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Dedicated to Academician Yu.A. Zolotov in the year of his 90th birthday

Coordination Polymers of Cadmium with Di(pyrazol-1-yl)alkane-4,4'-dicarboxylic Acids: Synthesis, Crystal Structures, and Luminescence Properties

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Abstract—Coordination polymers of cadmium(II) with the di(pyrazol-1-yl)alkane derivatives, bis(3,5-dimethylpyrazol-1-yl)methane-4,4'-dicarboxylic acid (H_2L^1) and 1,3-bis(pyrazol-1-yl)propane-4,4'-dicarboxylic acid (H_2L^2), are synthesized. The crystal structures of the products are determined by X-ray diffraction (CIF files CCDC nos. 2172853 (**I**) and 2172854 (**II**)). The Cd^{2+} ions and dicarboxylic acid with one methylene group between the pyrazole cycles form a three-dimensional coordination polymer with a single mutual intergrowing of coordination networks, whereas three methylene groups result in the formation of a two-dimensional coordination polymer, the layers of which are linked by hydrogen bonds involving water molecules in the coordination sphere of the Cd^{2+} ions. The luminescence spectra of the synthesized coordination polymers exhibit two bands: with the local intraligand excitation and with the metal–ligand charge transfer.

Keywords: coordination polymers, cadmium, pyrazole, dicarboxylic acids, luminescence

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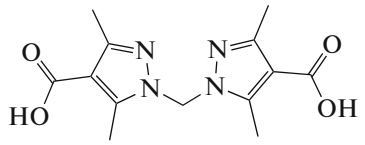
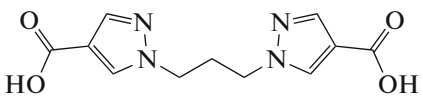
INTRODUCTION

Di(pyrazol-1-yl)alkanes are neutral bidentate ligands, the coordination chemistry of which was studied in rather detail, and the corresponding complexes with the majority of metal ions were characterized [1]. At the same time, the presence of only two nitrogen atoms in these ligands results, as a rule, in the formation of molecular complexes or nonporous coordination polymers [2]. The insertion into the pyrazole cycles of functional groups with donor atoms capable of forming additional coordination bonds with metal ions should substantially enlarge the variety of possible coordination polymers with these ligands. The carboxyl derivatives of pyrazole were successfully applied earlier for the synthesis of porous metal-organic frameworks with valuable sorption, catalytic, and luminescence properties [3–5]. However, the study of the coordination chemistry of the dicarboxyl derivatives of di(pyrazol-1-yl)alkanes is at the very beginning now and was restricted up to recently by the di(pyrazol-1-yl)methane derivatives [6, 7]. We recently developed procedures for the synthesis of the 4,4'-dicarboxyl derivatives of di(pyrazol-1-yl)alkanes with different lengths of the polymethylene linkers and bearing substituents in the pyrazole cycles [8, 9].

In this work we report the first examples of the synthesis of metal-organic frameworks with two of such ligands: bis(3,5-dimethylpyrazol-1-yl)methane-4,4'-dicarboxylic acid (H_2L^1) and 1,3-bis(pyrazol-1-yl)propane-4,4'-dicarboxylic acid (H_2L^2) (Scheme 1).



H_2L^1



H_2L^2

Scheme 1.

EXPERIMENTAL

Commercially available solvents and reagents (reagent grade) were used as received. Ligands H_2L^1 and H_2L^2 were synthesized using earlier developed procedures [8]. The starting di(pyrazol-1-yl)alkanes were synthesized as described previously [10, 11]. IR absorption spectra in KBr pellets in a range of 4000–400 cm^{-1} were recorded on a VERTEX 80 FT-IR spectrometer. Elemental analysis was carried out on a Vario MICRO cube CHNS analyzer. Powder X-ray diffraction patterns were detected on a Bruker D8 ADVANCE diffractometer (CuK_α radiation). Thermogravimetric (TG) analysis was carried out on a NETZSCH TG 209 F1 thermal analyzer with the linear heating of the samples at a rate of 10°C/min in a helium atmosphere.

