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Influence of the Synthesis Conditions and the Presence of Guest Molecules on the Structures of Coordination Polymers $[Fe_2MO(Piv)_6(L)_x]_n$ (L = 4,4'-Bipyridine, Bis(4-Pyridyl)ethane) with the Labile Crystal Lattice

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Abstract—Coordination polymers $[Fe_2MO(Piv)_6(L^1)_x]_n \cdot n$Solv ($L^1$ = 1,2-bis(4-pyridyl)ethane, M = Ni (**I**), Co (**II**), $x = 1.5$; M = Co (**III**), $x = 2$) are synthesized. Depending on the synthesis conditions, compounds **II** (cross diffusion of reactants) or **III** (fast mixing of reactant solutions) of different compositions are formed. It is shown by X-ray diffraction analysis (CIF files CCDC 1550804 (**I**) and 1550805 (**III**)) that compound **I** is a porous coordination polymer built of parallel 2D layers and compound **III** is a 1D coordination polymer. The crystals of complexes **I** and **II** are isostructural. The mutual arrangement of the 2D layers in compound **II** depends on the solvent in which this coordination polymer is formed. The desolvation of polymers **I** and **II** leads to the collapse of the crystal lattice. Unlike the complexes with L^1, $[Fe_2NiO(Piv)_6(L^2)_{1.5}]_n \cdot n$Solv (**IV** · nSolv) is formed in the case of 4,4'-bipyridine (L^2), regardless of the solvent nature, and its crystal lattice is formed by interpenetrating 2D layers. The mutual arrangement of the 2D layers in the crystal lattice of compound **IV** varies with the solvent used for the synthesis of this coordination polymer or for the resolvation of a sample of polymer **IV**. It is found that the parameters of the ^{57}Fe Mössbauer spectra for compounds **IV** and **IV** · nDEF (DEF is N,N-diethylformamide) differ, which can be explained by a decrease in the symmetry of the coordination environment of the Fe^{3+} ions when the pores are filled with DEF molecules.

Keywords: porous coordination polymers, bipyridine, dipyridylethane, iron(III), nickel(II), cobalt(II), pivalate, lability, Mössbauer spectroscopy

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INTRODUCTION

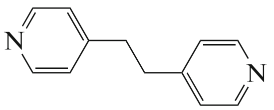
Porous coordination polymers are considered as a basis for the production of materials for gas storage, selective sorption, or separation of substances of different nature [1]. Some porous coordination polymers have rigid crystal lattices, whose structure remains unchanged upon the solvation/desolvation of the porous coordination polymer [2], whereas other porous coordination polymers (labile or flexible) undergo changes during these processes [3]. The flexibility of the porous coordination polymers can be caused by the possibility of changing the mutual arrangement of the bonded fragments of the structure (for example, metal-containing 1D chains and organic ligands linking these chains [4]), the conformations of the organic ligands [5], and the mutual arrangement of interpenetrating 2D layers or 3D networks that are not bonded by covalent bonds [6, 7]. The above listed changes in the crystal structure of the porous coordination polymer, its so-called "breathing," can be due to the desorption–resorption guest molecules [8]. Thus, the pore volume in the crystal lattices of flexible porous coordination polymers accessible for guest molecules depends on the ability of the latter to undergo the initial structural rearrangement [9]. Since these processes can change the magnetic properties, luminescence, and conductivity of the porous coordination polymers [10, 11], the study of the factors affecting the structures of the porous coordination polymers with flexible crystal lattices is an important task of coordination chemistry.

We have previously described the 1D and 2D polymers containing the trinuclear fragments $\{Fe_2MO(Piv)_6\}$ (M = Ni(II), Co(II)) and rigid (4,4'-bipyridine (L^2); *trans*-1,2-bis(4-pyridyl)ethylene (Dpe)) or flexible (bis-1,3-(4-pyridyl)propane) ligands [12, 13]. It is established on the basis of an analysis of the crystal structures and sorption properties of these compounds that the crystal lattices of the porous coordination polymers $[Fe_2MO(Piv)_6(L)_{1.5}]_n$ (L = L^2, Dpe) are labile, namely, their structures depend substantially on the presence of guest molecules. The replacement of the solvent (N,N-dimethylformamide (DMF) by N,N-diethylformamide (DEF)) in $[Fe_2MO(Piv)_6(L^2)_{1.5}]_n \cdot n$Solv results in a change in the mutual arrangement of the 2D layers in the crystal lattice with the retention of its topology [14].

The binding of the trinuclear fragments $\{Fe_2MO(Piv)_6\}$ (M = Ni(II), Co(II)) by Dpe molecules was found to result in the formation of the 2D polymer $[Fe_2MO(Piv)_6(Dpe)_{1.5}]_n$, whereas the partial photoisomerization of Dpe to *cis*-bis(4-pyridyl)ethylene (*cis*-Dpe) in the reaction medium leads to the formation of the 1D polymer $[\{Fe_2CoO(Piv)_6(cis\text{-}Dpe)\}_2(Dpe)]_n$ [13]. It could be expected that the replacement of *trans*-bis(4-pyridyl)ethylene by conformationally flexible 1,2-bis(4-pyridyl)ethane (L^1) would result in the formation of a higher diversity of porous coordination polymers depending on the conditions of their formation.

It is known that the mutual arrangement of polymer networks or chains of porous coordination polymers can change (with the retention of the structure of a single lattice or chain) depending on the composition of the reaction medium [15] or the presence of a template during the formation of a porous coordination polymer [16, 17]. For example, it was shown [16] that the introduction of oxalic acid into the reaction medium of the synthesis of the porous coordination polymer PCN-6 (copper(II) triazinetribenzoate) resulted in the formation of the porous coordination polymer PCN-6'. The structures of the crystal lattices of compounds PCN-6 and PCN-6' are distinguished by the presence or absence of the interpenetration of the polymer networks, and the surface areas of these porous coordination polymers differ by 1.4 times [16].

The purpose of this work is to determine the influence of the conditions of synthesis of the coordination polymers based on the trinuclear complexes $Fe_2MO(Piv)_6(HPiv)_3$ (M = Co(II), Ni(II)) and ligands of the bipyridine series (bis-1,2-(4-pyridyl)ethane (L^1) and 4,4'-bipyridine (L^2)) on the molecular and crystal structures of the formed compounds and to reveal the influence of the solvent and the method of its inclusion into the pores (capture during the formation of the coordination polymer in the solvent or post-synthetic resolvation of the coordination polymer) on the structures of the coordination polymers $[Fe_2NiO(Piv)_6(L^2)_{1,5}]_n \cdot n$Solv.



