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Structure Forming Role of Alkaline Metal Cations in the Formation of Chromium(III) Complexes with Anions of Cyclopropane-1,1-Dicarboxylic Acid

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Abstract—The reactions of $Cr(NO_3)_3 \cdot 9H_2O$ with potassium, sodium, and lithium salts of cyclopropane-1,1-dicarboxylic acid (H_2Cpdc) in a ratio of 1 : 3 are studied in order to elucidate the chemical assembling processes of the coordination polymers with Cr^{3+} and alkaline metal ions. The nature of the reacted alkaline metal cation affects the compositions and structures of the formed compounds. The reaction of $Cr(NO_3)_3 \cdot 9H_2O$ with $K_2(Cpdc)$ affords the 3D polymeric complex $[KCr(Cpdc)_2(H_2O)_2]_n$ (**I**) formed by the bis-chelate anionic fragments $[Cr(Cpdc)_2(H_2O)_2]^-$. Under similar conditions, the use of $Na_2(Cpdc)$ and $Li_2(Cpdc)$ results in the formation of the 3D polymers $[Na_4Cr(Cpdc)_3(H_2O)_6(NO_3)]_n$ (**II**) and $\{[Li_8Cr_2(Cpdc)_8(H_2O)_5] \cdot H_2O\}_n$ (**III**), respectively, containing the tris-chelate anionic fragments $[Cr(Cpdc)_3]^{3-}$. A distinctive feature of compound **III** is the presence in its structure of the $\{Li(Cpdc)\}^-$ fragments in which the $Cpdc^{2-}$ anion forms a six-membered chelate cycle with the Li^+ ion. The crystal structures of compounds **I**–**III** are determined by X-ray diffraction (CIF files CCDC nos. 2031258 (**I**), 2031260 (**II**), and 2031261 (**III**)).

Keywords: chromium(III) complexes, cyclopropane-1,1-dicarboxylic acid, alkaline metals, synthesis, X-ray diffraction

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INTRODUCTION

Intensive studies in the recent decade in the area of the chemistry of substituted malonic acids ($H_2R^1R^2Mal$) made it possible to elucidate their wide coordination capabilities for the design of polynuclear compounds and coordination polymers of various structures with diverse combinations of metal atoms (*s*–*d*, *d*–*d*', and *d*–*f*) and to determine regularities of changing the crystal structures and physicochemical properties depending on the nature of the initial metal compounds, synthesis conditions, and solvents or geometric characteristics of the substituent in the malonate anion [1–6]. In particular, it was shown for the oxovanadium(IV) compounds forming the bis-chelate anionic "block" $\{VO(R^1R^2Mal)_2\}^{2-}$ with anions $R^1R^2Mal^{2-}$ that an increase in the substituent size on going from cyclopropane-1,1-dicarboxylic acid (H_2Cpdc) to butylmalonic acid (H_2BuMal) favored a decrease in the dimensionality of the polymeric structure and the formation of compounds with the layered or chain structures [7, 8]. In the synthesis of the copper(II) coordination polymers with alkaline-earth metal cations, the $Cpdc^{2-}$ anions containing the rigid cyclopropane fragment, on the contrary, favor the formation of the 3D framework porous structures [9], whereas 2D polymeric compounds are formed in the case of the homometallic complexes of transition 3*d* metals and lanthanides [10–13].

Alkaline and alkaline-earth metal cations introduced into the reaction as components of the dicarboxylic acid salt can also play the structure forming role in both the formation of new *s*–3*d* molecules and crystal growth affecting the crystal packing and spatial architecture of the formed system. Ions of *s* elements participate in the self-organization of the supramolecular crystal structure of the compound due to the formation of ionic M–O bonds with the metal-containing bis-malonate fragments. The ionic radius of the alkaline metal cation, which is larger, as a rule, than the radii of 3*d* elements, often affects the type and dimensionality of the structure. For example, lithium cations with a small radius ($r(M^+)$, Å: Li (0.68), Na (0.98), K (1.33)) close to the radii of double-charge cations of 3*d* metals and Cr^{3+} (0.64 Å) [14] favor the formation of molecular compounds in the malonate systems, whereas sodium and potassium cations form layered or framework structures depending on the substituent geometry [4]. Numerous examples of the self-assembling directed by alkaline metal cations are known for the supramolecular architectures and polynuclear complexes in the systems with other polyfunctional ligands [15–27].

As shown previously, the reactions of chromium(III) with malonate anions can afford both the bis-chelate $[Cr(Mal)_2(H_2O)_2]^-$ and tris-chelate fragments $[Cr(Mal)_3]^{3-}$, as well as the binuclear hydroxocarboxylate anions $[Cr_2(OH)_2(Mal)_4]^{4-}$ [28–35], which in combination with the steric effects of substituents in the malonate ligand and variation of the synthesis conditions makes it possible to extend the variety of the formed structures [36, 37].

In this work, the reactions of chromium(III) nitrate with salts of cyclopropane-1,1-dicarboxylic acid (M_2Cpdc, M = K, Na, Li) in a ratio of 1 : 3 in an aqueous medium was studied. The effect of the nature of the alkaline metal on the compositions and crystal structures of the formed chromium(III) complexes with the $Cpdc^{2-}$ anions was studied.