Photoluminescence and luminescence excitation spectra and photoluminescence lifetimes were obtained on a Fluorolog-3 spectrofluorimeter (Horiba Jobin Yvon) with a cooled PC177CE-010 photon registration module equipped with an R2658 photoelectron multiplier. The instrument was equipped with a system for the measurement of fluorescence lifetimes based on the technology of time-correlated single photons counting (TCSPC) for measuring the emission decay kinetics. The instrument was completed with a set of solid state lasers of various wavelengths for measuring lifetimes in the nanosecond range.

X-ray diffraction (XRD). The crystallographic data for compounds **I** and **II** were obtained at 170 K on an Agilent Xcalibur automated diffractometer equipped with an Atlas S2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode with an increment of 0.5°). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the CrysAlisPro software [12]. The crystal structures were solved using the SHELXT software [13] and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELXL software [14]. The crystallographic data and XRD experimental details are listed in Table 1.

The coordinates of atoms and other parameters for compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC nos. 2172853 (**I**) and 2172854 (**II**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Synthesis of coordination polymer {[Cd(L^1)]·DMF}$_n$ (I). A 4-mL glass vial with a screw-top was loaded with $Cd(NO_3)_2·4H_2O$ (16 mg, 0.052 mmol) and dicarboxylic acid H_2L^1 (15 mg, 0.051 mmol), and a DMF–H_2O–EtOH (4 : 2 : 1) mixture (1 mL) was added. The reaction mixture was hold in an oven at 100°C for 48 h. Precipitated yellowish crystals were filtered off, washed with ethanol, and dried in air. The yield was 18 mg (75%).

IR (ν, cm^{-1}): 3022 ν(C–H_{aliph}), 2926 ν(C–H_{aliph}), 1657 $\nu_{as}(COO^-)$, 1572 ν(Pz), 1485 $\nu_s(COO^-)$, 1008 ν(Pz).

For $C_{16}H_{21}N_5O_5Cd$

Anal. calcd., %	C, 40.39	H, 4.45	N, 14.72
Found, %	C, 40.4	H, 4.5	N, 14.3

Synthesis of coordination polymer {[Cd(L^2)(H_2O)$_2$]·DMF}$_n$ (II) was carried out similarly to that of compound **I** from $Cd(NO_3)_2·4H_2O$ (16 mg, 0.052 mmol) and dicarboxylic acid H_2L^2 (14 mg, 0.053 mmol) in a DMF–H_2O–EtOH (4 : 2 : 1) mixture (10 mL). The yield of colorless crystals was 16 mg (64%).

IR (ν, cm^{-1}): 3287 br ν(O–H), 3130 ν(C–H_{arom}), 2941 ν(C–H_{aliph}), 1659 $\nu_{as}(COO^-)$, 1562 ν(Pz), 1429 $\nu_s(COO^-)$, 1004 ν(Pz).

For $C_{14}H_{21}N_5O_7Cd$

Anal. calcd., %	C, 34.76	H, 4.38	N, 14.48
Found, %	C, 34.6	H, 4.0	N, 14.1

RESULTS AND DISCUSSION

Coordination polymers **I** and **II** were synthesized by the reactions of cadmium nitrate with dicarboxylic acids H_2L^1 or H_2L^2 under the solvothermal conditions in a DMF–H_2O–EtOH (4 : 2 : 1) mixture of solvents at 100°C. The synthesis conditions were optimized by the variation of the temperature and solvent composition in order to obtain single crystals suitable for XRD.

Compound **I** crystallizes in the tetragonal crystal system in the chiral space group $P4_32_12$ (Table 1). The asymmetric unit includes one molecule of ligand L^1 in the deprotonated form and one Cd^{2+} ion. The unit cell contains eight formula units. The Cd^{2+} ion exists in a distorted octahedral environment and coordinates three anions of ligand L^1: two anions are coordinated by the carboxyl groups via the bidentate mode and one anion is coordinated due to the nitrogen atoms in positions 2 of the pyrazole cycles via the bidentate cyclic coordination mode (Fig. 1a). As a result, the anions of ligand L^1 bind the Cd^{2+} ions in three directions to form the 3D coordination polymer (Fig. 1b). Ligands L^1 binding the adjacent Cd^{2+} ions are arranged helically, which predetermines the chiral character of the whole structure. Two networks of the coordination polymer are mutually concatenated when packing (Fig. 1c).