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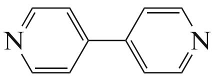

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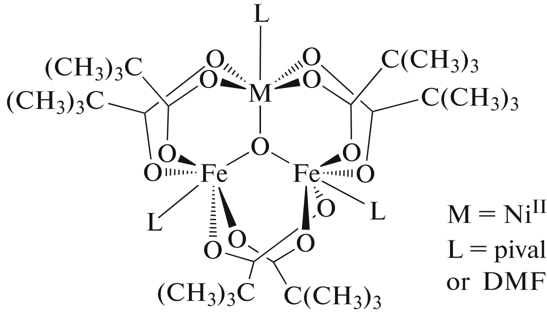


M = Ni^{II} or Co^{II}
L = pivalic acid
or DMF (in solution)

Porous coordination polymers $[Fe_2MO(Piv)_6(L)_{1.5}]_n$ (L = L^1, M = Ni(II) (**I**), Co(II) (**II**); L = L^2, M = Ni(II) (**IV**)) and $[Fe_2CoO(Piv)_6(L^2)_2]_n$ (**III**) were obtained in this work. The influence of the solvent on the structures of the coordination polymers formed by the reaction of $[Fe_2NiO(Piv)_6(HPiv)_3]$ with L^2 was studied to determine the possibility of forming a porous coordination polymer with L^2 and without interpenetration of the 2D layers in the crystal lattice. The samples were characterized using X-ray phase analysis. Complexes **IV** and **IV** · 2DEF were studied by Mössbauer spectroscopy. The structures of compounds **I** and **III** were determined by X-ray diffraction analysis. The isostructural character of the crystals of compounds **I** and **II** follows from a similarity of the unit cell parameters of the single crystals.

EXPERIMENTAL

All procedures related to the synthesis of new complexes were carried out in air using commercially available solvents and reagents (DMF, chloroform, dioxane, acetonitrile, ethanol, dimethoxyethane, ethyl acetate, dioctyl phthalate, 1,2-bis(4-pyridyl)ethane, and 4,4'-bipyridine). The starting trinuclear complexes $[Fe_2MO(Piv)_6(HPiv)_3]$ (M = Ni, Co) and coordination polymers $[Fe_2NiO(Piv)_6(L^2)_{1.5}]_n$ were synthesized using known procedures [12, 13].

Synthesis of $[Fe_2NiO(Piv)_6(L^1)_{1.5}]_n \cdot 2n$DMF (I · 2*n*DMF). Weighed samples of $Fe_2NiO(Piv)_6(HPiv)_3$ (55 mg, 0.05 mmol) and pivalic acid (25 mg) were dissolved in DMF (10 mL), and the obtained solution was placed in a tube. Onto this solution DMF (5 mL) and a solution (5 mL) containing L^1 (15 mg, 0.08 mmol) in acetonitrile were consequently layered. In 2 weeks, the formed crystals were collected and dried in air. The yield was 27 mg (36%). The crystals for X-ray diffraction analysis were stored under a solvent layer.

Synthesis of $[Fe_2CoO(Piv)_6(L^1)_{1.5}]_n \cdot m$Solv (II · *m*Solv). Weighed samples of $Fe_2CoO(Piv)_6(HPiv)_3$ (55 mg, 0.05 mmol) and pivalic acid (25 mg) were dissolved in DMF (10 mL), and the obtained solution was placed in a tube. Onto this solution DMF (5 mL) and a solution (5 mL) containing L^1 (15 mg, 0.08 mmol) in a chosen solvent (acetonitrile, ethanol, dimethoxyethane, or ethyl acetate) were consequently layered. In 2 weeks, the formed crystals were collected under a solvent layer for X-ray diffraction analysis.

Synthesis of $[Fe_2CoO(Piv)_6(L^1)_2]_n \cdot m$Solv (III · *m*DMF). A weighed sample of $Fe_2CoO(Piv)_6(HPiv)_3$ (55 mg, 0.05 mmol) was dissolved in DMF (10 mL). Pivalic acid (50 mg, 0.5 mmol) and a solution (10 mL) of L^1 (15 mg, 0.08 mmol) in acetonitrile were consequently added to the obtained solution, which resulted in the formation of a brown precipitate. The reaction mixture with the precipitate was left to stay, and a minor amount of brown crystals suitable for X-ray diffraction analysis was formed in the reaction mixture after several weeks.

Synthesis of $[Fe_2NiO(Piv)_6(L^2)_{1.5}]_n \cdot m$Solv (IV · *m*DMF) was carried out by the reaction of $Fe_2NiO(Piv)_6(HPiv)_3$ (55 mg, 0.05 mmol) and L^2 (12 mg, 0.075 mmol) in the corresponding solvents (chloroform, dioctyl phthalate) or by the slow diffusion of a solution of the ligand in a chosen solvent (ethyl acetate, ethanol) to a solution of the trinuclear complex in DMF. The single crystals were sampled for the determination of the unit cell parameters. The bulky samples were filtered off, washed with the corresponding solvent or a mixture of solvents, and dried in air.

Elemental analysis (C, H, N) was carried out on a Carlo Erba 1106 automated C,H,N analyzer. X-ray diffraction analysis was conducted using a Bruker D8 ADVANCE diffractometer (CuK_α radiation, λ = 1.54056 Å).

The sorption capacity toward nitrogen at 77 K was estimated by the method of nitrogen thermodesorption from the ratio of the peak surface areas of nitrogen desorbed from the surface of the studied porous coordination polymer and standard (silica gel with S_{BET} = 271 m^2/g).

The ^{57}Fe Mössbauer spectra were recorded on a Wiesel electrodynamic spectrometer (Germany) at 16, 78, and 300 K using a helium cryostat (Janis, model CCS 850) with a temperature regulator (Lake Shore Cryotronics, model 332). The accuracy of temperature maintenance was 0.1 K. The radiation source was ^{57}Co(Rh) with an activity of 1.1 GBq. Isomeric shifts were counted from the center of the magnetic hyperfine structure of metallic iron. The Mössbauer spectra were processed using the Loren (Semenov Institute of Chemical Physics, Russian Academy of Sciences) and NORMOS (Germany) (by least squares assuming that the shape is described by the Lorentz function) standard programs. A sample of **IV** · 2DEF was measured under a DEF layer to warrant its unchanged solvate composition.