EXPERIMENTAL

New compounds were synthesized in air using distilled water, $Cr(NO_3)_3\cdot 9H_2O$ (99%, Acros Organics), KOH (99+%), NaOH (99+%), $LiOH\cdot H_2O$ (99+%), and H_2Cpdc (97%, Sigma Aldrich). IR spectra were recorded in a frequency range of 4000–400 cm^{-1} on a Spectrum 65 FTIR spectrophotometer (PerkinElmer) equipped with a Quest ATR accessory (Specac) using the attenuated total reflection (ATR) method. Elemental analyses were carried out on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $[KCr(Cpdc)_2(H_2O)_2]_n$ (I). A solution of K_2Cpdc, which was synthesized by the reaction of H_2Cpdc (0.146 g, 1.11 mmol) with KOH (0.125 g, 2.22 mmol) in water (20 mL) at 90°C, was added to a solution of $Cr(NO_3)_3\cdot 9H_2O$ (0.15 g, 0.37 mmol) in distilled water (10 mL) at 90°C. The reaction mixture was stirred at 90°C for 4 h, and the resulting bluish-green solution was kept for slow evaporation (T = 22°C) for 2 months. Crimson-colored crystals suitable for X-ray diffraction were separated from the mother liquor by filtration, washed with water (T = 5°C), and dried in air. The yield of compound **I** was 0.085 g (59.2% based on $Cr(NO_3)_3\cdot 9H_2O$).

For $C_{10}H_{12}O_{10}KCr$

Anal. calcd., %	C, 31.34	H, 3.16
Found, %	C, 31.10	H, 3.27

IR (ATR; ν, cm^{-1}: 3146 m.br ν(O–H), 3027 w, 2826 m.br, 1577 s $\nu_{as}(COO^-)$, 1560 s, 1435 m, 1412 m, 1383 s $\nu_s(COO^-)$, 1237 s, 1209 m, 1193 m, 1088 m, 1042 w, 988 w, 975 w, 937 s, 868 s, 817 m, 795 m, 770 s, 756 s, 738 s, 660 s, 555 s, 524 s, 470 s, 430 w.

Synthesis of $[Na_4Cr(Cpdc)_3(H_2O)_6(NO_3)]_n$ (II). A solution of Na_2Cpdc, which was synthesized by the reaction of H_2Cpdc (0.146 g, 1.11 mmol) and NaOH (0.090 g, 2.22 mmol) in water (25 mL) at 90°C, was added to a solution of $Cr(NO_3)_3\cdot 9H_2O$ (0.15 g, 0.37 mmol) in distilled water (10 mL) at 90°C. The reaction mixture was stirred at 90°C for 3 h, and the resulting green solution was kept for slow evaporation (T = 22°C) for a month. Dark blue crystals suitable for X-ray diffraction were separated from the mother liquor by filtration and dried in air. The yield of compound **II** was 0.100 g (38.3% based on $Cr(NO_3)_3\cdot 9H_2O$).

For $C_{15}H_{22}NO_{21}Na_4Cr$

Anal. calcd., %	C, 25.87	H, 3.18	N, 2.01
Found, %	C, 25.67	H, 3.45	N, 2.12

IR (ATR); ν, cm^{-1}: 3385 m.br ν(O–H), 3039 vw, 1678 w, 1578 s $\nu_{as}(COO^-)$, 1422 s, 1390 s $\nu_s(COO^-)$, 1348 s, 1237 s, 1208 m, 1082 m, 1060 vw, 992 vw, 979 vw, 933 s, 869 s, 826 w, 807 w, 792 w, 769 m, 757 m, 740 s, 687 m, 591 m, 553 s, 515 s, 463 s.

Synthesis of $\{[Li_8Cr_2(Cpdc)_8(H_2O)_5]\cdot H_2O\}_n$ (III). A solution of Li_2Cpdc, which was synthesized by the reaction of H_2Cpdc (0.146 g, 1.11 mmol) and $LiOH\cdot H_2O$ (0.094 g, 2.22 mmol) in water (25 mL) at 90°C, was added to a solution of $Cr(NO_3)_3\cdot 9H_2O$ (0.15 g, 0.37 mmol) in distilled water (10 mL) at 90°C. The reaction mixture was stirred at 90°C for 3 h and kept at 22°C for a month. A green solution was filtered from a finely dispersed green precipitate, and the resulting filtrate was kept for slow evaporation (T = 22°C) for 2 months. Dark blue crystals suitable for X-ray diffraction were separated from the mother liquor by filtration and dried in air. The yield of compound **III** was 0.054 g (23.6% based on $Cr(NO_3)_3\cdot 9H_2O$).

For $C_{35}H_{35}O_{38}Li_8Cr_2$

Anal. calcd., %	C, 34.37	H, 2.88
Found, %	C, 34.04	H, 3.16

IR (ATR; ν, cm^{-1}: 3458 m.br ν(O–H), 3394 m.br ν(O–H), 3124 vw, 3022 vw, 1558 s $\nu_{as}(COO^-)$, 1435 s, 1400 s $\nu_s(COO^-)$, 1243 s, 1214 s, 1082 m, 1045 w, 978 m, 944 s, 871 s, 811 m, 801 m, 754 s, 555 s, 487 s.

