Structures and sorption properties of the coordination polymers built up of 3d metal carboxylate polynuclear complexes

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The reaction of trinuclear acetate complexes $Fe_2MO(AcO)_6(H_2O)_3$ ($M = Ni^{2+}, Co^{2+}$) with 4,4´-bipyridine (bpy) results, depending on the reaction conditions, in porous coordination polymers with the composition $Fe_2MO(AcO)_6(bpy)_{1.5}$ (with retention of the metal core $Fe_2MO(AcO)_6$) or nonporous coordination polymers with the composition $M_2(AcO)_4(bpy)_2$ (with destruction of the metal core $Fe_2MO(AcO)_6$). The adsorption and desorption properties of the compounds $Fe_2MO(AcO)_6(bpy)_{1.5}$ with respect to nitrogen and hydrogen were studied. The reaction of hexanuclear benzoate complex $Mn_6O_2(PhCOO)_{10}(MeCN)_4$ with bpy or *trans*-1,2-bis(4-pyridyl)ethylene (bpe) in DMF results in destruction of the metal core $Mn_6O_2(PhCOO)_{10}$ and formation of nonporous coordination polymers, while the pivalate complex $Mn_6O_2(Piv)_{10}(EtOH)_3(HPiv)$ under the same conditions gives rise to the coordination polymer containing $Mn_6O_2(Piv)_{10}$ structural blocks.

Key words: coordination polymers, polynuclear complexes, nitrogen adsorption, hydrogen adsorption.

The interest in porous coordination polymers (PCP) built up of 3d metals is caused by several reasons, in particular, by the possibility of creation of polyfunctional materials on the base of such compounds that can find application as magnetic materials with controlled properties as well as active components of sensors.[1—3] The porous coordination polymers can possess the combination of properties that is unattainable in the case of other classes of compounds, for example, the ability to adsorb certain substrates (including gases) along with nontrivial magnetic properties caused by the exchange interaction of unpaired electrons. However, the problem of effective directed synthesis of the compounds comprising predetermined polynuclear structural units has not been solved to date. Therefore, the preparation of PCP by cross-linking of polynuclear blocks by appropriate bridging ligands is of special interest. In the overwhelming majority of examples of PCP having polynuclear blocks published to date, crystal lattices are formed by self-assembly in the reaction mixtures (for example, the polymers having trinuclear blocks Fe_3O^{7+}).[4] The examples of the preparation of PCP using polynuclear complexes as the building blocks, in which the metal-organic core is retained during the reaction, are scarce.[5] As a rule, cross-linking of polynuclear complexes (blocks) by bridging ligands results in nonporous structures.[6—8] Thus, the preparation of PCP where the basic structure of polynuclear blocks would be retained is topical. In this case, the physical properties of a polynuclear complex (for example, magnetic and spectral) will, at least partially, predetermine the properties of the resulting coordination polymer, which will allow obtaining the compounds with the desired properties.

The aim of the present work was to study a possibility of using the polynuclear complexes with homonuclear (Mn_6O_2) and heteronuclear (Fe_2MO, where M = Co, Ni) cores for the preparation of PCP by cross-linking with conformationally rigid ligands (4,4´-bipyridine (bpy) and *trans*-1,2-bis(4-pyridyl)ethylene (bpe)), to determine conditions of PCP formation, and to study their sorption properties.

In the present work, hexanuclear Mn^{II} and Mn^{III} pivalates and benzoates ($Mn_6O_2(Piv)_{10}(EtOH)_3(HPiv)$ and $Mn_6O_2(PhCOO)_{10}(MeCN)_4$, respectively) and trinuclear heterometal acetate complexes $Fe_2MO(AcO)_6(H_2O)_3$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1192—1198, June, 2010.

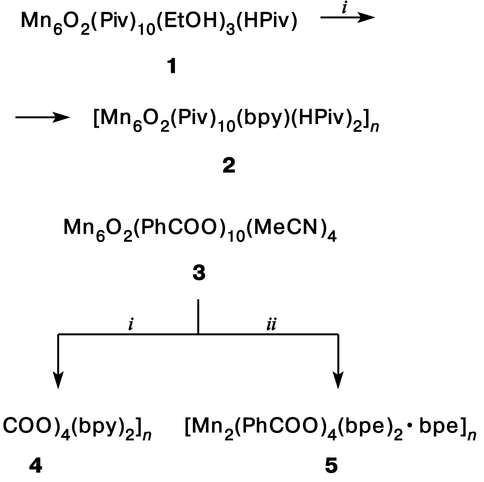
(M = Co, Ni) were used as the starting polynuclear complexes. These hexa- and trinuclear complexes have coordinated solvent molecules (four and three, respectively), which could be replaced by bridging ligands to obtain two-dimensional cross-linked polymers. The reactions of these compounds with bpy and bpe depending on the conditions resulted in coordination polymers with the starting polynuclear blocks or their destruction products. The conditions were determined that allowed one to retain the polynuclear metal cores in resulting coordination polymers. The sorption properties of the prepared PCP were studied.

