5)	O(4)Cd(1)N(4)	84.81(6)
O(31)Cd(1)N(4)[a]	86.43(5)	N(2)Cd(1)N(4)[a]	173.21(6)
O(4)Cd(1)O(21)	82.83(5)	N(1)Cd(1)O(1)	95.95(6)
N(1)Cd(1)O(21)	99.23(5)	O(4)Cd(1)O(1)	122.05(6)
O(31)Cd(1)O(21)	132.32(5)	N(2)Cd(1)O(1)[a]	100.32(7)
N(4)Cd(1)O(21)[a]	86.52(5)	N(4)Cd(1)O(1)	85.68(7)
O(4)Cd(1)O(32)	80.53(5)	N(1)Cd(1)O(5)	88.06(6)
N(1)Cd(1)O(32)	80.85(5)	N(2)Cd(1)O(5)[a]	86.56(6)
N(4)Cd(1)O(32)[a]	111.04(5)	N(4)Cd(1)O(5)	87.23(7)
O(21)Cd(1)O(32)	162.41(5)	O(1)Cd(1)O(5)	171.83(6)
O(4)Cd(1)O(22)	81.61(5)	N(1)Cd(1)O(2)	147.00(6)
N(1)Cd(1)O(22)	149.16(5)	O(4)Cd(1)O(2)	71.88(6)
O(31)Cd(1)O(22)	80.18(5)	N(2)Cd(1)O(2)[a]	90.90(7)
N(4)Cd(1)O(22)[a]	79.38(5)	N(4)Cd(1)O(2)	90.42(7)
O(32)Cd(1)O(22)	129.96(4)	O(5)Cd(1)O(2)	124.91(6)
d(H...A), *d*(D...A), ∠DHA			
O(4)–H...O(21)[b]	2.18, 2.901, 176.7	N(2)–H...N(3)[b]	2.30, 3.172, 173.5
O(4)–H...O(33)[c]	2.00, 2.785, 167.6	N(2)–H...N(1S)	2.19, 3.001, 171.8
N(4)–H...O(23)[d]	2.10, 2.948, 159.6	N(4)–H...O(2)[c]	2.42, 3.236, 158.0
N(4)–H...N(13)	2.29, 3.093, 166.9		

* Symmetry codes: [a] $1 - x, 1 - y, 1 - z$; [b] $1 - x, -y, -z$, [c] $1 - x, -y, 1 - z$, [d] $1 + x, 1 + y, 1 + z$ (**I**); [a] $1 + x, y, z$; [b] $1 - x, 1 + y, z$; [c] $1 - x, y, z$ (**II**).

hydrogen bonds with the O atoms of the NO_3 groups of the adjacent molecules of the complex. This hydrogen bonding results in the formation of a three-dimensional supramolecular network, which is additionally strengthened by intermolecular stacking interactions between the aromatic fragments of 3-Aq of the adjacent molecules (the distance between the centroids of the pyridine and benzene rings is 3.686 Å, and the shortest distance is C(4)...C(10) ($2 - x, 1 - y, 1 - z$) 3.346 Å (Fig. 1b).

Compound **II** crystallizes as a solvate with one MeCN molecule in the triclinic space group $P\bar{1}$. The

