ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 11, pp. 709–717. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © E.S. Bazhina, G.G. Aleksandrov, M.A. Kiskin, A.A. Sidorov, I.L. Eremenko, 2017, published in Koordinatsionnaya Khimiya, 2017, Vol. 43, No. 11, pp. 641–649.

Examples of Cation Exchange in New Ionic Oxovanadium(IV) Complexes with Anions of Cyclobutane-1,1-Dicarboxylic Acid

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Received May 19, 2017

Abstract—The results on the synthesis and study of the crystal structures of compounds based on anionic fragments $\{VO(Cbdc)_2\}^{2-}$ formed by oxovanadium(IV) (vanadyl, VO^{2+}) and two chelate-bound anions of cyclobutane-1,1-dicarboxylic acid ($H_2Cbdc = C_4H_6(COOH)_2$) are presented. The use of ammonium cation NH_4^+ as a counterion in the synthesis leads to the formation of the mononuclear complex $(NH_4)_2[VO(Cbdc)_2(H_2O)] \cdot 2H_2O$ (**I**). In the case of K^+ cation, compound $[K_4(VO)_2(Cbdc)_4(H_2O)_4]_n$ (**II**) with the 3D polymeric crystal structure is formed. The reaction of compound **II** with $Mg(NO_3)_2 \cdot 6H_2O$ in an aqueous solution involves the partial substitution of K^+ by Mg^{2+} cations to form 1D polymeric compound $\{[KMg_{0.5}(VO)(Cbdc)_2(H_2O)_{6.5}] \cdot 3H_2O\}_n$ (**III**), while a similar reaction of compound **I** does not afford the product of substitution of $NH_4{}^+$ by Mg^{2+} cations (CIF files CCDC 1551021–1551023 for compounds **I–III**, respectively).

Keywords: oxovanadium(IV), cyclobutane-1,1-dicarboxylate, carboxylate complexes, X-ray diffraction

DOI: 10.1134/S107032841711001X

INTRODUCTION

One of approaches to the synthesis of polynuclear coordination compounds of transition metals is the use of polydentate ligands capable of forming with the metal center stable anionic complexes containing functional groups free for coordination. These complex anions can act as metal-containing ligands and can form heterometallic polynuclear compounds upon the interaction with metal cations of different nature. From the practical point of view, it seems interesting to find the conditions for the formation of compounds promising for the preparation of new magnetic materials, porous coordination polymers with high sorption capacity, and precursors of oxide materials [1–5].

Anions of malonic acid (H_2Mal) and its substituted analogs (H_2R_2Mal) can serve as convenient polydentate ligands for the synthesis of metal-containing units. In aqueous solutions these anions form with the most part of doubly charged transition metal cations stable bis-chelate anion $[M(Mal)_2]^{2-}$ in which the metal center coordinates two anions of dicarboxylic acid via the chelate mode. The oxygen atoms of the ligand form the equatorial plane of the coordination polyhedron of the metal (square planar environment), and the free axial positions can be occupied by one (square pyramid $[M(Mal)_2(H_2O)]^{2-}$) or two water molecules (octahedron $[M(Mal)_2(H_2O)_2]^{2-}$) [6–10]. In the most cases, the interaction of the bis-chelate anions with transition metal cations leads to the formation of the 1D coordination polymers [11–13]. However, in the systems with anions of substituted malonic acid and alkaline and alkaline-earth metal cations, the dimensionality of polymeric structures can vary from 1D to 3D depending on the size of the metal cation and substituent at the methylene carbon atom in the R_2Mal^{2-} anion. The influence of these factors on the crystal structure was studied in more detail for the oxovanadium(IV) compounds [13–19].

We have previously shown that substituted malonates of copper(II) can successfully be used as the starting reagents for the synthesis of new polynuclear compounds via the partial or complete substitution of alkaline and alkaline-earth cations by Mg^{2+} and *d*-element cations, for example, Ni^{2+}, Co^{2+}, and Cd^{2+} [7, 12], and the bis-chelate moieties with the Cu(II) atom is retained in the structures of the new compounds. In this work, we synthesized two new oxovanadium(IV) compounds with anions of cyclobutane-1,1-dicarboxylic acid (H_2Cbdc) in which the bis-chelate moieties $\{VO(Cbdc)_2\}^{2-}$ are formed. The possibility of substitution of NH_4^+ and K^+, which are present in these compounds as counterions, by Mg^{2+} cations was also studied.

[†] Deceased.

EXPERIMENTAL

All procedures related to the synthesis of new complexes were carried out in air using distilled water and ethanol (reagent grade). The following reagents were used for the preparation of new compounds: $VOSO_4 \cdot 3H_2O$ (analytical grade), NH_4HCO_3 (reagent grade), K_2CO_3 (reagent grade), KOH (analytical grade), $Mg(NO_3)_2 \cdot 6H_2O$ (reagent grade), and H_2Cbdc (98%, Acros Organics). The IR spectra of the compounds were recorded on a Spectrum 65 FT-IR spectrophotometer (PerkinElmer) using the attenuated total reflectance (ATR) method in a frequency range of 4000–400 cm^{-1}. Elemental analysis was carried out on a EuroEA 3000 CHNS-analyzer (EuroVector).