X-ray diffraction analyses of the single crystals of coordination polymers **I** and **III** were carried out on a Bruker Apex II diffractometer (CCD detector, MoK_α, λ = 0.71073 Å, graphite monochromator). The structures were solved by direct methods and refined in the full-matrix anisotropic approximation for all nonhydrogen 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-97 program package [18]. The disordered solvate molecules in compound **I**, which we failed to localize, were removed using the SQUEEZE procedure [19].

The crystallographic parameters and refinement details for the structures studied are as follows.

Compound I: greenish-brown crystals as hexagonal prisms, $C_{105}H_{165}Fe_4N_9Ni_2O_{29}$, 2358.28 g/mol, T = 173(2) K, triclinic crystal system, space group $P\bar{1}$, a = 11.933(1), b = 27.683(3), c = 30.421(4) Å, α = 65.023(2)°, β = 83.520(2)°, γ = 85.419(2)°, V = 9046(2) Å^3, Z = 2, ρ_{calcd} = 0.866 g/cm^3, μ = 0.564 mm^{-1}, θ_{max} = 26.44°, number of measured reflections 83 061, number of independent reflections 37098, R_{int} = 0.1267, GOOF = 0.763, R_1 ($I > 2\sigma(I)$) = 0.0719, wR_2 ($I > 2\sigma(I)$) = 0.1773. Some disordered solvent molecules were not localized, and the corresponding electron density was corrected using the SQUEEZE procedure from the PLATON package [20].

Compound III: brown crystals as hexagonal prisms, $C_{54}H_{78}CoFe_2N_4O_{13}$, 1161.83 g/mol, T = 296(2) K, monoclinic crystal system, space group $P2_1/c$, a =

Table 1. Unit cell parameters of compound **II** in various solvents

Solvent	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	V, Å^3
MeCN	11.940(6)	27.45(1)	28.96(1)	110.306(6)	92.377(7)	95.951(7)	8906(7)
EtOAc	11.82(2)	27.26(4)	28.69(4)	110.9(3)	92.41(4)	95.35(5)	8573(17)
$(MeO)_2C_2H_4$	11.84(2)	27.54(6)	30.28(6)	65.3(3)	82.56(4)	85.18(4)	8890(30)
EtOH	11.8(1)	30.2(3)	31.5(3)	67.2(2)	89.1(4)	84.8(3)	10320(60)

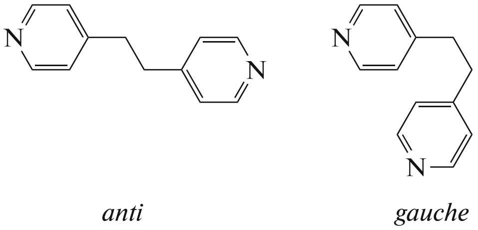
12.091(9), $b = 20.43(2)$, $c = 31.65(2)$ Å, $\beta = 96.73(2)°$, $V = 7764(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.994$ g/cm^3, $\mu = 0.627$ mm^{-1}, $\theta_{max} = 25.69°$, number of measured reflections 22 176, number of independent reflections 13 094, $R_{int} = 0.1769$, GOOF = 0.555, R_1 ($I > 2\sigma(I)$) = 0.0984, wR_2 ($I > 2\sigma(I)$) = 0.2592. Some disordered solvent molecules were not localized, and the corresponding electron density was corrected using the SQUEEZE procedure from the PLATON package [20].

The unit cell parameters of compound **II** depending on the solvent used are presented in Table 1.

The coordinates of atoms and other parameters for the structures of compounds **I** and **III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1550804 (**I**) and 1550805 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The syntheses of compounds **I–III** are based on the substitution of coordinated molecules of pivalic acid and/or DMF molecules in $Fe_2MO(Piv)_6(HPiv)_x(DMF)_{3-x}$ (M = Ni(II), Co(II); x = 0–3, formed from $Fe_2MO(Piv)_6(HPiv)_3$ upon dissolution in DMF) by the nitrogen atoms of the pyridine groups of L^1. Molecules L^1 are conformationally flexible and can take both *gauche* (angular) and *anti* (linear) conformations (Scheme 1) [21].



(L^1)

Scheme 1.

The 1D chains $[Fe_2MO(Piv)_6(anti\text{-}L^1)]_n$ formed by filling two coordination vacancies in the trinuclear block by the pyridine groups of *anti*-L^1 can be distinguished in the crystal lattices of compounds **I–III**. In the case of compounds **I** and **II**, these chains are linked by the *anti*-L^1 molecules (which leads to the formation of the 2D network), whereas the coordination vacancies in these chains in compound **III** are filled by *gauche*-L^1 acting as a monodentate nonbridging ligand.

The slow diffusion of the $[Fe_2MO(Piv)_6(HPiv)_3]$ complex (M = Ni, Co) and ligand L^1 leads to the formation of crystals of 2D polymers **I** and **II** with an insignificant impurity of an amorphous precipitate. The fast mixing of solutions of $Fe_2MO(Piv)_6(HPiv)_3$ and L^1 with the same ratio of the reactants as in the case of diffusion results in the formation of a precipitate with a variable composition containing a minor amount of the crystals of 1D polymer **III** in the case of M = Co(II). The reaction of trinuclear pivalate with ligand L^1 of the bipyridine series leading to the formation of compound **III** differs substantially from the reactions of the same trinuclear complexes with conformationally rigid bipyridines L^2 and Dpe, resulting in the formation of the 2D polymers [12, 13]. The difference in the compositions of the porous coordination polymers formed under various conditions (namely, the ratio of the contents of $Fe_2MO(Piv)_6$ and L^1 in them) can be explained by several factors, among which the different contributions of the diffusion rates of the reactants are probably significant: in the case of the fast mixing of solutions, the ratio of $Fe_2MO(Piv)_6$ and L^1 in the whole bulk of the reaction mixture corresponds to their amounts, whereas this ratio in the part of the reaction mixture, where the reactants interact, depends primarily on the diffusion rate in the case of the layering of solutions of the reactants. It can be assumed that the concentration of the reactants is low in the region of crystal growth in the case of slow diffusion, which results in a slow growth of particles of the most stable (under the synthesis conditions) coordination polymer. At the same time, the fast mixing of the reactants results in the formation of particles containing ligand L^1 in different conformations (probably, the *gauche* and *anti* forms of L^1 are permanently equilibrated in the solution), whose combination can lead to the formation of crystals of compound **III**.

