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Layered *trans*-1,4-Cyclohexanedicarboxylates of Divalent Metals: Synthesis, Crystal Structures, and Thermal Properties

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Abstract—The reactions of magnesium nitrate with *trans*-1,4-cyclohexanedicarboxylic acid (H_2Chdc) in *N*,*N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) as solvents afford new coordination polymers [Mg_3(DMF)$_4$(Chdc)$_3$] (**I**), [Mg_3(DMF)$_2$(NMP)$_2$(Chdc)$_3$] (**II**), and [Mg_3(NMP)$_4$(Chdc)$_3$] (**III**). Coordination polymer [Ca_3(NMP)$_4$(Chdc)$_3$] (**IV**) is synthesized from calcium acetate and H_2Chdc in NMP. The reaction of cadmium nitrate with H_2Chdc and urotropine (Ur) in DMF gives coordination polymer [Cd(Ur)(DMF)(Chdc)] (**V**). The structures of the synthesized compounds are determined by single-crystal X-ray diffraction (XRD) (CIF files CCDC nos. 2120662 (**I**), 2120666 (**II**), 2120664 (**III**), 2120663 (**IV**), and 2120665 (**V**)). The coordination polymers of alkaline-earth metals (**I**–**IV**) are based on trinuclear carboxylate blocks {$M_3(OOC)_6$} linked by the dicarboxylate linkers into trigonal layers. The cadmium compound (**V**) is built of the mononuclear fragments {Cd(N_{Ur})$_2$(DMF)(OOC)$_2$} linked by bridging *trans*-1,4-cyclohexanedicarboxylates and urotropine molecules into polymer layers. Compounds **I**–**III** are characterized by IR spectroscopy, elemental analysis, and thermogravimetric analysis.

Keywords: alkaline-earth metals, cadmium, coordination polymers, metal-organic frameworks, synthesis, aliphatic ligands, layered compounds, X-ray diffraction, thermal stability

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INTRODUCTION

Metal-organic frameworks (MOF) have actively been used during the recent two decades as promising sorbents, catalysts, luminophores, and sensors. A significant part of MOF is based on polynuclear fragments or clusters, the use of which makes it possible to specify topology, connectivity, and necessary physicochemical properties of the coordination lattice [1–7], whereas the variation of the length and nature of the bridging ligand provides a possibility of controlling the porosity and sorption properties of the polymer [8–13].

The synthesis and study of low-dimensional coordination polymers are of great interest for the preparation of functional films, membranes, and catalytically active materials [14–18]. The use of topologically “planar” metallocenters, including polynuclear metallocenters, is a method for the targeted generation of 2D structures.

Cations of light metals (Li^+, Mg^{2+}, Al^{3+}, Ca^{2+}, and Sc^{3+}) are of interest for the synthesis of MOF. A low atomic mass of the metallocenter makes it possible to maximize the specific physicochemical characteristics [19–26]. On the one hand, salts of light alkaline-earth metals are easily available and cheap. However, a few MOF were prepared from them. On the other hand, although Cd^{2+} is highly toxic, it is widely used in the chemistry of MOF due to interesting optical and luminescence properties of its coordination compounds [27–32].

Five new layered *trans*-1,4-cyclohexanedicarboxylates of divalent alkaline-earth metals and cadmium were synthesized: [Mg_3(DMF)$_4$(Chdc)$_3$] (**I**), [Mg_3(DMF)$_2$(NMP)$_2$(Chdc)$_3$] (**II**), [Mg_3(NMP)$_4$(Chdc)$_3$] (**III**), [Ca_3(NMP)$_4$(Chdc)$_3$] (**IV**), and [Cd(Ur)(DMF)(Chdc)] (**V**). Their crystal structures were determined and physicochemical characterization was performed in this work.

EXPERIMENTAL

All starting substances were used as commercially available reagents without additional purification. *N*,*N*-Dimethylformamide (DMF) (reagent grade), *N*-methylpyrrolidone (NMP) (analytical grade), and a mixture of DMF with NMP served as solvents.