Synthesis of $\{(NH_4)_2[VO(Cbdc)_2(H_2O)]\} \cdot 2H_2O$ (I). A solution of $VOSO_4 \cdot 3H_2O$ (0.1 g, 0.46 mmol) in distilled water (15 mL) was added with H_2Cbdc (0.133 g, 0.92 mmol). The reaction mixture was stirred for 10 min at 22°C. A solution of NH_4HCO_3 (0.146 g, 1.84 mmol) in distilled water (10 mL) was poured to the obtained solution, and the mixture was stirred for 10 min. The resulting blue solution was kept at 22°C. The blue crystals suitable for X-ray diffraction formed in 2 days. The crystals were separated from the mother liquor by decantation, washed with cold water ($T \sim 5°C$) and ethanol ($T \sim 22°C$), and dried in air. The yield of compound **I** was 0.125 g (61.5% based on $VOSO_4 \cdot 3H_2O$).

For $C_{12}H_{26}N_2O_{12}V$

Anal. calcd., %: C, 32.66; H, 5.94; N, 6.35.

Found, %: C, 32.86; H, 5.88; N, 6.42.

IR (ATR; ν, cm^{-1}): 3594 w (ν(O–H)), 3444 w (ν(O–H)), 3378 w (ν(O–H)), 3168 m (ν(O–H)), 3067 s ($\nu(N^+–H)$), 2953 w (ν(C–H)), 2876 w (ν(C–H)), 1646 m, 1617 m, 1575 vs ($\nu_{as}(COO^-)$), 1456 s, 1423 s, 1379 vs ($\nu_s(COO^-)$), 1319 s, 1258 m, 1240 m, 1223 m, 1165 w, 1128 s, 1050 m, 1021 m, 955 s (ν(V=O)), 912 s, 885 m, 865 w, 811 vw, 784 s, 757 s, 703 s (δ(OCO)), 652 m (δ(OCO)), 555 s, 440 vs, 412 s [20, 21].

Synthesis of $[K_4(VO)_2(Cbdc)_2(H_2O)_4]_n$ (II). A solution of $VOSO_4 \cdot 3H_2O$ (0.15 g, 0.69 mmol) in distilled water (15 mL) was added with H_2Cbdc (0.199 g, 1.38 mmol). The reaction mixture was stirred for 10 min at 22°C. A solution of K_2CO_3 (0.286 g, 2.07 mmol) in distilled water (10 mL) was poured to the obtained solution, and the mixture was stirred for 10 min. The resulting dark blue solution was kept at 22°C. The formed brown precipitate was separated by filtration. The blue crystals suitable for X-ray diffraction formed in 2 months. The crystals were separated from the mother liquor by filtration, washed with cold water ($T \sim 5°C$) and ethanol ($T \sim 22°C$), and dried in air. The yield of compound **II** was 0.136 g (42.4% based on $VOSO_4 \cdot 3H_2O$).

For $C_{24}H_{32}O_{22}K_4V_2$

Anal. calcd., %: C, 30.97; H, 3.47.

Found, %: C, 30.94; H, 3.51.

IR (ATR; ν, cm^{-1}): 3534 w (ν(O–H)), 3398 w (ν(O–H)), 3288 vw (ν(O–H)), 3216 w (ν(O–H)), 3009 vw (ν(C–H)), 2964 w (ν(C–H)), 1628 vs ($\nu_{as}(COO^-)$), 1587 vs ($\nu_{as}(COO^-)$), 1458 w, 1425 w, 1367 vs ($\nu_s(COO^-)$), 1250 m, 1227 m, 1159 vw, 1119 s, 1063 w, 999 s (ν(V=O)), 974 s, 952 m, 924 s, 873 w, 776 s, 712 m (δ(OCO)), 648 s (δ(OCO)), 545 vs, 482 s, 473.61 s, 473 s, 461 s, 451 vs, 422 s [20, 21].

Synthesis of $\{[KMg_{0.5}(VO)(Cbdc)_2(H_2O)_{5.5}] \cdot 2.5H_2O)_8\}_n$ (III). A solution of $VOSO_4 \cdot 3H_2O$ (0.1 g, 0.46 mmol) in distilled water (10 mL) was added with a solution of K_2Cbdc, which was obtained by the neutralization of H_2Cbdc (0.133 g, 0.92 mmol) and KOH (0.103 g, 1.84 mmol) in water (15 mL). The reaction mixture was stirred for 10 min at 40°C. The obtained solution was added with $Mg(NO_3)_2 \cdot 6H_2O$ (0.236 g, 0.92 mmol), and the mixture was stirred for 10 min. The resulting blue solution was kept at 22°C. The blue crystals suitable for X-ray diffraction formed in 1 month. The crystals were separated from the mother liquor by decantation, washed with cold water ($T \sim 5°C$) and ethanol ($T \sim 22°C$), and dried in air. The yield of compound **III** was 0.133 g (52.8% based on $VOSO_4 \cdot 3H_2O$).

For $C_{12}H_{28}KMg_{0.5}O_{17}V$

Anal. calcd., %: C, 26.37; H, 4.26.

Found, %: C, 29.23; H, 4.17.

IR (ATR; ν, cm^{-1}): 3571 vw (ν(O–H)), 3358 m br (ν(O–H)), 3262 m br (ν(O–H)), 2996 w (ν(C–H)), 2960 w (ν(C–H)), 1578 vs ($\nu_{as}(COO^-)$), 1537 s, 1463 w, 1389 s ($\nu_s(COO^-)$), 1332 m, 1259 w, 1243 w, 1224 w, 1159 vw, 1124 m, 1055 vw, 1020 w, 977 s (ν(V=O)), 919 m, 761 s, 703 s (δ(OCO)), 662 s (δ(OCO)), 558 vs, 459 s, 447 vs, 430 s, 416 s [20, 21].