The structures of coordination polymers **I** and **III** were determined by X-ray diffraction analysis. They contain the neutral trinuclear fragments $\{Fe_2MO(Piv)_6\}$, where M = Ni(II) and Co(II) (Fig. 1), in which three metal ions occupy the vertices of the triangle and are indiscernible by the X-ray diffraction method. Each metal ion exists in the distorted octahedral environment O_5N.

The M–M interatomic distances in the trinuclear cores of polymers **I** and **III** range from 3.259(3) to 3.298(5) Å, the M–(μ_3-O) bond lengths are 1.880(6)–1.92(8), M–$O_{carboxylate}$ are 1.971(13)–2.09(2), and M–$N_{pyridine}$ are 1.912(6)–2.222(9) Å, which is consistent with the interatomic distances and bond lengths in the trinuclear blocks of similar coordination polymers and complexes [12–14, 22].

The crystal lattice of compound **I** is formed by 2D layers similar to "honeycombs." These layers are formed due to the binding of the trinuclear fragments $\{Fe_2MO(Piv)_6\}$ by the L^1 molecules in the *anti* conformation and are similar to the 2D layers in the porous coordination polymers $[Fe_2NiO(Piv)_6(L)_{1.5}]_n$ (L = L^2, Dpe) [12, 13]. The distances between the μ_3-O atoms of the adjacent trinuclear blocks $Fe_2NiO(Piv)_6$ within one layer in compound **I** are 17.247(8) and 17.316(11) Å (similar distances in $[Fe_2NiO(Piv)_6(Bpe)_{1.5}]_n$ are 17.213(9)–17.331(9) Å), and the distances between the μ_3-O atoms of the trinuclear fragments $\{Fe_2MO(Piv)_6\}$ lying on the diagonal of the hexagonal plane are 31.732(12)–37.933(9) Å (similarly to 33.12(1)–35.88(1) Å in $[Fe_2NiO(Piv)_6(Dpe)_{1.5}]_n$) [13]. The torsion angles between the pyridine groups in L^1 in compound **I** relative to the $-CH_2CH_2-$ bridge range from 170(2)° to 178(1)°. Unlike compounds $[Fe_2NiO(Piv)_6(L)_{1.5}]_n$ (L = L^2, Dpe), no interpenetration of the 2D layers is observed in the crystal lattice of coordination polymer **I**. These layers are parallel to the crystallographic plane {100}. The distances between the adjacent 2D layers in the crystal lattice of compound **I** differ. They can be divided into pairs: the distance between the layers in the pair is 3.078(2) Å and that between the nearest 2D layers of the adjacent pairs is 8.855(3) Å (the distances between the layers were determined as distances between the planes passing through six μ_3-O atoms of one "honeycomb"). The layers within one pair are shifted relative to each other by 11.70(2) Å (determined as a shift of centroids of six μ_3-O atoms of one "honeycomb") (Fig. 2).

The above described arrangement of the 2D layers in the crystal lattice of polymer **I** results in the formation of a two-dimensional system of pores that can be presented as channels arranged along the crystallographic axes *a* and *b* (Fig. 3). The total volume filled by the solvent molecules is 47% (calculated using the PLATON program for the probe molecule with $r = 1.4$ Å [20]). The positions of three DMF molecules (per formula unit) were localized by X-ray diffraction analysis. The methyl groups of DMF are located near the *tert*-butyl groups of the trinuclear fragments $\{Fe_2MO(Piv)_6\}$ and the pyridine groups of ligand L^1, whereas the oxygen atoms are directed to the center of ligand L^1.

According to the X-ray phase analysis data, the desolvation of compound **I** results in the complete loss of crystallinity, which can indicate the collapse and complete disordering of the crystal lattice (Fig. 4). Thus, the stability of the crystal lattice of compound **I** differs substantially from that of coordination polymers $[Fe_2NiO(Piv)_6(L)_{1.5}]_n$ (L = L^2, Dpe) in which interpenetration favors a relative retention of their structures [13, 14]. The estimation of the sorption capacity of desolvated sample **I** toward nitrogen at 77 K gives a surface area of ~5 m²/g, which corresponds to nitrogen adsorption on the external surface of microparticles of the sample and confirms the conclusion about the disappearance of the system of pores due to the disordering of the crystal lattice of this coordination polymer.

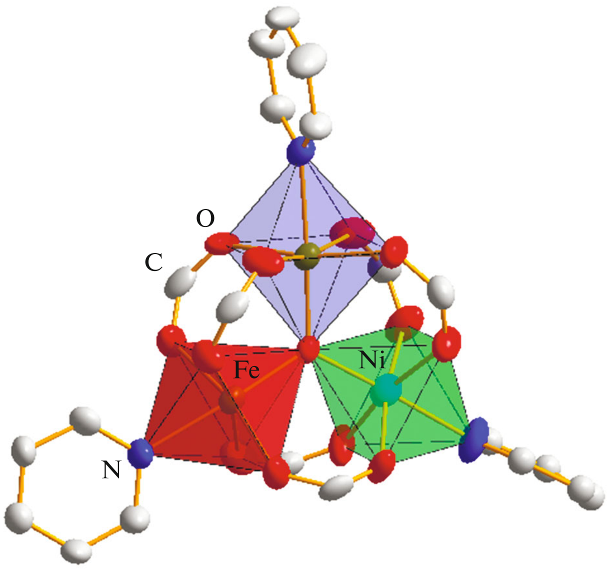


Fig. 1. Structure of the trinuclear block $Fe_2NiO(Piv)_6(Py)_3$ in compound **I**. The *tret*-butyl groups and hydrogen atoms are omitted.

