ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 11, pp. 730–740. © Pleiades Publishing, Ltd., 2015.
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The Formation of Polymeric Structures in the M^{2+}–VO^{2+} Systems (M^{2+} = Sr^{2+}, Ca^{2+}) Containing Substituted Malonate Anions

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Received April 6, 2015

Abstract—The synthesis and crystal structures of the polymeric compounds of vanadyl (VO^{2+}) and alkaline-earth metal cations (Sr^{2+} and Ca^{2+}) with the anions of substituted malonic acid analogs, $R(COOH)_2$, were described. Reactions of vanadyl sulfate ($VOSO_4 \cdot 3H_2O$) with calcium and strontium salts of cyclopropane-1,1-dicarboxylic (H_2Cpdc, $C_3H_4(COOH)_2$), cyclobutane-1,1-dicarboxylic (H_2Cbdc, $C_4H_6(COOH)_2$), and butylmalonic acids (H_2BuMal, $C_4H_{10}(COOH)_2$) gave polymeric structures with different (from 1D to 3D) dimensionality. The structure and dimensionality of the compound depends on the size of the substituent in the carboxylate dianion and the radius of the alkaline-earth metal ion.

DOI: 10.1134/S1070328415110019

INTRODUCTION

The design of coordination polymerics is one of the leading areas in modern coordination and supramolecular chemistry and provides the most promising method for synthesis of substances having technologically useful (magnetic, sorptive, catalytic, luminescent, etc.) properties [1–7]. The dianion of malonic acid, for which numerous substituted analogs are known, tends to show chelation as well as many chelating–bridging and bridging coordination modes. For this reason, malonate dianion is a convenient ligand when forming structural blocks of polymerics to bind various metal centers. By varying the substituents in the carbon chain of the malonate ligand, one can diversify the structure and crystal packing of the resulting compounds. The nature of metal atoms involved in the polynuclear architecture can affects the final molecular structure since metal atoms are formally structure-forming centers in the construction of a metal framework in polynuclear molecules or in the formation of structural blocks for the design of coordination polymerics with different dimensionality. Moreover, metal atoms are often of functional importance because of their physical and chemical properties such as magnetism, photo-, redox, and catalytic activity, etc. The construction of a polymeric architecture from individual blocks provides the most targeted and efficient method for the synthesis of coordination polymerics. In such systems, the metal centers (or the entire metal-containing blocks) can be bridged by organic molecules (or their anions) as well as by the blocks containing other metals. Such blocks based on alkali or alkaline-earth metal ions can contain coordinated molecules of water or other solvents (acetonitrile, THF, ethanol, etc.) [8–11]. It is known that such polymeric carboxylates—e.g., tartrate and malonate coordination polymerics of some 3*d* metals (Mn(II), V(IV), Fe(II), Ni(II), and Co(II))—that contain alkaline-earth metal ions (Ca^{2+}, Sr^{2+}, or Ba^{2+}) can be used as convenient precursors to compound perovskite-like mixed oxides having unique physical and chemical characteristics [12–18]. This gives impetus to the development of new approaches to the synthesis of substituted malonates combining 3*d*- and *s*-metals, *viz.*, vanadium and an alkaline-earth metal, as possible molecular precursors the preparation of compound oxides. It is known that such vanadium-containing oxides can exhibit high-temperature superconductivity [15–22]. Here we describe the synthesis of such systems, analyze the structures of resulting compounds $\{[M^{2+}(VO)(L)_2(H_2O)_x] \cdot yH_2O\}_n$ ($M^{2+} = Ca^{2+}$, Sr^{2+}; L is the substituted malonate anion), and try to elucidate the role of the bridging groups (such as Ca^{2+} and Sr^{2+} ions and water molecules) that link the structural blocks of substituted vanadium(IV) malonates. Earlier, we have found that the crystal structures in Ba^{2+}-containing systems monotonically decrease in dimensionality as the bulkiness of the substituent(s) in malonic acid increases [23, 24]. A similar trend has been observed for the analogous systems $\{[Na^{+}(VO)(L)_2(H_2O)_x] \cdot yH_2O\}_n$ [25]. It should be noted that the use of malonate anions containing a bulky substituent and small cations may lead to the limiting cases of the dimensionality decrease for the resulting coordination polymerics, as illustrated with the polynuclear structure $[Li_4(VO)_2(BuMal)_4(H_2O)_8] \cdot H_2O$ (H_2BuMal is butylmalonic acid) forming a molecular crystal [26].

