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Porous homo- and heterochiral cobalt(II) aspartates with high thermal stability of the metal-organic framework

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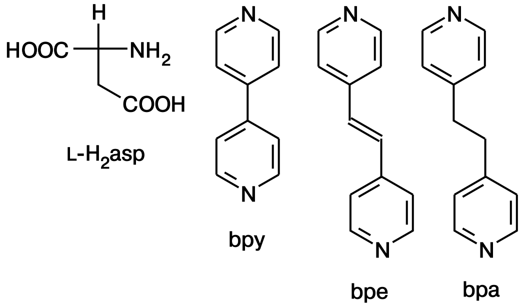
Metal-organic coordination polymers with the compositions $[Co_2(L\text{-asp})_2(bpy)]\cdot MeOH\cdot H_2O$ (**1**), $[Co_2(L\text{-asp})_2(bpe)]\cdot 0.28(bpe)\cdot H_2O$ (**2**), and $[Co_2(D\text{-asp})(L\text{-asp})(bpa)]\cdot 0.25(bpa)\cdot 1.5H_2O$ (**3**) (H_2asp is aspartic acid, bpy is 4,4´-bipyridine, bpe is *trans*-bis(4-pyridyl)ethylene, and bpa is 1,2-bis(4-pyridyl)ethane) were synthesized on heating cobalt(II) aspartate and N-donor ligands (bpy, bpe, or bpa) in an aqueous-methanol mixture. The structures of compounds **1**—**3** were established by X-ray diffraction analysis and confirmed by X-ray powder crystallography, IR spectroscopy, thermogravimetry, and elemental analysis. The stability of the synthesized coordination polymers was studied. It was shown that they retain the framework structure on heating to 300 °C.

Key words: cobalt(II) complexes, coordination polymers, framework structures, chiral complexes, amino acids, aspartic acid, X-ray powder diffraction, X-ray diffraction analysis.

Homochiral (enantiopure) porous metal-organic frameworks formed of inorganic and chiral organic building blocks[1—3] are promising materials for use in asymmetric catalysis[4—7] or for the selective separation of enantiomers.[8—11] The development along this important direction is restricted because of low accessibility of the chiral organic ligands, which should possess in addition to optical centers, substantial length and conformational rigidity necessary for the formation of stable homochiral porous structures. Therefore, search for new chiral building blocks and new ways to approach the synthesis of homochiral porous metal-organic frameworks are urgent. Natural amino acids are promising starting compounds for the synthesis of homochiral porous metal-organic compounds, because they are accessible in the optically pure state from natural materials. Coordination chemistry of amino acids is well studied[12]; however, only several examples for the synthesis and use of metal-organic porous frameworks can be found in the published literature. The aspartate anion is a polyfunctional ligand and can coordinate metal ions according to various modes to form mononuclear complexes and polymer structures.[13,14] The first porous cobalt(II) aspartate with high thermal stability has recently[15] been synthesized. It was shown[5,10,16] that the frameworks based on aspartic acid and other transition metals (Cu, Ni) possess interesting catalytic and sorption properties. Polymer structures based on glutamic acid, proline, and some other amino acids are known.[17—19] In the present work, we describe the synthesis, structures, and results of studying the thermal stability of three metal-organic coordination polymers: cobalt(II) aspartates containing the bidentate bridging N-donor ligands $[Co_2(L\text{-asp})_2(bpy)]\cdot MeOH\cdot H_2O$ (**1**), $[Co_2(L\text{-asp})_2(bpe)]\cdot 0.28(bpe)\cdot H_2O$ (**2**), and $[Co_2(D\text{-asp})(L\text{-asp})(bpa)]\cdot 0.25(bpa)\cdot 1.5H_2O$ (**3**) (H_2asp is aspartic acid, bpy is 4,4´-bipyridine, bpe is *trans*-bis(4-pyridyl)ethylene, and bpa is 1,2-bis(4-pyridyl)ethane).



Results and Discussion

We have recently[8] proposed a new approach for the synthesis of homochiral porous coordination polymers. A specific feature of the approach is the use in the synthesis of two simple ligands, namely, the chiral polyfunctional ligands forming chiral complexes with metal cations and the rigid bridging ligand that links these complexes to

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form a porous framework. The main advantage of the proposed method is the possibility to use rather simple and accessible optically pure ligands for synthesis. This approach has successfully been used[20,21] for the synthesis of several homochiral porous frameworks: zinc lactataterephthalate and copper and zinc camphorates with N-donor ligands. In the present work, the method proposed was used for the preparation of three coordination polymers: cobalt(II) aspartates containing the N-donor bridging ligands bpy, bpe, and bpa. L-Aspartic acid was chosen as the chirality carrier. The reaction of cobalt(II) aspartate with N-donor ligands taken in access were carried out in sealed ampules in an aqueous-methanol (1 : 1 vol/vol) solution at 130 °C. The starting cobalt L-aspartate is a polymer and insoluble in water or alcohol. By introducing the corresponding N-donor bidentate ligand in the reaction we were able to isolate compounds **1**—**3** as crimson-colored crystals. The phase purity of the sample was confirmed by X-ray diffraction analysis (see below). The change in the concentration, reactant ratios, or temperature of the synthesis results in the formation of a violet noncrystalline precipitate.

