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# Synthesis and Photoluminescence of Zinc(II) Complexes with Tetrafluoroterephthalic Acid ($H_2L$). Crystal Structure of Coordination Polymer $[Zn(H_2O)_4(L) \cdot 4H_2O]_n$

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**Abstract**—Complexes $Zn(H_2O)_4(L)$ (**I**) and $Zn(H_2O)(L)$ (**II**) ($H_2L$ = *p*-$HOOCC_6F_4COOH$) are synthesized. Single crystals of compound $[Zn(H_2O)_4(L) \cdot 4H_2O]_n$ (**III**) are grown. According to the X-ray diffraction data, the crystal structure of compound **III** is built of zigzag chains of coordination polymer $Zn(H_2O)_4(L)$ and molecules of water of crystallization. The chain contains ions $Zn^{2+}$, whose octahedral coordination sphere includes the O atoms of four water molecules and two O atoms of the deprotonated carboxyl groups. The chains in structure **III** are joined by a system of hydrogen bonds of coordinated water molecules and molecules of water of crystallization. The photoluminescence spectrum of $H_2L$ exhibits the band with $\lambda_{max}$ = 368 nm. The spectra of compounds **III**, **I**, and **II** contain bands at 322, 340, and 353 nm, respectively.

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Presently, considerable attention is given to the synthesis and studies of the structure and properties of coordination of metals with aromatic acids bearing several carboxyl groups. This is due to various polymeric structures of the solid phases formed, resulting in the formation of pores of various diameters. Specific features of the structure of the coordination polymers provide the inclusion of various compounds into pores of molecules and the manifestation of diverse functional properties (luminescence, hydrogen storage) [1, 2]. One of the simplest representatives of the studied dibasic aromatic acids is terephthalic acid *p*-$HOOCC_6H_4COOH$ (**$H_2L^1$**). Coordination polymer compounds $H_2L^1$ with ions $Zn^{2+}$ [3, 4], $Cr^{3+}$, and $Fe^{3+}$ were synthesized [5–8]. The Zn(II) compounds $Zn(H_2O)_2(L^1)$ and $Zn(H_2O)(L^1)$ exhibit photoluminescence at $\lambda_{max}$ = 402 nm ($\lambda_{exc}$ = 260 nm) and 344, 385 nm ($\lambda_{exc}$ = 279 nm), respectively [4]. The synthesis of the luminescent Zn(II) complexes is a topical problem [9, 10]. Therefore, it is of interest to synthesize the Zn(II) compounds with perfluorinated aromatic dicarboxylic acids, because the introduction of F atoms into the composition of organic ligands favors luminescence [11, 12].

This work is aimed at synthesizing the Zn(II) complexes with tetrafluoroterephthalic acid *p*-$HOOCC_6F_4COOH$ and at studying their structures and luminescence properties.

## EXPERIMENTAL

Terephthalic acid was synthesized according to a known procedure [13]. The following reagents were used in the synthesis of the complex: $Zn(CH_3COO)_2 \cdot 2H_2O$ and ZnO (reagent grade), EtOH (rectificate), and MeOH (high-purity grade). Alcohols were not dehydrated.

**Synthesis of (μ-tetrafluoroterephthalato)tetraaquazinc $Zn(H_2O)_4(L)$ (I). Procedure 1.** Warm (~50°C) solutions of $H_2L$ (0.48 g, 2 mmol) in EtOH (3 ml) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.37 g, 1.7 mmol) in EtOH (3 ml) were mixed, and the mixture was stored at room temperature. A finely crystalline white powder gradually precipitated from the solution. Next day the precipitate was filtered off with suction, washed with EtOH and hexane, and dried in air. The yield was 0.55 g (87%).