Single crystal X-ray diffraction study of **I–III** was carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector (MoK_α, λ = 0.71073 Å, graphite monochromator) [38]. A semiempirical absorption correction was applied using the SADABS program [39]. The hydrogen atoms at the

Table 1. Crystallographic data and structure refinement details for structures **I**–**III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{10}H_{12}O_{10}KCr$	$C_{15}H_{22}N_4O_{21}NaCr$	$C_{35}H_{35}O_{38}Li_8Cr_2$
M, g/mol	383.30	696.29	2446.30
T, K	150	296	273
Crystal system	Trigonal	Trigonal	Monoclinic
Space group	$R\bar{3}c$	$P3_121$	$C2/m$
a, Å	12.7944(3)	9.5533(7)	27.30(4)
b, Å	12.7944(3)	9.5533(7)	14.87(2)
c, Å	42.9765(10)	24.9257(16)	13.97(2)
α, deg	90	90	90
β, deg	90	90	117.76(4)
γ, deg	120	120	90
V, Å^3	6092.6(3)	1970.1(4)	5020(13)
Z	18	3	2
ρ_{calc}, g cm^{-3}	1.880	1.761	1.618
μ, mm^{-3}	1.205	0.599	0.545
θ_{min}–θ_{max}, deg	2.64–26.39	2.46–27.77	2.59–27.10
F(000)	3510	1065	2484
T_{min}/T_{max}	0.577/0.745	0.887/0.970	0.332/0.746
Ranges of reflection indices	$-15 \le h \le 15$, $-12 \le k \le 15$, $-53 \le l \le 53$	$-8 \le h \le 11$, $-8 \le k \le 11$, $-28 \le l \le 30$	$-30 \le h \le 30$, $-16 \le k \le 16$, $-15 \le l \le 15$
Number of measured reflections	12872	9623	12190
Number of independent reflections	1382	2584	3826
R_{int}	0.0260	0.0531	0.0953
Reflections with $I > 2\sigma(I)$	1325	2229	2594
GOOF	1.062	1.057	1.025
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0281$, $wR_2 = 0.0831$	$R_1 = 0.0562$, $wR_2 = 0.1438$	$R_1 = 0.1079$, $wR_2 = 0.2645$
R factors for all reflections	$R_1 = 0.0292$, $wR_2 = 0.0842$	$R_1 = 0.0657$, $wR_2 = 0.1506$	$R_1 = 0.1519$, $wR_2 = 0.2999$
Residual electron density ($\Delta\rho_{min}/\Delta\rho_{max}$), e/Å^3	–0.835/0.404	–0.478/0.710	–1.405/ 3.311

carbon atoms of the organic ligands and water molecules were generated geometrically and refined using the riding model. The hydrogen atoms of the OH groups in structures **I** and **II** were localized from the difference Fourier maps, and those in **III** were generated geometrically and refined by the riding model. The calculations were performed using the SHELX-2018 program package [40] using Olex 2 1.3 [41]. In the structure of **II**, the Na(1) atom was disordered over two positions (Na(1A) and Na(1B)) with equal occupancies of 0.5. In the structure of **III**, the Li(1) atom has a occupancy of 0.5, and the water molecules (O(10) and O(17)) were disordered over two positions (O(10A), O(10B) and O(17A), O(17B), respectively) with occupancies of 0.5. The crystallographic parameters and structure refinement details for structures **I**–**III** are presented in Table 1.

The structural data were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2031258 (**I**), 2031260 (**II**), and 2031261 (**III**); deposit@ccdc.cam.ac.uk; http:// www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of $Cr(NO_3)_3·9H_2O$ with K_2Cpdc (synthesized by the reaction of H_2Cpdc and KOH in

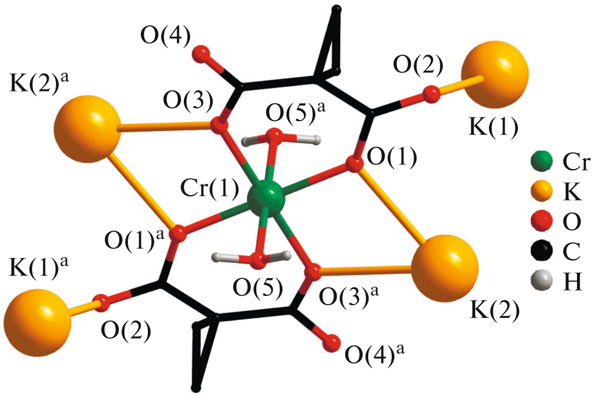

Fig. 1. Structure of the mononuclear anions [Cr$(Cpdc)_2(H_2O)_2]^-$ and their binding by the potassium atoms in structure of **I** (hydrogen atoms of the cyclopropane fragments are omitted). Symmetry codes: ^{a} 0.66667 – *x*, 0.33333 – *y*, 1.33333 – *z*.

an aqueous solution) in a molar ratio of 1 : 3 in an aqueous solution at 90°C resulted in the formation of crimson-colored crystals of compound $[KCr(Cpdc)_2(H_2O)_2]_n$ (**I**). The replacement of K_2Cpdc by Na_2Cpdc, under the same conditions, gave dark blue crystals of $[Na_4Cr(Cpdc)_3(H_2O)_6(NO_3)]_n$ (**II**), whereas the use of Li_2Cpdc in a similar reaction led to the crystallization of compound $\{[Li_8Cr_2(Cpdc)_8(H_2O)_5]\cdot H_2O\}_n$ (**III**).

The structure of **I** is formed by the mononuclear anionic fragments $[Cr(Cpdc)_2(H_2O)_2]^-$ in which the Cr(1) atom is in the octahedral environment coordinating two chelate dianions $Cpdc^{2-}$ and two monodentate water molecules (Fig. 1). Four O atoms of the carboxylate ligands lie in the equatorial plane of the polyhedron and form Cr–O bonds similar in length (Table 2), and the O atoms of the water molecules occupy the axial positions of the octahedron (Cr–O(H_2O) 1.9930(13) Å). Note that the formation of the bis-chelate anion $[Cr(R^1R^2Mal)_2(H_2O)_2]^-$ was earlier observed in the compound K–Cr(III) with the $Cbdc^{2-}$ anions. This compound crystallizes in ethanol, but it is characterized by the 2D polymeric structure rather than 3D structure, which can be explained by the steric effect of the more bulky cyclobutane fragment in the malonate anion [37].