Compound **II** crystallizes in the monoclinic crystal system in the centrosymmetric space group $P2_1/n$ (Table 1). The asymmetric unit contains one Cd^{2+} ion, one molecule of ligand L^2 in the deprotonated form,

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

Parameter	Value	
	I	**II**
Formula	$C_{13}H_{14}N_4O_4Cd$	$C_{14}H_{21}N_5O_7Cd$
FW	402.69	483.77
Crystal system	Tetragonal	Monoclinic
Space group	$P4_32_12$	$P2_1/n$
Z	8	4
a, Å	12.4691(5)	11.1572(3)
b, Å	12.4691(5)	12.0791(3)
c, Å	21.1780(12)	13.1659(4)
β, deg	90	91.814(2)
V, Å^3	3292.7(3)	1773.47(8)
ρ_{calc}, g cm^{-3}	1.625	1.812
μ, cm^{-1}	1.35	1.28
F(000)	1600	976
Measured reflections	8851	8648
Independent reflections (R_{int})	3714 (0.046)	3943 (0.020)
Reflections with $I > 2\sigma(I)$	3431	3514
Number of parameters	203	256
R_1	0.055	0.023
wR_2	0.129	0.049
GOOF	1.25	1.040
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.39/–0.73	0.38/–0.34
Fleck parameter	0.04(3)	

two water molecules, and one DMF molecule. The unit cell contains four formula units. The Cd^{2+} ion exists in an insignificantly distorted octahedral environment and coordinates three anions of ligand L^2: two anions are coordinated by the carboxyl groups with the monodentate coordination and one anion is coordinated due to the nitrogen atoms in positions 2 of the pyrazole cycles via the bidentate cyclic coordination mode to form the eight-membered chelate (Fig. 2a). Two coordination sites of the Cd^{2+} ion are occupied by two water molecules. As a whole, compound **II** is a 2D coordination polymer, the layers of which are parallel to the crystallographic plane *ab* (Fig. 2b). The layer packing results in the formation of channels oriented along the crystallographic axis *c* filled by solvate DMF molecules. The layers in the packing are coupled by hydrogen bonds between the coordinated water molecules (Fig. 2c, interatomic distance O(5)–O(6) 2.849(2) Å) and between the water molecules and oxygen atoms of the carboxylate groups (distance O(3)–O(5) 2.665(2) Å). The water molecules also form hydrogen bonds with the oxygen atoms of the solvate DMF molecules (O(5)–O(7) 2.662(2) Å) and oxygen atoms of the carboxyl groups within one layer (O(1)–O(6) 2.583(2) Å).

The bond lengths in the coordination polyhedra of the Cd^{2+} ions in compounds **I** and **II** are listed in Table 2.

The phase and chemical purities of compounds **I** and **II** were confirmed by phase XRD and elemental analyses. The calculated and experimental XRD patterns are shown in Fig. 3.

According to the TG data, compound **I** undergoes nearly no mass loss on heating to 300°C, and then the inserted solvent molecules are lost with the simultaneous decomposition of the framework (Fig. 4). The thermal decomposition of compound **II** proceeds in several stages. Two coordinated water molecules and partially solvated DMF molecules are lost in a range of 85–125°C. The complete removal of the DMF molecules comes to the end at 280°C, and the coordination polymer begins to decompose above this temperature (Fig. 4).