EXPERIMENTAL

All manipulations dealing with the synthesis of new compounds were performed in air. Distilled water and ethanol (reagent grade) were used. Other reagents included $VOSO_4 \cdot 3H_2O$ (analytical grade), $Sr(OH)_2 \cdot 8H_2O$ (Sigma-Aldrich), $Ca(OH)_2$ (reagent grade), cyclopropane-1,1-dicarboxylic acid (H_2Cpdc, 98%, Acros Organics), cyclobutane-1,1-dicarboxylic acid (H_2Cbdc, 98%, Acros Organics), and butylmalonic acid (H_2BuMal, 99%, ABCR GmbH & Co). IR spectra (KBr pellets) were recorded on a Spectrum 65 FTIR spectrophotometer (PerkinElmer) in the 4000–400 cm^{-1} range. Elemental analysis was carried out on a EuroEA 3000 CHNS analyzer (EuroVector).

Synthesis of $\{[Ca(VO)(Cpdc)_2(H_2O)_5] \cdot H_2O\}_n$ (I). Calcium hydroxide (0.068 g, 0.92 mmol) was added to a solution of H_2Cpdc (0.120 g, 0.92 mmol) in distilled water (25 mL). The reaction mixture was stirred at room temperature for 15–20 min. Then a solution of $VOSO_4 \cdot 3H_2O$ (0.1 g, 0.46 mmol) in distilled water (10 mL) was added with vigorous stirring. Stirring was continued for an additional 15 min. The resulting blue solution was left at room temperature for a month and a half; the white precipitate that formed was filtered off. Slow evaporation of the filtrate gave blue-violet crystals suitable for X-ray diffraction, which were washed with distilled water and ethanol and dried in air. The yield of compound **I** was 0.120 g (55.2% based on the initial amount of $VOSO_4 \cdot 3H_2O$).

For $C_{10}H_{20}CaO_{15}V$
anal. calcd., %: C, 25.49; H, 4.28.
Found, %: C, 25.65; H, 3.98.

IR (KBr; ν, cm^{-1}): 3790.5–3065.4 s.br, 3032.63 s, 3065.4–2704.7 s.br, 2583.77 vw, 1956.05 vw, 1657.64 s, 1621.08 s, 1567.95 vs, 1557.57 vs, 1428.29 s, 1416.35 vs, 1235.56 s, 1209.97 s, 1182.88 m, 1145.4 m, 1116.52 m, 1091.38 m, 1080.19 m, 1043.20 w, 984.38 s, 944.52 s, 868.12 s, 845.07 s, 776.70 s, 752.07 s, 550.57 s, 480.69 s.

Synthesis of $[Sr(VO)(Cbdc)[Sr(VO)(Cbdc)_2(H_2O)_5]_n$ (II). Strontium hydroxide (0.244 g, 0.92 mmol) was added to a solution of H_2Cbdc (0.1325 g, 0.92 mmol) in distilled water (25 mL). The reaction mixture was stirred at room temperature for 15–20 min. Then a solution of $VOSO_4 \cdot 3H_2O$ (0.1 g, 0.46 mmol) in distilled water (10 mL) was added with vigorous stirring. Stirring was continued for an additional 15 min. The bright blue solution together with a precipitate of $SrSO_4$ was kept at room temperature for ~5 h and then filtered. The filtrate was left at room temperature for nine days. The resulting bright sky-blue crystals suitable for X-ray diffraction were washed with distilled water and ethanol and dried in air. The yield of compound **II** was 0.1415 g (58.1% based on the initial amount of $VOSO_4 \cdot 3H_2O$).