The structure of compound **I** contains crystallographically independent K atoms of two types (K(1) and K(2)). The K(2) atoms form bonds with the O atoms of the carboxylate ligands involved in the chelating of Cr(1) and bind the $[Cr(Cpdc)_2(H_2O)_2]^-$ fragments into polymeric layers (Cr(1)···K(2) ~ 3.723 Å) (Fig. 2, Table 2). The shortest Cr···Cr distance in the layer is 6.3966 Å. In turn, the polymeric layers are joined into the 3D polymeric structure (Fig. 3) due to the coordination of the K(1) potassium atoms to the O atoms of the carboxyl groups, which are not involved in chelating. Each $[Cr(Cpdc)_2(H_2O)_2]^-$ fragment in this structure is surrounded by four potassium cations. The environment of the potassium atoms is formed only by the O atoms of the carboxyl groups, and the water molecules in the structure of **I** are coordinated only to the Cr atoms. The crystal structure of **I** is additionally stabilized due to the formation of hydrogen bonds between the H atoms of the water molecules and O atoms of the carboxyl groups of the adjacent $[Cr(Cpdc)_2(H_2O)_2]^-$ fragments in the polymeric layer and between the H atoms of the cyclopropane fragments and O atoms of the water molecules of the adjacent polymeric layers (Table 3).

In the structure of compound **II**, the Cr(1) atoms form the tris-chelate anionic fragments $[Cr(Cpdc)_3]^{3-}$ arranged on the 2-fold axis. The chromium atom coordinates six O atoms of three chelate anions $Cpdc^{2-}$ that form the octahedral environment of the metal center with similar values of the Cr–O bond lengths and the OCrO angles (Fig. 4, Table 2). The structure of **II** contains two types of crystallographi-

Table 2. Selected bond lengths (*d*) and angles (ω) in the structures of compounds **I**–**III**

Bond	*d*, Å		
	I (M = K)	**II** (M = Na)	**III** (M = Li)
Cr–O (Cpdc)	1.9365(12)–1.9534(12)	1.949(3)–1.956(3)	1.948(6)–1.980(6)
M–O (Cpdc)	2.7138(13)–2.7983(12)	2.261(4)–2.468(7)	1.87(4)–2.58(2)
M–O (H_2O)		2.215(8)–2.78(1)	1.88(3)–2.446(11)
Angle	ω, deg		
OCrO (adjacent)	87.81(6)–92.19(6)	88.64(15)–92.2(2)	86.4(3)–95.8(3)

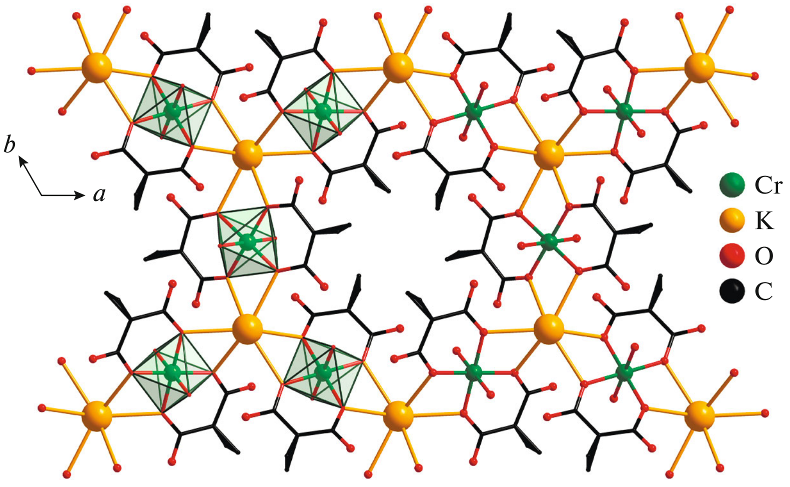

Fig. 2. Structure of the polymeric layer in the structure of compound **I** (hydrogen atoms are omitted).

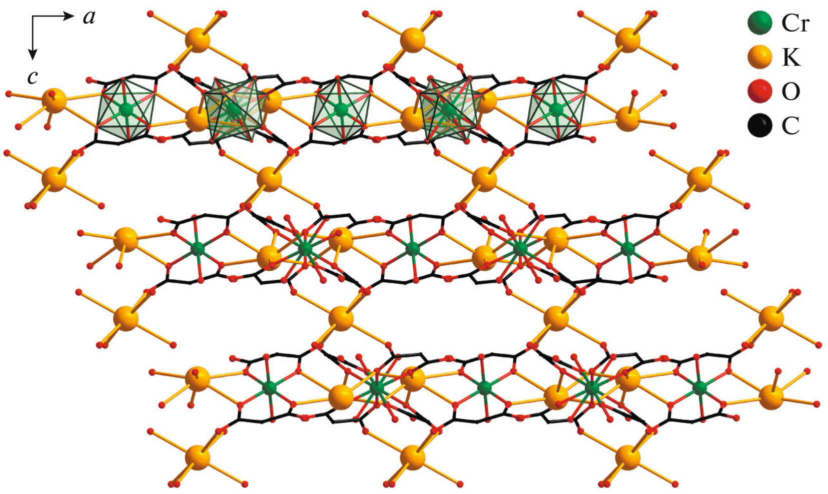

Fig. 3. Fragment of the 3D polymeric structure of compound **I** (cyclopropane fragments of the acid anions and hydrogen atoms are omitted).