The IR spectra of coordination polymers contain characteristic intense bands of stretching vibrations of the pyrazole cycles near 1560 and 1005 cm^{-1} and

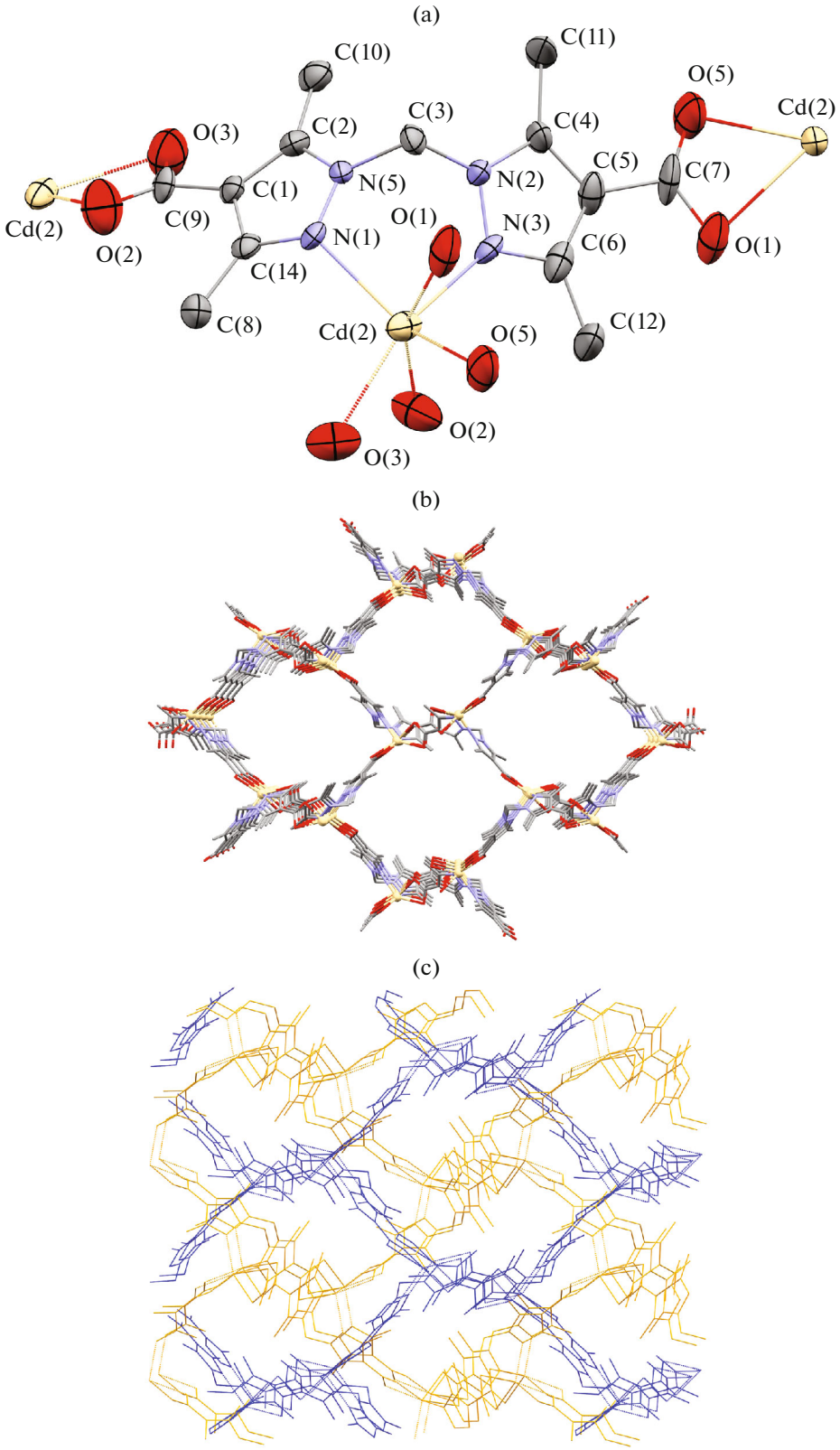


Fig. 1. (a) Elementary unit of coordination polymer **I**, (b) structure of the 3D network of compound **I**, and (c) fragment of the crystal structure of compound **I** showing the single intergrowing of the coordination networks. Thermal ellipsoids are given with 50% probability, and hydrogen atoms are omitted.