Results and Discussion

Since the hexanuclear pivalate $Mn_6O_2(Piv)_{10}(EtOH)_3(HPiv)$ (**1**, Piv = Me_3CCOO^-) has the coordinated molecules of ethanol and pivalic acid, one could expect that the cross-linking of the metal-containing blocks $Mn_6O_2(Piv)_{10}$ by N-donating bpy and bpe will occur in, at least, two dimensions. It was found that the reaction of hexanuclear complex **1** with bpy in DMF or in mixtures of solvents containing DMF (with addition of acetonitrile or ethyl acetate) resulted in 1D-coordination polymer $[Mn_6O_2(Piv)_{10}(bpy)(HPiv)_2]_n$ (**2**), whose structure has earlier[6] been described (the fact that both compounds were isostructural was confirmed by determination of unit cell parameters by single crystal X-ray analysis, Table 1). We failed to find conditions for the reactions, where two terminal ligands (EtOH and HPiv) in complex **1** could be replaced by two bridging molecules of bpy, which is necessary for the formation of a two-dimensional layer, where the blocks $\{Mn_6\}$ are connected through bpy molecules. Regardless of the ratio Mn_6 : bpy (1 : 1 and 1 : 2), only polymer **2** crystallized from the reaction mixture, which could be caused by its lower solubility (Scheme 1, Fig. 1, *a*).

In an attempt to prepare similar coordination polymers on the base of the benzoate analog, hexanuclear complex $Mn_6O_2(PhCOO)_{10}(MeCN)_4$ (**3**), we isolated the coordination polymers $[Mn_2(PhCOO)_4(bpy)_2]_n$ (**4**) and $[Mn_2(PhCOO)_4(bpe)_2 \cdot bpe]_n$ (**5**) upon reactions in DMF.

Scheme 1



i. bpy; *ii*. bpe

They contain the binuclear fragments formed due to destruction of the hexanuclear structural block Mn_6O_2 (see Scheme 1). Compound **4** (see Table 1) was isolated as a single crystal and was isostructural to the known polymer with the same composition.[9] In this compound, the chains of the fragments $\{Mn(\mu\text{-}OOCPh)_2\}$ are linked by bpy molecules forming a 2D network; the nitrogen atoms of bpy occupy the *trans*-positions in the coordination spheres of the Mn^{2+} ions completing them to the distorted octahedra N_2O_4 (see Scheme 1, Fig. 1, *b*).

In complex **5**, the bpe molecules link the dimeric fragments $\{Mn_2(PhCOO)_4\}$ in 1D chains (Fig. 2), which are packed parallel to each other in the lattice. The dimeric fragments $\{Mn_2(PhCOO)_4\}$ have two types of benzoate ions: two ions $PhCO_2^-$ play the bridging role linking two Mn^{2+} atoms, and two ions $PhCO_2^-$ form chelates with two metal atoms (see Fig. 2). Each Mn atom possesses the distorted octahedral environment of N_2O_4. The structural parameters, some interatomic distances, and angles are given in Tables 2 and 3. The free space between

Table 1. The parameters of cell units for complexes **2**, **4**, **8**, and **9***

Parameter	**2**	**4**	**8**	**9**
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Orthorhombic
Space group	P_{nna}	P_{bcn}	$P\bar{1}$	P_{nnm}
T/K	200(2)	293(2)	150(2)	293(2)
a/Å	29.397(15)	18.707(5)	7.953(3)	11.272(12)
b/Å	24.254(12)	11.669(5)	9.106(4)	11.554(10)
c/Å	13.466(7)	9.497(5)	10.641(4)	10.792(13)
α/deg	—	—	109.669(6)	—
β/deg	—	—	99.864(6)	—
γ/deg	—	—	100.818(6)	—

* The literature data for complexes **2, 4, 8**, and **9** are given in Refs 6,9—11, respectively.

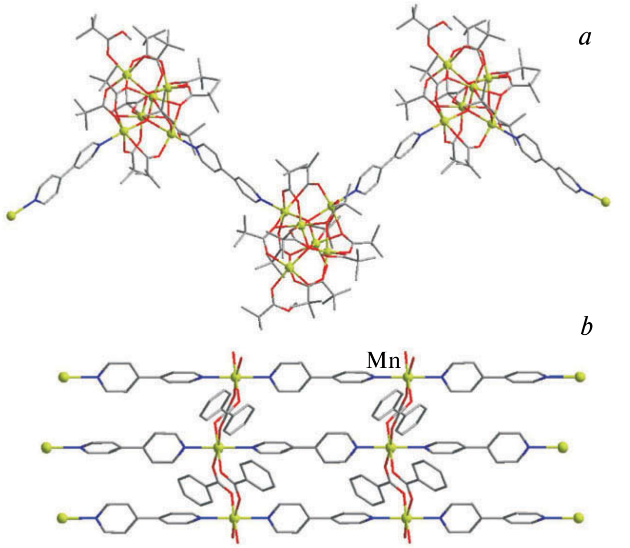


Fig. 1. The structures of polymers **2** (*a*) and **4** (*b*) according to X-ray studies.*

the one-dimensional chains $[Mn_2(PhCOO)_4(bpe)_2]_n$ is occupied by the bpe molecules, and the prepared compound does not have pores in the lattice.