X-ray diffraction analysis for single crystals of compounds **I–III** was carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) [22]. A semiempirical absorption correction was applied for all compounds [23]. The structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms at the carbon atoms of the organic ligands were generated geometrically and refined in the riding model. The Mg atom in structure **III** is disordered over two positions with the site occupancy factor 0.5. The calculations

Table 1. Crystallographic data and calculation parameters for the crystal structures of compounds **I–III**

Parameter	Value		
	I	**II**	**III**
FW	441.29	930.78	546.54
T, K	150(2)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pbcn$	$C2/c$	$C2/c$
a, Å	8.8659(7)	33.809(6)	24.831(3)
b, Å	16.1222(13)	9.6694(18)	10.1266(12)
c, Å	12.3529(10)	23.668(4)	18.068(2)
β, deg	90.00	116.343(3)	106.645(2)
V, Å^3	1765.7(2)	6934(2)	4353.1(9)
Z	4	8	8
ρ_{calcd}, g cm^{-3}	1.660	1.783	1.668
μ, mm^{-1}	0.631	1.109	0.743
Range of data collection for 2θ, deg	2.62–29.10	2.29–27.74	2.35–28.18
F(000)	924	3792	2272
T_{min}/T_{max}	0.6342/0.7459	0.5876/0.7456	0.6429/0.7452
Ranges of reflection indices	$-11 \le h \le 12$, $-15 \le k \le 22$, $-14 \le l \le 17$	$-43 \le h \le 38$, $-11 \le k \le 12$, $-30 \le l \le 30$	$-26 \le h \le 32$, $-13 \le k \le 13$, $-24 \le l \le 24$
Measured reflections	11766	22999	13027
Independent reflections	2514	7995	5349
R_{int}	0.0437	0.0519	0.0318
Reflections with $I > 2\sigma(I)$	2007	6194	4250
GOOF	1.001	1.001	1.001
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0331$, $wR_2 = 0.0889$	$R_1 = 0.0667$, $wR_2 = 0.1924$	$R_1 = 0.0608$, $wR_2 = 0.1682$
R factors for all reflections	$R_1 = 0.0457$, $wR_2 = 0.0965$	$R_1 = 0.0860$, $wR_2 = 0.2046$	$R_1 = 0.0753$, $wR_2 = 0.1811$
Residual electron density (min/max), e/Å^3	−0.354/0.455	−0.718/0.998	−1.348/1.408

were performed using the SHELX-97 program package [24]. The crystallographic parameters and details for structure refinement are presented in Table 1. Selected bond lengths and angles in compounds **I–III** are given in Tables 2 and 3. The structural data for compounds **I–III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1551021–1551023, respectively; http://www.ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

Mononuclear ionic complex **I** was obtained by the reaction of $VOSO_4 \cdot 3H_2O$ with H_2Cbdc and NH_4HCO_3 taken in a molar ratio of 1 : 2 : 4 in an aqueous solution. Compound **II** with the 3D polymeric crystal structure was obtained by a procedure similar to the synthesis of compound **I** using 3 moles of K_2CO_3 instead of 4 moles of NH_4HCO_3. The reaction of complex **I** with $Mg(NO_3)_2 \cdot 6H_2O$ does not afford a

Table 2. Selected bond lengths (*d*, Å) in compounds **I–III**

Bond	*d*, Å		
	I	**II**	**III**
V=O	1.6072(16)	1.600(4), 1.602(4)	1.593(3)
V–O(Cbdc)	1.9983(10), 2.0109(10)	1.939(4)–2.002(4)	1.992(2)–2.021(2)
V–O(H_2O)	2.2819(18)		2.270(3)
K–O(Cbdc)		2.565(4)–3.245(4)	2.718(3)–2.837(2)
K–O(H_2O)		2.664(5) –2.826(5)	2.732(7)–3.037(3)
Mg–O(Cbdc)			2.094(4)
Mg–O(H_2O)			1.931(4)–2.238(5)

Table 3. Selected bond angles (ω, deg) characterizing the vanadium coordination polyhedra in compounds **I–III**

Angle	ω, deg		
	I	**II**	**III**
$O_{oxo}VO_{eq}$	100.51(3), 101.88(3)	101.07(19)–109.32(19)	98.72(13)–102.35(12)
$O_{oxo}VO_{ax}$	180.0		177.64(13)
$O_{eq}VO_{eq}$	86.88(4), 88.82(4) 156.24(7), 158.98(7)	82.80(15)–88.64(16) 143.78(17)–156.96(17)	87.16(10)–99.08(12) 158.57(10), 160.56(11)
$O_{eq}VO_{ax}$	78.12(3), 79.49(3)		78.84(10)–80.38(11)

new compound, and only crystals of the starting complex **I** are formed as a result. In the case of compound **II**, a similar reaction leads to the formation of crystals of compound **III**, which is the product of the partial substitution of potassium ions in the starting structure **II** by magnesium ions (Scheme 1).

$$\mathrm{VOSO_4 + 2H_2Cbdc + 4NH_4HCO_3 \xrightarrow{H_2O} \{(NH_4)_2[VO(Cbdc)_2(H_2O)]\} \cdot 2H_2O} \qquad \mathbf{(I)}$$

$$\begin{tikzcd} \mathrm{VOSO_4 + 2H_2Cbdc + 3K_2CO_3} \arrow[r, "\mathrm{H_2O}"] & \mathrm{[K_4(VO)_2(Cbdc)_4(H_2O)_4]_n} \arrow[d, "\mathrm{+2Mg(NO_3)_2}"] & \mathbf{(II)} \\ \mathrm{VOSO_4 + 2H_2Cbdc + 4KOH + 2Mg(NO_3)_2} \arrow[r, "\mathrm{H_2O}"] & \mathrm{\{[KMg_{0.5}(VO)(Cbdc)_2(H_2O)_{5.5}] \cdot 2.5H_2O\}_n} & \mathbf{(III)} \end{tikzcd}$$

Scheme 1.

