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Effect of Synthesis Conditions on the Composition and Structure of Chromium(III) Complexes with Cyclobutane-1,1-Dicarboxylic Acid Anions

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Abstract—The reaction of $Cr(NO_3)_3{\cdot}9H_2O$ with potassium cyclobutane-1,1-dicarboxylate ($K_2(Cbdc)$) in 1 : 3 ratio was studied. It was shown that, depending on the reaction conditions and the solvents used for synthesis and crystallization, compounds of various compositions and structures can be isolated from the reaction system. Conducting the reaction in water followed by recrystallization from ethanol and methanol results in isolation of 2D polymeric complexes $[KCr(Cbdc)_2(H_2O)_2]_n$ (**I**) and $\{[K_4Cr_2(OMe)_2(Cbdc)_4(MeOH)_6]{\cdot}MeOH\}_n$ (**II**), respectively. The addition of excess KOH to the same reaction mixture and recrystallization from alcohols gives rise to the crystals of 3D polymeric compound $[K_3Cr(Cbdc)_3(H_2O)_2]_n$ (**III**). Conducting the reaction in methanol followed by slow diffusion of diethyl ether affords complex $[K_3Cr(Cbdc)_3(MeOH)_2(H_2O)_2]_n$ (**IV**) with a 2D polymeric structure. The crystal structures of compounds **I**–**IV** were determined by X-ray diffraction (CIF files CCDC nos. 2006090 (**I**), 2006109 (**II**), 2006116 (**III**), and 2006117 (**IV**)).

Keywords: chromium(III), cyclobutane-1,1-dicarboxylic acid, carboxylate complexes, synthesis, X-ray diffraction

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INTRODUCTION

The interest in the synthesis of transition metal complexes with carboxylate ligands has been increasing in recent years, first of all, owing to the magnetic [1–5] and luminescent properties [6–8] of these compounds, and also to their catalytic [9, 10] and biological (antibacterial, antifungal, and antitumor) activities [11–13]. Bridging carboxylate ligands are widely used to assemble coordination polymers and porous metal-organic frameworks, which are applied to design ion selective and electrochemical sensors [14–16], catalysts [17], and sorbents for the separation and storage of gases [18–20].

Substituted malonic acid analogues ($H_2R^1R^2Mal$), combining chelation and various types of bridging coordination, can serve for the synthesis of heterometallic complexes and coordination polymers composed of anionic "blocks" with two chelating acid anions $\{M(R^1R^2Mal)_2\}^{2-}$ ($M = VO^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}). In these compounds, hydrated cations of *s*-, 3*d*-, 4*d*-, and 4*f*-elements usually function as the bridging groups connecting malonate blocks, with the solubility, structure, and properties of the complexes being dependent on the substituent geometry in the malonate ligand [21]. Substituted malonic acid anions, unlike the anion of unsubstituted malonic acid, can in some cases participate in reactions in organic solvents, which enables the formation of products of a different structure [22, 23].

The anions of cyclobutane-1,1-dicarboxylic acid (H_2Cbdc) exhibit the same coordination modes as malonic acid anions and other substituted analogues; however, owing to the presence of the cyclic hydrocarbon substituent, they increase the stability of heterometallic complexes, which was demonstrated for oxidovanadium(IV) compounds. In this case, the use of $Cbdc^{2-}$ anions made it possible to isolate and structurally characterize heterometallic K–V(IV) and K–Ln(III)–V(IV) compounds, whereas reactions with other substituted malonic acids did not produce crystals of the target products [24, 25]. Being a flexible bridging ligand able to assume different conformations, the $Cbdc^{2-}$ anion is convenient for the design of Mn(II), Cu(II), Zn(II), and Cd(II) coordination polymers with N-donor ligands possessing useful functional properties [26–30].

The currently known heterometallic transition metal compounds with the $Cbdc^{2-}$ anions contain oxidovanadium(IV), copper(II), and nickel(II) ions [21, 24, 25, 31]. For chromium(III), malonate complexes have been obtained only for unsubstituted malonic acid [32–39].

This study deals with the reaction of chromium(III) nitrate with the potassium salt of cyclobutane-1,1-dicarboxylic acid (K_2Cbdc) taken in 1 : 3 ratio in water and in organic solvents. The effect of reaction conditions and the nature of solvents on the composition and crystal structure of the resulting chromium(III) complexes with $Cbdc^{2-}$ anions was investigated.

EXPERIMENTAL

The new compounds were synthesized in air using distilled water, ethanol (95%), methanol (99.9%), diethyl ether (99.7%), $Cr(NO_3)_3 \cdot 9H_2O$ (99%, Acros Organics), KOH (99+%), and H_2Cbdc (99%, Fluorochem). The attenuated total reflection (ATR) IR spectra of the compounds were measured in the frequency range of 4000–400 cm^{-1} on a Spectrum 65 (PerkinElmer) Fourier transform IR spectrometer equipped with a Quest ATR Accessory (Specac) attachment. Elemental analysis was carried out on a EuroEA 3000 (EuroVector) CHNS analyzer.

Synthesis of $[KCr(Cbdc)_2(H_2O)_2]_n$ (I). A solution of K_2Cbdc, prepared by neutralization of H_2Cbdc (0.216 g, 1.5 mmol) with KOH (0.168 g, 3 mmol) in 20 mL of water at 100°C, was added at 100°C to a solution of $Cr(NO_3)_3 \cdot 9H_2O$ (0.2 g, 0.5 mmol) in 10 mL of distilled water. The reaction mixture was stirred for 2 h at 100°C, and the resulting green-colored solution was allowed to stand at 22°C for 10 days. Ethanol (20 mL) was added to the resulting glass-like compound and colorless crystals, and the mixture was stirred for 3 h at 70°C. The green solution was filtered to separate the white amorphous precipitate and kept in an Erlenmeyer flask for slow evaporation at 22°C for 1 month. The pale lilac-colored crystals suitable for X-ray diffraction were separated from the mother liquor by filtration and dried in air. The yield of compound **I** was 0.042 g (20.4% based on $Cr(NO_3)_3 \cdot 9H_2O$).