IR spectra were recorded in a range of 4000–400 cm^{-1} in KBr pellets on a Scimitar FTS 2000 FTIR spectrometer. Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 F1 thermoanalyzer with the linear heating of the samples in a He atmosphere at a rate of 10 deg min^{-1}. Elemental analysis was conducted on a varioMICROcube CHNS analyzer.

Synthesis of [$Mg_3(DMF)_4(Chdc)_3$] (I). Magnesium nitrate hexahydrate (375 mg, 1.45 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (250 mg, 1.45 mmol), and DMF (12.5 mL) were mixed in a glass pot with a screw cover. The mixture was treated in an ultrasonic bath for 5 min and heated to 120°C for 24 h. The formed colorless coarsely crystalline precipitate was filtered off on a porous paper filter, washed with DMF (2 × 10 mL) and acetone (5 mL), and dried in air. The structure of the product was determined by XRD. The yield was 147 mg (35%). IR (KBr; ν, cm^{-1}): 3440 br.w ν(O–H), 2916 m ν(Csp^3–H), 2854 m ν(Csp^3–H), 1660 s ν(C=O), 1616 s ν(C=O), 1570 m ν_{as}(COO), 1417 s ν_s(COO). TGA: mass loss in a range of ~240–280°C Δ*m* = 33% (calculation based on 4DMF).

For $C_{36}H_{54}O_{16}Mg_3$

Anal. calcd., %	C, 49.4	H, 6.7	N, 6.4
Found, %	C, 49.4	H, 6.7	N, 6.4

Synthesis of [$Mg_3(DMF)_2(NMP)_2(Chdc)_3$] (II). Magnesium nitrate hexahydrate (375 mg, 1.45 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (250 mg, 1.45 mmol), NMP (6.25 mL), and DMF (6.25 mL) were mixed in a glass pot with a screw cover. The mixture was treated in an ultrasonic bath for 5 min and heated at 120°C for 24 h. The formed colorless coarsely crystalline precipitate was filtered off on a porous paper filter, washed with DMF (2 × 10 mL) and acetone (5 mL), and dried in air. The structure of the product was determined by XRD. The yield was 148 mg (33%).

IR (KBr; ν, cm^{-1}): 3430 br.vw ν(O–H), 2940, 2913 m ν(Csp^3–H), 2853 m ν(Csp^3–H), 1661 s ν(C=O), 1614 s ν(C=O), 1563 m ν_{as}(COO), 1416 s ν_s(COO). TGA: mass loss at ~220°C Δ*m* = 16% (based on 2DMF); in a range of 280–380°C Δ*m* = 21% (based on 2NMP).

For $C_{40}H_{58}O_{16}Mg_3$

Anal. calcd., %	C, 51.8	H, 6.7	N, 6.0
Found, %	C, 51.3	H, 6.2	N, 6.1

Synthesis of [$Mg_3(NMP)_4(Chdc)_3$] (III). Magnesium nitrate hexahydrate (100 mg, 0.39 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (67 mg, 0.39 mmol), and NMP (5.00 mL) were mixed in a glass pot with a screw cover. The mixture was treated in an ultrasonic bath for 10 min and heated at 120°C for 48 h. The formed colorless coarsely crystalline precipitate was filtered off on a porous paper filter, washed with NMP (2 × 10 mL) and acetone (5 mL), and dried in air. The structure of the product was determined by XRD. The yield was 102 mg (27%). IR (KBr; ν, cm^{-1}): 3420 br.w ν(O–H), 2941, 2910 s ν(Csp^3–H), 2853 m ν(Csp^3–H), 1665 m ν(C=O), 1562 m ν_{as}(COO), 1412 s ν_s(COO). TGA: mass loss at ~190°C Δ*m* = 21% (based on 2NMP); in a range of 200–350°C Δ*m* = 20% (based on 2NMP).

For $C_{44}H_{62}O_{16}Mg_3$

Anal. calcd., %	C, 53.9	H, 6.8	N, 5.7
Found, %	C, 54.8	H, 6.9	N, 5.9

Synthesis of [$Ca_3(NMP)_4(Chdc)_3$] (IV). Calcium acetate (16.0 mg, 0.101 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (17.0 mg, 0.099 mmol), and NMP (1.00 mL) were mixed in a glass ampule. The mixture was treated in an ultrasonic bath for 10 min, and the ampule was sealed and heated at 130°C for 24 h. The formed coarse crystals were sampled for XRD. The structure and composition of the product were determined by XRD.