For $C_8H_8F_4O_8Zn$

| | | | | |
|---|---|---|---|---|
| anal. calcd., %: | C, 25.7; | H 2.1; | F, 20.4; | Zn, 17.5. |
| Found, %: | C, 26.0; | H 2.0; | F, 20.6 | Zn, 18.1. |

**Procedure 2.** Zinc oxide (0.2 g, 2 mmol) was added to a warm solution of $H_2L$ (0.64 g, 2.7 mmol) in MeOH (20 ml). The mixture was stirred at room temperature for 6 h, and the precipitate was filtered off with suction, washed with EtOH and hexane, and dried in air. The yield was 0.66 g (72%).

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[1] Deceased.

For $C_8H_8F_4O_8Zn$

| | | | | |
|---|---|---|---|---|
| anal. calcd., %: | C, 25.7; | H, 2.1; | F, 20.4; | Zn, 17.5. |
| Found, %: | C, 25.9; | H, 2.0; | F, 20.5; | Zn, 17.8. |

The thermal analysis (TA) of complex **I** showed that its mass loss on heating occurred in three stages. According to the thermal gravimetry (TG) data, the mass loss was 14.6% at the first stage (50–80°C). This corresponds to the loss of three water molecules (the calculated content of three water molecules in compound **I** is 14.5%). The endotherm is observed at 70°C in the DTA (differential thermal analysis) curve. The product formed is stable up to 150°C. At the second stage (150–195°C) the mass loss is 4.7%, which corresponds to the loss of one more water molecule. The endotherm in the DTA curve at 190°C corresponds to this process. The total mass loss in two stages is 19.3%, and the calculated water content in $Zn(H_2O)_4(L)$ is also 19.3%. The third stage of mass loss corresponding to the decomposition of the dehydrated complex begins at 270°C. The process is accompanied by the exotherm at 375°C.

**Synthesis of (μ-tetrafluoroterephthalato)aquazinc $Zn(H_2O)(L)$ (II).** A weighed sample of complex **I** was heated in a desiccator at 100°C for 3 h. The mass loss was 14.5%.

For $C_8H_2F_4O_5Zn$

Found, %: Zn 20.8.
anal. calcd., %: Zn 20.5.

The substance is stable on storage in air.

**Synthesis of (μ-tetrafluoroterephthalato)tetraaquazinc tetrahydrate $[Zn(H_2O)_4(L) \cdot 4H_2O]_n$ (III).** A weighed sample of compound **I**, which was synthesized according to procedure 2, was dissolved on heating in a minimum amount of $H_2O$, and the beaker with the solution was covered with a watch crystal and left to stand in air. Transparent crystals precipitated after several days. Outside the mother liquor the crystals in air gradually grew turbid and disintegrated.

Analyses to C, H, and F were carried out similarly to a procedure described [14]. The Zn content was determined by complexonometric titration (Trilon B, eriochrome black T as an indicator). The TA curves were obtained using a TG 209 F1 Iris® thermobalance (NETZSCH). The sample weight was 20 mg (Al crucible, helium atmosphere, heating rate 10 deg/min, temperature range 20–600°C). The experimental results were processed using the standard Proteus Analysis program package [15]. The excitation and photoluminescence (PLM) spectra of compounds $H_2L$ and **I**–**III** in the solid phase were obtained on a Cary Eclipse spectrofluorimeter at 300 K under equivalent conditions for all samples (500 V, 5-nm gap). X-ray phase analysis was carried out on a DRON-3M automated power diffractometer ($R = 192$ mm, $CuK_\alpha$ radiation, Ni filter) in the 2θ range from 3° to 60°.

**X-ray diffraction analysis of compound III.** Unit cell parameters and reflection intensities were measured at low temperature (150 K) on a Bruker X8 Apex CCD automated diffractometer equipped with a two-coordinate detector according to a standard procedure ($MoK_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator). The crystallographic characteristics and details of the X-ray diffraction experiment and structure refinement for compound **III** are given in Table 1. The structure was solved by a direct method and refined by the full-matrix least-squares method on $F^2$ in the anisotropic (for non-hydrogen atoms) approximation using the SHELXL-97 program package [16]. The positions of the hydrogen atoms of the water molecules were localized from the difference electron density synthesis and included into refinement in the isotropic approximation along with non-hydrogen atoms. Selected interatomic distances and bond angles are listed in Table 2. The full tables of the coordinates of atoms, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (no. 802247); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