Table 2. The main crystallographic data and refining parameters for structure **5**

Parameter	Value
Molecular formula	$C_{64}H_{50}Mn_2N_6O_8$
Molecular weight	1140.98
Dimensions/mm	0.20×0.20×0.10
Crystal system	Triclinic
Space group	$P\bar{1}$
T/K	293(2)
λ/Å	0.71073
a/Å	9.2849(17)
b/Å	12.227(2)
c/Å	13.083(2)
α/deg	70.076(3)
β/deg	85.715(3)
γ/deg	1370.1(4)
V/Å^3	1370.1
Z	1
d_{calc}/g cm^{-3}	1.383
μ/mm^{-1}	0.524
Number of measured reflections	9456
Number of independent reflections	3944
R_{int}	0.1373
wR (gt)	0.0693
R (gt)	0.1386

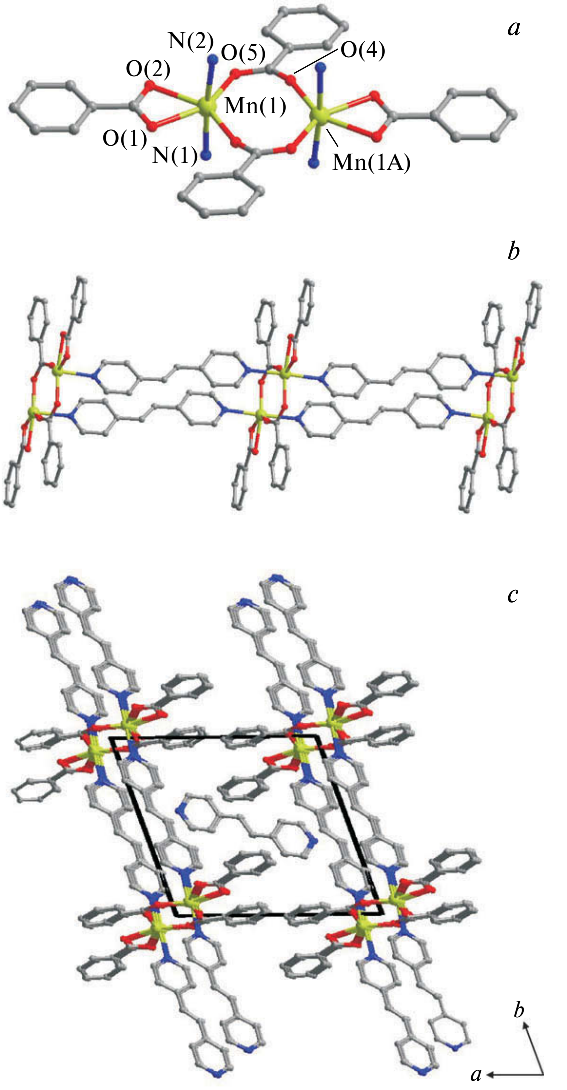


Fig. 2. The structure of compound **5**: (*a*) the structure of the binuclear fragment $\{Mn_2(PhCOO)_4(bpe)_4\}$ (only nitrogen atoms of the coordinated bpe molecule are shown); (*b*) the structure of the polymeric chain; (*c*) the chains packing in unit cell. The hydrogen atoms are not shown.

The formation of different products in the reactions of hexanuclear complexes $Mn_6O_2(Piv)_{10}(EtOH)_3(HPiv)$ (**1**) and $Mn_6O_2(PhCOO)_{10}(MeCN)_4$ (**3**) with bpy (and its analog, bpe) in the polar coordinating solvents could be explained by different influence of the substituents in the carboxylates. Thus the higher stability of Mn^{II} and Mn^{III} pivalates as compared with benzoates could be connected with the fact that the electron-donating *tert*-butyl group increases the electron density on the oxygen atoms, which favors the formation of a stronger Mn—O bond, whereas the electron-withdrawing phenyl substituent weakens the Mn—O bond. In addition to different electronic effect of substituents in the carboxylates, the steric shielding of

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* Figures 1—3 are available in full color in the on-line version of the journal (http://www.springerlink.com).

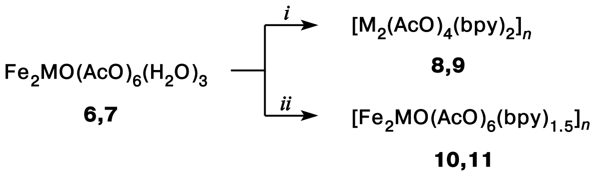
Table 3. The main bond lengths (*d*) and bond angles in complex **5**

Parameter	Value	Parameter	Value	Parameter	Value
Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Mn(1)—N(1)	2.265(5)	O(4)—Mn(1)—O(5)	121.13(17)	O(1)—Mn(1)—O(2)	57.51(16)
Mn(1)—N(2)	2.269(5)	O(4)—Mn(1)—O(1)	89.47(17)	N(1)—Mn(1)—O(2)	91.48(17)
Mn(1)—O(1)	2.259(4)	O(5)—Mn(1)—O(1)	149.33(17)	O(4)—Mn(1)—N(2)	88.46(18)
Mn(1)—O(2)	2.268(4)	O(4)—Mn(1)—N(1)	87.78(17)	O(5)—Mn(1)—N(2)	91.03(17)
Mn(1)—O(4)	2.084(4)	O(5)—Mn(1)—N(1)	88.19(17)	O(1)—Mn(1)—N(2)	91.86(17)
Mn(1)—O(5)	2.117(4)	O(1)—Mn(1)—N(1)	91.29(17)	N(1)—Mn(1)—N(2)	175.08(18)
		O(4)—Mn(1)—O(2)	146.96(17)	O(2)—Mn(1)—N(2)	93.40(17)
		O(5)—Mn(1)—O(2)	91.84(17)		

Mn^{2+} ions in the hexanuclear block, which prevents the substitution of terminal ligands and destruction of the hexanuclear framework, should not be ruled out.