For $C_{12}H_{16}O_{10}KCr$

Anal. calcd., %	C, 35.04	H, 3.92
Found, %	C, 35.19	H, 4.03

IR (ATR; ν, cm^{-1}): 3091 br.m (ν(O–H)), 3008 m, 2962 m, 2866 m, 1599 s (ν_{as}(COO$^-$)), 1568 s (ν_{as}(COO$^-$)), 1447 m, 1379 s (ν_s(COO$^-$)), 1256 m, 1245 m, 1228 s, 1161 w, 1118 s, 1058 w, 998 m, 949 m, 919 s, 839 m, 757 s, 722 s, 661 s, 547 s, 509 s, 449 s, 416 s.

Synthesis of $\{[K_4Cr_2(OMe)_2(Cbdc)_4(MeOH)_6] \cdot MeOH\}_n$ (II). A solution of K_2Cbdc, prepared by neutralization of H_2Cbdc (0.162 г, 1.12 mmol) with KOH (0.126 g, 2.25 mmol) in 20 mL of water, was added at 100°C to a solution of $Cr(NO_3)_3 \cdot 9H_2O$ (0.15 g, 0.375 mmol) in 15 mL of distilled water. The reaction mixture was stirred for 1 h at 100°C, and the resulting green solution was allowed to stand at 22°C for 1 month. Methanol (20 mL) was added to the resulting glass-like compound and colorless crystals, and the mixture was stirred for 3 h at 70°C. The green solution was filtered to remove the white amorphous precipitate and kept in an Erlenmeyer flask for slow evaporation at 22°C for 2 weeks. Methanol (20 mL) was added to the precipitated green and colorless crystals, and the crystals were dissolved at 70°C. Green solution was filtered to remove the white amorphous precipitate and kept in a Schlenk flask at 22°C for 2 months. The resulting green crystals suitable for X-ray diffraction were separated from the mother liquor by decanting and dried in air. The yield of compound **II** was 0.051 g (25.1% based on $Cr(NO_3)_3 \cdot 9H_2O$).

For $C_{16}H_{27}O_{12}K_2Cr$

Anal. calcd., %	C, 35.48	H, 5.03
Found, %	C, 35.61	H, 5.14

IR (ATR; ν, cm^{-1}): 3543 w (ν(O–H)), 3409 vw (ν(O–H)), 3178 vw (ν(O–H)), 3008 vw, 2963 w, 2866 vw, 1657 w, 1592 s (ν_{as}(COO$^-$)), 1575 s (ν_{as}(COO$^-$)), 1449 m, 1419 m, 1371 s (ν_s(COO$^-$)), 1258 s, 1242 m, 1225 m, 1158 w, 1116 s, 1097 s, 1052 s, 1014 s, 956 m, 915 s, 884 w, 867 m, 849 m, 782 s, 719 s, 685 m, 660 m, 614 m, 541 s, 505 s, 492 s, 448 s, 423 m.

Synthesis of $[K_3Cr(Cbdc)_3(H_2O)_2]_n$ (III). A solution of K_2Cbdc, prepared by neutralization of H_2Cbdc (0.108 g, 0.75 mmol) with KOH (0.113 g, 2 mmol) in 20 mL of water, was added at 100°C to a solution of $Cr(NO_3)_3 \cdot 9H_2O$ (0.1 g, 0.25 mmol) in 10 mL of distilled water. After stirring for 1 h at 100°C, the green solution was allowed to stand at 22°C for 1 week. Ethanol (20 mL) was added to the resulting glass-like compound and colorless crystals, and the mixture was stirred for 3 h at 70°C. The green solution was filtered to remove the white amorphous precipitate and kept in an Erlenmeyer flask for slow evaporation at 22°C for 2 weeks. The precipitated green crystals suitable for X-ray diffraction were separated from the mother liquor by decanting, washed with EtOH, and dried in air. The yield of compound **III** was 0.070 g (44.3% based on $Cr(NO_3)_3 \cdot 9H_2O$).

For $C_{18}H_{22}O_{14}K_3Cr$

Anal. calcd., %	C, 34.23	H, 3.51
Found, %	C, 34.39	H, 3.80

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

Parameter	Value			
	I	**II**	**III**	**IV**
M, g/mol	411.35	541.57	631.65	695.74
T, K	296	120	296	150
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	9.1802(9)	11.2052(7)	8.4516(8)	8.6240(9)
b, Å	8.1659(10)	12.6600(7)	17.3830(15)	10.9551(11)
c, Å	10.7250(12)	17.6107(10)	17.1707(14)	15.6353(16)
α, deg	90	78.7070(10)	90	73.204(2)
β, deg	99.687(4)	86.6970(10)	103.176(3)	79.928(2)
γ, deg	90	67.7540(10)	90	77.236(2)
V, Å^3	792.53(15)	2267.1(2)	2456.2(4)	1369.4(2)
Z	2	4	4	2
$\rho_{calcd.}$, g cm^{-3}	1.724	1.587	1.708	1.687
μ, mm^{-3}	1.035	0.930	1.043	0.949
θ_{min}–θ_{max}, deg	3.15–25.99	1.77–30.68	2.34–26.37	1.97–28.31
F(000)	422	1124	1292	718
T_{min}/T_{max}	0.621/0.746	0.489/0.746	0.674/0.746	0.833/0.981
Ranges of reflection indices	$-11 \le h \le 11$ $-9 \le k \le 10$ $-12 \le l \le 11$	$-15 \le h \le 16$ $-18 \le k \le 17$ $-25 \le l \le 25$	$-10 \le h \le 10$ $-21 \le k \le 21$ $-21 \le l \le 21$	$-11 \le h \le 11$ $-14 \le k \le 14$ $-20 \le l \le 20$
Number of measured reflections	5068	30594	22482	14612
Number of unique reflections	1549	13996	5023	6750
R_{int}	0.0758	0.0259	0.1273	0.0241
Number of reflections with $I > 2\sigma(I)$	1231	12061	3075	5637
GOOF	1.057	1.036	1.038	1.171
R-factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0530$ $wR_2 = 0.1442$	$R_1 = 0.0410$ $wR_2 = 0.1067$	$R_1 = 0.0797$ $wR_2 = 0.1469$	$R_1 = 0.0556$ $wR_2 = 0.1255$
R-factors for all reflections	$R_1 = 0.0652$ $wR_2 = 0.1541$	$R_1 = 0.0493$ $wR_2 = 0.1112$	$R_1 = 0.1391$ $wR_2 = 0.1719$	$R_1 = 0.0668$ $wR_2 = 0.1294$
Residual electron density (min/max), e/Å^3	–0.605/0.675	–1.280/0.865	–0.547/0.783	–0.681/0.976