It was found that compound **III** can be synthesized in a higher yield by the direct interaction of $VOSO_4 \cdot 3H_2O$ with salt K_2Cbdc (obtained by the reaction of H_2Cbdc and KOH in an aqueous solution) and $Mg(NO_3)_2 \cdot 6H_2O$ (see Experimental). An attempt to substitute Na^+ cations by Mg^{2+} cations in the earlier described compound $[Na_2(VO)(Cbdc)_2(H_2Cbdc)(H_2O)_3]_n$ [17] does not give the product Na–Mg–V(IV) as in the case of complex **I**.

Compound **I** consists of the bis-chelate anion $[VO(Cbdc)_2(H_2O)]^{2-}$, two cations NH_4^+, and two solvate water molecules. The $[VO(Cbdc)_2(H_2O)]^{2-}$ anion has the crystallographic symmetry C_2: the 2-fold axis C_2 passes through the V(1), O(1), and O(1*w*) atoms. The equatorial plane of the coordination octahedron of the vanadium atom is occupied by four O atoms of two chelate-coordinated anions of cyclobutane-1,1-dicarboxylic acid. The axial positions are occupied by the O atoms of the vanadyl group {V=O} and water molecule (Fig. 1a, Tables 2 and 3). The six-membered vanadium-malonate rings V(1)O(4)C(1)C(2)C(3)O(2) have a distorted half-chair conformation: the V(1), O(4), C(1), C(3), and O(2) atoms are coplanar within 0.099 Å, and the C(2) atom deviates from this plane by 0.797 Å. The dihe-

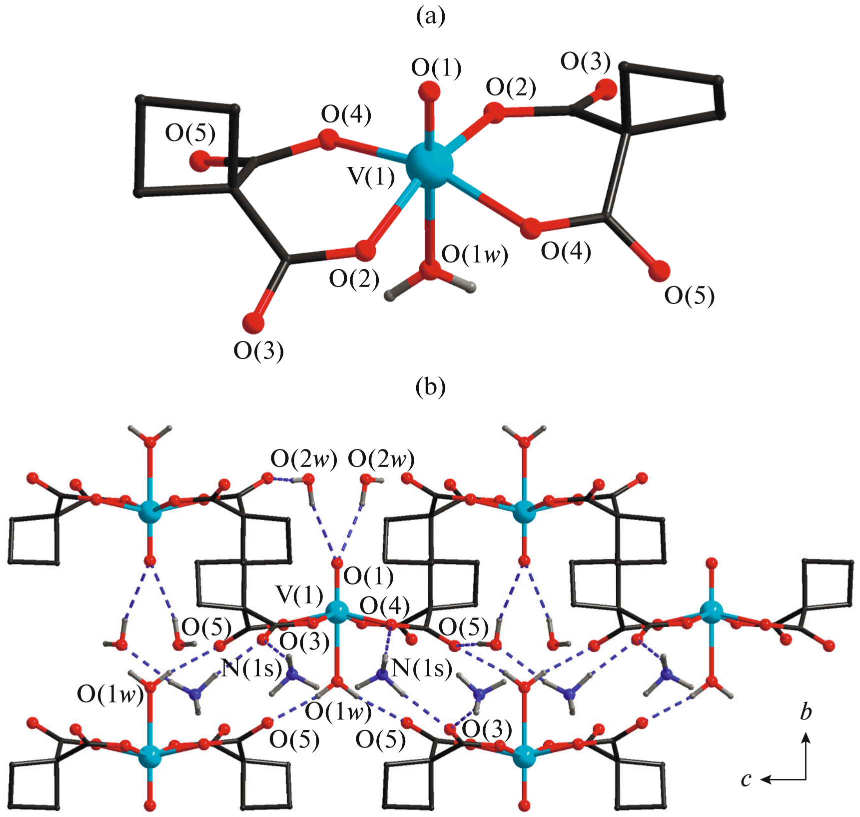

Fig. 1. (a) Structure of the bis-chelate dianion $[VO(Cbdc)_2(H_2O)]^{2-}$ and (b) the crystal packing fragment of compound **I**. Hydrogen bonds are shown by dashed lines.

dral angle between the V(1)O(4)C(1)C(3)O(2) and C(1)C(2)C(3) planes is 56.2°. In crystal, the bis-chelate anions $[VO(Cbdc)_2(H_2O)]^{2-}$ are bound to the NH_4^+ cations due to hydrogen bonds between the hydrogen atoms of the NH_4^+ cations, the O(3), O(4), and O(5) atoms of the $Cbdc^{2-}$ ligand, and solvate water molecules O(2*w*). In addition, the O(1) atom of the vanadyl group is involved in hydrogen bonding (Fig. 1b). The parameters of hydrogen bonds are given in Table 4.