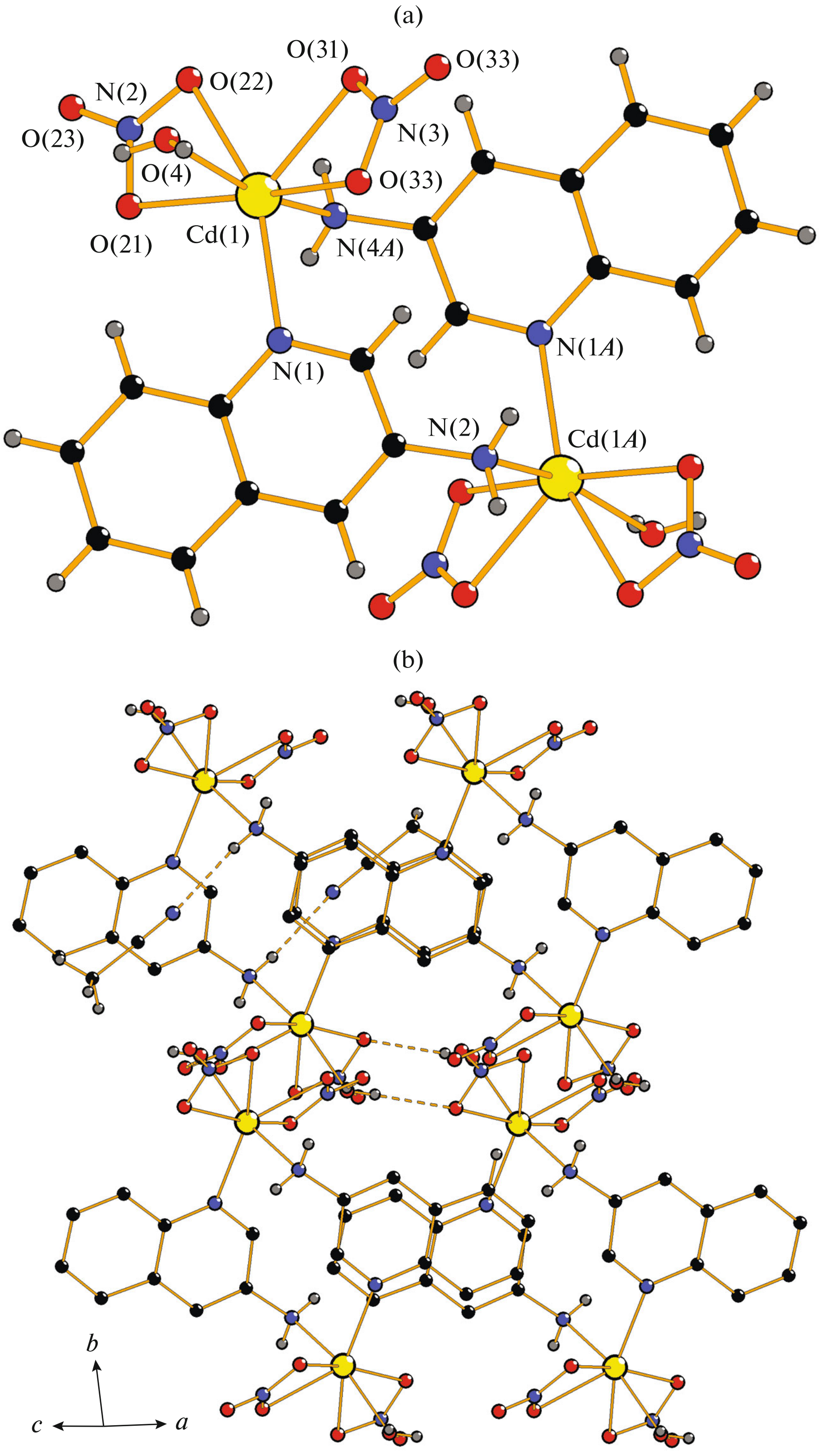

Fig. 1. (a) Molecular structure and (b) the fragment of the crystal packing of complex **I**. The hydrogen atoms at the carbon atoms of 3-Aq are omitted, and the intermolecular hydrogen bonds are shown by dash.

inversion center is localized between the Cd atoms of two polymeric chains. The elementary unit of the coordination polymer is the mononuclear fragment consisting of two chelate anions NO_3^-, the monodentate molecule 3-Aq coordinated by the atom of the NH_2 group, and two N atoms of two bridging molecules 3-Aq (Fig. 2a, Table 2). The geometry of the environment of the Cd atom (CdN_3O_4) corresponds to a pentagonal bipyramid with the O atoms and the N atom of the pyridine cycle in the equatorial positions.