Table 2. Selected bond lengths (d) and angles (ω) in compounds **I–IV**

Bond	d, Å			
	I	**II**	**III**	**IV**
Cr–O (Cbdc)	1.903(2), 1.984(2)	1.9390(14)–1.9727(13)	1.941(4)–1.968(4)	1.936(3)–2.005(3)
K–O (Cbdc)	2.765(2)–3.302(2)	2.5675(15)–3.3539(15)	2.618(5)–3.277(6)	2.618(3)–3.172(3)
K–O (H_2O)			2.661(6), 2.817(5), 2.851(5)	2.830(3)–3.286(3)
K–O (MeOH)		2.615(2)–2.8061(19)		2.642(4), 2.817(3)
Angle	ω, deg			
OCrO (adjacent)	74.39(9)–105.61(9)	79.04(5)–97.14(6)	85.87(17)–98.28(18)	85.70(11)–96.12(12)

IR (ATR; ν, cm^{-1}): 3545 w (ν(O–H)), 3407 w (ν(O–H)), 3262 w (ν(O–H)), 3011 vw, 2992 vw, 2969 vw, 2950 vw, 1657 w, 1600 s ($\nu_{as}(COO^-)$), 1575 s ($\nu_{as}(COO^-)$), 1451 w, 1419 m, 1371 s ($\nu_s(COO^-)$), 1328 s, 1257 m, 1225 m, 1187 vw, 1164 vw, 1118 s, 1053 vw, 1014 w, 955 w, 915 s, 891 w, 878 w, 849 vw, 770 m, 718 m, 652 m, 617 m, 542 s, 507 m, 459 s, 447 s, 412 s.

Synthesis of $[K_3Cr(Cbdc)_3(MeOH)_2(H_2O)_2]_n$ (IV). A solution of K_2Cbdc, prepared by neutralization of H_2Cbdc (0.162 g, 1.12 mmol) with KOH (0.126 g, 2.25 mmol) in 30 mL of MeOH, was added at 70°C to a solution of $Cr(NO_3)_3 \cdot 9H_2O$ (0.15 g, 0.375 mmol) in 10 mL of MeOH. The reaction mixture was stirred for 1 h at 70°C and cooled to 22°C, and the green solution was separated from the white amorphous precipitate by filtration. The solution (5 mL) in a small vessel was placed into a sealed container with 10 mL of Et_2O on the bottom and kept at 22°C for 7 days. The green crystals suitable for X-ray diffraction were separated from the mother liquor by decanting and dried in air. The yield of compound **IV** was 0.043 g (16.7% based on $Cr(NO_3)_3 \cdot 9H_2O$).

For $C_{20}H_{30}O_{16}K_3Cr$

Anal. calcd., %	C, 35.03	H, 2.94
Found, %	C, 35.25	H, 3.12

IR (ATR; ν, cm^{-1}): 3545 w (ν(O–H)), 3400 w (ν(O–H)), 3266 w (ν(O–H)), 3010 vw, 2987 w, 2956 w, 2865 vw, 2831 vw, 1593 s ($\nu_{as}(COO^-)$), 1436 w, 1358 s ($\nu_s(COO^-)$), 1256 m, 1242 m, 1230 m, 1160 w, 1118 s, 1097 m, 1042 m, 1021 m, 1007 m, 957 w, 917 s, 874 vw, 855 vw, 769 s, 740 m, 718 m, 661 m, 545 s, 504 s, 474 s, 451 s, 416s, 410 s.

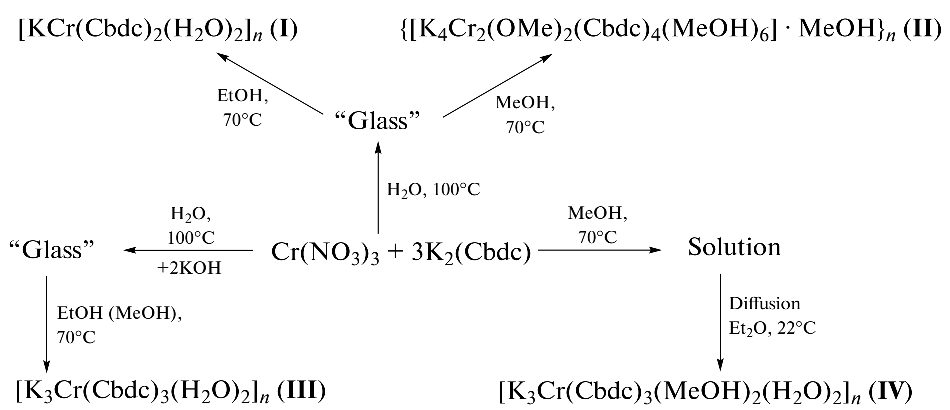
Single crystal X-ray diffraction study of **I–IV** was carried out on a Bruker SMART APEX II diffractometer with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [40]. A semiempirical absorption correction was applied by the SADABS program [41]. The structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of organic ligands were generated geometrically and refined using the riding model. The hydrogen atoms of the OH groups in structures **I–III** were located from difference Fourier maps. The calculations were carried out by the SHELX-2014 program package [42] using Olex2 1.3 [43]. In the structure of **II**, the K(3) atom, the O(21) atom of the potassium-coordinated MeOH molecule, and the C(18) atom of one cyclobutane moiety of the ligand are disordered over two positions with occupancies of 0.078(2) and 0.922(2) (K(3*a*) and K(3)); 0.312(10) and 0.688(10) (O(21*a*) and O(21*b*)); and 0.842(6) and 0.158(6) (C(18*a*) and C(18*b*)), respectively. Crystallographic parameters and structure refinement details for **I–IV** are given in Table 1. Selected bond lengths and angles in I-IV are summarized in Table 2.