## RESULTS AND DISCUSSION

The Zn(II) compounds with terephthalic acid, $Zn(H_2O)_2(L^1)$ and $Zn(H_2O)(L^1)$, were synthesized [4] by the hydrothermal reaction of ZnO and the acid in water (autoclave, 160°C, 48 h). We synthesized compound **I** using two procedures by the reaction of tetrafluoroterephthalic acid (having higher acidity) with $Zn(CH_3COO)_2 \cdot 2H_2O$ or ZnO in alcohol media at temperatures not higher than 50°C without an autoclave. Water in complex **I** synthesized by the second procedure is present due to its formation in the reaction and to the presence of water in methanol. The diffraction patterns of the samples of complex **I** synthesized using two procedures are identical, indicating their similar structures. Compared to the Zn(II) complexes with terephthalic acid [4], complex **I** contains more water molecules (four). It is most likely that the coordination to the $Zn^{2+}$ ions of fluorine-containing anions $L^{2-}$, whose donor ability is lower than that of the terephthalic acid anions, enhances the capability of the acceptors ($Zn^{2+}$ ions) of adding water molecules. The TA data indicate the difference in binding of water molecules during the dehydration of complex **I**. In addition, these data showed the possibility to obtain product **II** containing only one water molecule by heating of complex **I**.

According to the X-ray diffraction data, single crystals of compound **III** have the composition $Zn(H_2O)_4(L) \cdot 4H_2O$. Crystal structure **III** consists of

**Table 1.** Crystallographic characteristics and experimental and refinement details for the structure of compound **III**

| Parameter | Value |
|---|---|
| Empirical formula | $C_8H_{16}F_4O_{12}Zn$ |
| FW | 445.58 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$, Å | 6.8435(2) |
| $b$, Å | 6.8435(2) |
| $c$, Å | 8.7154(3) |
| α, deg | 88.605(1) |
| β,deg | 70.943(1) |
| γ, deg | 88.916(1) |
| $V$, Å$^3$ | 388.00(2) |
| $Z$; ρ(calcd.), mg/cm$^3$ | 1; 1.907 |
| μ, mm$^{-1}$ | 1.690 |
| Crystal sizes, mm | 0.50 × 0.32 × 0.20 |
| can range, θ, deg | 2.47–35.00 |
| Number of measured reflections | 4596 |
| Number of independent reflections | 3218 |
| $R_{\text{int}}$ | 0.0116 |
| Number of reflections with $I > 2\sigma(I)$ | 3168 |
| Number of refined parameters | 147 |
| Goodness-of-fit on $F^2$ | 1.061 |
| $R$ factor ($I > 2\sigma(I)$) | $R_1 = 0.0193$,<br>$wR_2 = 0.0535$ |
| $R$ factor (on all $I_{hkl}$): | $R_1 = 0.0196$<br>$wR_2 = 0.0536$ |
| Residual electron density (max/min) $e$/Å$^3$ | 0.534/–0.520 |