For $C_{12}H_{22}O_{14}SrV$
anal. calcd., %: C, 27.25; H, 4.19.
Found, %: C, 27.34; H, 4.34.

IR (KBr; ν, cm^{-1}): 3739.5–3050.8 s.br, 3017.31 w, 3003.4 w, 2970.95 m, 2872.3 vw, 1665.91 s, 1645.93 s, 1594.84 vs, 1581.84 vs, 1394.71 s, 1327.53 s, 1259.71 m, 1230.43 m, 1160.62 vw, 1126.55 s, 1059.45 w, 1017.64 m, 959.62 s, 941.1 m, 923.38 m, 875.64 vw, 842.71 vw, 795.72 w, 771.80 m, 714.51 m, 663.55 m, 558.58 s, 462.11 s, 443.57 m.

Synthesis of $\{[Ca(VO)(Cbdc)_2(H_2O)_4] \cdot H_2O\}_n$ (III). Vanadyl sulfate (0.1 g, 0.46 mmol) and H_2Cbdc (0.1325 g, 0.92 mmol) were dissolved in distilled water (40–50 mL) at room temperature. Then $Ca(OH)_2$ (0.068 g, 0.92 mmol) was added, and the reaction mixture was stirred for 25–30 min. The resulting blue solution was left at room temperature for two weeks. The white precipitate that formed was filtered off. The resulting bright blue crystals suitable for X-ray diffraction were washed with distilled water and ethanol and dried in air. The yield of compound **III** was 0.083 g (35.9% based on the initial amount of $VOSO_4 \cdot 3H_2O$).

For $C_{12}H_{24}O_{15}CaV$
anal. calcd., %: C, 28.86; H, 4.85.
Found, %: C, 29.07; H, 5.05.

IR (KBr; ν, cm^{-1}): 3757.7–3043.5 s.br, 3002.24 m, 2964.17 m, 1651.40 s, 1590.87 s, 1458.46 w, 1442.37 m, 1379.02 vs, 1322.53 m, 1256.94 vw, 1247.99 vw, 1227.56 w, 1183.71 vw, 1158.75 vw, 1115.53 m, 1065.18 vw, 1002.62 s, 958.90 vw, 923.53 w, 882.23 vw, 857.29 vw, 842.71 vw, 776.90 m, 761.04 m, 721.51 m, 669.38 m, 649.18 m, 545.34 m, 467.27 w, 411.94 m.

The compound $\{[Sr_3(VO)_3(BuMal)_6(H_2O)_{12}] \cdot 2H_2O\}_n$ (IV) was obtained by a similar procedure for the synthesis of compound **II** using a respective amount of H_2BuMal instead of H_2Cbdc. The yield of compound **IV** was 0.223 g (87.4% based on the initial amount of $VOSO_4 \cdot 3H_2O$).

For $C_{42}H_{88}O_{41}Sr_3V_3$
anal. calcd., %: C, 30.30; H, 5.33.
Found, %: C, 30.15; H, 5.22.

IR (KBr; ν, cm^{-1}): 3612.0–3141.2 s.br, 2960.51 s, 2933.57 s, 2873.61 m, 2861.9 m, 1643.74 vs, 1590.94 vs, 1407.24 vs, 1364.05 s, 1339.0 s, 1312.97 s, 1285.80 s, 1197.01 w, 1135.66 vw, 1104.42 w, 1090.9 vw, 988.36 s, 957.34 m, 906.23 w, 806.41 m, 782.25 w, 745.77 m, 710.58 s, 650.0 m, 610.74 s, 576.12 s, 508.90 s, 440.94 s.