The structural data were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2006090 (**I**), 2006109 (**II**), 2006116 (**III**), and

2006117 (**IV**)); deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The interaction of $Cr(NO_3)_3 \cdot 9H_2O$ with K_2Cbdc (prepared by the reaction of H_2Cbdc with KOH in water) taken in 1 : 3 molar ratio in water at 100°C resulted in the formation of colorless potassium nitrate crystals and a green-colored glass-like product. Recrystallization of this mixture from ethanol at 70°C followed by separation of potassium nitrate as a white precipitate afforded lilac-colored crystals of $[KCr(Cbdc)_2(H_2O)_2]_n$ (**I**) with a 2D polymeric structure. Recrystallization of this mixture from methanol did not give crystals suitable for X-ray diffraction. However, preconcentration of the reaction mixture, repeated recrystallization from methanol, and separation of the precipitated potassium nitrate crystals yielded the 2D polymer $\{[K_4Cr_2(OMe)_2(Cbdc)_4(MeOH)_6] \cdot MeOH\}_n$ (**II**) as green crystals. The reaction of $Cr(NO_3)_3 \cdot 9H_2O$ with K_2Cbdc in 1 : 3 ratio in water with the addition of 2 moles of KOH also afforded a glass-like product, recrystallization of which from MeOH or EtOH resulted in the isolation of the 3D polymer $[K_3Cr(Cbdc)_3(H_2O)_2]_n$ (**III**) as green crystals. The reaction of $Cr(NO_3)_3 \cdot 9H_2O$ with K_2Cbdc in 1 : 3 ratio in methanol followed by slow diffusion of diethyl ether into the reaction solution gave the crystals of the 2D polymer $[K_3Cr(Cbdc)_3(MeOH)_2(H_2O)_3]_n$ (**IV**) (Scheme 1).



Scheme 1.

The centrosymmetric structure of **I** (the inversion center is at the Cr atom) is formed by mononuclear chromium-containing $[Cr(Cbdc)_2(H_2O)_2]^-$ anions linked by K^+ cations. The Cr atom is in an octahedral coordination environment, being coordinated by two chelate $Cbdc^{2-}$ dianions whose O atoms (O(2), O(4)) are located in the equatorial plane of the polyhedron and two water molecules whose O atoms (O(5)) occupy axial positions (Cr(1)–O(5) 2.126(2) Å) (Table 2, Fig. 1a). The metal coordination polyhedron is highly distorted: the adjacent OCrO angles significantly deviate from 90° (Table 2). In the crystal packing of **I**, the $\{Cr(Cbdc)_2(H_2O)_2\}$ anionic moieties are connected into a layered structure via coordination to potassium by carboxylate O atoms (O(1), O(2), O(3), O(4)) (Table 2), with the bonds of the K atom with O(1) and O(4) atoms (3.293(3) and 3.302(2) Å, respectively) being longer than similar bonds with the O(2) and O(3) atoms (2.765(2) and 2.990(3) Å). In the crystal of **I**, each chromium-containing moiety is surrounded by four crystalographically equivalent K atoms, so that the shortest Cr···K distance is 4.0830 Å and the Cr···Cr distances are identical and equal to 6.7399 Å (Fig. 1b). The polymeric layer is additionally stabilized by hydrogen bonds involving carboxylate O(1) and O(3) atoms and coordinated water molecules (Table 3).

The basic structural unit of **II** is the binuclear $[Cr_2(OMe)_2(Cbdc)_4]^{4-}$ tetraanion in which both Cr atoms are chelated by $Cbdc^{2-}$ dianions and are connected by two μ-bridging OMe groups (Cr–O, 1.9783(14)–1.9921(14) Å). The Cr coordination polyhedron is an octahedron, which is distorted due to the difference between the Cr–O bond lengths (Table 2). In the structure of **II**, there are two types of such units containing crystalographically independent Cr(1) and Cr(2) atoms with slightly different Cr–O bond lengths and four types of non-equivalent K atoms (K(1), K(2), K(3), K(4)). The K(3) atom is disordered over two positions (K(3*a*) and K(3)) with occupancies of ~0.1 and ~0.9, respectively. The Cr(1)···Cr(1) and Cr(2)···Cr(2) distances are similar: 3.0658 and 3.0574 Å, respectively. The alternating binuclear $\{Cr(1)_2(OMe)_2(Cbdc)_4\}$ and $\{Cr(2)_2(OMe)_2(Cbdc)_4\}$ moieties are linked by the K(1), K(2), K(3), and K(4) atoms to form polymeric chains (Table 2, Fig. 2a). Each of the four non-equivalent K atoms coordinates one MeOH molecule (O(19), O(20), O(21), O(24)),