The reactions of trinuclear heterometallic acetate complexes $Fe_2MO(AcO)_6(H_2O)_3$ (M = Co^{2+} (**6**), Ni^{2+} (**7**)) in DMF also result in destruction of the metal trinuclear core. Thus the reaction of **6** and **7** with bpy results in the coordination polymers with the composition $[M_2(AcO)_4(bpy)_2]_n$ (M = Co (**8**), Ni (**9**)) (Scheme 2, Table 1). The cell parameters of polymers **8** and **9** were identical to those described earlier for complexes $[Co_2(AcO)_4(bpy)_2]_n$ (see Ref. 10) and $[Ni_2(AcO)_4(bpy)_2]_n$ (see Ref. 11). However, in spite of similar compositions, they are not isostructural analogs. Polymers **8** and **9** are constructed by cross-linking of the binuclear blocks $\{M_2(AcO)_4\}$ through the bpy molecules whose nitrogen atoms occupy the axial positions in the coordination spheres of the metal ions (Fig. 3).

Scheme 2



M = Co^{2+} (**6**), Ni^{2+} (**7**), Co (**8**, **10**), Ni (**9**, **11**)
i. bpy, DMF; *ii*. bpy, DMF, MeCN.

The treatment of **6**, **7** with bpy in a mixture of DMF and MeCN (volume ratio 1 : 6; molar ratio 1 : 9) affords crystals of coordination polymers $[Fe_2MO(AcO)_6(bpy)_{1.5}]_n$ (M = Co (**10**), Ni (**11**)) (see Scheme 2), whose composition was confirmed by the data from elemental analysis and energy dispersive spectroscopy (the ratio Fe : Ni and Fe : Co was 2). Scanning electron microscopy showed that the samples are homogeneous and fine-crystalline. The attempts to obtain single crystals of these polymers failed. The compositions of complexes **10** and **11** corresponds to the compounds, where all nitrogen atoms of the bpy molecules are coordinated to the Fe^{3+} and M^{2+} ions in the trinuclear blocks $\{Fe_2MO(AcO)_6\}$. Previously, such compounds have been obtained on the base of the trinuclear ruthenium acetate complexes $Ru_3O(AcO)_6$ and pyrazine.[12] Presumably, complexes **10** and **11** also have polymeric structures, and, most probably, are built up of two-dimensional layers. As will be shown below, this assumption agrees with the results of sorption measurements.

The formation of different complexes in the reaction of trinuclear acetates $Fe_2MO(AcO)_6(H_2O)_3$ (**6**, **7**) with bpy depending on the solvent could be connected with different amount of DMF in the reaction mixture. Owing to the high solvation ability, good donating ability of the oxygen atom, and high dielectric permeability, DMF, probably, favors dissociation of the polynuclear complexes with destruction of the polymetal frameworks and formation of the mononuclear units (for example, $M(AcO)_2(DMF)_4$, where M = Co^{2+}, Ni^{2+}). Another possible reason for the formation of different products in the reaction of **6** and **7** with bpy depending on the solvent could be connected with the reaction time. The increase in DMF content favors better solvation as well as the blocking of vacant coordination sites in the coordination spheres of the metal ions, which prevents formation of the insoluble coordination polymer and results in higher solubility of the possible reaction products. As a consequence, the time of existence of a polynuclear species in a solution increases. This can lead to the increase in concentration of

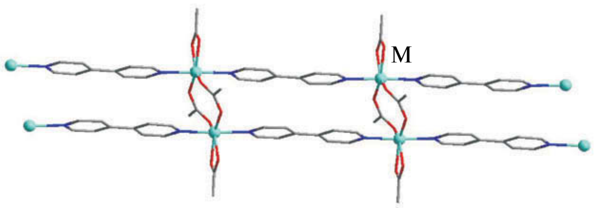


Fig. 3. The structures of polymers **8** (M = Co) and **9** (M = Ni) according to X-ray studies.

the dissociation products and to crystallization of the compound comprising "building blocks", which are the decomposition products of the trinuclear complexes. It can not be excluded that the formation of coordination polymers $[Fe_2MO(AcO)_6(bpy)_{1.5}]_n$ (**10**, **11**) in the reaction of $Fe_2MO(AcO)_6(H_2O)_3$ with bpy in a mixture of DMF and MeCN is connected with short time of existence of the trinuclear species in the solution, *i.e.*, the crystallization of these polymers occurs rapidly under the conditions far from equilibrium (therefore, we failed to obtain the single crystals of $[Fe_2MO(AcO)_6(bpy)_{1.5}]_n$ for X-ray study). The reaction under conditions more close to equilibrium (the reduction of crystallization time by increasing the solubility of the reaction products could be achieved by increasing the DMF content in the reaction mixture) led to destruction of the trinuclear core and crystallization of the homometalic polymers. Similar reaction, *i.e.*, destruction of the trinuclear complex $Fe_3O(AcO)_6(H_2O)_3$ in the reaction with bpy and formation of a coordination polymer $[Fe(bpy)_3(H_2O)_2](PF_6)_2 \cdot 2(bpy) \cdot 5H_2O$, occurs in an aqueous medium, which agrees with the assumption of destruction of trinuclear cores Fe_2MO in the reaction with bipyridine in polar coordinating solvents.[13]

The thermal stability of complexes **10** and **11** was estimated by derivatography in an atmosphere of argon with the mass spectrometric determination of gaseous decomposition products with *m/z* 16—18 (H_2O), 40—44 ($H_2C=C=O$ and CO_2), and 59—60 (AcOH). The heating of the samples up to 100 °C leads to dehydration, no mass loss occurred upon further heating in the range 100—220 °C (Fig. 4). Above 220 °C, the decomposition of the samples begins, which apparently proceeds stepwise; however, the steps could not be differentiated. In the mass spectra of the decomposition products at temperature higher then 220 °C, all the studied species, *viz.*, H_2O, CO_2, ketene, and acetic acid, were detected. The decomposition process is finished at 320 °C, the further temperature increase does not lead to the mass change. The temperatures of decomposition of complexes **10** and **11** are the same, evidencing that thermal stability of these compounds does not depend on the metal nature in the trinuclear core $\{Fe_2M\}$ (M = Co, Ni).