The compound $\{[Ca(VO)(BuMal)_2(H_2O)_5] \cdot H_2O\}_n$ (V) was obtained by a similar procedure for the synthesis of compound III using a respective amount of H_2BuMal instead of H_2Cbdc. The yield of compound **V** was 0.074 g (30.4% based on the initial amount of $VOSO_4 \cdot 3H_2O$).

For $C_{14}H_{30}CaO_{14}V$ (without the solvate water molecule)

anal. calcd., %:	C, 32.75;	H, 5.89.
Found, %:	C, 32.63;	H, 5.71.

IR (KBr; ν,$^{-1}$): 3658.36 vw, 3632.4–3076.2 s.br, 2959.98 m, 2933.9 w, 2872.53 w, 1578.05 vs, 1417.37 s, 1364.8 w, 1340.50 w, 1322.42 w, 1202.22 vw, 1138.02 vw, 1103.96 vw, 988.77 m, 960.17 w, 908.27 vw, 804.37 w, 716.56 w, 609.84 w, 583.67 w, 513.05 w.

Single-crystal X-ray diffraction studies of compounds **I–V** were performed on a Bruker SMART APEX I diffractometer equipped with a CCD detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) [27]. For each compound, a semiempirical absorption correction was applied [28]. The structures were solved by direct methods and refined anisotropically (for all non-hydrogen atoms) by the full-matrix least-squares method. The H atoms at the carbon atoms of the organic ligands were located geometrically and refined using a riding model. The H atoms of the hydrate molecules in structures **I** and **III** were located in difference electron-density maps and refined by imposing constraints on the lengths of equivalent O–H bonds (~0.85 Å) and on the HOH angles (~109°). The H atoms of the hydrate molecules in structures **IV** and **V** were not located, probably because of twinning in structure **IV** (the crystals of compound **IV** are monoclinic pseudoorthorhombic; the β angle is nearly 90°). In structure **V**, the Ca^{2+} ion is disordered over two positions (Ca(1)···Ca(1*A*) 0.62 Å) with occupancies of ~0.7 and ~0.3, respectively. All calculations were performed with the SHELX-97 program package [29]. Crystallographic parameters and the data collection and refinement statistics for structures **I–V** are summarized in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. X-ray data for compounds **I–V** have been deposited with the Cambridge Structural Database (CCDC nos. 1032991–1032995, respectively; http://www.ccdc.cam.ac.uk/Community/Requestastructure/ Pages/DataRequest.aspx).

RESULTS AND DISCUSSION

Earlier, we have demonstrated that $VOSO_4 \cdot 3H_2O$ reacts with Ba(Cpdc) or Sr(Cpdc) in a ratio of 1 : 2 in an aqueous solution to give the crystals of compound $\{[Ba_2(VO)_2(Cpdc)_4(H_2O)_8] \cdot 2H_2O\}_n$ and $[Sr(VO)(Cpdc)_2(H_2O)_6]_n$ **(VI)**. Their 3D-polymeric structures are constructed of vanadium(IV)-containing mononuclear bis-chelate moieties linked by the cationic polyhedra of the Ba^{2+} or Sr^{2+} ions, respectively [23].