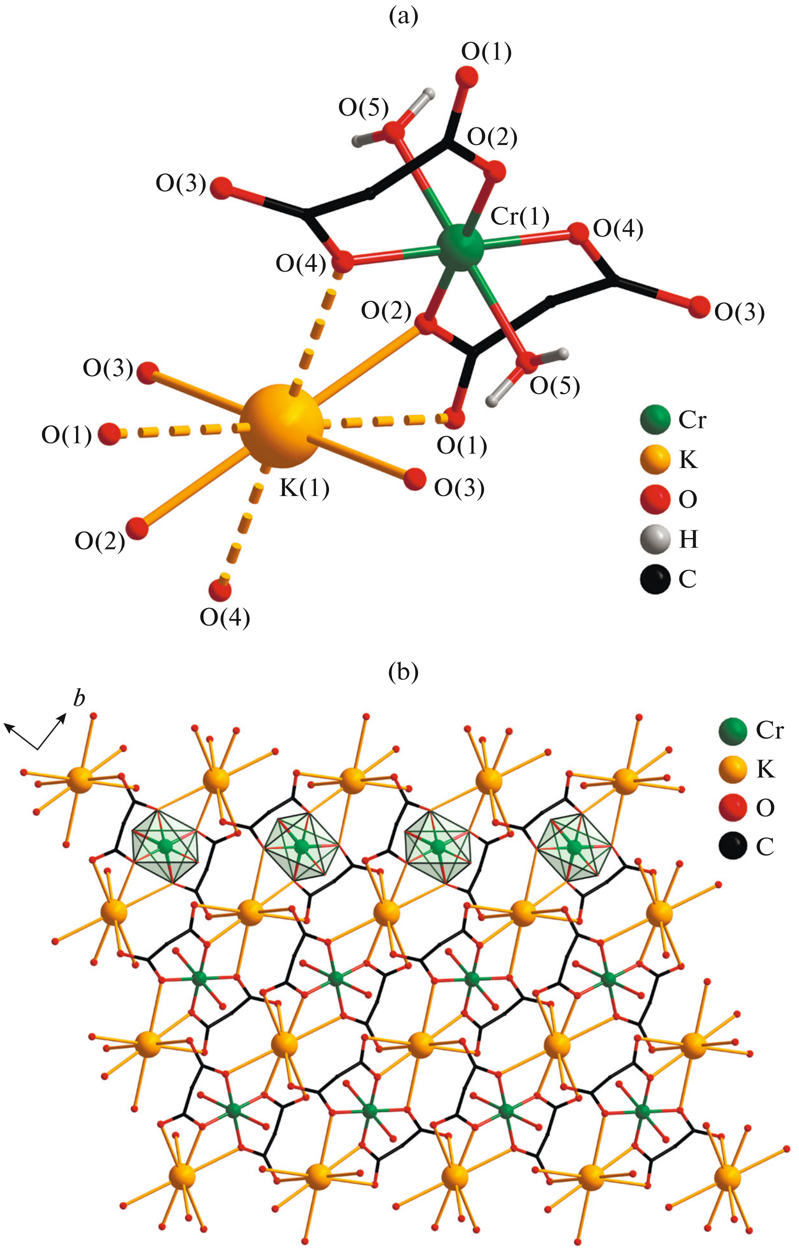


Fig. 1. Structure of the $[Cr(Cbdc)_2(H_2O)_2]^-$ anions, environment of K atoms (a), and formation of the layered structure in **I** (b). (a) The dashed lines show elongated K–O bonds (a). The cyclobutane moieties of acid anions (a, b) and hydrogen atoms of water molecules (b) are omitted.

with K(1) and K(4), K(2), and K(3) atoms, respectively, being connected by μ-bridging MeOH molecules (O(22) and O(23)) (K(1)···K(4) 3.5220, K(2)···K(3) 4.4179, K(4)···K(3) 4.7184, K(1)···K(3) 3.796, K(4)···K(2) 6.0034 Å) (Table 2). The K(4) atom is additionally bound to the O(9) atom of the bridging OMe group of the $\{Cr(1)_2(OMe)_2(Cbdc)_4\}$ moiety (2.8905(13) Å); the corresponding distance between K(3) and O(18) of the OMe group of $\{Cr(2)_2(OMe)_2(Cbdc)_4\}$ is much longer (3.3896(15) Å). The chains are connected into polymeric layers via coordination of carboxylate atoms (O(8) and O(13)) by the K(1) and K(2) atoms of neighboring chains (K–O 2.6001(14), 2.7982(16) Å; K(2)···K(2) 4.2338 Å) (Fig. 2b). The polymeric layer is additionally stabilized by a network of hydrogen bonds involving carboxylate oxygen atoms (O(2), O(4), O(5), O(7), O(15), and O(17)) and coordinated methanol molecules (Table 3).

The structure of **III** is formed by the $[Cr(Cbdc)_3]^{3-}$ anions in which Cr has an octahedral coordination environment, being coordinated by three $Cbdc^{2-}$

Table 3. Geometric parameters of hydrogen bonds in structures **I**–**IV***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
I				
O(5)–H(5*a*)···O(1)^{i}	0.87	1.77	2.581(3)	155
O(5)–H(5*b*)···O(3)^{ii}	0.87	1.70	2.540(3)	160
II				
O(23)–H(23)···O(5)	0.85	1.90	2.7310(19)	169
O(19)–H(19)···O(4)^{i}	0.86	1.93	2.783(2)	175
O(20)–H(20)···O(17)^{ii}	0.85	1.89	2.709(2)	161
O(21*b*)–H(21*b*)···O(15)	0.85	2.07	2.876(4)	157
O(24)–H(24)···O(2)^{iii}	0.84	1.94	2.7688(19)	170
O(22)–H(22)···O(7)^{iv}	0.85	2.02	2.763(2)	145
III				
O(13)–H(13*a*)···O(8)^{i}	0.85	2.35	2.926(8)	125
O(13)–H(13*b*)···O(12)^{ii}	0.85	2.48	2.799(7)	104
O(14)–H(14*a*)···O(8)^{iii}	0.85	2.14	2.815(8)	136
O(14)–H(14*b*)···O(10)^{iv}	0.85	2.57	2.899(7)	104
IV				
O(5*w*)–H(5*wa*)···O(7)^{i}	0.90	1.88	2.769(4)	167
O(1*s*)–H(1*s*)···O(12)^{ii}	0.95	1.90	2.708(7)	142
O(5*w*)–H(5*wb*)···O(7)^{iii}	0.87	2.23	3.072(4)	164
O(2*s*)–H(2*s*)···O(4)	0.83	1.86	2.670(5)	166
O(4*w*)–H(4*wa*)···O(5*w*)^{i}	0.84	2.05	2.772(5)	142
O(4*w*)–H(4*wb*)···O(2*s*)	0.92	2.10	2.939(5)	152