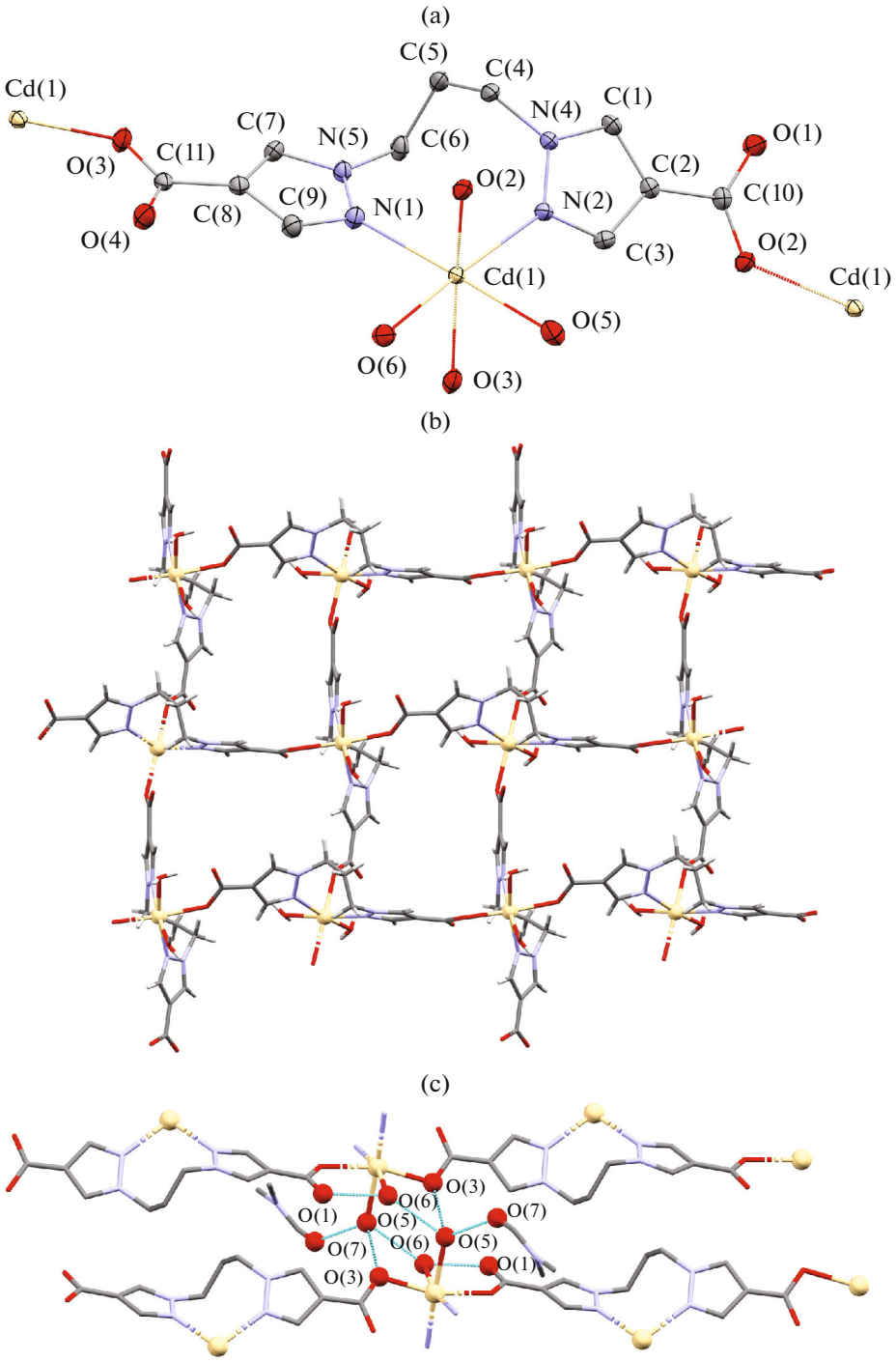


Fig. 2. (a) Elementary unit of coordination polymer **II**, (b) structure of the 2D network of compound **II**, and (c) fragment of the crystal structure of compound **II** showing the formation of hydrogen bonds involving water molecules. Thermal ellipsoids are given with 50% probability, and hydrogen atoms and solvate DMF molecules are omitted.