According to the X-ray diffraction data, compounds **1** and **2** are homochiral metal-organic coordination polymers and contain only L-aspartate anions; they crystallize in the chiral space groups $P2_12_12$ and $P2_1$, respectively. The adequate values of the absolute structure parameters were obtained by the refinement of structures **1** and **2** (Table 1). Under the synthesis conditions of compound **3**, L-aspartic acid is racemized, and compound **3** crystallizes in the centrosymmetric space group $P2_1/n$. Structure **3** simultaneously contain residues of both L- and D-aspartic acid coordinated to the cobalt atoms. Compound **1** is isostructural to the recently[15] obtained complex $[Co_2(L\text{-}asp)_2(bpy)] \cdot 1.5H_2O$, but differs in the synthesis method and the composition of the host molecules. In spite of the racemization of the amino acid residue, the structure of compound **3** is also identical in topology to structures **1** and **2**. It is well known[22] that, when racemic mixtures of the ligands are used, the structures of the obtained metal-organic coordination polymers do not necessarily replicate the topology of the frameworks obtained using the optically pure ligands. The coordination environment of the cobalt ions in compounds **1**—**3** is the same and has a slightly distorted octahedral geometry. The coordination polyhedron of the metal contains two nitrogen atoms (one atom from the amino group of aspartic acid, and the second atom from the N-donor ligand) and four oxygen atoms (from the carboxyl groups of two aspartate ions, Fig. 1). The Co—N and Co—O bond lengths in structures **1**—**3** fall in the normal bond length distribution for the octahedral Co^{II} complexes (Tables 1—3). The aspartate ion acts as a tridentate bridging ligand, *i.e.*, it is coordinated to the cobalt cation through the carboxyl and amino group according to the *gran*-type and to two adjacent cobalt cations through the oxygen atoms of the carboxyl groups to form infinite layers $\{Co(asp)\}_\infty$ lying in the *ac* plane (see Fig. 2). These layers are homochiral for compounds **1** and **2** and contain only L-asp (see Fig. 2, *a*). In structure **3**, the layers of cobalt(II) aspartate contain equal amounts of L-asp and D-asp, alternating in the chess order (see Fig. 2, *b*). The coordination environment of cobalt in the layer is supplemented by the nitrogen atom of the pyridine rings of the bridging ligands. Due to this coordination mode, metal-organic framework structures are formed (see Fig. 3), which results in the formation of channels in structures **1**—**3**. The dimensions of the channels determined by the length of the bridging ligands are 4×5 Å^2 for **1** and 4×7 Å^2 for **2** and **3**, which is consistent with the length of the bidentate bridging ligand used in the synthesis of porous cobalt aspartates.

Table 1. Selected bond lengths (*d*) and angles (ω) in structure **1**

Parameter	Value
Bond length	*d*/Å
Co(1)—O(1)	2.167(3)
Co(1)—O(2)^a	2.016(4)
Co(1)—N(1)	2.110(3)
Co(1)—O(3)	2.058(3)
Co(1)—O(4)^b	2.184(3)
Co(1)—N(2)	2.132(16)
Co(1)—N(2´)	2.151(16)
O(1)—C(1)	1.242(6)
Angle	ω/deg
O(1)—Co(1)—O(4)^b	177.15(15)
O(2)^a—Co(1)—O(1)	94.74(16)
O(2)^a—Co(1)—N(1)	104.57(15)
O(2)^a—Co(1)—O(3)	175.07(14)
O(2)^a—Co(1)—O(4)^b	87.05(13)
O(2)^a—Co(1)—N(2)	91.3(4)
O(2)^a—Co(1)—N(2´)	82.8(4)
N(1)—Co(1)—O(1)	84.05(13)
N(1)—Co(1)—O(4)^b	97.66(13)
N(1)—Co(1)—N(2)	163.9(4)
N(1)—Co(1)—N(2´)	166.0(4)
Angle	ω/deg
O(3)—Co(1)—O(1)	89.02(14)
O(3)—Co(1)—N(1)	78.97(14)
O(3)—Co(1)—O(4)^b	89.08(15)
O(3)—Co(1)—N(2)	85.3(4)
O(3)—Co(1)—N(2´)	94.4(4)
N(2)—Co(1)—O(1)	92.7(4)
N(2)—Co(1)—O(4)^b	85.1(4)
N(2)—Co(1)—N(2´)	13.1(3)
N(2´)—Co(1)—O(1)	83.4(4)
N(2´)—Co(1)—O(4)^b	94.6(4)

[a] The atoms were multiplied by the symmetry procedure $-x + 3/2, y - 1/2, -z + 1$.
[b] $-x + 3/2, y - 1/2, -z + 2$.