Synthesis of [Cd(Ur)(DMF)(Chdc)] (V). Cadmium nitrate tetrahydrate (30.0 mg, 0.097 mmol), *trans*-1,4-cyclohexanedicarboxylic acid (17.0 mg, 0.099 mmol), urotropine (30.0 mg, 0.214 mmol), DMF (1.00 mL), and a 65% aqueous solution of $HClO_4$ (0.216 mmol, 20.0 μL) were mixed in a glass pot with a screw cover. The mixture was treated in an ultrasonic bath for 5 min and heated at 90°C for 48 h. The formed colorless coarsely crystalline precipitate was filtered off on a porous paper filter, washed with DMF (3 × 2 mL), and dried in air. The structure and composition of the product were determined by XRD. The yield was 6.7 mg (14%).

IR (KBr; ν, cm^{-1}): 3394 br.s ν(O–H), 2990 w ν(Csp^2–H), 2934, 2917 s ν(Csp^3–H), 2853 m ν(Csp^3–H), 1650 s ν(C=O), 1556 s ν_{as}(COO), 1412 s ν_s(COO).

XRD. Diffraction data for single crystals of compounds **I–IV** were obtained at 130 K on an Agilent Xcalibur automated diffractometer equipped with an AtlasS2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha)$ = 0.71073 Å, ω scan mode). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the CrysAlisPro program package [33]. The diffraction data for single crystals of compound **V** were accumulated at the Belok station of the Kurchatov Synchrotron Radiation Source (Rayonix SX165 detector, λ = 0.79272 Å). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the XDS program package [34]. The crystal structures were solved using the SHELXT program [35] and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELXL program [36]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined by the riding model. The crystallographic data and experimental XRD details are listed in Table 1.

Table 1. Crystallographic parameters and experimental XRD details for the structures of compounds **I**–**V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
Empirical formula	$C_{36}H_{58}N_4O_{16}Mg_3$	$C_{40}H_{62}N_4O_{16}Mg_3$	$C_{44}H_{66}N_4O_{16}Mg_3$	$C_{44}H_{66}N_4O_{16}Ca_3$	$C_{17}H_{29}N_5O_5Cd$
FW	875.79	927.86	979.93	1027.24	495.85
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	*Pbca*	$P2_1/c$	$P2_1/n$
a, Å	14.1965(12)	14.3851(12)	9.7689(4)	27.4596(10)	11.464(2)
b, Å	9.8578(8)	9.7670(6)	17.7212(7)	10.4047(3)	9.728(2)
c, Å	16.8763(14)	17.1475(13)	27.0559(13)	17.7601(6)	17.056(3)
α, deg	90	90	90	90	90
β, deg	111.143(10)	112.257(9)	90	104.697(4)	92.82(3)
γ, deg	90	90	90	90	90
V, $Å^3$	2202.8(3)	2229.7(3)	4683.8(3)	4908.2(3)	1899.8 (6)
Z	2	2	4	4	4
ρ_{calc}, g cm^{-3}	1.320	1.382	1.390	1.390	1.734
μ, mm^{-1}	0.14	0.14	0.14	0.41	1.57
F(000)	932	988	2088	2184	1016
Crystal size, mm	0.30 × 0.07 × 0.07	0.30 × 0.13 × 0.04	0.52 × 0.49 × 0.05	0.26 × 0.25 × 0.08	0.24 × 0.24 × 0.04
Scan range over θ, deg	3.31–25.35	3.31–25.35	3.45–29.46	3.45–25.35	2.3–28.5
Range of indices *hkl*	$-17 \le h \le 17$, $-8 \le k \le 11$, $-20 \le l \le 16$	$-14 \le h \le 17$, $-11 \le k \le 11$, $-20 \le l \le 17$	$-13 \le h \le 8$, $-24 \le k \le 15$, $-21 \le l \le 33$	$-32 \le h \le 33$, $-10 \le k \le 12$, $-21 \le l \le 21$	$-13 \le h \le 3$, $-11 \le k \le 11$, $-20 \le l \le 20$
Measured reflections/ independent (R_{int})	10 118/4000 (0.0366)	10238/4058 (0.0291)	16 873/5627 (0.0230)	24 119/8956 (0.0327)	12 057/3459 (0.0621)
Reflections with $I > 2\sigma(I)$	3177	3283	4618	7932	3023
GOOF	1.122	1.019	1.031	1.230	1.038
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0700$, $wR_1 = 0.154$	$R_1 = 0.0595$, $wR_1 = 0.1428$	$R_1 = 0.0414$, $wR_1 = 0.0934$	$R_1 = 0.0600$, $wR_1 = 0.1195$	$R_1 = 0.0321$, $wR_1 = 0.0725$
R factors (for all reflections)	$R_2 = 0.0883$, $wR_2 = 0.1610$	$R_2 = 0.0786$, $wR_2 = 0.1560$	$R_2 = 0.0556$, $wR_2 = 0.0986$	$R_2 = 0.0694$, $wR_2 = 0.1223$	$R_2 = 0.0382$, $wR_2 = 0.0750$
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	0.69/–0.52	0.86/–0.88	0.43/–0.39	0.61/–0.56	0.57/–0.68