It was found for a series of coordination polymers **II** synthesized in various solvents that the replacement of an aprotic solvent by a protic one exerts the highest effect on the crystal lattice parameters. For example, in the case of the layering of a solution of L^1 in acetonitrile, ethyl acetate, or dimethoxyethane, the unit cell volume of the obtained coordination polymer lies within 8573(17)–8906(7) Å³, whereas the unit cell volume increases to 10 320 Å³ in the case of ethanol. It should be mentioned that all unit cell parameters for the samples obtained from acetonitrile and ethyl acetate are similar. It can be assumed that for the synthesis of compound **I**, on the one hand, the most favorable conformation of the ligand can somewhat change depending on the solvent and can affect, in turn, the structure of an individual 2D layer in the course of its formation and, as a consequence, can influence on the *a*, *b*, and γ parameters. On the other hand, the inclusion of molecules of different nature into the pores of

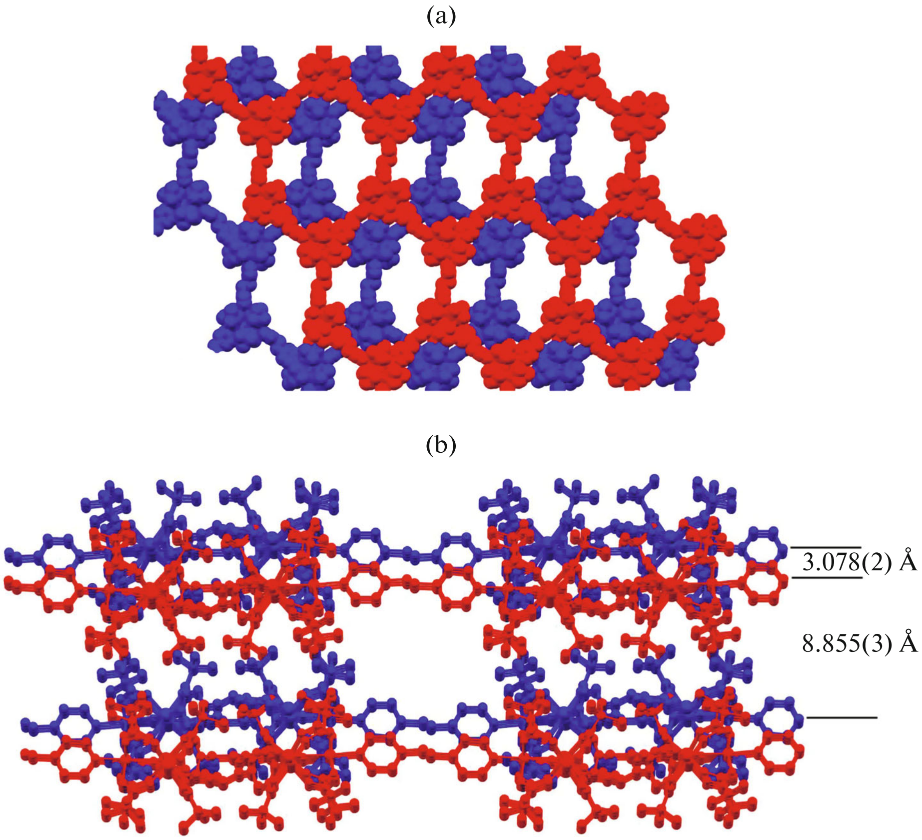


Fig. 2. (a) Pair of the 2D layers and (b) their mutual arrangement in the crystal lattice of compound **I**. The hydrogen atoms and solvate DMF molecules are omitted.

this coordination polymer can affect the mutual arrangement of the 2D layers relative to each other and the c, α, θ, and β parameters.

The crystal lattice of compound **III** is built of zigzag 1D chains formed by the binding of the trinuclear fragments $\{Fe_2CoO(Piv)_6\}$ by molecules L^1 in *anti* conformations (Fig. 5a). In the crystal lattice, these chains are packed parallel to each other along the crystallographic axis c. The third "free" coordination position in each trinuclear fragment $\{Fe_2CoO(Piv)_6\}$ is occupied by the pyridine group of the terminal L^1 molecule in the *gauche* conformation, and the second pyridine group of this molecule remained uncoordinated. The torsion angles between the pyridine groups relative to the $-CH_2CH_2-$ bridge in L^1 are 176(2)° for *anti*-L^1 and 79(3)° for *gauche*-L^1. In the case of *anti*-L^1, the pyridine groups are nearly mutually perpendicular (the dihedral angle between the planes passed through the C and N atoms of the pyridine rings is 88.4(8)°, and a similar angle in *gauche*-L^1 is 39.6(9)°). The crystal lattice of compound **III** contains 1D channels with a cross section of ~4 × 9 Å oriented along the crystallographic axis a (Fig. 5) and filled with the solvate DMF molecules.

Unlike the earlier described porous coordination polymers $[Fe_2MO(Piv)_6(L)_{1.5}]_n$ (L = L^2, Dpe), the layers are parallel in porous coordination polymers **I** and **II**. Taking into account the fact that a change in the synthesis conditions can lead to the formation of "isomeric" porous coordination polymers differed by the presence or absence of interpenetration [16], we studied the structures of the porous coordination polymers formed by the reaction of complex $[Fe_2NiO(Piv)_6(HPiv)_3]$ with L^2 in various solvents. It was established that porous coordination polymers of similar structure (interpenetration of 2D layers in the crystal lattice) were formed in all cases studied. It could be expected that the formation of the coordination polymer in the reaction of $[Fe_2NiO(Piv)_6(HPiv)_3]$ and L^2 using the solvent (dioctyl phthalate), the size of molecules of which exceeds the pore size in the known porous coordination polymer **IV** [14], would avoid interpenetration. However, it turned out that the porous coordination polymer of the known structure formed and large molecules did not enter into the pores as described below.

Since the desolvation of compounds **I** and **II** results in the collapse of their crystal lattices and in the formation of compounds amorphous to X-rays, the study

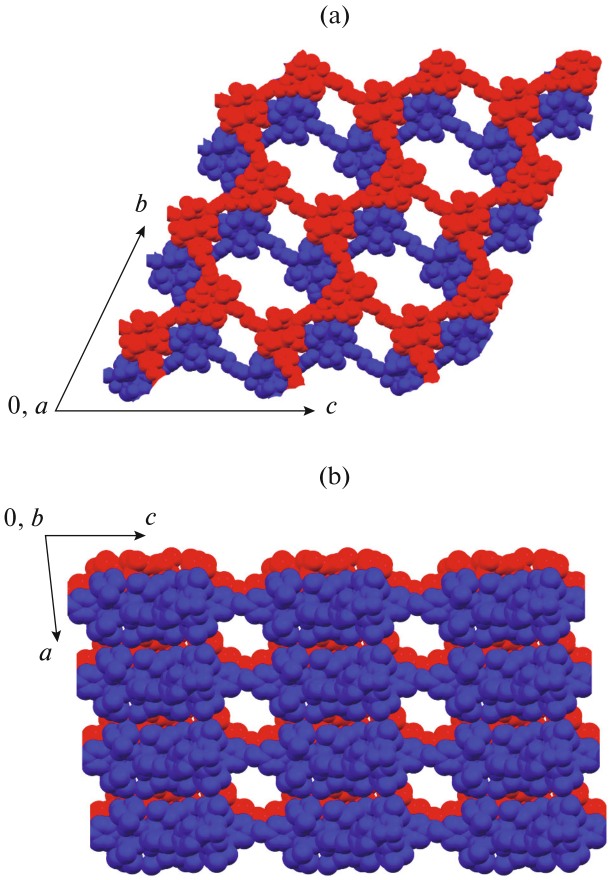


Fig. 3. Channels in compound **I** along the crystallographic axes (a) *a* and (b) *b*.