cally independent sodium atoms (Na(1) and Na(2)). The Na(1) atom is disordered over two positions (Na(1A) and Na(1B)) with an occupancy of 0.5 each. The Na(2) atom is linked with the adjacent metal atoms (Na(1A) and Na(1B)) by the bridging water molecules (O(1w), O(2w), and O(3*w*)) and the oxygen atoms of the carboxyl groups (O(1) and O(4)) to form zigzag 1D polymeric chains in the *ab* plane (the distances are as follows: Na(1A)···Na(2) 3.028(6), 3.184(6) Å; Na(1B)···Na(2) 3.302(6), 3.545(7) Å). The sodium atoms Na(1A) and Na(1B) complete their environments by the coordination of the oxygen atom (O(1N)) of the bridging anion NO_3^-, linking the polymeric chains into the cationic layer $\{Na_4(H_2O)_6(NO_3)\}_n^{3n+}$ (Na···O(NO_3) 2.161(11), 3.193(13) Å) (Fig. 5). In the crystal structure of compound **II**, the Na atoms coordinate the O atoms of the carboxyl groups of the $\{Cr(Cpdc)_3\}$ fragments (each $\{Cr(Cpdc)_3\}$ fragment is surrounded by ten Na atoms) that bind the cationic layers $\{Na_4(H_2O)_6(NO_3)\}_n^{3n+}$ into the framework structure (Cr···Cr 9.553(7) Å, Cr···Na 4.821–6.341 Å) (Fig. 6). The structure of complex **II** is additionally stabilized by a wide network of intramolecular hydrogen bonds, whose formation involves the water molecules and oxygen atoms of the carboxyl groups and nitrate anions (Table 3).

Similarly to compound **II**, the structure of compound **III** is formed by the mononuclear anionic fragments $[Cr(Cpdc)_3]^{3-}$ in which the Cr(1) atom coordinates three chelate dianions $Cpdc^{2-}$ and has an octahedral coordination environment (Fig. 7, Table 2). Ten crystallographically independent lithium atoms

Table 3. Geometric parameters of hydrogen bonds in the structures of compounds **I**–**III***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
I				
O(5)–H(1a)···O(4)$^{\text{i}}$	0.74	1.85	2.5822(18)	169
O(5)–H(1b)···O(2)$^{\text{ii}}$	0.90	1.81	2.706(2)	175
C(5)–H(5a)···O(5)$^{\text{iii}}$	0.99	2.56	3.530(3)	165
II				
O(2*w*)–H(2*w*a)···O(1N)	0.70	2.32	2.940(10)	148
O(2*w*)–H(2*w*b)···O(3)$^{\text{i}}$	0.82	2.02	2.837(5)	171
O(3*w*)–H(3*w*a)···O(5)$^{\text{ii}}$	0.85	2.01	2.856(6)	173
O(3*w*)–H(3*w*b)···O(1N)	0.85	2.40	2.997(9)	128
O(3*w*)–H(3*w*b)···O(3*w*)$^{\text{iii}}$	0.85	2.60	3.045(9)	114
O(1*w*)–H(1*w*a)···O(2N)$^{\text{iv}}$	0.85	1.95	2.794(11)	177
O(1*w*)–H(1*w*b)···O(2)	0.85	2.33	2.924(6)	127
O(1*w*)–H(1*w*b)···O(5)	0.85	2.45	3.251(7)	157
III				
O(7*w*)–H(7*w*a)···O(4)$^{\text{i}}$	0.85	2.09	2.865(16)	151
O(7*w*)–H(7*w*b)···O(4)$^{\text{ii}}$	0.85	2.30	2.865(16)	125
O(11*w*)–H(11a)···O(10*B*)	0.86	2.54	3.21(3)	135
O(12*w*)–H(12a)···O(7)$^{\text{iii}}$	0.85	2.07	2.904(12)	167
O(12*w*)–H(12b)···O(8*w*)$^{\text{iv}}$	0.85	2.05	2.83(3)	153
C(13)–H(13a)···O(16)$^{\text{v}}$	0.97	2.40	3.334(14)	161

* Symmetry codes: $^{\text{i}}$ $2/3 + x - y, 1/3 + x, 4/3 - z$; $^{\text{ii}}$ $-1/3 + y, 1/3 - x + y, 4/3 - z$; $^{\text{iii}}$ $2/3 - x + y, 1/3 + y, -1/6 + z$ (**I**). $^{\text{i}}$ $-x, 1 + y, z$; $^{\text{ii}}$ $y, 1 + x, 1 - z$; $^{\text{iii}}$ $y, x, 1 - z$; $^{\text{iv}}$ $x, 1 + y, z$ (**II**). $^{\text{i}}$ $1 - x, y, 1 - z$; $^{\text{ii}}$ $1 - x, 1 - y, 1 - z$; $^{\text{iii}}$ $1/2 - x, -1/2 + y, 1 - z$; $^{\text{iv}}$ $1/2 - x, 1/2 + y, 1 - z$; $^{\text{v}}$ $1/2 - x, 1/2 + y, 2 - z$ (**III**).