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

anions, which form six-membered chelate rings with the metal atoms (Table 2), three types of crystallographically independent K atoms (K(1), K(2), K(3)) and two H_2O molecules (Fig. 3a). The {Cr(Cbdc)$_3$} moieties are connected in pairs to form ribbon type polymeric layers via coordination of the carboxylate O atoms of the Cbdc^{2-} anions by K(1), K(2), and K(3) atoms (Cr(1)···K(1) 3.7601, K(1)···K(2) 4.429, K(1)···K(3) 4.434, K(3)···K(2) 4.249 Å) (Table 2, Fig. 3b). The shortest Cr···Cr distance within the layer is 8.280 Å. The K(1) and K(3) atoms participate in binding the polymeric layers into 3D framework via the bridging water molecule (K(1)–O(14) 2.830(5), K(3)–O(14) 2.862(6) Å) and O(6) carboxylate oxygen (K(1)–O(6) 2.620(5) Å) (Fig. 4). The K(2) atom monodentately coordinates the second H_2O molecule (K(2)–O(13) 2.652(6) Å) and does not participate in

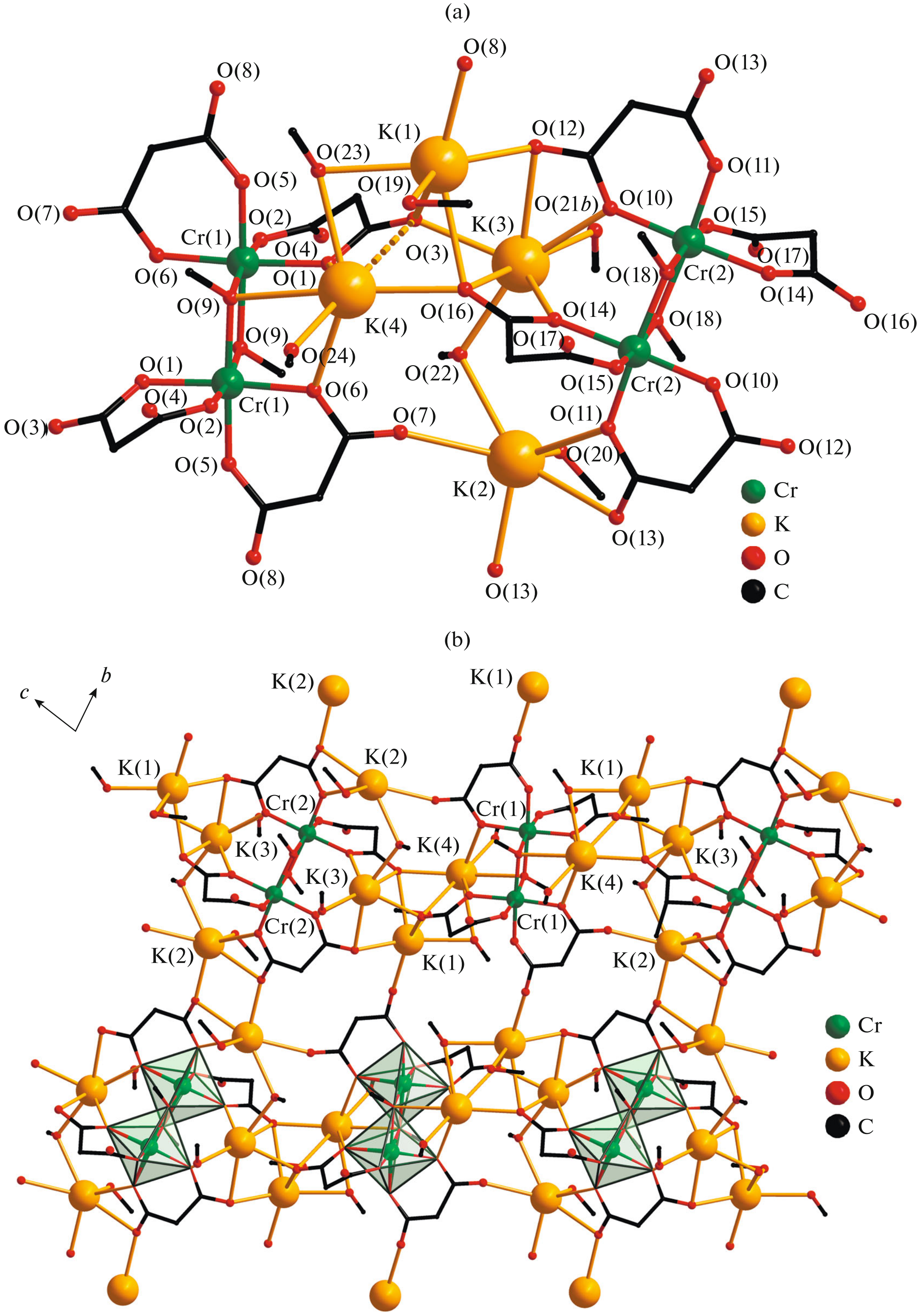


Fig. 2. Structure of the $[Cr_2(MeO)_2(Cbdc)_4]^{4-}$ anions, their connection into a chain by K atoms (a), and formation of the layered structure in **II** (b). Positions of K(3*a*) and O(21*a*) (a) andcyclobutane moieties of acid anions and hydrogen atoms of methanol molecules (a, b) are omitted.The dashed line shows the elongated K–O bond (a) .