A comparison of the powder X-ray diffraction patterns of a freshly prepared sample of complex **10** and the sample heated at 150 °C (**10′**) shows that the crystal structure of the complex is disordered upon heating (Fig. 5). The intensity of the reflexes in the diffraction pattern of sample **10′** was considerably lower then that of sample **10**, several reflexes disappear completely or are shifted a little. Such disordering can be connected with the change in the structure caused by the solvent removal on heating.

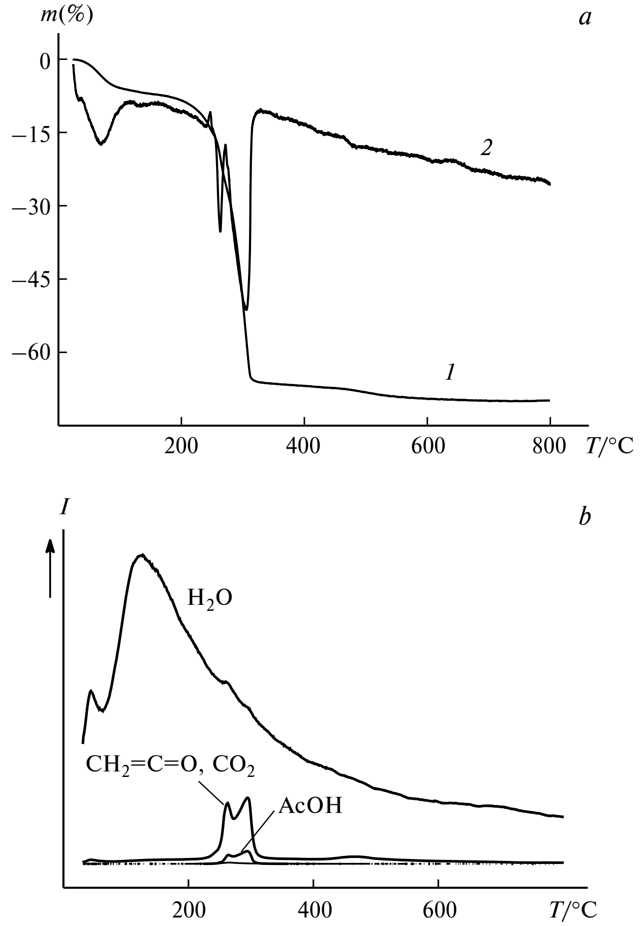


Fig. 4. The dependence of mass loss *vs.* temperature (*a*): *1* — weight change, *2* — heat flow and the dependence of the peak intensities in the mass spectra of the gaseous decomposition products (*b*) of complex **10** heated under argon atmosphere *vs.* temperature.

The measurements of nitrogen and hydrogen adsorption isotherms by complexes **10** and **11** (Fig. 6) at 77 K show that these compounds adsorb relatively large amounts of these gases. The sorption capacity of the complexes obviously exceeds the amounts of nitrogen and hydrogen that could be adsorbed by the surface of the particles evidencing for the presence of pores in their lattices. On the base of reversibility of adsorption (the curves of ad-

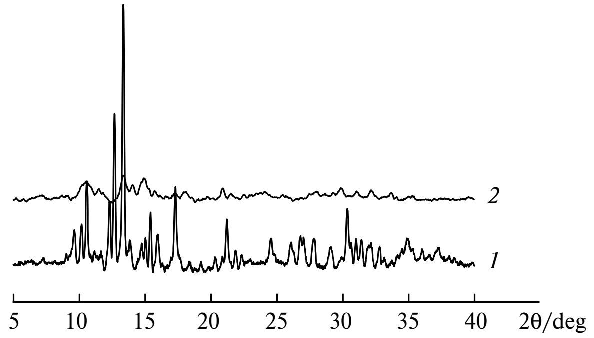


Fig. 5. The powder X-ray diffraction patterns of the freshly prepared sample of **10** before (*1*) and after heating to 150 °C (*2*) obtained under similar conditions.

sorption and desorption almost coincided), it can be concluded that compounds **10** and **11** possess conformationally rigid structures. The nitrogen adsorption isotherms of compounds **10** and **11** are close to type I according to the IUPAC classification (BDDT). The sharp increase in the isotherms at low P/P_S values could be caused by filling of micropores, and the increase at the P/P_S values close to 1 may be due to interparticle condensation of nitrogen. The surface areas (S) determined using the nitrogen adsorption isotherm by the BET (S_{BET}) and the Langmuir methods (S_{Lang}) were, respectively, 47 and 58 $m^2 g^{-1}$ for **10** and 36 and 44 $m^2 g^{-1}$ for **11**. The micropore volumes (V_0) determined using the Dubinin—Radushkevich equation were 0.021 and 0.016 $cm^3 g^{-1}$ for **10** and **11** respectively. The total pore volumes (V_T) determined using the nitrogen sorption capacity value at $P/P_S = 0.9$ are 0.022 and 0.023 $cm^3 g^{-1}$ for **10** and **11**, respectively, which are close to the micropore volume values. Thus, virtually all pores in compounds **10** and **11** are micropores.