are determined in the structure of compound **III** (Fig. 7). They form the "layers" containing chains of two types: {Li(4)···Li(10)··· Li(1)···Li(2)··· Li(1)···Li(10)} consisting of seven lithium atoms and polymeric chains $\{\cdots$Li(6)···Li(5)···Li(6)···(Li(9), Li(8), Li(7))···Li(3)–(Li(9), Li(8), Li(7))$\cdots\}_n$ (Fig. 8). In the chain of the first type, two Li(1) atoms (occupancy is 0.5) are linked with the central Li(2) atom by the bridging water molecules O(1*w*) and O(10A) (occupancy is 0.5) (Li(1)···Li(2) 3.08(4) Å). Each Li(1) atom is bound to Li(10) due to the bridging water molecules O(10B) (occupancy is 0.5) and O(17A) (occupancy is 0.5), and each Li(10) atom is linked with Li(4) due to the O(6) atoms of the carboxyl groups of the chromium-containing fragments $[Cr(Cpdc)_3]^{3-}$ (Li(1)···Li(10) 3.68(3), Li(10)···Li(4) 2.58(3) Å). The "central" Li(2) atom additionally coordinates one water molecule (O(2*w*)), whereas "terminal" Li(4) coordinates two monodentate water molecules (O(7*w*) and O(8*w*)) (Figs. 7 and 8). In the chain of the second type, the Li(9) atom coordinates one $Cpdc^{2-}$ anion that forms the six-membered chelate ring with the metal atom. Such coordination mode of the malonate anion has previously been observed in the structure of the Li(I)–Co(II) dimethylmalonate complex [42]. Further the $\{Li(9)(Cpdc)\}^-$ fragment binds three lithium atoms (Li(8), Li(7), and Li(6)) due to the carboxylate O atoms of the $Cpdc^{2-}$ anion, and each of the Li(8), Li(7), and Li(6) atoms forms bonds with two $[Cr(Cpdc)_3]^{3-}$ fragments of the adjacent layers (Li(6)···Li(9) 3.67(5), Li(7)···Li(9) 5.91(5), and Li(8)···Li(9) 3.33(4) Å). The binding of Li(9) with Li(3) in the chain occurs due to the coordination of the O(2) atoms of the carboxylate anions (Li(3)···Li(9) 2.64(4) Å). The Li(5) and Li(6) atoms are linked via

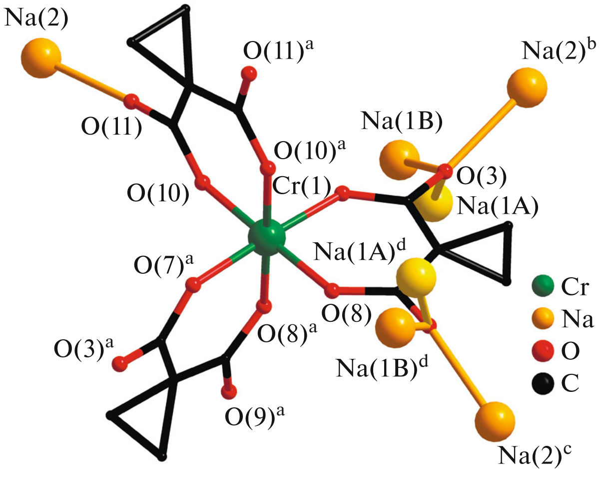

Fig. 4. Structure of the anionic fragment $[Cr(Cpdc)_3]^{3-}$ and its binding with the sodium atoms in the structure of compound **II** (hydrogen atoms are omitted). Symmetry codes: ^{a} $-x$, $-x + y$, $1.33333 - z$; ^{b} $1 + x$, y, z; ^{c} $-x$, $-1 - x + y$, $1.33333 - z$; ^{d} $1 - y$, $1 + x - y$, $0.33333 + z$.

one bridging water molecule (O(10*w*)) and the O(19) atoms of the carboxyl groups of the $[Cr(Cpdc)_3]^{3-}$ fragments belonging to the adjacent layers (Li(5)···Li(6) 2.63(2) Å). The Li(7) and Li(8) atoms additionally coordinate one water molecule each (O(11*w*) and O(9*w*), respectively) (Figs. 7 and 8). All types of the lithium atoms, except for Li(2), participate in the binding of the $[Cr(Cpdc)_3]^{3-}$ fragments between each other due to the coordination of the O atoms of the carboxyl groups that are not involved in the chelating of the Cr(1) atom (O(2), O(4), O(6), O(8), O(12), and O(19)). In thus formed 3D polymeric structure, the layers of the lithium cations alternate with the layers of the anionic fragments $[Cr(Cpdc)_3]^{3-}$ (Fig. 9). The shortest Cr···Cr distance within this layer is 7.33 Å, and that between the adjacent layers is 7.184 Å. The structure of complex **III** is additionally stabilized by the network of hydrogen bonds, the formation of which involves the solvate water molecules O(12*w*), water molecules O(7*w*), O(8*w*), and O(11*w*) coordinated to the Li(4) and Li(7) atoms, and carboxylate O atoms (Table 3).