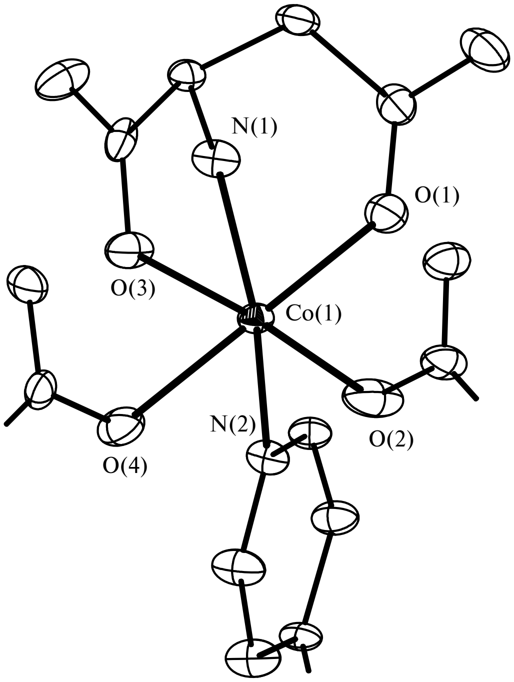

Fig. 1. Coordination environment of the Co^{2+} ion in structure **1** (ellipsoids of 50% probability).

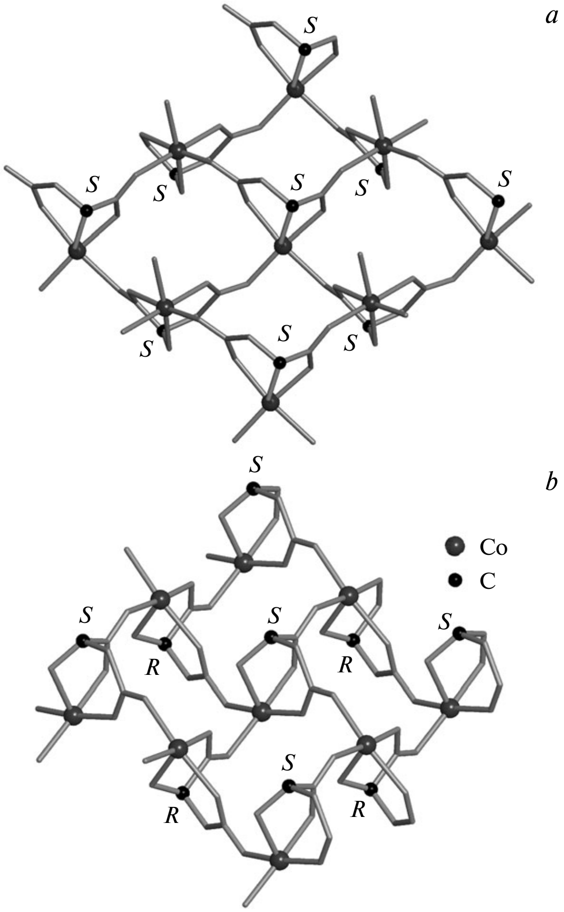

Fig. 2. Fragments of the layer of cobalt aspartate $\{Co(asp)\}_\infty$ in structures **1** (*a*) and **3** (*b*). The hydrogen atoms are omitted.

Table 2. Selected bond lengths (*d*) and angles (ω) in structure **2**

Parameter	Value
Bond length	*d*/Å
Co(1)—O(11)	2.039(2)
Co(1)—N(11)	2.125(3)
Co(1)—O(13)	2.147(2)
Co(1)—O(22)^a	2.124(2)
Co(1)—O(24)^b	2.039(2)
Co(1)—N(31)	2.160(3)
Co(2)—O(12)^c	2.232(3)
Co(2)—O(14)^d	2.012(2)
Co(2)—O(21)	2.057(2)
Co(2)—N(21)	2.117(3)
Co(2)—O(23)	2.168(2)
Co(2)—N(32)	2.139(3)
Angle	ω/deg
O(11)—Co(1)—N(11)	78.80(11)
O(11)—Co(1)—O(13)	89.63(10)
O(11)—Co(1)—O(22)^a	89.45(10)
O(11)—Co(1)—N(31)	87.70(11)
N(11)—Co(1)—O(13)	84.23(10)
N(11)—Co(1)—N(31)	165.93(11)
O(13)—Co(1)—N(31)	91.81(10)
O(22)^a—Co(1)—N(11)	94.83(10)
O(22)^a—Co(1)—O(13)	178.79(10)
O(22)^a—Co(1)—N(31)	88.93(10)
O(24)^b—Co(1)—O(11)	175.63(11)
O(24)^b—Co(1)—N(11)	105.37(11)
O(24)^b—Co(1)—O(13)	89.49(10)
O(24)^b—Co(1)—O(22)^a	91.49(9)
O(24)^b—Co(1)—N(31)	88.05(11)
O(14)^d—Co(2)—O(12)^c	89.15(10)
O(14)^d—Co(2)—O(21)	174.38(11)
O(14)^d—Co(2)—N(21)	100.51(10)
O(14)^d—Co(2)—O(23)	97.34(10)
O(14)^d—Co(2)—N(32)	86.46(11)
O(21)—Co(2)—O(12)^c	85.23(10)
O(21)—Co(2)—N(21)	80.19(10)
O(21)—Co(2)—O(23)	88.28(9)
O(21)—Co(2)—N(32)	93.71(10)
N(21)—Co(2)—O(12)^c	98.45(10)
N(21)—Co(2)—O(23)	82.72(10)
N(21)—Co(2)—N(32)	169.08(11)
O(23)—Co(2)—O(12)^c	173.10(9)
N(32)—Co(2)—O(12)^c	89.99(11)
N(32)—Co(2)—O(23)	88.09(10)

[a] The atoms were multiplied by the symmetry procedure $-x + 2, y - 1/2, -z + 2$.