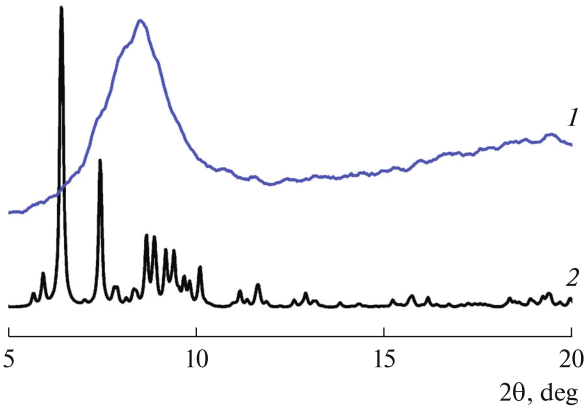


Fig. 4. (*1*) Powder diffraction pattern for a sample of compound **I** dried in air and (*2*) the calculated diffraction pattern of **I** · *n*Solv.

of their structures is difficult. A more detailed study of the solvent effect on the structures of the porous coordination polymers with labile crystal lattices was carried out using porous coordination polymer **IV**, which is an analog of compounds **I** and **II**. As mentioned above, the distinctions of these porous coordination polymers are the length and flexibility of the bridging ligands (L^2 and L^1, respectively) and the mutual arrangement of the 2D frameworks (interpenetrating and parallel, respectively) [12–14].

It has previously been shown that the replacement of DMF by DEF in the reaction of $[Fe_2NiO(Piv)_6(HPiv)_3]$ with L^2 affects only the mutual arrangement of the 2D layers in the crystal lattice of compound **IV** [14]. The desolvation of **IV** · ***n*Solv** changes the dihedral angle between the planes, cell parameters, and reflection positions in the X-ray powder diffraction patterns. Thus, an analysis of the diffraction patterns makes it possible to estimate the dihedral angle between the 2D layers and, as a consequence, the pore volume in the porous coordination polymer $[Fe_2NiO(Piv)_6(L^2)_{1.5}]_n$.

In the case of formation of this porous coordination polymer in the solvent, the shape of the molecule of which is close to DMF or DEF, the samples are obtained in which the mutual arrangement of the 2D layers is close, according to the X-ray phase diffraction data, to that in the samples with the maximum pore volume (these samples are formed when DEF is used [14]) (Fig. 6a). The use of nitromethane or a nitromethane–nitrobenzene mixture as a solvent affords the samples, whose X-ray powder patterns are close to those of the porous coordination polymers with the minimum pore volume (these samples can be obtained by the desolvation of $[Fe_2NiO(Piv)_6(L^2)_{1.5}]_n \cdot 2n$DMF [12, 14]) (Fig. 6b). It can be concluded that nitromethane molecules cannot efficiently slide apart the 2D layers in compound **IV**, which can be explained by a weak interaction of these molecules with the crystal lattice units of the porous coordination polymer.

Thus, the replacement of the solvent in the synthesis of the coordination polymers based on the trinuclear fragments $\{Fe_2MO(Piv)_6\}$ with L^1 affects the mutual arrangement of the 2D layers, whereas the change in the conditions of reactant mixing (slow diffusion or pouring together of the solutions) results in a change in the composition and structure of the formed coordination polymer. The use of conformationally rigid ligands (such as L^2, tris(4-pyridyl)pyridine, or tris(4-pyridyl)triazine) in the reaction with the trinuclear complexes $[Fe_2MO(Piv)_6(Solv)_3]$, as a rule, results in the formation of coordination polymers with the same trinuclear fragment–bridging ligand ratio and a similar sequence of bonds [23], while the mutual arrangement of the 2D layers relative to each other can depend on the solvent type in the reaction medium in the case of the flexible coordination polymer $[Fe_2MO(Piv)_6(L^2)_{1.5}]_n$.

It was shown by X-ray powder analysis that the resolvation of desolvated sample **IV** with methanol, ethanol, or toluene (Fig. 7) resulted in the moving apart of the 2D layers, possibly indicating that the sol-