The characteristics (S, V) of the porous structures of complexes **10** and **11** are close to the S and V values of the coordination polymer $[Zn(trz)F]_n$ (trz = 1,2,4-triazolate; $S_{BET} = 66$ $m^2 g^{-1}$, $V = 0.04$ $cm^3 g^{-1}$)[14] whose crystal structure has pores with diameter 5.3 Å, MOF-3 and MOF-9 ($S_{Lang} = 140$ and 127 $m^2 g^{-1}$, $V = 0.038$ and 0.035 $cm^3 g^{-1}$, respectively),[15] $[Mn(NDC)]_n$ (NDC is naphthalene-2,6-dicarboxylate; $S_{Lang} = 191$ $m^2 g^{-1}$, $V = 0.068$ $cm^3 g^{-1}$).[16] At the same time, it should be noted that, due to the small size of microcrystals of complexes **10** and **11**, the adsorption on surface of the particles can make a considerable contribution to the total sorption capacity.

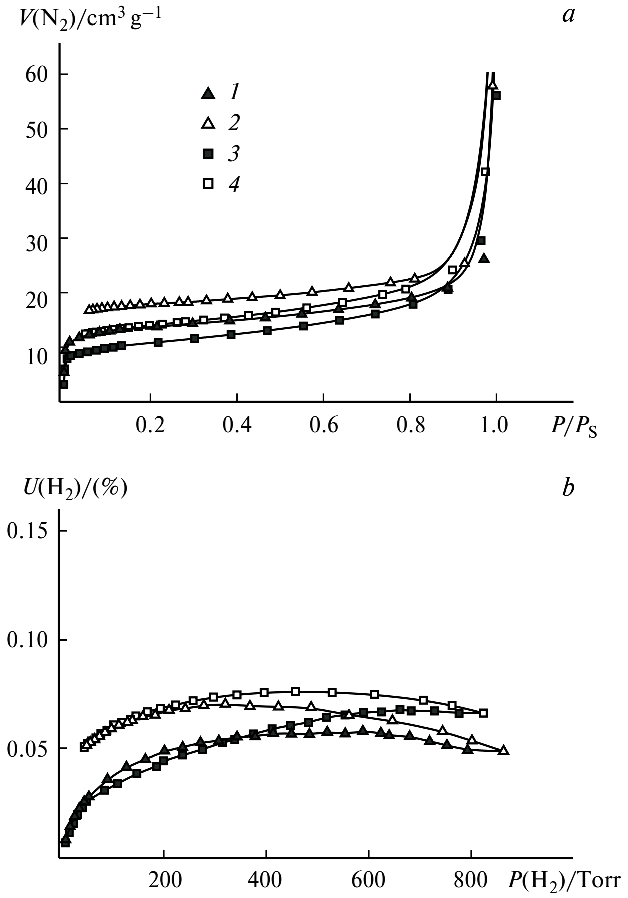


Fig. 6. The adsorption isotherm (*1*, *3*) and desorption isotherm (*2*, *4*) of nitrogen (*a*) and hydrogen (*b*) of compounds **10** (*1*, *2*) and **11** (*3*, *4*).

Unlike the nitrogen adsorption by compounds **10** and **11**, the shape of the isotherms of adsorption and desorption of hydrogen by these compounds (some reduction of the sorption capacity with an increase in P) could evidence for nonequilibrium character of the hydrogen adsorption process. The "opening" of ultramicropores in the lattice of compounds **10** and **11** may take place at certain hydrogen pressure resulting in an increase in the pore volume available for H_2. The change in the structure of PCP on hydrogen adsorption has been observed earlier.[17]

The maximum hydrogen sorption capacities of **10** and **11** are 0.055 and 0.068%, respectively. The assessment of hydrogen density in pores of these compounds at the maximum filling gives values 0.016 and 0.020 g cm^{-3} for **10** and **11**, respectively, and equals 23 and 28% of the hydrogen density at 20 K. These values of H_2 density in pores of the coordination polymers are close to those found earlier.[18]

In conclusion, in the present work we found the conditions for the formation of coordination polymers $Fe_2MO(AcO)_6(bpy)_{1.5}]_n$ (M = Co, Ni) in the reaction of trinuclear acetate complexes $Fe_2MO(AcO)_6(H_2O)_3$ with 4,4´-bipyridine. It was shown that the prepared compounds $[Fe_2MO(AcO)_6(bpy)_{1.5}]_n$ are able to adsorb nitrogen and hydrogen. It was found that the reactions of trinuclear acetate complexes $Fe_2MO(AcO)_6(H_2O)_3$ with 4,4´-bipyridine and hexanuclear manganese benzoate $Mn_6O_2(PhCOO)_{10}(MeCN)_4$ with 4,4´-bipyridine or *trans*-1,2-(4-pyridyl)ethylene in the polar coordinating solvent (DMF) lead to destruction of the polynuclear framework and formation of the nonporous coordination polymers, whereas analogous pivalate $Mn_6O_2(Piv)_{10}(EtOH)_3(HPiv)$ gave under the same conditions the coordination polymer containing structural blocks $Mn_6O_2(Piv)_{10}$. The differences in stabilities of the polynuclear complexes in the studied reactions could be explained by different polarity and different donating ability of the solvent and also by different electronic influence of the substituents in the carboxylate ligands.