asymmetric and symmetric stretching vibration bands of the carboxylate groups. In the IR spectrum of compound **I**, these bands are remoted at a shorter distance from each other ($\Delta = \nu_{as}(COO^-)-\nu_s(COO^-) = 172$ cm^{-1}) compared to the spectrum of compound **II** ($\Delta = 230$ cm^{-1}). The difference in positions of these bands is consistent with different coordination modes of the carboxylate groups: bidentate cyclic in compound **I** and monodentate in compound **II** [15].

Since the coordination compounds of cadmium(II) often exhibit pronounced luminescence [16, 17], we studied the luminescence properties of synthe-

Table 2. Selected bond lengths in the structures of compounds **I** and **II**

Compound **I**		Compound **II**	
Bond	*d*, Å	Bond	*d*, Å
Cd(2)–O(5)	2.237(7)	Cd(1)–O(3)	2.2625(14)
Cd(2)–O(2)^{i}	2.281(8)	Cd(1)–O(2)^{iii}	2.3076(14)
Cd(2)–N(1)^{ii}	2.319(6)	Cd(1)–N(2)^{iv}	2.3106(16)
Cd(2)–N(3)^{ii}	2.353(7)	Cd(1)–N(1)^{iv}	2.3322(16)
Cd(2)–O(30)^{i}	2.372(8)	Cd(1)–O(5)	2.3486(15)
Cd(20)–O(1)	2.487(8)	Cd(1)–O(6)	2.3552(15)
Cd(2)–C(7)	2.678(10)		
Cd(2)–C(9)^{i}	2.704(9)		

Symmetry transforms: ^{i} $-x+2, -y+1, z+1/2$; ^{ii} $x+1/2, -y+1/2, -z+5/4$; ^{iii} $x+1, y-1, z$; ^{iv} $-x+1/2, y-1/2, -z+3/2$.

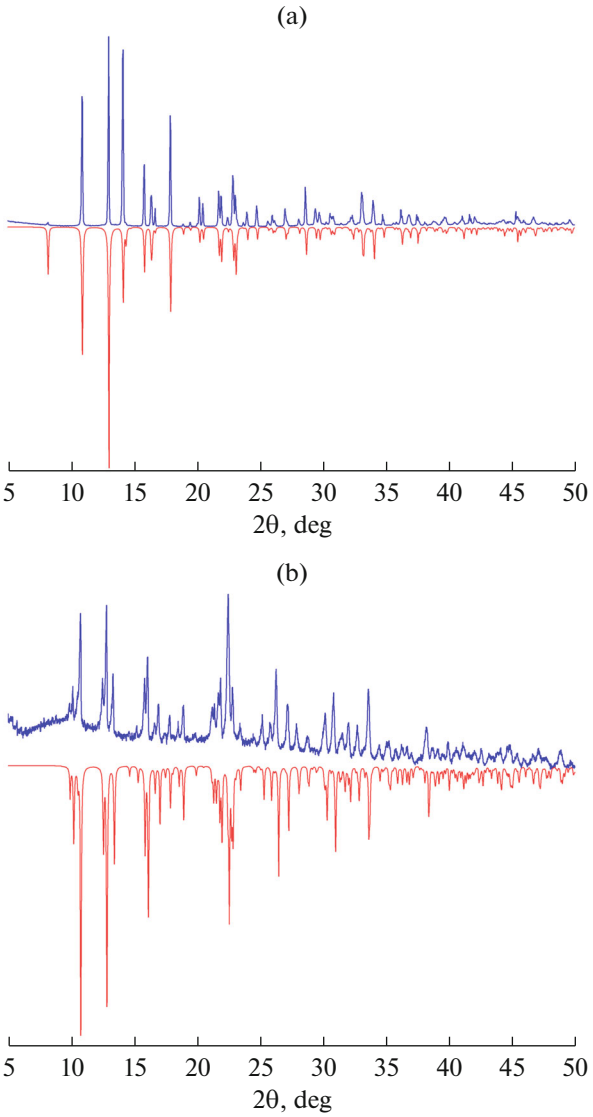


Fig. 3. Experimental (top) and calculated (bottom) powder XRD patterns of coordination polymers (a) **I** and (b) **II**.