**Table 2.** Selected interatomic distances and bond angles in the structure of compound **III**

| Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|
| Zn(1)–O(1) | 2.0944(6) | O(1)–H(11) | 0.81(2) |
| Zn(1)–O(2) | 2.1336(6) | O(1)–H(12) | 0.80(2) |
| Zn(1)–O(3) | 2.1027(6) | O(2)–H(21) | 0.87(2) |
| O(3)–C(1) | 1.2654(9) | O(2)–H(22) | 0.87(2) |
| O(4)–C(1) | 1.2474(9) | O(1*w*)–H(1a) | 0.78(2) |
| C(1)–C(2) | 1.510(1) | O(1*w*)–H(1b) | 0.87(2) |
| C(2)–C(4a) | 1.391(1) | O(2*w*)–H(2a) | 0.77(2) |
| C(2)–C(3) | 1.391(1) | O(2*w*)–H(2b) | 0.77(2) |
| C(3)–F(3) | 1.3418(9) | C(4)–F(4) | 1.3425(8) |
| C(3)–C(4) | 1.385(1) | | |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| O(1a)Zn(1)O(3) | 91.39(2) | C(4a)C(2)C(3) | 116.98(6) |
| O(1)Zn(1)O(3) | 88.61(2) | C(4a)C(2)C(1) | 120.90(6) |
| O(1a)Zn(1)O(2) | 91.47(2) | C(3)C(2)C(1) | 122.10(6) |
| O(1)Zn(1)O(2) | 88.53(2) | F(3)C(3)C(4) | 118.53(6) |
| O(3)Zn(1)O(2) | 88.61(2) | F(3)C(3)C(2) | 120.09(6) |
| O(3a)Zn(1)O(2) | 91.39(2) | C(4)C(3)C(2) | 121.37(7) |
| C(1)O(3)Zn(1) | 128.43(5) | F(4)C(4)C(3) | 118.42(6) |
| O(4)C(1)O(3) | 126.23(7) | F(4)C(4)C(2a) | 119.90(6) |
| O(4)C(1)C(2) | 117.99(6) | C(3)C(4)C(2a) | 121.65(7) |
| O(3)C(1)C(2) | 115.77(6) | | |

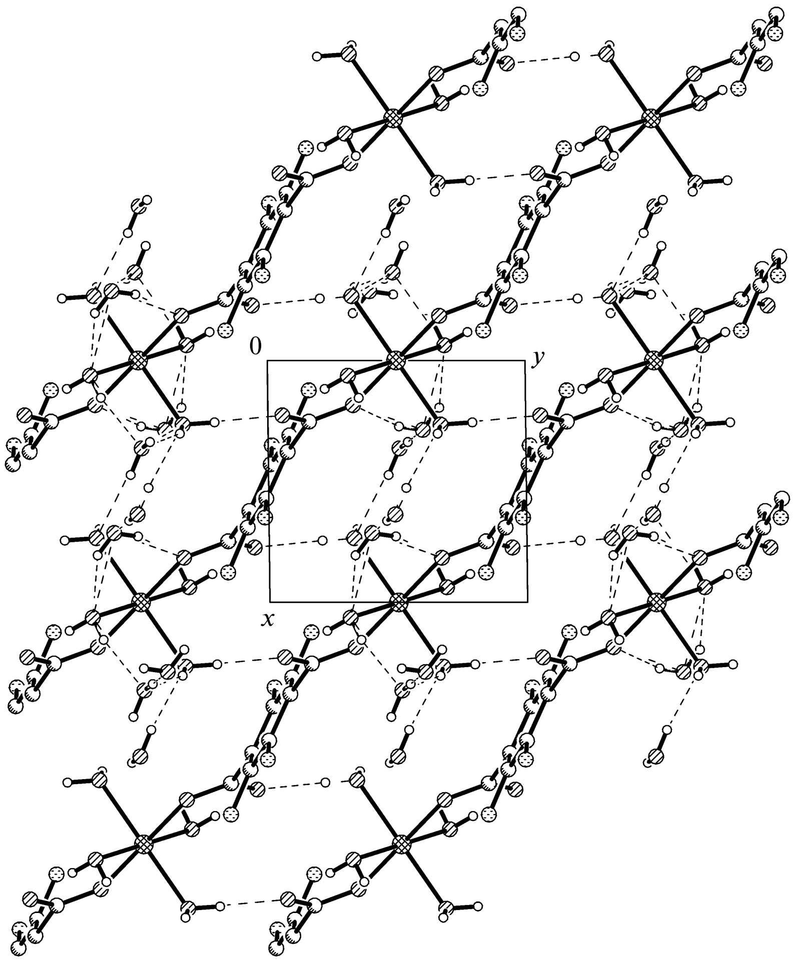

**Fig. 1.** Packing of one-dimensional chains of the coordination polymer $Zn(H_2O)_4(L)$ and molecules of water of crystallization in structure **III** in projection on the plane (001).