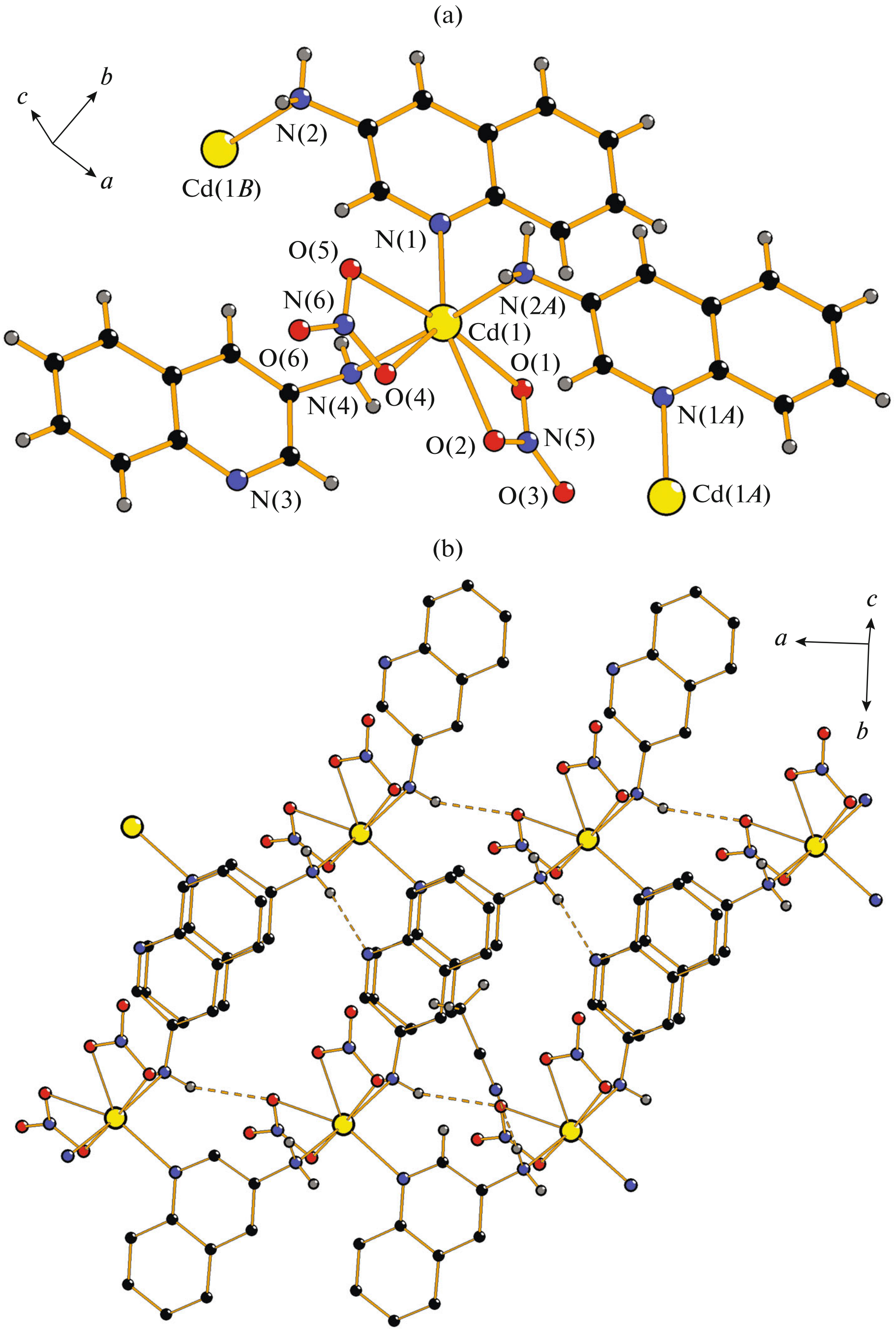

Fig. 2. (a) Fragments of the polymeric chain and (b) crystal packing of complex **II**. The hydrogen atoms at the carbon atoms of 3-Aq are omitted, and the intermolecular hydrogen bonds are shown by dash.

The H atoms of the NH_2 group of the bridging Aq molecule are involved in the formation of hydrogen bonds with the N atoms of the solvate MeCN molecule and the uncoordinated pyridine cycle of the adjacent chain (Table 2). The intramolecular hydrogen bond between the H atom of the NH_2 group of the 3-Aq molecule coordinated via the monodentate mode and the O atom of the NO_3 group is also observed. The chains are additionally linked to each other by intermolecular stacking interactions between the aromatic fragments of 3-Aq (the distances between the centroids of the aromatic rings are 3.587–3.778 Å, and the shortest distance is N(3)...C(9) (x, $-1 + y$, z) 3.366 Å).

The phase purity of compounds **I** and **II** was confirmed by X-ray diffraction analysis (Fig. S1).