To conclude, in the series of the synthesized and structurally characterized compounds M(I)–Cr(III) with the $Cpdc^{2-}$ anions (M(I) = Li, Na, K), the nature of the alkaline metal affects the composition and organization of the polymeric structure in crystal but exerts no effect on the dimensionality: all the three compounds are characterized by the 3D polymeric structure. In the case of the K^+ cations (compound **I**), in spite of the number of carboxylate anions in the reaction system sufficient for the formation of the $[Cr(Cpdc)_3]^{3-}$ complex (ratio Cr : $Cpdc^{2-}$ = 1 : 3), the $[Cr(Cpdc)_2(H_2O)_2]^-$ fragment is formed and contains only two anions of the acid. The tris-chelate anionic "block" $[Cr(Cpdc)_3]^{3-}$ is formed in the systems with Na^+ and Li^+ cations (compounds **II** and **III**). However, in the case of Na^+, the NO_3^- anions are additionally involved in the formation of the polymeric crystal structure, whereas the $\{Li(Cpdc)\}^-$ anionic fragments in which the dicarboxylic acid anion forms the six-membered chelate cycle with the Li^+ ion are additionally involved in structure formation in the case of Li^+. In addition, the crystal structures of compounds **II** and **III** are characterized by a similar layered organi-

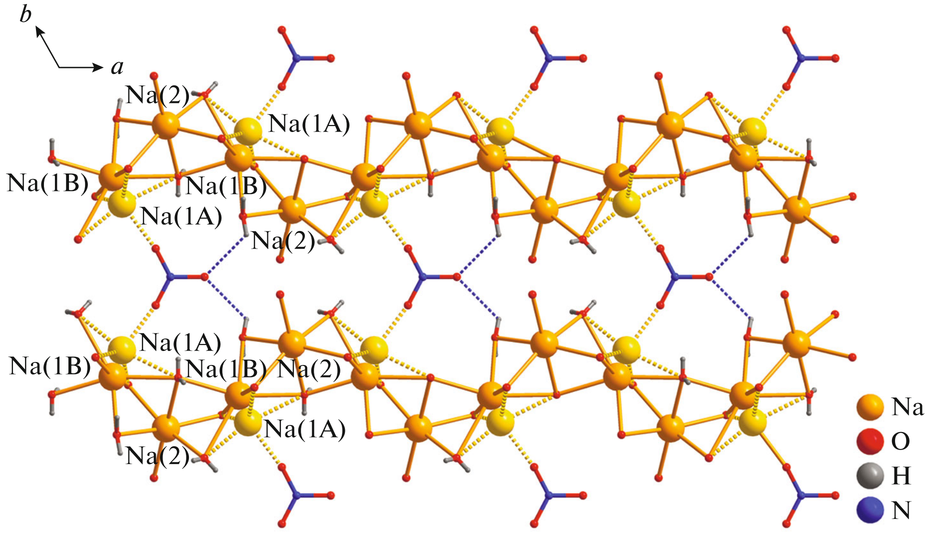

Fig. 5. Formation of the cationic layers $\{Na_4(H_2O)_6(NO_3)\}_n^{3n+}$ in the structure of compound **II**. Hydrogen bonds are shown by blue dashed lines.

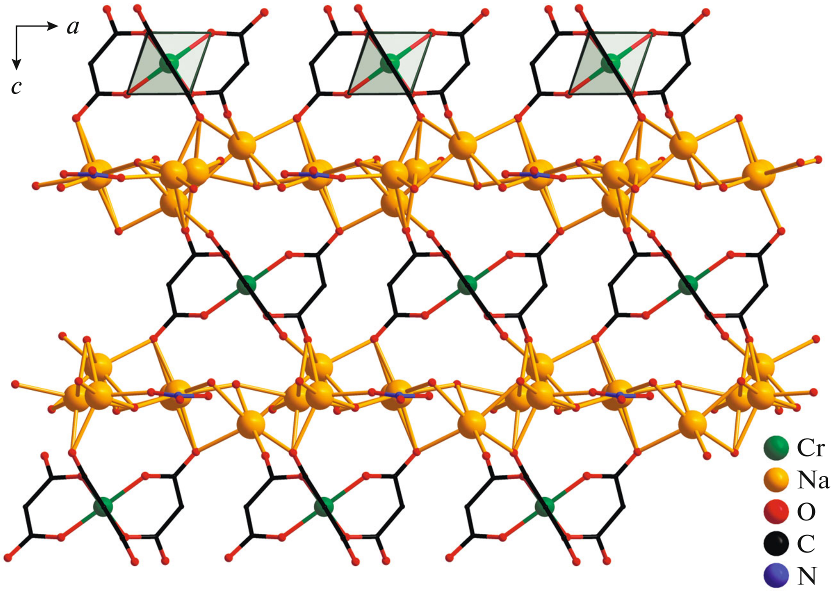

Fig. 6. Fragment of the 3D polymeric structure of compound **II** (cyclopropane fragments of the acid anions and hydrogen atoms of the water molecules are omitted).