sized coordination polymers **I** and **II** and their ligands. The photoluminescence excitation spectrum of ligand H_2L^1 exhibits a broad band with an absorption maximum at 272 nm and a shoulder about 310 nm corresponding to the $n-\pi^*$ and $\pi-\pi^*$ transitions in the pyrazole cycles. The emission band has a vibrational structure with a maximum at 380 nm, the position of which is independent of the excitation wavelength (Fig. 5a). The excitation and emission spectra of ligand H_2L^2 contain one band each with maxima at 277 and 343 nm, respectively.

The luminescence excitation spectra of compounds **I** and **II** are complicated and consist of several bands with maxima at 376 and 291 nm for compound **I** and at 376, 309, and 274 nm for compound **II** (Fig. 5b). The emission spectrum of compound **I** exhibits a band at 370 nm and a shoulder about 460 nm. Similarly, the emission spectrum of compound **II** contains a band with a maximum at 340 nm, and the long-

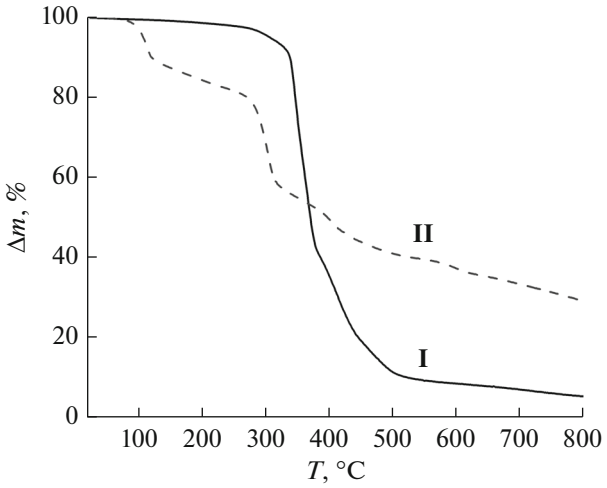


Fig. 4. Thermogravimetric curves for coordination polymers **I** and **II**.