The basic structural motif in compound **II** is formed by two mononuclear bis-chelate anions $[V(1)O(Cbdc)_2]^{2-}$ and $[V(2)O(Cbdc)_2]^{2-}$ containing crystallographically nonequivalent V(1) and V(2) atoms, four nonequivalent potassium atoms (K(1), K(2), K(3), K(4)), and four water molecules bound to the potassium atoms. Each vanadium atom is in the square pyramidal ($\tau = 0.0078$ for V(1) and $\tau = 0.0198$ for V(2) [25]) coordination environment of five oxygen atoms: four carboxylate O atoms of the $Cbdc^{2-}$ ligand and the O atom of the {V=O} group. The six-membered vanadium-malonate rings of both bis-chelate anions have a boat conformation. In the V(1)O(2)C(1)C(2)C(3)O(4) metallocycle, the O(2), C(1), C(3), and O(4) atoms are coplanar within 0.015 Å, and the V(1) and C(2) atoms deviate from this plane by 0.537 and 0.606 Å, respectively. The dihedral angles between the planes O(2)C(1)C(3)O(4), V(1)O(2)O(4) and O(2)C(1)C(3)O(4), C(1)C(2)C(3) are 21.9° and 44.6°, respectively. In the V(1)O(6)C(7)C(8)C(9)O(8) metallocycle, the O(6), C(7), C(9), and O(8) atoms are coplanar within 0.012 Å, and the V(1) and C(8) atoms deviate from this plane by 0.494 and 0.506 Å, respectively. The dihedral angles between the planes O(6)C(7)C(9)O(8), V(1)O(6)O(8) and O(6)C(7)-C(9)O(8), C(7)C(8)C(9) are 20.4° and 37.4°, respectively. In the V(2)O(13)C(13)C(14)C(15)O(11) metallocycle, the O(13), C(13), C(15), and O(11) atoms are coplanar within 0.027 Å, and the V(2) and C(14) atoms deviate from this plane by 0.414 and 0.552 Å, respectively. The dihedral angles between the planes O(13)C(13)C(15)O(11), V(2)O(11)O(13) and O(13)C(13)C(15)O(11), C(13)C(14)C(15) are 16.7° and 41.1°, respectively. In the V(2)O(15)-C(19)C(20)C(21)O(17) metallocycle, the O(15), C(19), C(21), and O(17) atoms are coplanar within 0.019 Å, and the V(2) and C(20) atoms deviate from this plane by 0.448 and 0.493 Å, respectively. The dihedral angles between the planes O(15)C(19)-C(21)O(17), V(2)O(15)O(17) and O(15)C(19)-C(21)O(17), C(19)C(20)C(21) are 18.5° and 37.5°, respectively. In crystals of compound **II**, the

Table 4. 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(1*w*)–H(1*w*)···O(5)$^{\rm i}$	0.82	1.99	2.799(1)	169
O(2*w*)–H(2*w*a)···O(1)$^{\rm ii}$	0.83	2.36	3.138(2)	157
O(2*w*)–H(2*w*b)···O(5)$^{\rm iii}$	0.82	2.02	2.826(2)	165
N(1s)–H(1s)···O(4)$^{\rm iv}$	0.91	2.02	2.916(2)	171
N(1s)–H(2s)···O(3)$^{\rm v}$	0.93	1.96	2.880(2)	173
N(1s)–H(3s)···O(3)	0.92	1.99	2.872(2)	159
N(1s)–H(4s)···O(2*w*)$^{\rm vi}$	0.91	2.03	2.930(2)	170
		II		
O(1*w*)–H(1*w*1)···O(16)$^{\rm i}$	0.84	2.10	2.912(6)	163
O(1*w*)–H(2*w*1)···O(5)$^{\rm ii}$	0.83	1.93	2.745(5)	168
O(2*w*)–H(1*w*2)···O(16)	0.83	1.98	2.785(7)	163
O(2*w*)–H(2*w*2)···O(5)$^{\rm iii}$	0.83	2.08	2.813(6)	147
O(3*w*)–H(1*w*3)···O(9)$^{\rm iv}$	0.84	2.02	2.795(6)	153
O(3*w*)–H(2*w*3)···O(12)$^{\rm v}$	0.83	2.00	2.798(6)	164
O(4*w*)–H(1*w*4)···O(9)$^{\rm vi}$	0.83	1.99	2.818(6)	176
O(4*w*)–H(2*w*4)···O(12)$^{\rm vii}$	0.83	2.07	2.870(6)	161
		III		
O(1*w*)–H(1*w*a)···O(3)$^{\rm i}$	0.83	1.86	2.686(4)	174
O(1*w*)–H(1*w*b)···O(7)$^{\rm ii}$	0.83	1.84	2.669(4)	175
O(2*w*)–H(2*w*a)···O(1)$^{\rm iii}$	0.83	2.09	2.862(4)	153
O(2*w*)–H(2*w*b)···O(7)$^{\rm ii}$	0.83	1.98	2.809(4)	172
O(3*w*)–H(3*w*a)···O(8*w*)$^{\rm iv}$	0.83	2.04	2.821(9)	158
O(3*w*)–H(3*w*b)···O(3)$^{\rm v}$	0.83	1.96	2.767(4)	164
O(4*w*)–H(4*w*a)···O(2*w*)	0.85	1.88	2.610(6)	143
O(4*w*)–H(4*w*b)···O(5)	0.85	2.08	2.678(6)	127
O(5*w*)–H(5*w*a)···O(7*w*)	0.82	2.29	2.787(5)	11.9
O(5*w*)–H(5*w*b)···O(9*w*)$^{\rm vi}$	0.82	2.10	2.824(9)	147
O(6*w*)–H(6*w*a)···O(5)	0.83	2.01	2.830(4)	173
O(7*w*)–H(7*w*a)···O(6*w*)$^{\rm v}$	0.83	1.93	2.750(7)	180
O(8*w*)–H(8*w*a)···O(9*w*)	0.84	1.92	2.704(10)	155
O(9*w*)–H(9*w*b)···O(5)	0.89	2.44	2.882(9)	111