Experimental

Polynuclear complexes $Mn_6O_2(Piv)_{10}(EtOH)_3(HPiv)$, $Mn_6O_2(PhCOO)_{10}(MeCN)_4$, $Fe_2MO(AcO)_6(H_2O)_3$ (M = Co, Ni) were prepared according to the described methods.[19—21] 4,4´-Bipyridine, *trans*-1,2-(4-pyridyl)ethylene (Merck), AcOEt, AcOH, and DMF were used without further purification. Acetonitrile was distilled over P_2O_5 before use. Elemental analysis was performed using a Carlo Erba 1106 analyzer. The powder X-ray diffraction studies were carried out using a DRON-3 diffractometer (Fe-Kα radiation, λ = 1.936 Å). The N_2 and H_2 adsorption isotherms were obtained on a Sorptomatic 1990 instrument at 77 K. The adsorption measurements were performed using the samples preactivated by heating at 120 °C for 2 h *in vacuo*. The thermogravimetric studies were carried out on a LABSYS ATD/DSC1600 instrument with an attached Pfeiffer Omnistar mass spectrometer.

Poly(bis(μ_2-4,4´-bipyridine-*N*,*N*´)tetra(μ_2-benzoato-*O*,O´)-dimanganese(II)), $[Mn_2(PhCOO)_4(bpy)_2]_n$ (4). A solution of bpy (55 mg, 0.35 mmol) in AcOEt (10 mL) was added to a solution of $Mn_6O_2(PhCOO)_{10}(MeCN)_4$ (300 mg, 0.17 mmol) in DMF (10 mL). The obtained solution was kept at room temperature for two weeks. The precipitated yellow crystals were filtered off and air dried. Yield 130 mg (28%). Found (%): C, 63.80; H, 4.05; N, 6.23. $C_{48}H_{36}Mn_2N_4O_8$. Calculated (%): C, 63.60; H, 4.00; N, 6.18.

Poly(bis(μ_2-1,2-bis(4-pyridyl)ethylene-*N*,*N*´)tetra(μ_2-benzoato-*O*,*O*´)dimanganese(II)) *trans*-1,2-bis(4-pyridyl)ethyelene solvate, $[Mn_2(PhCOO)_4(bpe)_2 \cdot bpe]_n$ (5). A solution of bpe (100 mg, 0.55 mmol) in a mixture of DMF (5 mL) and AcOEt (10 mL) was added to a solution of $Mn_6O_2(PhCOO)_{10}(MeCN)_4$ (500 mg, 0.29 mmol) in DMF (10 mL). The obtained solution was kept at room temperature for one month, the yellow precipitate was filtered off and air dried. Yield 210 mg (21%). Found (%): C, 67.30; H, 4.35; N, 7.21. $C_{64}H_{50}Mn_2N_6O_8$. Calculated (%): C, 67.40; H, 4.42; N, 7.37.

Poly(bis(μ_2-4,4´-bipyridine-*N*,*N*´)tetra(μ_2-acetato-*O*,*O*´)dicobalt(II)), $[Co_2(AcO)_4(bpy)_2]_n \cdot H_2O$ ($8 \cdot H_2O$). $Fe_2CoO(AcO)_6(H_2O)_3$ (100 mg, 0.168 mmol) and bpy (60 mg, 0.384 mmol) were dissolved in DMF (10 mL) at 60—80 °C. The reaction mixture was filtered and kept for one week at room temperature, the crystalline precipitate was filtered off and air dried. Yield 40 mg (70%). Found (%): C, 49.30; H, 4.25; N, 8.24. $C_{28}Co_2H_{30}N_4O_9$. Calculated (%): C, 49.10; H, 4.42; N, 8.19.

Poly(bis(μ_2-4,4´-bipyridine-*N*,*N*´)tetra(μ_2-acetato-*O*,*O*´)dinickel (II)), $[Ni_2(AcO)_4(bpy)_2]_n$ (9). Complex **9** was prepared according to the procedure for compound **8**. Yield 20%. Found (%): C, 50.20; H, 4.35; N, 8.58. $C_{28}Ni_2H_{28}N_4O_8$. Calculated (%): C, 50.50; H, 4.24; N, 8.41.

Poly(tris(μ_2-4,4´-bipyridine-*N*,*N*´)di(μ_3-oxo)dodeca(μ_2-acetato-*O*,*O*´)tetrairon(III)dicobalt(II)), $[Fe_2CoO(AcO)_6(bpy)_{1.5}]_n \cdot 2H_2O \cdot 1.5MeCN$ ($10 \cdot 2H_2O \cdot 1.5MeCN$). MeCN (10 mL) and AcOH (0.5 mL) were added directly to the freshly prepared solution of $Fe_2CoO(AcO)_6(H_2O)_3$ (300 mg, 0.5 mmol) in DMF (5 mL). Then a solution of bpy (118 mg, 0.75 mmol) in MeCN (20 mL) was added at room temperature with stirring. After several hours, the crystals precipitated were filtered off, washed with acetonitrile and air dried. Yield 230 mg (60%). Found (%): C, 41.40; H, 4.43; N, 7.09. $C_{30}CoFe_2H_{38.5}N_{4.5}O_{15}$. Calculated (%): C, 41.30; H, 4.45; N, 7.22.