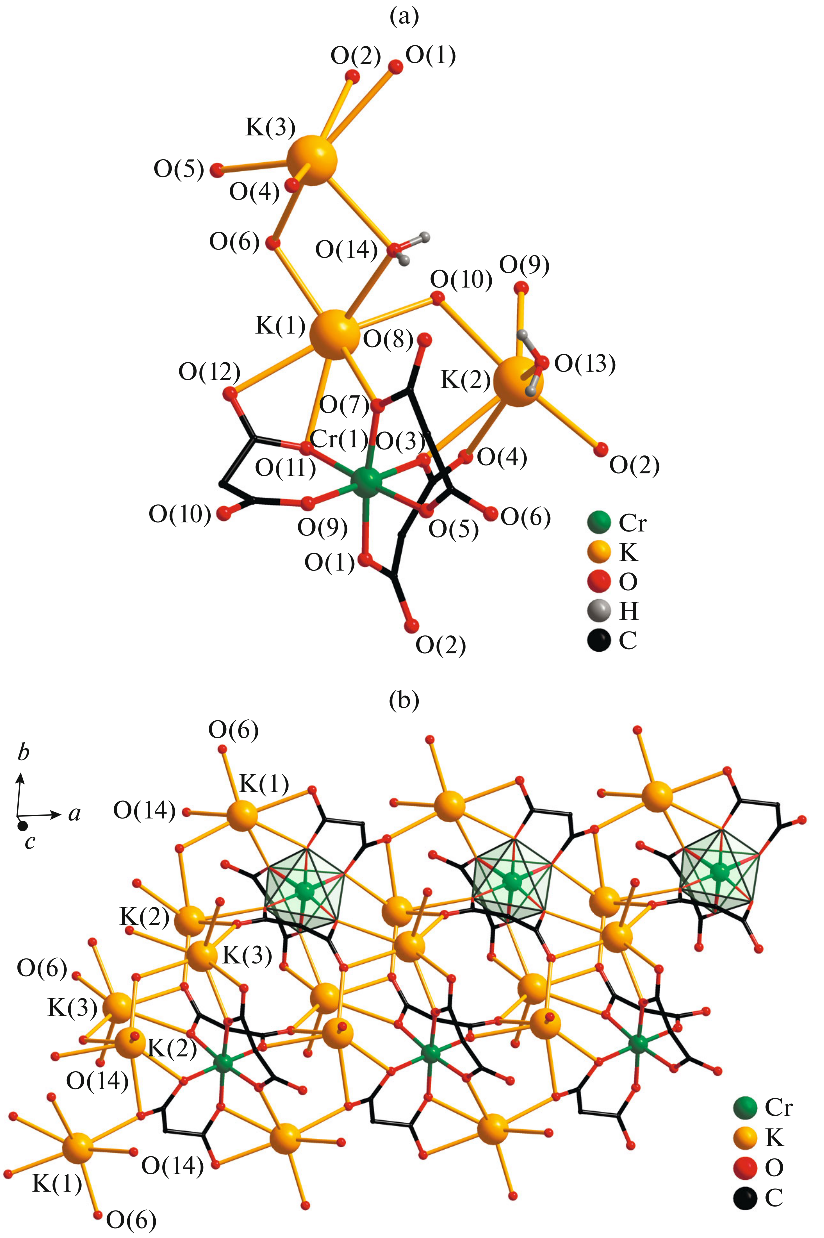


Fig. 3. Structure of the $[Cr(Cbdc)_3]^{3-}$ anion, environment of linked K atoms (a), and (b) formation of the polymeric layer in the structure of **III** (b). The cyclobutane moieties of acid anions (a, b) andhydrogen atoms of water molecules (b) are omitted.

the binding of layers (Figs. 3a, 4). The polymeric structure of **III** is additionally stabilized by hydrogen bonding involving oxygen atoms of carboxyl groups (O(8), O(10), and O(12)) and coordinated water molecules (Table 3).

The crystal structure of **IV**, like that of **III**, is formed by mononuclear $[Cr(Cbdc)_3]^{3-}$ anions in which the Cr atom is chelated by three $Cbdc^{2-}$ ligands, three types of crystalographically independent K atoms (K(1), K(2), K(3)), and two water molecules. However, unlike **III**, the structure of **IV** contains two methanol molecules (Table 2, Fig. 5a). The Cr atom in **IV**, like that in **III**, has an octahedral coordination environment, with the OCrO adjacent angles slightly deviating from 90° (Table 2). In the crystal of **IV**, the $\{Cr(Cbdc)_3\}$ tris-chelate moieties are connected in pairs by the K(1), K(2), and K(3) atoms to form polymeric chains (Cr(1)···K(2) 3.5561, K(1)···K(3) 4.1906, K(2)···K(3) 3.5961 Å). The K(1) and K(2) atoms coordinate each one terminal MeOH molecule (O(1*s*) and O(2*s*)), while K(3) coordinates the H_2O molecule (O(5*w*)) (Table 2, Fig. 5a). The chains are bound into a layered structure via coordination of K(1) and K(2) to the carboxylate O(8) and O(6) atoms, respectively,

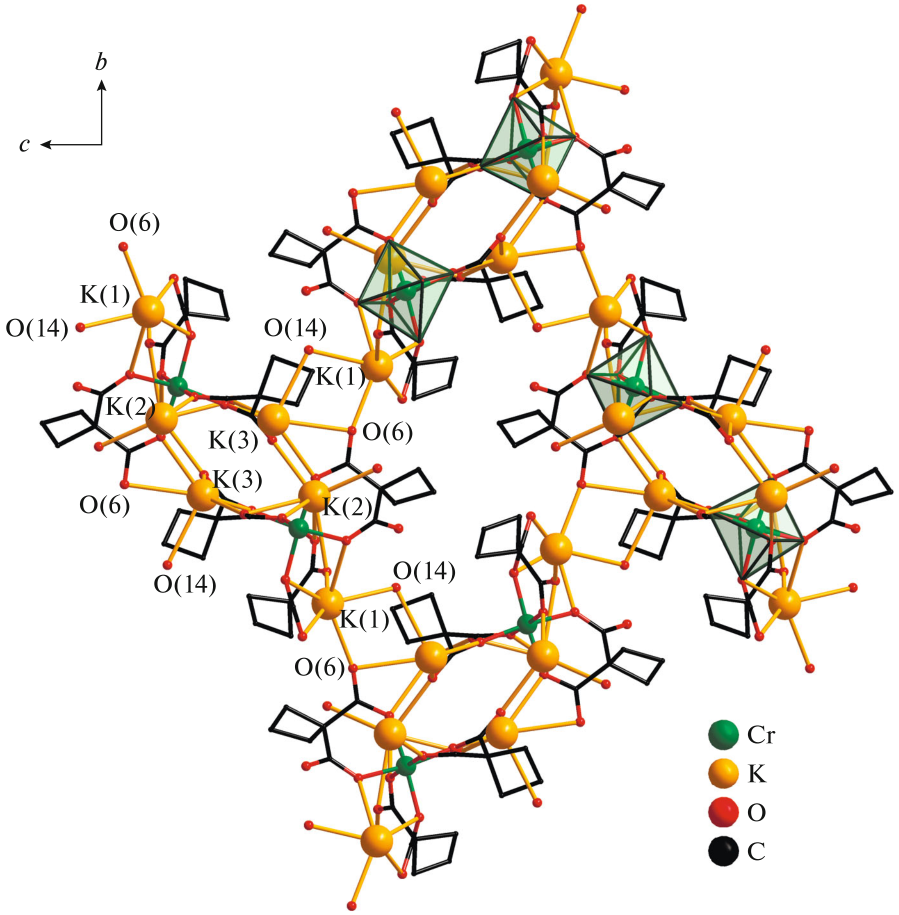


Fig. 4. Fragment of the framework structure in the crystals of **III** (hydrogen atoms are omitted).