* Symmetry codes; $^{\rm i}\,x, -y + 1, z + 1/2$; $^{\rm ii}\,-x + 1/2, y + 1/2, z$; $^{\rm iii}\,-x, -y + 1, -z$; $^{\rm iv}\,x + 1, y, z$; $^{\rm v}\,-x + 1, -y + 1, -z$; $^{\rm vi}\,-x + 1, y, -z + 1/2$ (**I**). $^{\rm i}\,-x, y - 1, -z + 1/2$; $^{\rm ii}\,-x + 1/2, -y + 1/2, -z + 1$; $^{\rm iii}\,x - 1/2, -y + 3/2, z - 1/2$; $^{\rm iv}\,x, -y + 1, z + 1/2$; $^{\rm v}\,x, y - 1, z$; $^{\rm vi}\,-x + 1/2, -y + 3/2, -z + 1$; $^{\rm vii}\,-x + 1/2, y - 1/2, -z + 3/2$ (**II**). $^{\rm i}\,-x + 5/2, y + 1/2, -z + 1/2$; $^{\rm ii}\,-x + 5/2, y - 1/2, -z + 1/2$; $^{\rm iii}\,x, -y + 3, z + 1/2$; $^{\rm iv}\,-x + 2, -y + 3, -z$; $^{\rm v}\,x, y + 1, z$; $^{\rm vi}\,-x + 2, y, -z + 1/2$ (**III**).

$[\mathrm{V(1)O(Cbdc)_2}]^{2-}$ and $[\mathrm{V(2)O(Cbdc)_2}]^{2-}$ anions are linked by ionic interactions K–O between the potassium cations and carboxylate O atoms of the Cbdc^{2-} anions. The V(1)···V(2) distance in the elementary structural unit is 6.514(2) Å. Four water molecules are bound to the potassium atoms. Two of them are bridging: O(3*w*) binds the K(2) and K(3) atoms, and O(2*w*) connects two K(4) atoms of the adjacent structural units. Thus, the layer of the polymeric structure of compound **II** represents a series of chains linked by the bridging molecules O(2*w*) (Fig. 2b). The framework structure in crystals of compound **II** is formed due to ionic bonds K(1)–O(1) and K(3)–O(10) (2.806(4) and 2.808(4) Å) between the potassium cations and O atoms of the vanadyl groups {V=O} in the adjacent layers (Fig. 2c). The shortest V···V distance in structure **II** is observed between the V(1) atoms of the adjacent layers (5.510(2) Å). The crystal structure of compound **II** is additionally stabilized by a network of hydrogen bonds (Table 4).

The crystal structure of compound **III** is formed by the bis-chelate anions $[VO(Cbdc)_2(H_2O)]^{2-}$ in which the vanadium atom, unlike the starting compound **II**, is in the distorted octahedral coordination environment: the O atom of the coordinated water molecule is localized in the *trans* position to the O atom of the vanadyl group {V=O} (Fig. 3a). The V–O bond lengths with the O atoms of the carboxylate ligand are comparable with those in compounds **I** and **II** (Table 2) and those in the earlier described oxovanadium(IV) compounds with the $Cbdc^{2-}$ anions [17–19]. The six-membered vanadium-malonate rings of the bis-chelate anion have a boat conformation. In the V(1)O(2)C(1)C(2)C(3)O(4) metallocycle, the O(2), C(1), C(3), and O(4) atoms are coplanar within 0.031 Å, and the V(1) and C(2) atoms deviate from this plane by 0.413 and 0.641 Å, respectively. The dihedral angles between the O(2)C(1)C(3)O(4), V(1)O(2)O(4) and O(2)C(1)C(3)O(4), C(1)C(2)C(3) planes are 16.4° and 47.6°, respectively. In the V(1)O(6)-C(7)C(8)C(9)O(8) metallocycle, the O(6), C(7), C(9), and O(8) atoms are coplanar within 0.056 Å, and the V(1) and C(8) atoms deviate from this plane by 0.444 and 0.571 Å, respectively. The dihedral angles between the O(6)C(7)C(9)O(8), V(1)O(6)O(8) and O(6)C(7)C(9)O(8), C(7)C(8)C(9) planes are 17.9° and 42.8°, respectively. In crystals of compound **III**, each bis-chelate dianion $[VO(Cbdc)_2(H_2O)]^{2-}$ is linked with two potassium atoms by ionic interactions K–O between the O atoms of the carboxylate groups of the bis-chelate dianions and water molecules O(1*w*) coordinated to the vanadium atoms (K–O 3.023(3) and 3.037(3) Å, angle K(1)O(1*w*)K(1) 174.30(10)°). In crystals of compound **III**, 1D polymeric chains are formed (Fig. 3b) in which the distances between the adjacent vanadium atoms are the same and equal to 6.6033(9) Å. The site occupancy of the Mg atoms in structure **III** is 0.5 and, hence, only 50% of all the bis-chelate fragments $[VO(Cbdc)_2(H_2O)]^{2-}$ that present in the crystal of compound **III** are bound to the magnesium atom (Fig. 3b). The Mg atom is in a distorted octahedral environment and coordinates five water molecules in addition to the bond with the carboxylate O atom. Two of them (O(3*w*) and O(4*w*)) are bridging (Mg–O, 2.038(4) and 2.238(5) Å) and bind the magnesium and potassium atoms (K–O, 2.732(7) and 2.933(4) Å), whereas three water molecules are terminal (Mg–O, 1.931(4), 1.969(4) and 2.038(5) Å). One