one-dimensional chains of the molecular coordination polymer $Zn(H_2O)_4(L)$ and molecules of water of crystallization (Fig. 1). It is seen in projection on the plane (001) that the chains are zigzag and the angle Zn(1)O(3)C(1) is 128.4°. The polymer chains contain the $Zn^{2+}$ ions occupying the partial positions in the symmetry centers. The octahedral coordination sphere of the $Zn^{2+}$ ion includes the O atoms of four coordinated water molecules (Zn–O 2.0944(6) and 2.1336(6) Å) and two O(3) atoms of the deprotonated carboxyl groups of two bridging ligands $L^{2-}$ (Zn–O 2.1027(6) Å). The distance Zn···Zn in the chain is 11.238 Å. The structure contains strong hydrogen bonds O–H···O between the uncoordinated O atoms of ligands $L^{2-}$ and two of four coordinated water molecules (O(1)···O(4a) 2.665(1) Å, angle O(1)H(12)O(4a) 161°). This results in the formation of six-membered H-cycles $ZnCO_3H$ related by the symmetry center (Figs. 2a, 2b). The cycle has an envelope conformation with the Zn(1) atom shifted by 0.411(3) Å from the plane of five atoms O(3)O(4)C(1)O(1a)H(12a); the average deviation of the atoms of this fragment being 0.035(5) Å.

The polymeric Zn(II) complex with $H_2L^1$, $Zn(H_2O)_2(L^1)$, is also one-dimensional and chain in structure, but the coordination polyhedron of the Zn atom is the $ZnO_4$ tetrahedron [4]. The octahedral coordination polyhedron $ZnO_6$ has previously been found in the ionic compound $[\{Zn(H_2O)_4BETC\}^{2-} C_4H_{12}N_2^{2+} \cdot 4H_2O]_n$ (BETC = 1,2,4,5-benzenetetracarboxylate ion) in which the fragment $Zn(H_2O)_4BETC^{2-}$ is a chain coordination polymer [17]. The crystal structure of this compound contains the same number of molecules of water of crystallization as in structure **III**.

The polymer chains in the structure of compound **III** are joined by the system of hydrogen bonds of the coordinated and crystallization water molecules. Fig-