[b] $-x + 2, y - 1/2, -z + 1$.

[c] $-x + 3, y + 1/2, -z + 2$.

[d] $-x + 3, y + 1/2, -z + 1$.

The bridging ligand bpy in structure **1** is disordered over two orientations (I and II) with halved occupancy (Fig. 4). The planes of two pyridine rings in the bpy molecule are unfolded relative to each other by 36.2 and 30.8° in positions I and II, respectively. The angle between the

Table 3. Selected bond lengths (*d*) and angles (ω) in structure **3**

Parameter	Value
Bond length	*d*/Å
Co(1)—O(1)	2.080(2)
Co(1)—O(2)^a	2.062(2)
Co(1)—N(1)	2.107(3)
Co(1)—O(3)	2.158(2)
Co(1)—O(4)^b	2.133(2)
Co(1)—N(11)	2.139(3)

Parameter	Value
Angle	ω/deg
O(1)—Co(1)—N(1)	80.41(9)
O(1)—Co(1)—O(3)	87.22(9)
O(1)—Co(1)—O(4)^b	85.02(9)
O(1)—Co(1)—N(11)	92.43(9)
O(2)^a—Co(1)—O(1)	176.17(9)
O(2)^a—Co(1)—N(1)	100.69(9)
O(2)^a—Co(1)—O(3)	96.54(9)
O(2)^a—Co(1)—O(4)^b	91.20(9)

Parameter	Value
Angle	ω/deg
O(2)^a—Co(1)—N(11)	86.96(9)
N(1)—Co(1)—O(3)	83.11(10)
N(1)—Co(1)—O(4)^b	96.84(10)
N(1)—Co(1)—N(11)	169.41(10)
O(4)^b—Co(1)—O(3)	172.14(9)
O(4)^b—Co(1)—N(11)	90.26(9)
N(11)—Co(1)—O(3)	88.79(9)

[a] The atoms were multiplied by the symmetry procedure $x + 1/2, -y + 1/2, z + 1/2$.

[b] $x + 1/2, -y + 1/2, z - 1/2$.

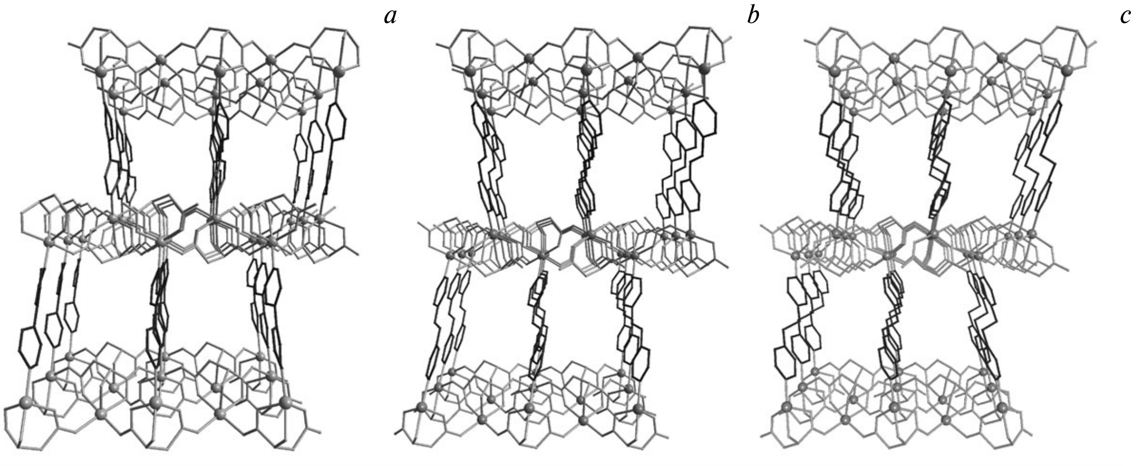

Fig. 3. Structure of metal-organic frameworks **1** (*a*), **2** (*b*), and **3** (*c*) (view along the porous channels). The aspartate ions are gray, and the linear bridging N-donor ligands are black.

planes of the pyridine rings, which are in orientations I or II, is 33.3°. In structure **2**, the bridging ligand bpe has an almost planar geometry, the average deviation of the atoms from the plane being 0.094 Å. The planes of the pyridine rings are unfolded relative to each other by 5.5°. In structure **3**, the $CH_2—C_5H_4N$ fragments of the bridging ligand bpa do not lie in the same plane but are localized in two parallel planes.