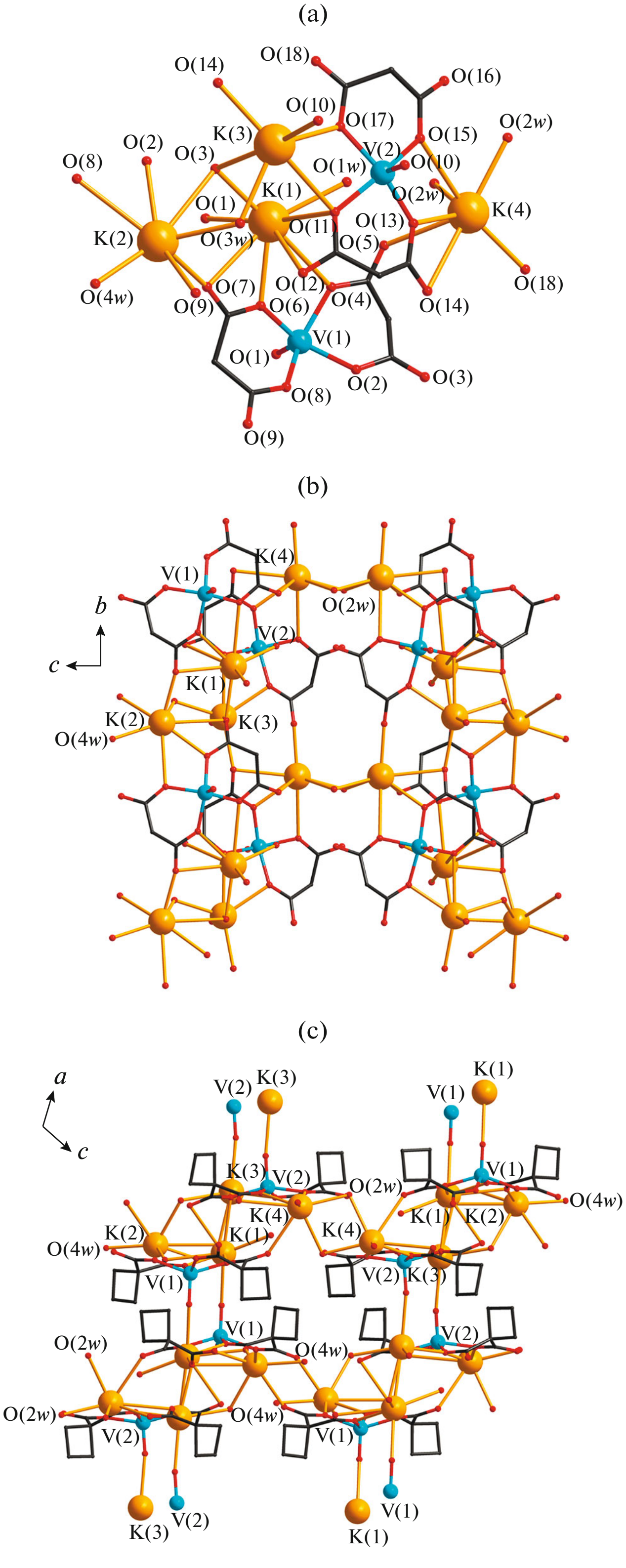

Fig. 2. (a) Basic structural fragment of compound **II** and the formation of (b) the layer and (c) three-dimensional crystal structure in crystal of compound **II**. The cyclobutane fragments of the ligand (a, b) and hydrogen atoms are omitted.