When Sr(Cpdc) in this reaction system is replaced by Ca(Cpdc), the solution produces the compound $\{[Ca(VO)(\mu_3\text{-Cpdc-}\kappa^2O,O')(\text{Cpdc-}\kappa^2O,O')(\mu\text{-}H_2O)(H_2O\text{-}\kappa O)_4] \cdot H_2O\}_n$ **(I)** having a layered structure. As in compound **VI**, the $[VO(Cpdc)_2(H_2O)]^{2-}$ dianions in structure **I** are formed by from the crystallographically equivalent V(1) atoms chelating two cyclopropane-1,1-dicarboxylate dianions. The electron-donating O atoms of the dianions of the ligand $Cpdc^{2-}$ are in the equatorial plane of the coordination polyhedron of vanadium (V(1)–O(Cpdc), 1.985(2)–1.998(2) Å). The vanadyl O(1) atom occupies an axial position (V(1)=O(1), 1.604(2) Å). This bond length falls within the range observed for the well-known vanadyl compounds with unsubstituted malonate anions [30–32]. The O(2) atom of the coordinated water molecule is *trans* to O(1); the V(1)–O(2) bond is lengthened (2.308(4) Å). This O atom completes the distorted octahedral environment of vanadium. The distortion parameters of the coordination polyhedron of the V atom in structure **I** are given in Table 3. The six-membered vanadium-malonate rings V(1)–O(2)–C(1)–C(2)–C(3)–O(4) and V(1)–O(6)–C(6)–C(7)–C(8)–O(8) adopt a distorted half-chair conformation. The bis-chelate dianions $[VO(Cpdc)_2(H_2O)]^{2-}$ in structure **I** are bound to the calcium atoms by ionic interactions to form zigzag chains (Fig. 1a). As in compound **VI**, only one Cpdc2- anion involved in binding the bis-chelate moieties in structure I and perform a m3,k2 coordination mode. The other $Cpdc^{2-}$ dianion acts as a chelating ligand only.

The network layered structure **I** is formed by zigzag polymeric chains united through interactions between the Ca^{2+} ions of one chain and the O atoms of the calcium-coordinated water molecules of another chain (Ca–O, 2.716(2) Å) (Fig. 1b). The coordination sphere of each Ca atom is completed with the O atoms of four water molecules. The distance between the Ca atoms in adjacent chains is 4.2784(6) Å. The shortest V···V distance (7.0468(6) Å) is found between the metal atoms of adjacent chains in the network packing.

Replacement of Sr(Cpdc) by Sr(Cbdc) in a reaction like that used to obtain compound **VI** resulted in the formation of the crystalline compound $[Sr(VO)(\mu\text{-Cbdc-}\kappa^2O,O')_2(H_2O\text{-}\kappa O)_5]_n$ **(II)** having a chain structure. The polymeric chains of compound **II** consist of the structurally equivalent bis-chelate dianions $[VO(Cbdc)_2(H_2O)]^{2-}$ containing the V(1) atom. These dianions are structurally similar to the bis-chelate moieties in compounds **VI** and **I**, except for the slightly lengthened V=O bond (1.612(8) Å). Earlier, such V=O bond lengths have been noted for vanadyl tartrate compounds with Ca^{2+}, Sr^{2+}, and Ba^{2+} cations [15–17]. The six-membered vanadium-malonate