The full tables of interatomic distances and bond angles, atomic coordinates, and atomic shift parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2120662 (**I**), 2120666 (**II**), 2120664 (**III**), 2120663 (**IV**), and 2120665 (**V**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available on request from the authors.

RESULTS AND DISCUSSION

Magnesium compounds **I**–**III** were synthesized under similar solvothermal conditions by the reaction of magnesium nitrate hexahydrate and *trans*-1,4-cyclohexanedicarboxylic acid (H_2Chdc) at 120°C. Compounds **I** and **II** are isostructural to each other and crystallize in the monoclinic crystal system with the space group $P2_1/n$ and $Z = 2$. Compound **III** unexpectedly obtained in NMP is not isostructural to its analogs **I** and **II** synthesized in the presence of DMF and crystallizes in the orthorhombic crystal system with the space group *Pbca* and $Z = 4$.

The independent moiety of compounds **I**–**III** contains two magnesium atoms. The Mg(1) ion occupies the partial position and exists in the octahedral environment close to regular and consisting of two O atoms of coordinated molecules of the amide solvents, two O atoms from two bridging carboxyl groups, and two O atoms of the chelating carboxyl group. The $Mg(1)–O_{amide}$ bond lengths range from 2.0344(12) to 2.1332(11) Å. The $Mg(1)–O_{COO}$ bond lengths range from 2.0141(11) to 2.182(3) Å. The Mg(2) ion exists in the common position and adopts the regular octahedral environment of six O atoms from six carboxyl groups with $Mg(2)–O_{COO}$ bond lengths ranging from 2.0256(19) to 2.1272(10) Å. Two Mg(1) ions and one Mg(2) ion are joined into trinuclear carboxylate blocks $\{Mg_3(O)_4(\kappa^1,\kappa^1\text{-}OOCR)_4(\kappa^1,\kappa^2\text{-}OOCR)_2\}$ (Figs. 1a–1c), which are very popular for Mg^{2+} and a series of divalent cations of transition metals, such as Zn^{2+}, Co^{2+}, and Mn^{2+} [37–42]. The blocks are connected by bridging *trans*-1,4-cyclohexanedicarboxylates to form trigonal layers (Figs. 2a, 2b) with the single-layer (AA) packing for compounds **I** and **II** and bilayered (ABAB) packing in the case of compound **III**. The crystal structures of compounds **I–III** is close-packed and contains no cavities.