According to the X-ray diffraction data, the channels of framework **1** are filled up with disordered water and methanol molecules. The channels of framework **3** contain disordered water and bpa molecules. The bpa molecules are oriented along the *a* axis in the channels and disordered over two half-occupied positions in such a way that the second pyridine ring of the first position overlaps the first ring of the second position, which creates illusion of an infinite chain of the alternating pyridine rings and $CH_2—CH_2$ fragments (Fig. 5). An analysis of interatomic distances in structures **1** and **3** revealed no specific interactions of the framework walls with the host molecules of water, alcohol, and bpa, except for the van der Waals interactions. Based on the data of X-ray diffraction analysis, TGA (see further), and elemental analysis (C, H, N), the following compositions were ascribed to compounds **1** and **3**: $[Co_2(\text{L-asp})_2(bpy)] \cdot MeOH \cdot H_2O$ (**1**)

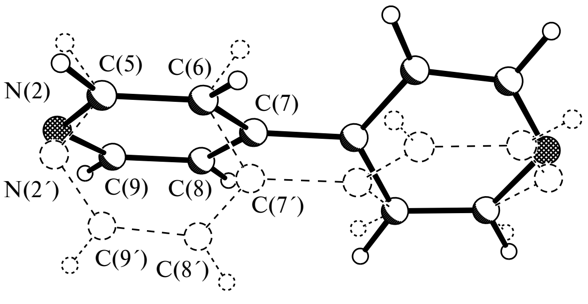

Fig. 4. Two independent orientations of the bpy molecule in **1**: I (solid lines) and II (dash).

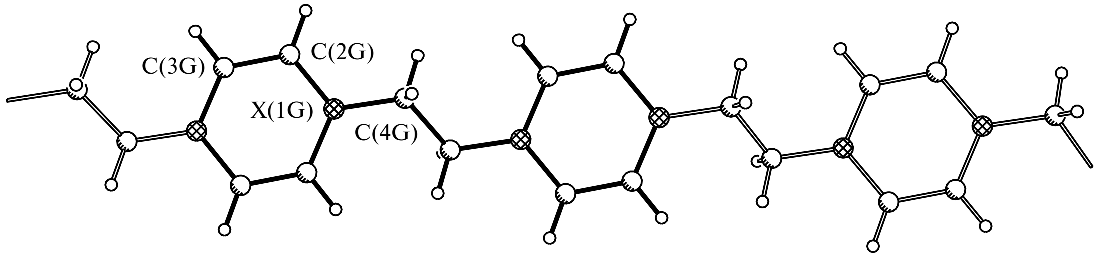

Fig. 5. Arrangement of the guest bpa molecules over two alternating positions with the overlapping of the pyridine rings (X = 1/2 C + 1/2 N).

and $[Co_2$(D-asp)(L-asp)(bpa)$]\cdot0.25$(bpa)$\cdot1.5H_2O$ (**3**). No adequate model was found when refining structure **2** for disordered guest molecules located in cavities of the coordination framework and, therefore, the SQUEEZE procedure using the PLATON package was applied.[23] The results of SQUEEZE (36 e^- in 170 Å^3), TGA, and elemental analysis (C, H, N) suggest that a formula unit in structure **2**, $[Co_2$(L-asp)$_2$(bpe)$]\cdot0.28$(bpe)$\cdot H_2O$, contains 0.28 bpe molecule and one water molecule. The phase purity of compounds **1—3** was confirmed by X-ray powder diffraction (Fig. 6). The accessible volume calculated by the PLATON program (filling of cavities with probe walls with a radius of 1.2 Å with the increment 0.2 Å) in the absence of guest molecules was 22.2 (0.147 cm^3 g^{-1}), 25.6 (0.181 cm^3 g^{-1}), and 22.4% (0.155 cm^3 g^{-1}) for structures **1**, **2**, and **3**, respectively. To confirm that the channels of compounds **2** and **3** contain guest molecules bpe and bpa, the samples obtained were heated in the mass spectrometer cell. The appearance of the intense molecular peaks of the guest molecules bpe and bpa was observed in the mass spectra at 200 °C (the metal-organic frameworks decompose at >300 °C, see further). The guest molecules bpe and bpa can completely be removed from frameworks **2** and **3** only on heating at 200—220 °C and evacuation to 10^{-4} Torr.

The thermal stability of the synthesized compounds was studied by TGA and X-ray powder diffraction. According to the TGA data, the weight loss of compound **1** in the temperature range from room temperature to 100 °C was 8.8%, which can be assigned to the removal of the guest water and alcohol molecules (calculated for $MeOH\cdot H_2O$ in **1**: 8.5%). The considerable weight loss upon heating at >350 °C is ascribed to the decomposition of the metal-organic framework (Fig. 7, *a*). The TGA data showed that compound **2** loses 2.76% weight on heating from room temperature to 100 °C. This can be explained by the loss of one guest molecule, because, according to the calculation, removal of one H_2O molecule from compound **2** corresponds to the weight loss of 2.85%. In the TGA diagram of compound **3** 12% weight loss in the range from room temperature to 300 °C is attributed to the removal of 1.5 guest water molecules and 0.25 bpa molecule (calculated for 0.25bpa$\cdot1.5H_2O$ in **3**: 10.8%). The further weight loss upon heating compounds **1—3** from 350 °C is related to the decomposition of the metal-organic framework. The thermal stability of copper and nickel aspartates has earlier[5,10,16] been studied. It was shown that the