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures **I–V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
Empirical formula	$C_{10}H_{20}O_{15}CaV$	$C_{12}H_{22}O_{14}SrV$	$C_{12}H_{24}O_{15}CaV$	$C_{42}H_{88}O_{41}Sr_3V_3$	$C_{14}H_{32}O_{15}CaV$
M	471.28	528.86	499.33	1659.76	530.41
T, K	173(2)	296(2)	296(2)	120(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$Pnna$	$P2_1/c$	$P2_1/c$
a, Å	8.0293(3)	14.538(16)	11.299(3)	16.4108(10)	10.1909(15)
b, Å	15.2558(6)	16.577(19)	24.568(6)	12.3632(8)	20.737(3)
c, Å	13.7127(5)	9.350(11)	14.021(4)	32.3951(19)	11.9009(18)
β, deg	100.6290(10)	125.388(15)	90	90.0100(10)	112.620(2)
V, Å^3	1650.89(11)	1837(4)	3892.3(18)	6572.6(7)	2321.5(6)
Z	4	4	8	4	4
ρ_{calcd}, g cm^{-3}	1.896	1.912	1.704	1.677	1.518
μ, mm^{-3}	0.995	3.485	0.849	2.925	0.716
θ_{min}–θ_{max}, deg	2.58–27.53	2.11–29.47	1.66–30.28	0.63–27.60	2.24–29.22
F(000)	972	1068	2072	3384	1112
T_{min}/T_{max}	0.6661/0.7456	0.3141/0.7459	0.7116/0.8976	0.4545/0.7585	0.7775/0.9190
Ranges of h, k, and l indices	$-10 \le h \le 10$, $-19 \le k \le 19$, $-12 \le l \le 17$	$-15 \le h \le 19$, $-22 \le k \le 9$, $-12 \le l \le 11$	$-15 \le h \le 15$, $-34 \le k \le 25$, $-19 \le l \le 19$	$-19 \le h \le 21$, $-16 \le k \le 8$, $-30 \le l \le 42$	$-13 \le h \le 13$, $-24 \le k \le 28$, $-16 \le l \le 15$
Number of measured reflections	12330	3869	30232	36684	14747
Number of unique reflections	3807	2479	5702	14911	6189
R_{int}	0.016	0.083	0.0501	0.0443	0.0470
Number of reflections with $I > 2\sigma(I)$	3592	1196	4224	12568	3777
GOOF	1.000	1.000	1.001	1.001	1.000
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0340$, $wR_2 = 0.1090$	$R_1 = 0.0650$, $wR_2 = 0.1570$	$R_1 = 0.0434$, $wR_2 = 0.1158$	$R_1 = 0.0518$, $wR_2 = 0.1324$	$R_1 = 0.0699$, $wR_2 = 0.1882$
R factors for all reflections	$R_1 = 0.0358$, $wR_2 = 0.1106$	$R_1 = 0.1402$, $wR_2 = 0.1949$	$R_1 = 0.0659$, $wR_2 = 0.1386$	$R_1 = 0.0688$, $wR_2 = 0.1447$	$R_1 = 0.1291$, $wR_2 = 0.2185$
Residual electron density (min/max), e/Å^3	–1.090/0.602	–1.067/1.651	–0.395/1.085	–0.968/1.695	–1.332/1.396

Table 2. Selected geometrical parameters of compounds **I**–**V**

Bond	Bond length (*d*), Å				
	L = Cpdc	L = Cbdc		L = BuMal	
	M = Ca	M = Sr	M = Ca	M = Sr	M = Ca
	I	**II**	**III**	**IV**	**V**
V=O	1.604(2)	1.612(8)	1.582(2)	1.584(5)–1.587(5)	1.583(4)
V–O (H_2O-κO)	2.308(4)	2.295(9)		2.275(6)–2.439(5)	2.313(3)
V–O (L-κ^2O,O')	1.985(2)–1.998(2)	1.995(6), 2.023(5)	1.977(2)–2.007(2)	1.966(5)–2.035(6)	2.000(3)–2.014(3)
M–O (H_2O)	2.452(2)–2.513(2)	2.540(6), 2.654(7)	2.376(2)–2.458(2)	2.546(4)–2.809(4)	2.252(7)–2.480(8)
M–O (V=O)		2.735(8)			
M–O (μ-L)	2.375(2), 2.455(2)	2.580(6)	2.466(2)–2.518(2)	2.508(5)–2.816(5)	2.348(4)–2.475(6)

Table 3. Distortion parameters of the coordination polyhedra of vanadium in structures **I**–**V**