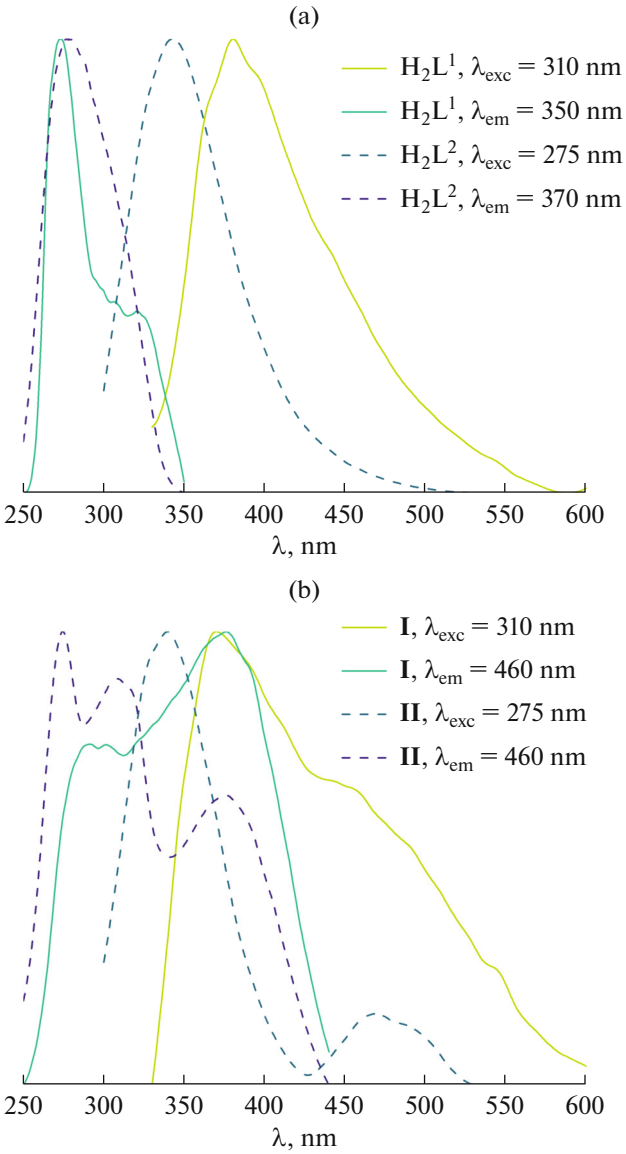


Fig. 5. Photoluminescence excitation and emission spectra of (a) dicarboxylic acids H_2L^1 and H_2L^2 and (b) coordination polymers **I** and **II**.

wavelength band has a pronounced maximum at 470 nm instead of the shoulder (Fig. 5b). Since the positions of the absorption and emission maxima of the short-wavelength bands are close to the corresponding bands in the spectra of the free ligands, they can be attributed to intraligand fluorescence, and the long-wavelength bands appeared in the emission spectra of coordination polymers **I** and **II** should be assigned to the metal–ligand transitions.

Thus, the coordination polymers of cadmium with the dicarboxyl derivatives of di(pyrazol-1-yl)alkanes were synthesized and structurally characterized. The obtained characteristics demonstrate a potential of these new ligands for the construction of coordination polymers of different dimensionalities. Coordination polymer **II** is the first example of coordination compound with dicarboxylic acid H_2L^2, and compound **I** is the second example of coordination compound with anions of acid H_2L^1 as ligands.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Pettinari, C. and Pettinari, R., *Coord. Chem. Rev.*, 2005, vol. 249, p. 663.
2. Potapov, A.S., Domina, G.A., Petrenko, T.V., et al., *Polyhedron*, 2012, vol. 33, p. 150.
3. Liu, Q., Song, Y., Ma, Y., et al., *J. Am. Chem. Soc.*, 2019, vol. 141., p. 488.
4. Belousov, Y.A., Drozdov, A.A., Taydakov, I.V., et al., *Coord. Chem. Rev.*, 2021, vol. 445, p. 214084.
5. Wu, T., Huang, S., Yang, H., et al., *ACS Mater. Lett.*, 2022, vol. 4, p. 751.
6. Kivi, C.E., Gelfand, B.S., Dureckova, H., et al., *Chem. Commun.*, 2018, vol. 54, p. 14104.
7. Gimeno-Fonquernie, P., Liang, W., Albalad, J., et al., *Chem. Commun.*, 2022, vol. 58, p. 957.
8. Burlutskiy, N.P. and Potapov, A.S., *Molecules*, 2021, vol. 26, p. 413.
9. Pershina, E.A., Pavlov, D.I., Burlutskiy, N.P., and Potapov, A.S., *Molbank*, 2021, no. 4, p. M1298.
10. Potapov, A.S., Domina, G.A., Khlebnikov, A.I., and Ogorodnikov, V.D., *European J. Org. Chem.*, 2007, p. 5112.
11. Potapov, A.S. and Khlebnikov, A.I., *Polyhedron*, 2006, vol. 25, p. 2683.
12. *CrysAlisPro. Agilent Technologies. Version 1.171.34.49* (release 20-01-2011 CrysAlis171.NET).
13. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Cryst. Adv.*, 2015, vol. 71, p. 3.
14. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
15. Deacon, G.B. and Phillips, R.J., *Coord. Chem. Rev.*, 1980, vol. 33, p. 227.
16. Kovalev, V.V., Kokunov, Y.V., Shmelev, M.A., et al., *Russ. J. Coord. Chem.*, 2021, vol. 47, p. 272. https://doi.org/10.1134/S1070328421040047
17. Pavlov, D.I., Ryadun, A.A., Samsonenko, D.G., et al., *Russ. Chem. Bull.*, 2021, vol. 70, p. 857. https://doi.org/10.1007/s11172-021-3159-6

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