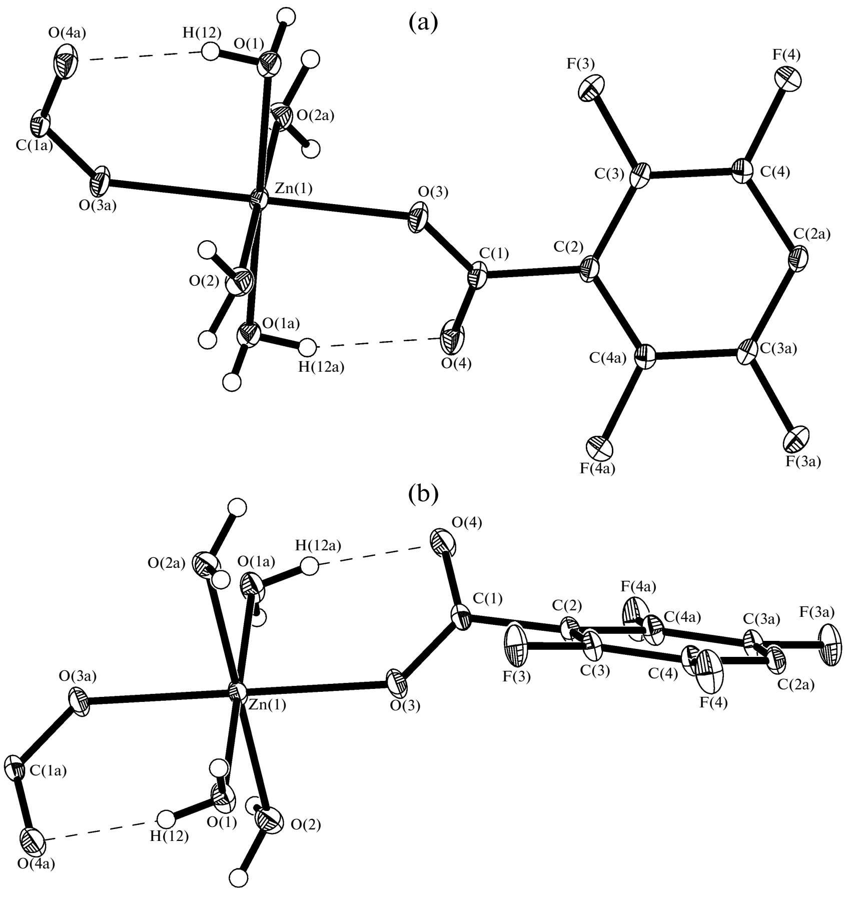

**Fig. 2.** Structure of the independent fragment of the chain coordination polymer $Zn(H_2O)_4(L)$ in structure **III** in two projections (a, b) with enumerated non-hydrogen atoms (thermal ellipsoids are shown at the 50% probability level).

ure 3 shows the mutual arrangement of polymer chains in structure **III**, whose packing forms channels along the direction [100] ~3 × 3 Å in size. The channels are occupied by molecules of water of crystallization. Therefore, complex **III** can be classified as an inclusion compound.

We believe that the structure of complex **I** is analogous to that of the coordination polymer $Zn(H_2O)_4(L)$ in structure **III**. The structure of complex **II** seems to be more complicated by analogy to the trimeric complex $Zn(H_2O)(L^1)$.

The PLM excitation spectrum of acid $H_2L$ exhibits two bands with $\lambda_{max} = 290$ and 340 nm (Fig. 4). The excitation spectra of complexes **I** and **II** contain only one broad band with $\lambda_{max}$ ~293 and ~292 nm, respectively. The band is broader for complex **II**. Based on these data, we chose the excitation wavelength during recording the PLM spectra ($\lambda_{exc} = 290$ nm). The PLM spectrum of acid $H_2L$ exhibits one somewhat asymmetric band in the UV spectral region ($\lambda_{max} = 368$ nm) possessing rather high PLM intensity (Fig. 4). The PLM spectra of the samples of complex **I** synthesized by two procedures has the asymmetric band with $\lambda_{max} = 340$ nm. The PLM spectrum of compound **II**, unlike that of $Zn(H_2O)(L^1)$, contains one asymmetric band with $\lambda_{max} = 353$ nm. The PLM spectrum of inclusion compound **III** exhibits one band with $\lambda_{max} = 322$ nm. Therefore, there is a considerable hypsochromic shift of the bands in the PLM spectra of compounds **I**–**III** compared to the spectrum of $H_2L$. The shift increases with an increase in the amount of water molecules in these compounds. The PLM intensity of complexes **I** and **II** decreases slightly compared to $H_2L$. The PLM intensity of inclusion compound **III** bearing four molecules of water of crystallization is much lower than that of complexes **I** and **II**. Therefore, the coordination of the tetrafluoroterephthalate anions to the $Zn^{2+}$ ions does not increases the PLM intensity of compounds **I**–**III** compared to the PLM intensity of acid $H_2L$.