Poly(tris(μ_2-4,4´-bipyridine-*N*,*N*´)di(μ_3-oxo)dodeca(μ_2-acetato-*O*,*O*´)tetrairon(II)dinickel(II)), $[Fe_2NiO(AcO)_6(bpy)_{1.5}]_n \cdot 2H_2O \cdot MeCN$ ($11 \cdot 2H_2O \cdot MeCN$). Compound **11** was prepared according to the procedure for compound **10**. Yield 230 mg (60%). Found (%): C, 40.70; H, 4.39; N, 6.92. $C_{29}Fe_2H_{37}N_4NiO_{15}$. Calculated (%): C, 40.90; H, 4.38; N, 6.58.

X-Ray diffraction studies of single crystals of compounds **2**, **4**, **5**, **8**, and **9** were carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector and monochromatic irradiation source (Mo-K$_\alpha$, λ = 0.71073 Å) using a standard procedure.[22] Structure of **5** was solved by direct methods and refined by the full-matrix method with anisotropic displacement parameters for all nonhydrogen atoms (see Table 1). The hydrogen atom coordinates were geometrically calculated and refined using the riding model. The calculations were carried out using SHELXS-97 and SHELXL-97 programs.[23] The parameters of unit cells for **2**, **4**, **8**, and **9** are given in Table 1.

This work was financially supported by the National Academy of Sciences of the Ukraine (the target complex program of scientific researches "Fundamental problems of hydrogen energetics"), cooperation agreement between NAS of the Ukraine and National Center for Scientific Research of France (CNRS), the State Foundation for Basic Research of the Ukraine (Project F28.3/014 "Chemistry and physics of polynuclear complexes and coordination polymers on the base of carboxylates, oximes and their analogs"), the Russian Foundation for Basic Research (Projects Nos 08-03-00091, 08-03-00343, 09-03-12122, and 09-03-90441), Program of Presidium RAS, the Council for Grants at the President of the Russian Federation (Program for the State Support of Young PhD Scientists, Grants MK-156.2009.3, NSh-3672.2010.3) and the Federal Science and Innovation Agency (State Contract No. 02.513.12.3094).

References

1. L. Ouahab, T. Enoki, *Eur. J. Inorg. Chem.*, 2004, 933.
2. D. Maspoch, N. Domingo, N. Roques, K. Wurst, J. Tejada, C. Rovira, D. Ruiz-Molina, J. Veciana, *Chem. Eur. J.*, 2007, **13**, 8153.
3. L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 2763.
4. A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Côté, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 7110.
5. C. Serre, F. Millange, S. Surblé, G. Férey, *Angew. Chem., Int. Ed.*, 2004, **43**, 6286.
6. K. Nakata, H. Miyasaka, K. Sugimoto, T. Ishii, K. Sugiura, M. Yamashita, *Chem. Lett.*, 2002, 658.
7. S. Wang, H.-L. Tsai, K. Folting, J. D. Martin, D. N. Hendrickson, G. Christou, *J. Chem. Soc., Chem. Commun.*, 1994, 671.
8. D. Visinescu, G. I. Pascu, M. Andruh, J. Magull, H. W. Roesky, *Inorg. Chim. Acta*, 2002, **340**, 201.
9. H. Chen, W.-G. Wang, C.-B. Ma, C.-N. Chen, Q.-T. Liu, D.-Z. Liao, L.-C. Li, *Jiegou Huaxue* (*Chinese J. Struct. Chem.*), 2007, **26**, 687.
10. J. Lu, C. Yu, T. Niu, T. Paliwala, G. Crisci, F. Somosa, A. J. Jacobson, *Inorg. Chem.*, 1998, **37**, 4637.
11. Y.-L. Fu, Z.-W. Xu, J.-L. Ren, S. W. Ng, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m1897.
12. S. Nikolaou, H. E. Toma, *Eur. J. Inorg. Chem.*, 2008, 2266.
13. N. V. Izarova, M. N. Sokolov, A. Rothenberger, L. Ponikiewski, D. Fenske, V. P. Fedin, *C. R. Chim.*, 2005, **8**, 1005.

14. W. Ouellette, B. S. Hudson, J. Zubieta, *Inorg. Chem.*, 2007, **46**, 4887.
15. M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
16. H. R. Moon, N. Kobayashi, M. P. Suh, *Inorg. Chem.*, 2006, **45**, 8672.
17. X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science*, 2004, **306**, 1012.
18. S. V. Kolotilov, V. V. Pavlishchuk, *Teor. Eksp. Khim.*, 2009, **45**, 67 [*Theor. Exp. Chem.* (*Engl. Transl.*), 2009, **45**, 75].
19. M. A. Kiskin, I. G. Fomina, G. G. Aleksandrov, A. A. Sidorov, V. M. Novotortsev, Y. V. Rakitin, Z. V. Dobrokhotova, V. N. Ikorskii, Y. G. Shvedenkov, I. L. Eremenko, I. I. Moiseev, *Inorg. Chem. Commun.*, 2005, **8**, 89.
20. K. S. Gavrilenko, S. V. Punin, O. Cador, S. Golhen, L. Ouahab, V. V. Pavlishchuk, *Inorg. Chem.*, 2005, **44**, 5903.
21. A. B. Blake, A. Yavari, W. E. Hatfield, C. N. Sethulekshmi, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 2509.
22. *SMART (Control) and SAINT (Integration) Software*, *Version 5.0*, Bruker AXS, Inc., Madison (WI), 1997.
23. G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, University of Göttingen, Germany, 1997.

Received December 9, 2009;
in revised form April 14, 2010