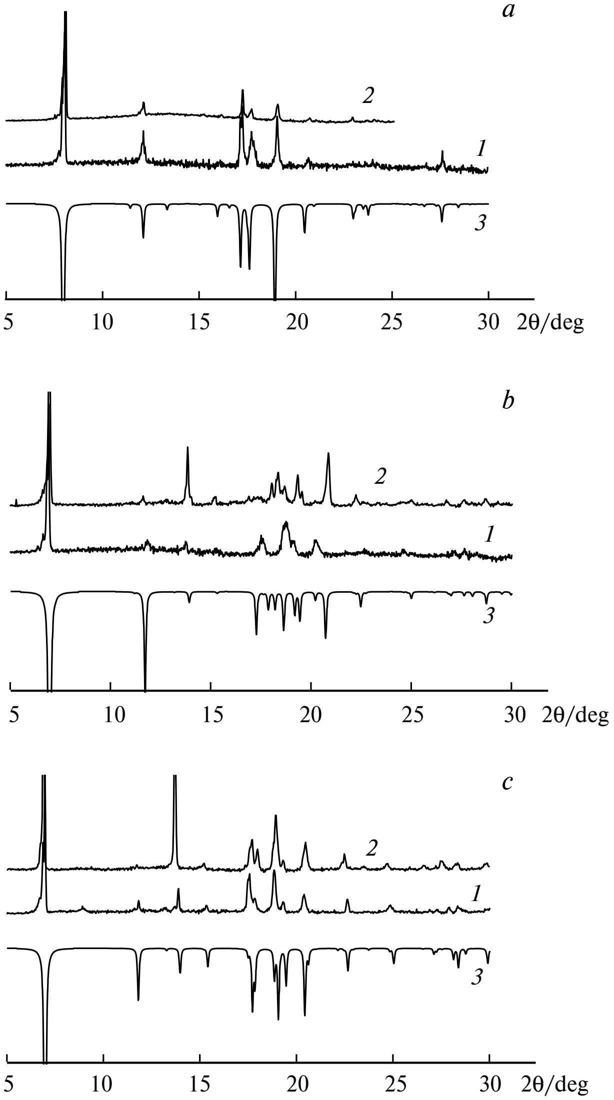

Fig. 6. Comparison of the experimental diffraction patterns for **1** (*a*), **2** (*b*), and **3** (*c*) obtained for the freshly synthesized (*1*) and heated at 300 °C (*2*) samples with those calculated by the X-ray diffraction data (*3*, "reflected" plot).

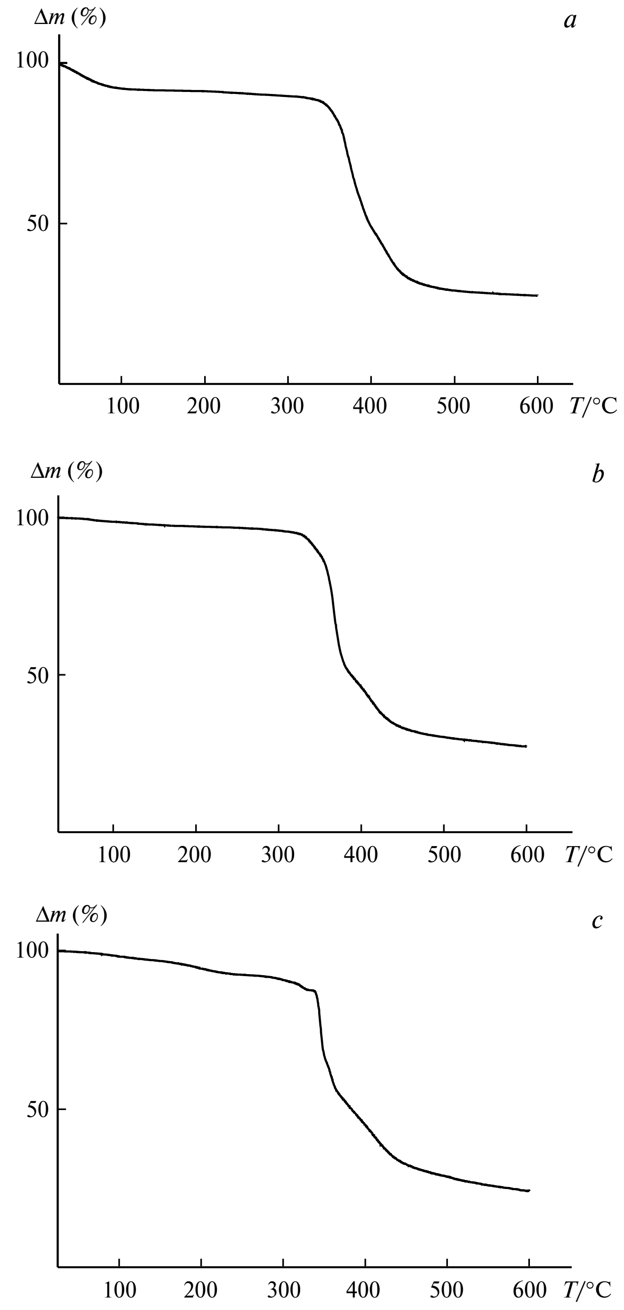

Fig. 7. TGA curves for compounds **1** (*a*), **2** (*b*), and **3** (*c*).