Compound **IV** was synthesized by the reaction of calcium acetate and H_2Chdc in NMP at 130°C. This compound is not isostructural to magnesium compounds **I–III** and crystallizes in the monoclinic crystal system with the space group $P2_1/c$ and $Z = 4$. The independent moiety contains three calcium atoms. The coordination geometry of Ca(1) and Ca(3) takes the shape of a one-capped octahedron with the coordination number 7 due to the change of the coordination mode by one more carboxyl group from κ^1,κ^1 to κ^1,κ^2. The $Ca(1/3)–O_{amide}$ bond lengths range from 2.287(2) to 2.363(3) Å. The $Ca(1/3)–O_{COO}$ bond lengths range from 2.308(2) to 2.509(2) Å. The Ca(2) ion has an octahedral environment with the $Ca(2)–O_{COO}$ bond lengths ranging from 2.284(2) to 2.348(2) Å. An increase in the coordination number of terminal Ca^{2+} from 6 to 7 thus results in trinuclear blocks $\{Ca_3(O)_4(\kappa^1,\kappa^1\text{-}OOCR)_2(\kappa^1,\kappa^2\text{-}OOCR)_4\}$ (Fig. 1d). In spite of a difference in the coordination mode, the blocks retain a connectivity of 6 and form analogous trigonal layers including bridging *trans*-1,4-cyclohexanedicarboxylates (Fig. 2c). The layers have the ABAB packing. The crystal structure of compound **IV** is also close-packed and contains no cavities.

Compounds **I–III** represent the first known examples of magnesium *trans*-1,4-cyclohexanedicarboxylates. One calcium *trans*-1,4-cyclohexanedicarboxylate $[Ca(H_2O)_2(Chdc)]\cdot H_2O$ with the three-dimensional structure built of polymer metal-carboxylate chains obtained in an aqueous medium has previously been described [43]. It is most likely that the chemical nature of an amide solvent (DMF or NMP) is a determining factor in the formation of new coordination polymers of alkaline-earth metals (**I–IV**).

Compound **V** was synthesized by the reaction of cadmium nitrate tetrahydrate, H_2Chdc, and urotropine Ur in DMF at 90°C. Strong perchloric acid $HClO_4$ in an equimolar amount was added to base Ur for the complete dissolution of the reagents. Compound **V** crystallizes in the monoclinic crystal system with the space group $P2_1/n$ and $Z = 4$. The independent moiety contains one cadmium atom. Its coordination environment consists of two nitrogen atoms from two bidentate bridging urotropine molecules, one oxygen atom of the coordinated DMF solvent, and four O atoms from two bidentate chelating carboxyl groups. The Cd–N bond lengths are 2.342(2) and 2.487(2) Å. The $Cd–O_{DMF}$ bond length is 2.406(2) Å. The $Cd–O_{COO}$ bond lengths range from 2.3190(18) to 2.4857(19) Å. Thus, the coordination number of Cd(II) is 7. The metallocenters (nodes) shown in Fig. 3a are tetraconnected and linked by *trans*-1,4-cyclohexanedicarboxylates along the crystallographic axis *c* into zigzag chains. The chains are connected by the bridging ligands Ur along the *b* axis to form 2D coordination layers (Fig. 3b). The bilayered (ABAB) packing of the layers in the three-dimensional crystal structure of compound **V** is also close-packed and contains no cavities.

Three cadmium *trans*-1,4-cyclohexanedicarboxylates synthesized without using additional N-donor ligands were known earlier. Chain compound $[Cd(H_2O)_2(C_8H_{10}O_4)]$ based on the mononuclear fragments was synthesized in an aqueous medium [38] using piperidine as a modulator of basicity of the medium. We have previously synthesized three-dimensional MOF $[Cd(H_2O)(Chdc)]\cdot 0.5CH_3CN$ formed of polymer metal-carboxylate chains in a mixture of water and acetonitrile using 1,4-diazabicyclo[2.2.2]octane (Dabco) as the basicity modulator [44]. The three-dimensional MOF $[Cd_2(DMF)(Chdc)_2]$ also built of polymer carboxylate chains was synthesized in DMF without modulators [45]. It is most likely that urotropine in a DMF medium is a rather strong ligand to form coordination lattices involving urotropine, unlike the above considered cases of piperidine in water and Dabco in water–acetonitrile mixtures. Similar examples of the dual nature of urotropine (base–ligand) in the synthesis of MOF were published earlier [40, 44, 46–48].