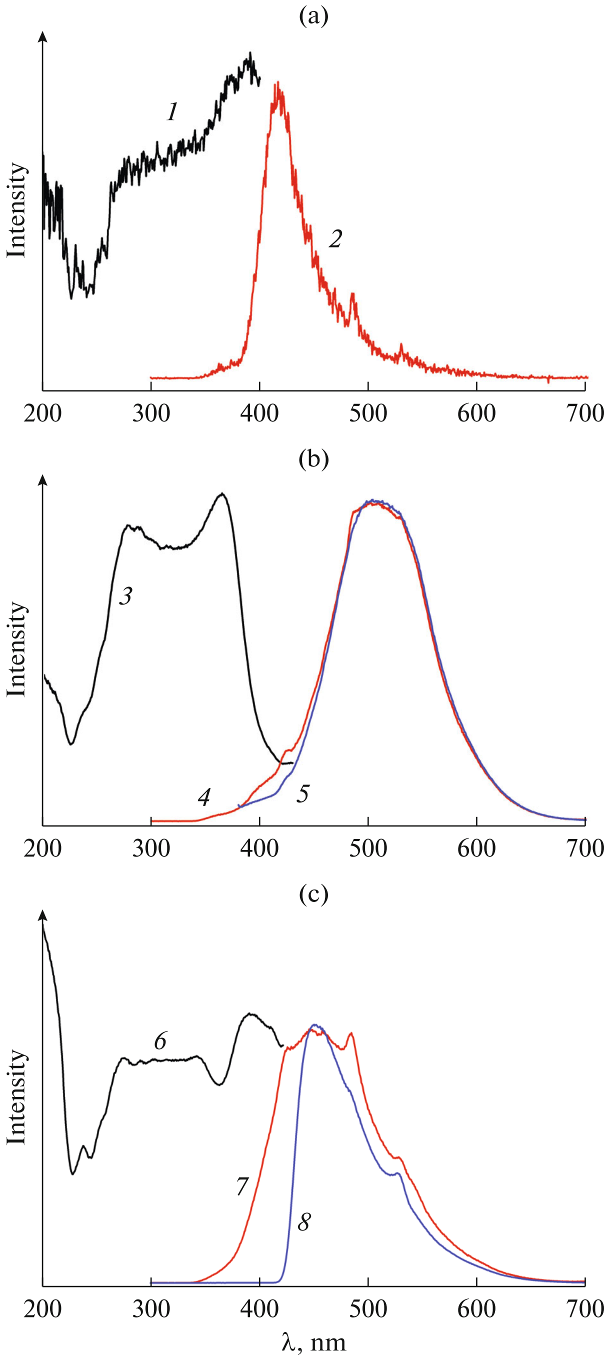

Fig. 3. Excitation (λ_{em} = (*1*) 417, (*3*) 510, and (*6*) 455 nm) and emission (λ_{exc} = (*2*) 280, (*4*) 280, (*5*) 365, (*7*) 275, and (*8*) 390 nm) spectra of the solid samples of (a) 3-Aq, (b) **I**, and (c) **II** at room temperature.

The emission and excitation spectra of the 3-Aq ligand and complexes **I** and **II** are shown in Fig. 3. The emission spectra of the samples contain intense broad nonsymmetric lines: 417 nm (λ_{exc} = 280 nm) for 3-Aq, 510 nm (λ_{exc} = 280 and 365 nm) for compound **I**, and 455 nm (λ_{exc} = 275 and 390 nm) for compound **II**. The emission bands are shifted to the red range by 93 and 38 nm for compounds **I** and **II**, respectively, compared to those of free 3-Aq. A similar red shift was observed in the emission spectra of the d^0-metal compounds with 8-aminoquinoline [11–13]. The emission is related to intraligand π–π transitions. The shift of the luminescence band to the red range in the spectrum of dimer **I** is higher than that for polymer **II**. Although the coordination number of the Cd ion is seven in both cases, the environments differ: in dimer **I** the coordination sites at the Cd ion are occupied by the amino groups of 3-Aq, and in polymer **II** these sites are occupied by one NH_2 group of 3-Aq and one O atom of the water molecule.

Thus, two new coordination compounds of cadmium nitrate in which 3-Aq performs the bridging function were synthesized by the reaction of cadmium nitrate with 3-aminoquinoline at various ratios of the reacting components and varied compositions of the solvents. The synthesized compounds represent the binuclear complex (L : Cd = 1 : 1) and 1D polymer (L : Cd = 2 : 1). In both cases, the coordination number of the cadmium atoms is seven, and the geometry of the polyhedra corresponds to a pentagonal bipyramid. The nitrate anions are coordinated to the cadmium atoms via the chelate mode. Both compounds luminescence in the red spectral range.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

SUPPLEMENTARY INFORMATION

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