copper-based framework are thermally unstable and decompose on heating to 150 °C, whereas for the nickel-based frameworks degradation occurs on heating above 250 °C. Thus, the metal-organic framework based on cobalt(II) aspartates prepared by us have high thermal stability and the loss of the crystallinity is observed only on heating above 300 °C. We carried out additional studied of stability of frameworks **1—3** at elevated temperatures. Evacuated ampules with samples **1—3** were maintained at 300 °C for 5 h. After cooling, the X-ray diffraction patterns were recorded for the powders obtained (see Fig. 6). The data obtained show that compounds **1—3** retain crystal structures at 300 °C. As far as we know, this is the highest value for homochiral porous coordination polymers. Slight changes in the powder diffraction patterns can be due to some flexibility and the "breathing" effect of the porous framework. Porous homochiral materials with high thermal stability are of great interest, for instance, being used as stationary phases in gas enantioselective chromatography.

Thus, the present work describes the synthesis and crystal structures of the family of metal-organic coordination polymers based on Co^{II} aspartates and bidentate N-donor bridging ligands **1—3**. Compounds **1** and **2** have the homochiral porous framework. The chiral ligand is racemized during the synthesis of compound **3**. Metal-organic frameworks **1—3** possess high thermal stability and retain structures on heating to 300 °C.

Experimental

L-Aspartic acid, 4,4′-bipyridine, *trans*-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyl)ethane, methanol, and basic cobalt(II) carbonate (reagent grade and higher grades) were used. Cobalt aspartate Co(asp) • $3H_2O$ was synthesized according to an earlier[10] described procedure. X-ray diffraction analysis was carried out on a Bruker Nonius X8Apex single-crystal diffractometer with a 4K CCD detector. IR spectra were recorded on a Scimitar FTS 2000 instrument with KBr pellets. Elemental analysis was carried out on a EURO EA 3000 instrument (EuroVector). Thermogravimetric analysis was carried out on a TG 209 F1 thermobalance (Natzsch); the samples were heated in an argon atmosphere with a heating rate of 10 deg min^{-1}. X-ray diffraction was measured on a Philips APD 1700 automated powder diffractometer (Cu-Kα radiation, λ = 1.54056 Å).

Catena{diaspartate-4,4′-bipyridyldicobalt(II)} methanol solvate monohydrate (1). A solution of Co(L-asp) • $3H_2O$ (0.244 g, 1.00 mmol) and 4,4′-bipyridine (0.312 g, 2.00 mmol) in a methanol—water (1 : 1) mixture (6.0 mL) was sealed in a glass tube and maintained at 130 °C for 48 h. The resulting crimson-colored crystals was washed several times with a water—methanol (1 : 1) mixture to remove unreacted reactants and dried in air. The yield was 0.150 g (50%). Found (%): C, 39.2; H, 4.05; N, 9.70. $C_{19}H_{24}Co_2N_4O_{10}$. Calculated (%): C, 38.9; H, 4,10; N, 9.55. IR, ν/cm^{-1}: 444 (m), 529 (m), 610 (s), 679 (m), 735 (w), 820 (m), 862 (m), 899 (m), 968 (m), 1028 (m), 1070 (m), 1213 (m), 1298 (s), 1419 (s), 1483 (m), 1597 (s), 1649 (s, sh), 1971 (w), 2918 (m), 3076 (w), 3179 (m), 3250 (m), 3356 (m, sh). TGA. Found: Δ*m* = 8.8%. Calculated for H_2O + MeOH in **1**: 8.5%.

Catena{diaspartate-*trans*-bis(4-pyridyl)ethylenedicobalt(II)} 0.28-*trans*-bis(4-pyridyl)ethylene solvate monohydrate (2) was synthesized under the conditions analogous to the synthesis of compound **1** but with the addition of *trans*-bis(4-pyridylethylene (0.364 g, 2.00 mmol) instead of bpy. The final product as crimson-colored crystals was washed with a methanol—water (1 : 1) mixture to remove unreacted reactants and then dried in air. The yield was 0.240 g (76%). Found (%): C, 44.2; H, 4.0; N, 9.9. $C_{23.36}H_{24.8}Co_2N_{4.56}O_9$. Calculated (%): C, 44.4; H, 3,96; N, 10.1. IR, ν/cm^{-1}: 546 (m), 608 (m), 681 (w), 833 (m), 897 (w), 968 (m), 1036 (m), 1105 (w), 1221 (m), 1296 (m), 1420 (s), 1555 (s), 1595 (s), 1653 (s), 2818 (w), 2918 (w), 3071 (w),