The thermal stability of magnesium compounds **I–III** was characterized by the TGA method (Fig. 4). Compound $[Mg_3(DMF)_4(Chdc)_3]$ (**I**) loses the coordinated solvent at 240–280°C. The weight of the solid residue at 600°C is 21% and corresponds to magnesium oxide (theor. 17%) with a carbon impurity formed, most likely, because the incomplete volatilization of organic linkers. Compound $[Mg_3(DMF)_2(NMP)_2(Chdc)_3]$ (**II**) stepwise loses the coordinated solvent at 220°C (DMF) and in a range of 280–380°C (NMP). The weight of the solid residue at 600°C is 20% and corresponds to magnesium oxide (theor. 13%) with the thermal decomposition products of the organic ligands. Compound $[Mg_3(NMP)_4$-

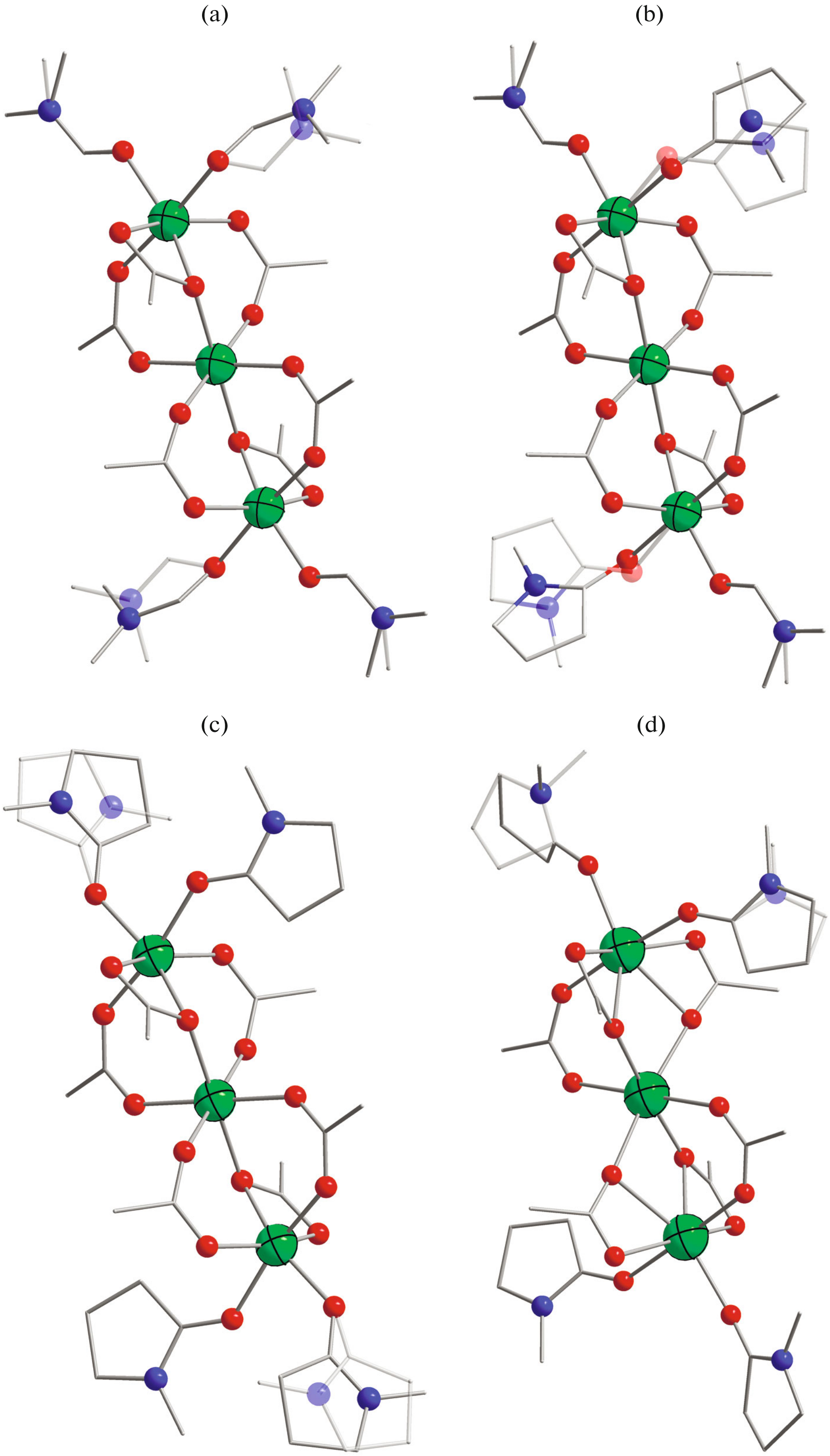

Fig. 1. Trinuclear carboxylate blocks $\{M_3(\text{amide})_4(\text{OOCR})_6\}$ in the structures of compounds (a) **I**, (b) **II**, (c) **III**, and (d) **IV**. The second positions of the disordered DMF and NMP molecules are semitransparent. In Figs. 1–3, M atoms are green, N atoms are blue, and O atoms are red; hydrogen atoms are omitted.

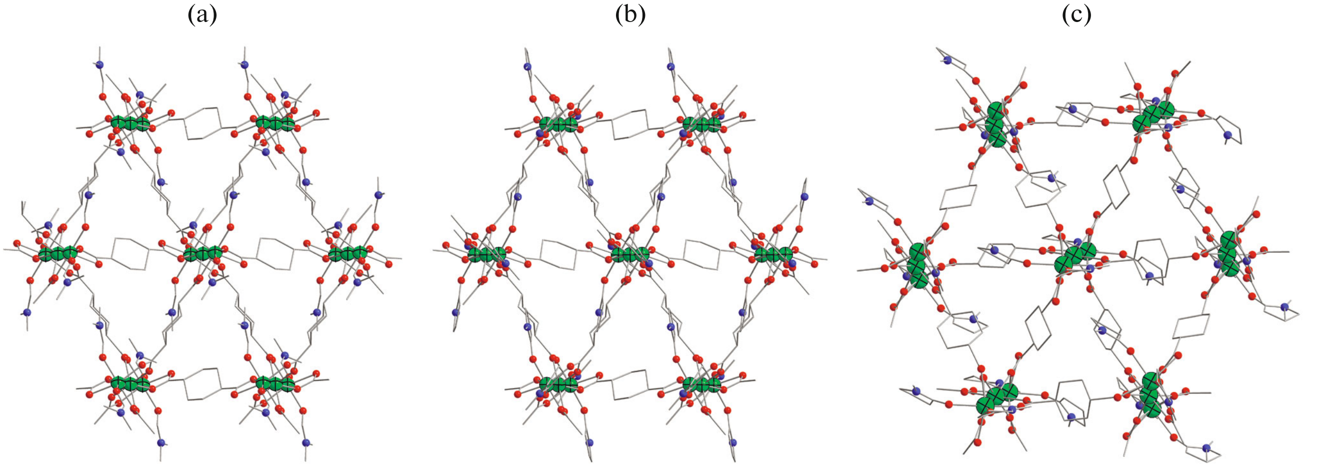

Fig. 2. Coordination layers $\{M_3(amide)_4(Chdc)_3\}$ in the structures of compounds (a) **I**, (b) **III**, and (c) **IV**. Only one of possible positions of DMF and NMP is shown.