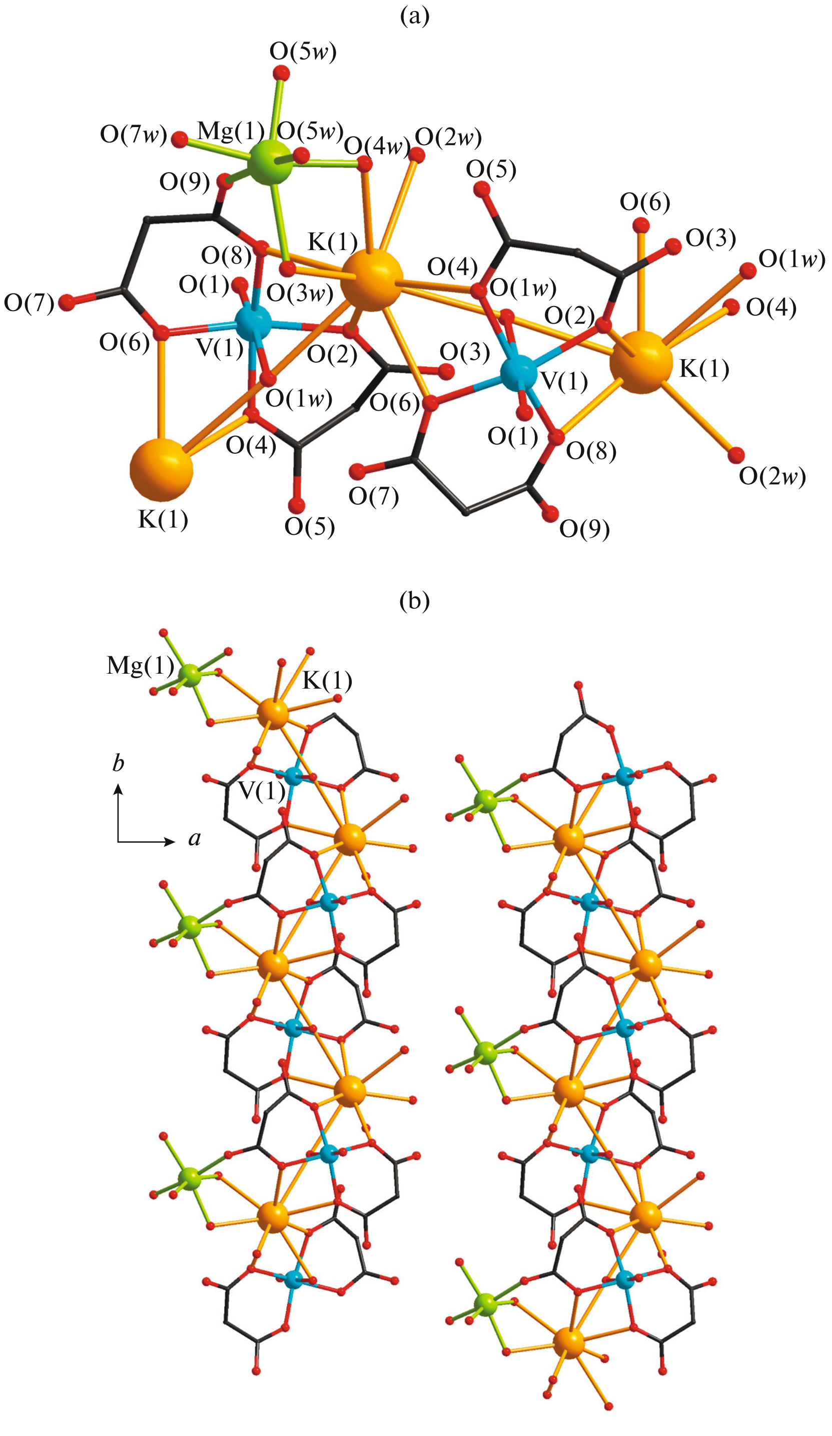

Fig. 3. (a) Fragment of the polymer chain in compound **III** and (b) the mutual arrangement of the polymeric chains in crystal of compound **III**. The cyclobutane fragments of the ligand and hydrogen atoms are omitted.

of the bound water molecules (O(7*w*)) is localized on the crystallographic axis 2 (its multiplicity is 0.5). Each potassium atom additionally coordinates one water molecules O(2*w*) (K–O, 2.920(4) Å) (Fig. 3a). The solvate water molecule O(6*w*) is also localized on the axis 2 and, hence, the overall number of water molecules per formula unit of compound **III** is equal to eight. The crystal structure of compound **III** is additionally stabilized by a network of hydrogen bonds (Table 4).

It can be assumed that each Mg atom substitutes only one K atom upon the interaction of the starting compound **II** with magnesium nitrate and, thus, the occupancy of Mg in the new structure becomes half.

The substitution of a halved number of K^+ ions (r_{ion} = 1.66 Å) by Mg^{2+} ions having the charge almost twice as large and a nearly halved ionic radius (0.74 Å) results in the degradation of the starting 3D polymeric structure and a decrease in the dimensionality of the new structure to 1D. As can be seen from Figs. 2b and 3b, the chain motif resembling that in compound **II** is retained in structure **III**, and the coordination of the magnesium atom prevents the binding of this motif with a similar adjacent motif.

In the previous works, we described the structures of the coordination polymers formed by the dianionic fragment $\{VO(R_2Mal)_2\}^{2-}$ and alkaline, alkaline-earth, or transition metal atoms [13–19]. A quite expected increase in the dimensionality of the structures with an increase in the radius and number of cations was demonstrated in the series of compounds Li–V(IV), Na–V(IV) and Ca–V(IV), Sr–V(IV), Ba–V(IV) with the same anion of substituted malonic acid. For the systems with alkaline ions and alkaline-earth ions having a close radius, the dimensionality was higher in the case of alkaline metal ions, because their number in the structure is twice as large; i.e., in the systems with the same anion of substituted malonic acid, the dimensionality of, e.g., compounds Na–V(IV) is higher than that of Sr–V(IV). Although we could not yet characterize the Mg–V(IV) systems, it can be assumed that these can be chain polymers or molecular complexes. This is indirectly confirmed by the data on the structures of compounds Mn–V(IV), since the radii of 3*d*-metal atoms are close to the radius of a magnesium atom. However, high structural changes are observed on going from one cation to another when synthesizing only bimetallic compounds. A combination of two types of counterions, for example, potassium and magnesium in the above described compound **III**, would allow one to increase structural diversity of coordination polymers based on the dianionic fragments $\{VO(R_2Mal)_2\}^{2-}$.

ACKNOWLEDGMENTS

X-ray diffraction analysis was carried out at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences).

E.S. Bazhina acknowledges the Council on Grants of the President of the Russian Federation (grant no. MK-3514.2017.3) for the support of the synthetic part of the work. M.A. Kiskin, A.A. Sidorov, and I.L. Eremenko acknowledge the Russian Science Foundation for the support of X-ray diffraction and spectral (IR spectroscopy) studies of the new compounds (project no. 14-23-00176-P).

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Translated by E. Yablonskaya