Table 4. Crystallographic characteristics and the diffraction experimental and refinement details for the structures of compounds **1—3**

Parameter	**1**	**2**	**3**
Empirical formula	$C_{19}H_{24}Co_2N_4O_{10}$	$C_{23.36}H_{24.8}Co_2N_{4.56}O_9$	$C_{23}H_{28}Co_2N_{4.5}O_{9.5}$
M	586.28	631.30	637.36
Crystal size/mm^3	0.24×0.14×0.10	0.13×0.10×0.10	0.25×0.20×0.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12$	$P2_1$	$P2_1/n$
a/Å	22.1923(18)	6.5597(2)	6.5634(2)
b/Å	6.9433(5)	25.4447(8)	25.3343(8)
c/Å	7.7302(6)	7.9129(2)	7.8400(2)
β/deg	90	91.950(1)	90.718(1)
V/Å^3	1191.13(16)	1319.97(7)	1303.53(7)
Z	2	2	2
T/K	150(2)	150(2)	100(2)
d_{calc}/g cm^{-3}	1.635	1.588	1.624
μ/mm^{-1}	1.454	1.316	1.335
F(000)	600	646	655
θ Range/deg	1.84—27.27	2.58—28.30	2.72—27.51
Parameters h, k, l	$-27 \le h \le 28$, $-8 \le k \le 8$, $-7 \le l \le 9$	$-7 \le h \le 8$, $-33 \le k \le 33$, $-10 \le l \le 7$	$-4 \le h \le 8$, $-32 \le k \le 32$, $-10 \le l \le 10$
Number of measured /independent reflections	7991/2655 (R_{int} = 0.0306)	10662/6447 (R_{int} = 0.0211)	9851/2993 (R_{int} = 0.0169)
Number of reflections with $F > 4\sigma(F)$	2364	5521	2740
T_{max}/T_{min}	0.868/0.722	0.880/0.848	0.731/0.776
Number of reflections/ applied restraints/ refined parameters	2655/96/221	6447/1/308	2993/46/208
Goodness-of-fit on F^2	1.114	1.059	1.100
R Indices for $F > 4\sigma(F)$	R_1 = 0.0409, wR_2 = 0.1046	R_1 = 0.0316, wR_2 = 0.0748	R_1 = 0.0473, wR_2 = 0.1104
R Indices for all data	R_1 = 0.0476, wR_2 = 0.1071	R_1 = 0.0397, wR_2 = 0.0769	R_1 = 0.0514, wR_2 = 0.1120
Absolute structure parameter	0.02(4)	0.099(15)	—
Largest diff. peak and hole /e • Å^{-3}, ρ_{max}/ρ_{min}	0.900/–0.712	0.379/–0.261	1.913/–0.776

3250 (w, sh), 3350 (w, sh). TGA. Found: Δm = 2.76%. Calculated for H_2O in **2**: 2.85%.

Catena{diaspartate-1,2-bis(4-pyridyl)ethanedicobalt(II)} 0.25-1,2-bis(4-pyridyl)ethane solvate 1.5-hydrate (3) was obtained under the conditions similar to those of synthesis of compound **1** but with the addition of 1,2-bis(4-pyridyl)ethane (0.368 g, 2.00 mmol) instead of bpy. The final product as crimson-colored crystals was washed with a methanol—water (1 : 1) mixture to remove unreacted reactants and then dried in air. The yield was 0.100 g (30%). Found (%): C, 43.5; H, 4.5; N, 9.7. $C_{23}H_{28}Co_2N_{4.5}O_{95}$. Calculated (%): C, 43.3; H, 4.43; N, 9.89. IR, ν/cm^{-1}: 440 (w), 527 (m), 606 (s), 681 (w), 833 (s), 897 (m), 968 (m), 1024 (w), 1103 (m), 1221 (m), 1296 (s), 14201 (s), 1557 (s), 1595 (s), 1653 (s), 1967 (w), 2916 (m), 3071 (w), 3181 (w), 3250 (m), 3348 (m, sh). TGA. Found: Δm = 12%. Calculated for 1.5 H_2O + 0.25bpa in **3**: 10.8%.

X-ray diffraction study of single crystals of compounds **1—3** was carried out on a Bruker—Nonius X8Apex CCD four-circle automated diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å) equipped with a two-coordinate detector. An absorption correction was applied by intensities of equivalent reflections using the SADABS program.[24] The structures were solved by a direct method and refined by full-matrix least squares in the anisotropic approximation (for non-hydrogen atoms) using the SHELX-97 program package.[25] Positions of the hydrogen atoms of aspartic acid and molecules of bpy, bpe, bpa, and methanol were calculated geometrically and refined by the riding model. We failed to localize hydrogen atoms for disordered molecules of water of crystallization in structures **1** and **3**. The crystallographic characteristics and the diffraction experimental and refinement details for crystal structures **1—3** are given in Table 4. Selected bond lengths and bond angles are listed in Tables 1—3. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC Nos 742 947 (**1**), 742 948 (**2**), and 742 949 (**3**); http://www.ccdc.cam.ac.uk/products/csd/request/) and are available from the authors.

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