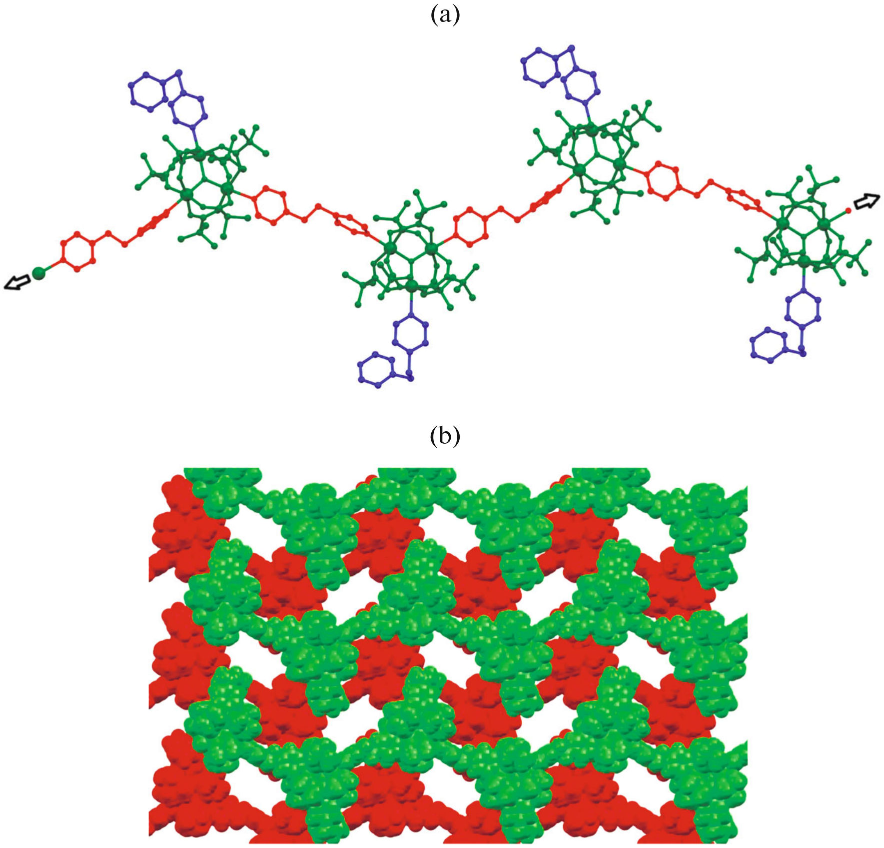


Fig. 5. (a) 1D chain and (b) channels in the crystal lattice of compound **III**.

vent molecules enter into the polymer pores. At the same time, the resolvation with dichloromethane does not result in a change in the crystal lattice of the porous coordination polymer, and the resolvation with ethyl acetate leads to insignificant changes in the reflection positions in the powder diffraction pattern. The difference in the reflection positions in the diffraction patterns of the sample obtained from ethyl acetate and the sample obtained from DMF and resolvated with ethyl acetate can be explained by the fact that the pore size is comparable to that of the ethyl acetate molecule and, as a consequence, it is difficult for ethyl acetate molecules to enter into the pores of the desolvated sample of compound **IV**. Thus, depending on the solvent resolvating a sample of compound **IV**, this process can favor both the maximum possible moving apart of the 2D layers, which is achieved in the synthesis of the coordination polymer (in the case of methanol, ethanol, or toluene), and an incomplete moving apart of the 2D layers (in the case of dichloromethane or ethyl acetate). This can be due to the energy of interaction of the crystal lattice units with the solvent molecules or to the correspondence of the solvent molecules to the pore geometry. The complete opening of pores in the case of alcohols is consistent with the results of adsorption measurements [14].

Since structural rearrangements of the crystal lattice containing iron(III) ions can result in a change in their coordination environment and, as a consequence, in a change in the electric field around them, the electronic structures of the Fe^{3+} ion in porous coordination polymer **IV** · 2DEF and in the desolvated sample were studied by ^{57}Fe Mössbauer spectroscopy at 300, 78, and 16 K (Table 2, Fig. 8). All spectra exhibit only one doublet of quadrupole splitting. The isomeric shift for all samples is close to those in the earlier described heterometallic trinuclear complexes [24–26] and corresponds to the high-spin Fe^{3+} ion. In spite of exchange interactions between the metal ions in the trinuclear fragment according to the magnetochemical data [12], no signs of exchange interactions are observed in the Mössbauer spectra. The high values of quadrupole splitting indicate a low symmetry of the environment of the Fe^{3+} ions, and the storage of the sample under the DEF layer decreases the symmetry, which can be attributed to a strong distortion of the bond lengths and angles near the metal ions when the pores are filled with DEF molecules. Thus, the parameters of the Mössbauer spectra depend on the presence of a solvent in the pores affecting the mutual arrangement of the crystal lattice units and, as a consequence, the geometry of the coordination environ-

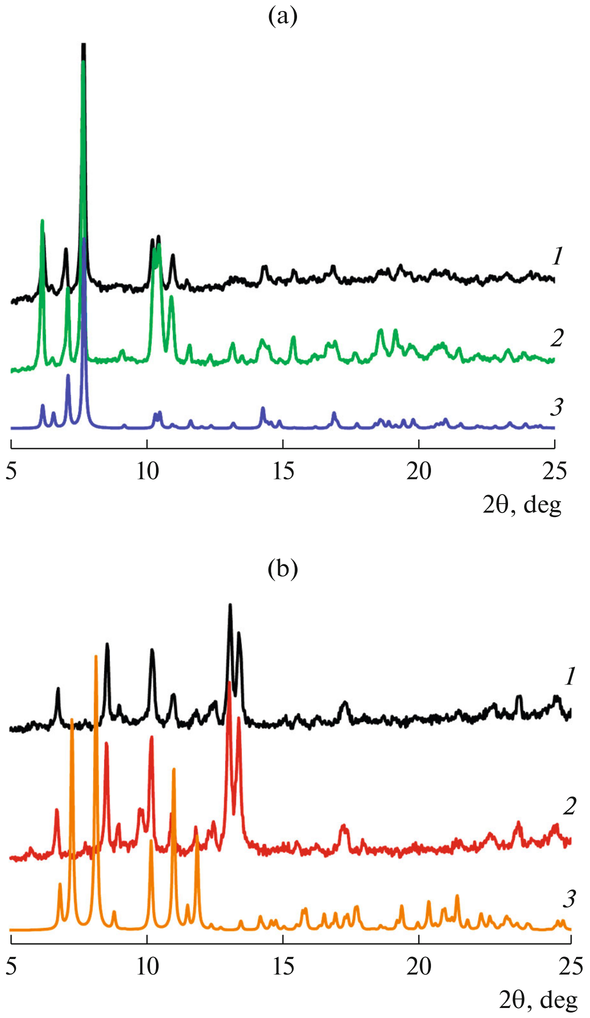


Fig. 6. Powder diffraction patterns of the samples of compound **IV** obtained from different solvents: (a) (*1*) nitromethane, (*2*) nitromethane–nitrobenzene (1 : 1), and (*3*) dimethylformamide, 296 K (theoretically calculated by the X-ray diffraction data); (b) (*1*) nitromethane, (*2*) nitromethane–nitrobenzene (1 : 1), and (*3*) dimethylformamide, 120 K (theoretically calculated by the X-ray diffraction data).