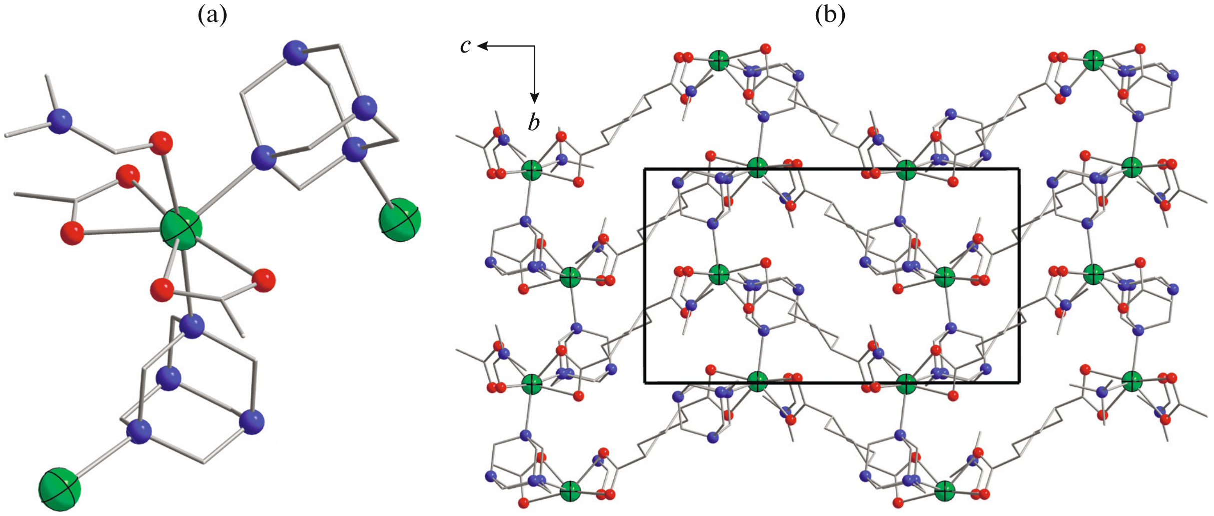

Fig. 3. (a) Fragment $\{Cd(DMF)(Ur)_2(OOCR)_2\}$ in compound **V** and its binding with the adjacent Cd(II) atoms and (b) coordination layer in compound **V** (view along the *a* axis).

$(Chdc)_3]$ (**III**) stepwise loses the coordinated solvent at 190°C (2NMP) and in a range of 200–350°C (2NMP). The weight of the solid residue at 600°C is 17% and also corresponds to magnesium oxide (theor. 12%) with the thermal decomposition products of the organic ligands. A decrease in the thermal stability in the order **I** > **II** > **III** demonstrates an unusual inverse dependence on the boiling point of the solvent (T_b(DMF) = 153°C < T_b(NMP) = 202°C), which is probably related to an increase in the molecular size of the solvent leading to "loosening" of the crystal structures of the coordination polymers shown by the order V/Z: 1101.4 Å^3 (**I**) < 1114.9 Å^3 (**II**) < 1171.0 Å^3 (**III**).

Thus, five new layered metal-organic frameworks, which are divalent metal *trans*-1,4-cyclohexanedicarboxylates, were synthesized and structurally characterized. Magnesium compounds **I**–**III** and calcium compound **IV** are based on the trinuclear carboxylate blocks $\{M_3(OOCR)_6\}$ that form hexaconnected coordination layers of trigonal geometry. Cadmium compound **V** is built of the mononuclear fragments $\{Cd(N_{Ur})_2(DMF)(OOCR)_2\}$. However, this compound is also layered due to the bridged coordination of ditopic urotropine and $Chdc^{2-}$. Compounds **I**–**III** were characterized by IR spectroscopy, elemental analysis, and thermogravimetric analysis. An unusual series of thermal stability for the similar magnesium MOF was obtained by the TGA data: $[Mg_3(DMF)_4(Chdc)_3]$ > $[Mg_3(DMF)_2(NMP)_2(Chdc)_3]$ > $[Mg_3(NMP)_4(Chdc)_3]$. The series demonstrates an inverse dependence on the boiling point of the coordinated solvent. This effect was assigned to an

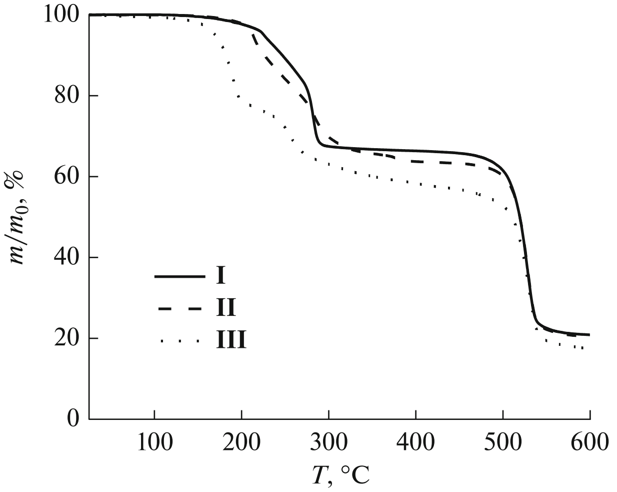

Fig. 4. TGA plots for compounds **I**–**III**.

increase in the molecular size of the solvent leading to "loosening" of the packing of the coordination lattices in the crystal.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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