belonging to the {Cr(Cbdc)$_3$} moieties of neighboring chains and via bridging water molecules (O(4*w*)), which connect K(2) and K(3) atoms belonging to neighboring chains (K(2)···K(3) 4.3718 Å) (Fig. 5b, 5c). The shortest Cr···Cr distance within the layer is that between the metal atoms of two neighboring chains (7.515 Å). The layered structure of **IV** is additionally stabilized by hydrogen bonds involving oxygen atoms of carboxyl groups (O(4), O(7), and O(12)) and coordinated water and methanol molecules (Table 3).

Thus, it was shown that K–Cr(III) compounds with Cbdc^{2-} anions (unlike the previously obtained K V(IV) complex [24]) are soluble in methanol and ethanol. This allowed studying the effect of these solvents and excess KOH taken in the reaction on the composition and structure of the products. The use of ethanol for recrystallization of the glass-like product, obtained by the reaction of $Cr(NO_3)_3$ with K_2Cbdc (1 : 3) in water, resulted in isolation of compound **I** containing $[Cr(Cbdc)_2(H_2O)_2]^-$ bis-chelate moieties, although the amount of Cbdc^{2-} anions in the reaction system was sufficient for the formation of a tris-chelate complex. Similar recrystallization from methanol yielded an unusual 2D polymeric, compound **II** formed by binuclear $[Cr_2(\mu\text{-OMe})_2(Cbdc)_4]^{4-}$ anions. Compounds **III** and **IV** containing $[Cr(Cbdc)_3]^{3-}$ tris-chelate moieties can be isolated upon the addition of excess KOH for the reaction in water followed by recrystallization from alcohols or upon conducting the reaction in methanol followed by slow diffusion of diethyl ether, respectively. However, in the case of **III**, a 3D polymeric structure is formed, while in the case of **IV**, a 2D polymer is produced due to coordination of methanol molecules.

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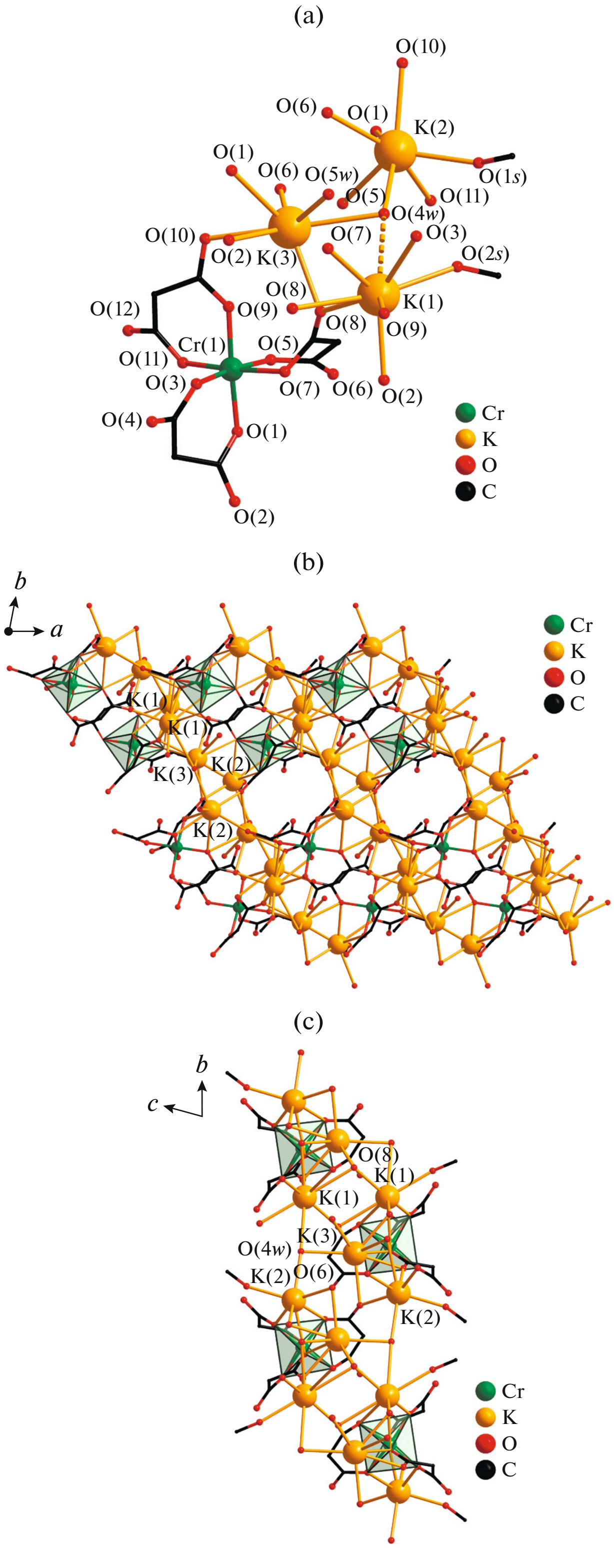

Fig. 5. Structure of the $[Cr(Cbdc)_3]^{3-}$ mononuclear anion, environment of linked K atoms (a), and fragment of the crystal packing of compound **IV**: projection on the *ab* plane (b) and *bc* plane (c). The cyclobutane moieties of acid anions and hydrogen atoms of methanol and water molecules are omitted. The dashed line shows the elongated K–O bond (a).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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