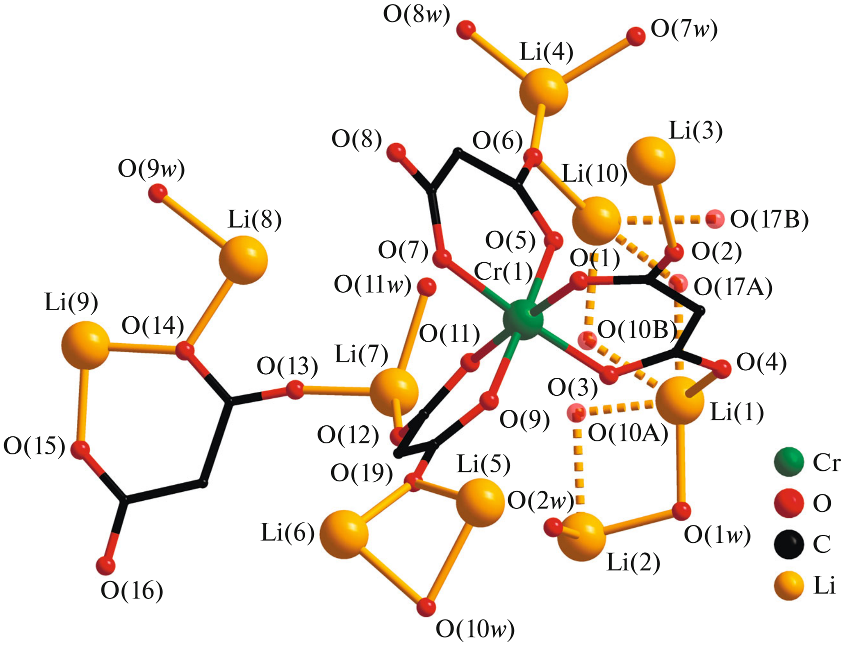

Fig. 7. Asymmetric unit of the polymeric structure of compound **III**: the structure of the anionic fragment $[Cr(Cpdc)_3]^{3-}$ and its binding with the nonequivalent lithium atoms (cyclopropane fragments of the acid anions and hydrogen atoms of the water molecules are omitted).

zation: the layers of the Na^+ or Li^+ cations bound to each other alternate with the layers formed by the $[Cr(Cpdc)_3]^{3-}$ fragments. Unlike them, the layers of the framework structure in compound **I** are formed by the anionic fragments $[Cr(Cpdc)_2(H_2O)_2]^-$ bound to each other via the K^+ cations.

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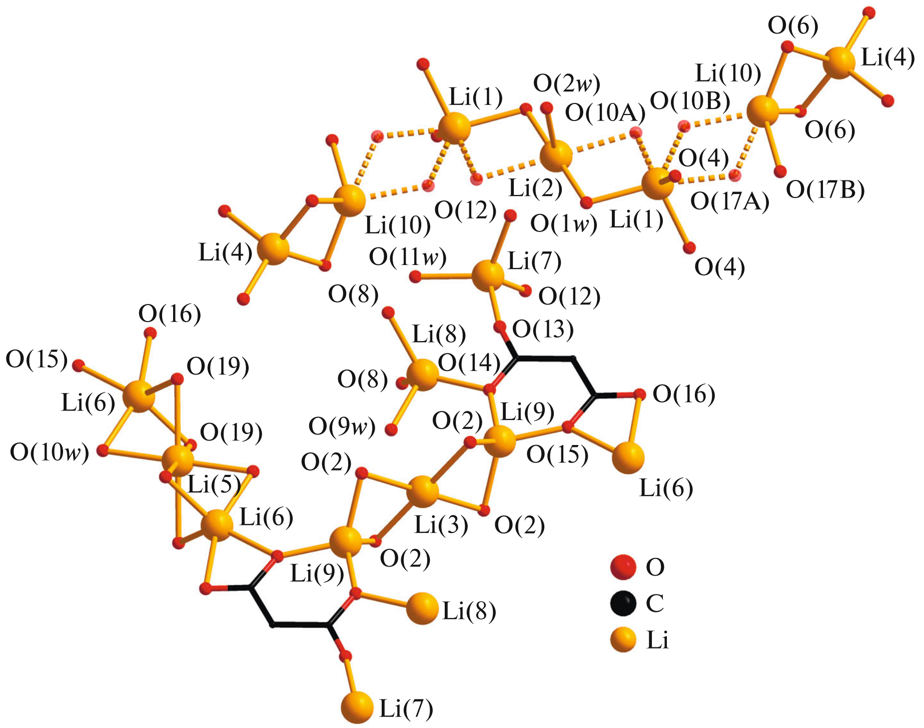

Fig. 8. Fragment of the layer formed by the lithium atoms in the structure of compound **III** (cyclopropane fragments of the acid anions and hydrogen atoms are omitted).

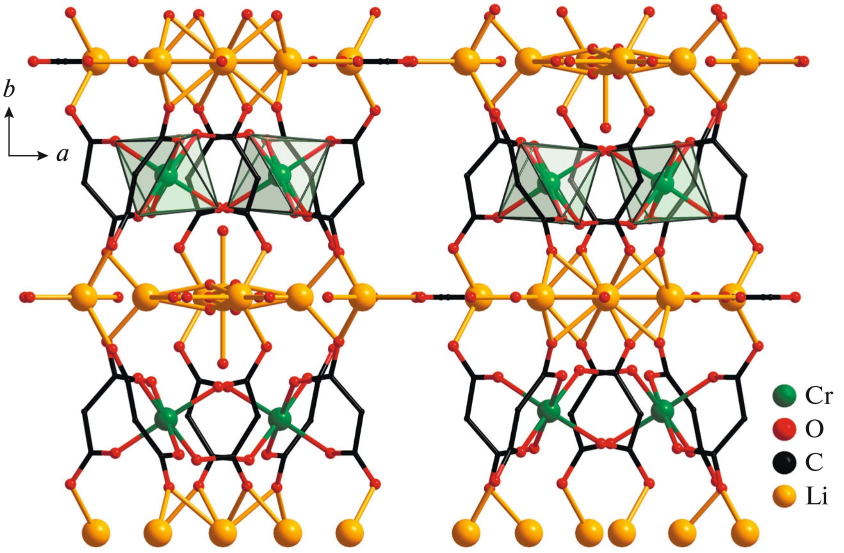

Fig. 9. Fragment of the framework structure of compound **III** formed by the layers of the mutually linked lithium atoms and anionic fragments $[Cr(Cpdc)_3]^{3-}$ (cyclopropane fragments of the acid anions and hydrogen atoms are omitted).

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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