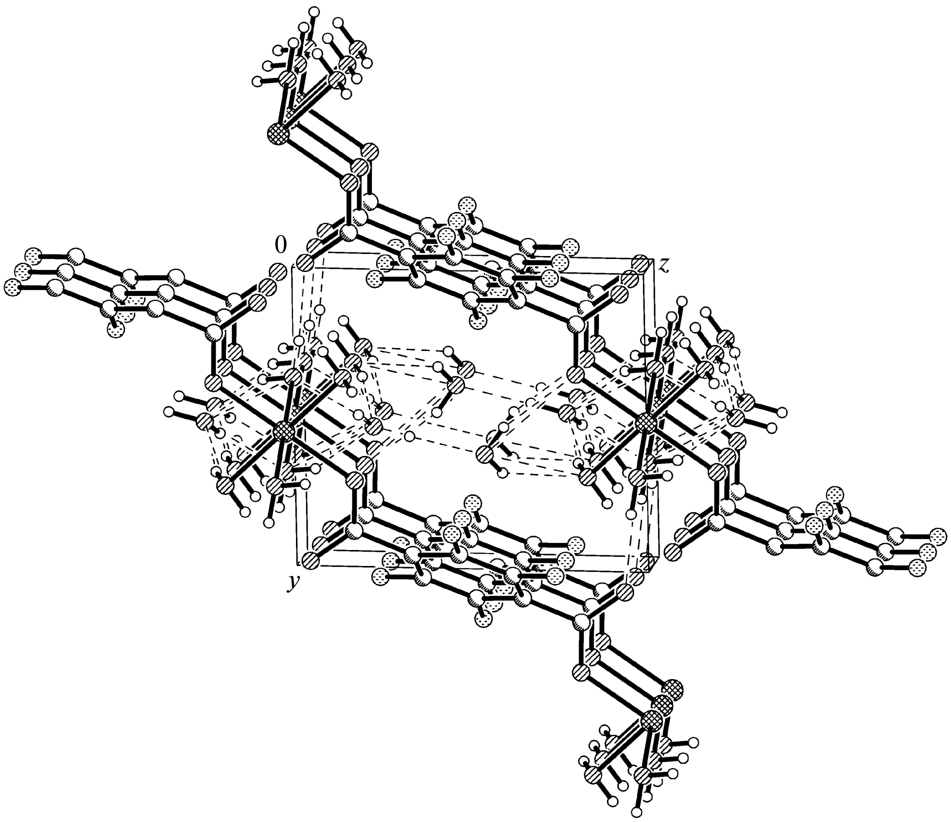

**Fig. 3.** Chain packing in crystal structure **III** in projection to the plane (100) and the arrangement of molecules of water of crystallization in the channels formed.

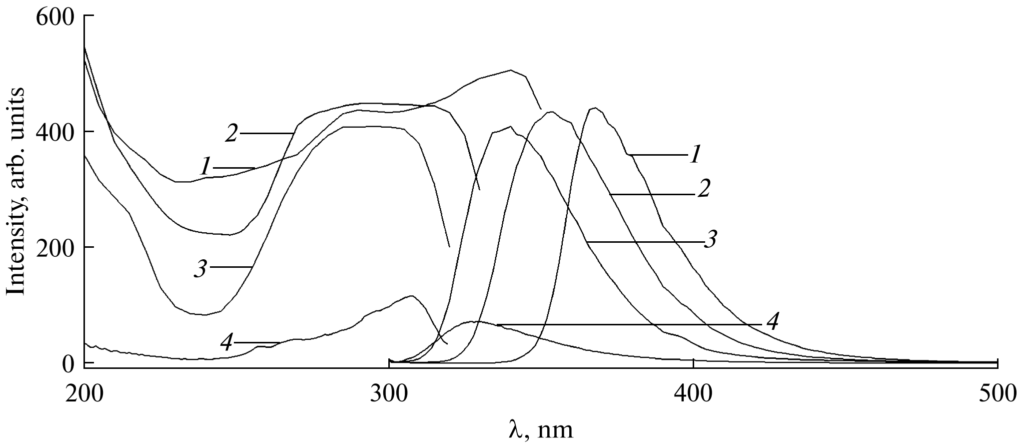

**Fig. 4.** Excitation and photoluminescence spectra of (*1*) $H_2L$, (*2*) $Zn(H_2O)(L)$, (*3*) $Zn(H_2O)_4(L)$, and (*4*) $[Zn(H_2O)_4(L) \cdot 4H_2O]_n$; $V = 500$ V, 5-nm gap, $\lambda_{exc} = 290$ nm.

The results of the studies showed that photoluminescent coordination polymers of zinc(II) can be synthesized from perfluoroaromatic dicarboxylic acids.

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