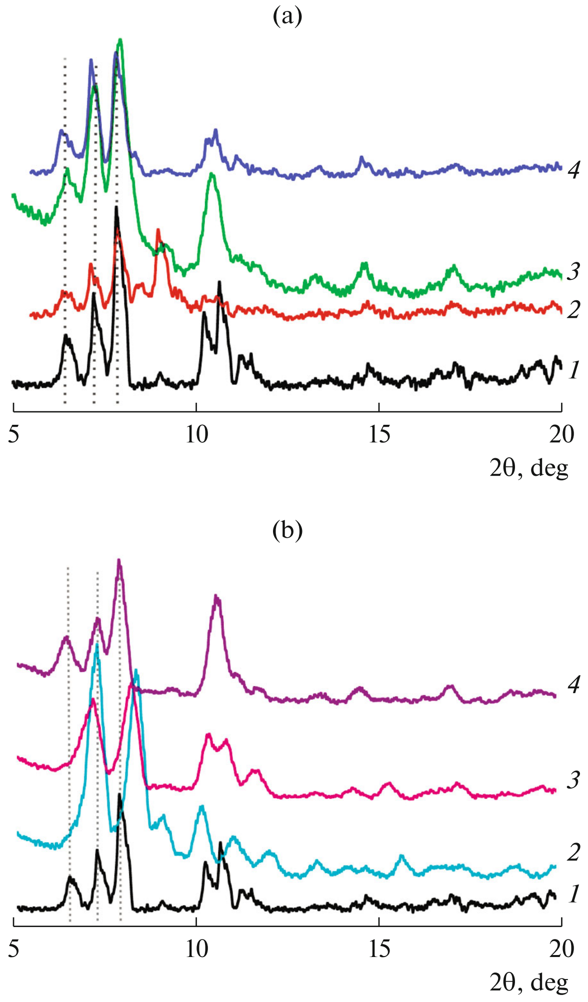


Fig. 7. Powder diffraction patterns of compound **IV** resolvated with different solvents: (a, b) (*1*) freshly prepared sample; (a) (*2*) sample after activation, (*3*) methanol, and (*4*) ethanol; (b) (*2*) dichloromethane, (*3*) ethylacetate, and (*4*) toluene.

Table 2. Mössbauer spectral parameters of porous coordination polymer **IV** in the desolvated state and under a DEF layer

Sample	T, K	Component	Δ*	Δ**	A***
			±0.03 mm/s		±0.05
IV	300	Fe^{3+} (paramagnetic)	0.42	0.98	1.00
	78	Fe^{3+} (paramagnetic)	0.52	1.01	1.00
	16	Fe^{3+} (paramagnetic)	0.54	1.05	1.00
IV · 2DEF	78	Fe^{3+} (paramagnetic)	0.52	1.13	1.00
	16	Fe^{3+} (paramagnetic)	0.53	1.18	1.00

* δ is the isomeric shift (relative to α-Fe).
** Δ is the quadrupole splitting.
*** A is the relative content of iron(III).

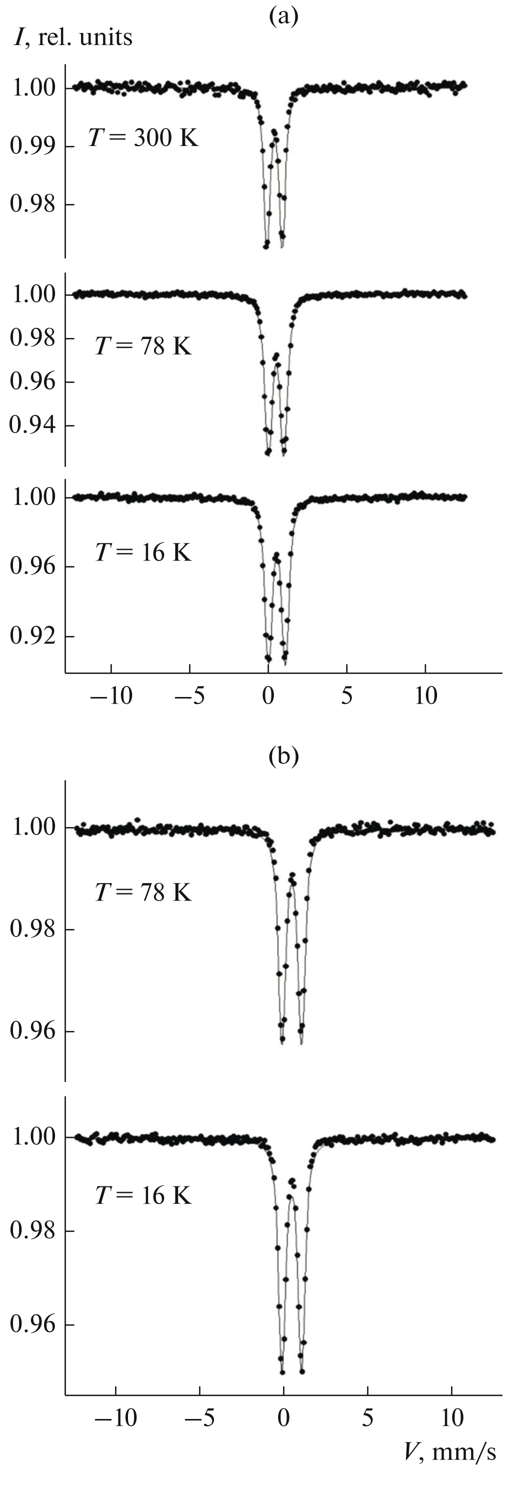


Fig. 8. Mössbauer spectra of compounds (a) **IV** and (b) **IV** · 2DEF.

ment of even coordinatively saturated Fe^{3+} ions, which is consistent wit the data of studying the change in the magnetic properties upon the desolvation of the sample [12]. Therefore, when interpreting the Mössbauer spectra, one should take into account not only the donor/acceptor influence of the ligands but also a possibility of changing the geometry of the environment of the metal ions.

To conclude, it is shown that the replacement of the solvent in the reaction medium for the synthesis of coordination polymer **IV** · *n*Solv affects only the mutual arrangement of the 2D layers in the crystal lattice, whereas a change in the method of reactant mixing (slow diffusion or mixing of solutions) in the case of conformationally flexible ligand L^1 changes the ratio of the amounts of the trinuclear fragments and ligands and results in the formation of the 1D coordination polymer. At the same time, in the case of conformationaly rigid ligand L^2, the method of reactant mixing exerts no effect on the structure of the coordination polymer. It is shown for compound **IV** as an example that the resolvation by various solvents can result in the complete or partial moving apart of the 2D layers. The influence of pore filling in coordination polymer **IV** on the Mössbauer spectral parameters of the Fe^{3+} ion was found, which can be due to insignificant changes in the geometry of the coordination environment during pore filling.

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