Parameter	**I**	**II**	**III**	**IV**	**V**
	L				
	Cpdc	Cbdc	Cbdc	BuMal	BuMal
Deviation of the V atom from the equatorial plane of its coordination polyhedron, Å	0.3167(4)	0.3824(17)	0.4433(4)	0.3362(10)–0.3855(12)	0.3562(8)
Bond angles	Values and ranges of the angles ω, deg				
V=O/V–O(L)	98.15(8)–100.11(8)	100.2(2), 102.0(2)	101.66(9)–104.19(9)	97.8(2)–102.4(2)	99.2(2)–100.6(2)
V=O/V–O(H_2O)	178.87(8)	180		171.9(2)–177.5(2)	176.8(2)
V–O(H_2O)/V–O(L)	79.99(7)–81.65(7)	78.0(1), 80.0(1)		73.9(2)–85.1(2)	77.7(1)–82.1(1)

rings V(1)–O(2)–C(1)–C(2)–C(3)–O(4) in the dianions $[VO(Cbdc)_2(H_2O)]^{2-}$ adopt a half-chair conformation. The bis-chelate dianions are linked in such a way that each Sr(1) cation is bound to three neighboring dianions $[VO(Cbdc)_2(H_2O)]^{2-}$ through two carboxylate O atoms of the ligands $Cbdc^{2-}$ (Sr–O, 2.580(6) Å) and a vanadyl O atom (Sr–O, 2.735(8) Å), thus uniting two chains into a ribbon structure (Fig. 2a). The vanadyl V=O group involved in linking of bis-chelate moieties (M–O=V bond formation) has also been found in the compound $\{[Ba(VO)(Me_2Mal)_2(H_2O)] \cdot H_2O\}_n$ [24] and unsubstituted oxovanadium(IV) malonates containing alkali metal cations [32]. The V···V and Sr···Sr distances in the chain of structure **II** are 5.647(5) and 7.238(6) Å, respectively. The coordination sphere of the Sr atoms is completed with the O atoms of four water molecules. In the crystal of compound **II**, the polymeric chains run parallel to each other (Fig. 2b) in such a way that the V···V and Sr···Sr distances between adjacent chains are nonbonding (7.846(6) and 6.555(6) Å, respectively).

The calcium vanadyl cyclobutane-1,1-dicarboxylate $\{[Ca(VO)(\mu_3\text{-}Cbdc\text{-}\kappa^2O,O')(\mu\text{-}Cbdc\text{-}\kappa^2O,O')(H_2O\text{-}\kappa O)_4] \cdot H_2O\}_n$ (**III**) obtained from vanadyl sulfate, H_2Cbdc, and $Ca(OH)_2$ in an aqueous solution has also a chain structure. In contrast to compounds **VI**, **I** and **II** discussed above, the ligand environment around the V atoms in structure **III** forms no distorted octahedron. Their coordination polyhedra are tetragonal pyramids with four carboxylate O atoms forming the base and with the vanadyl O atom as the apex. The six-membered vanadium-malonate rings V(1)–O(2)–C(1)–C(2)–C(3)–O(4) and V(1)–O(6)–C(7)–C(8)–C(9)–O(8) adopt a boat conformation. The vanadium-containing dianions $[VO(Cbdc)_2]^{2-}$ are linked in pairs by the Ca(1) atoms through the vanadium-chelating carboxylate O atoms (Ca(1)–O, 2.4757(16) and 2.5175(17) Å). Such trinuclear fragments {V(1)–Ca(1)–V(1)} form a chain by binding to the Ca(2) atoms through the carboxylate O atoms (Ca(2)–O, 2.466(2) Å) not involved in the chelation of the vanadium atoms (Fig. 3a). The shortest V···V distance (6.0729(16) Å) in the chain is found between the vanadium atoms of the adjacent trinuclear fragments {V(1)–Ca(1)–V(1)}. As with compound **I**, the crystal packing of compound **III** has a network structure. However, this structure shows no Ca···O···Ca bridges since the shortest Ca···Ca distance between adjacent chains is longer by ~1.55 Å (Fig. 3b).

A reaction of a solution of vanadyl sulfate with Sr(BuMal) resulted in crystallization of the compound $\{[Sr_3(VO)_3(\mu_3\text{-BuMal-}\kappa^2O,O')_4(\mu\text{-BuMal-}\kappa^2O,O')_2(\mu\text{-}H_2O)_4(H_2O\text{-}\kappa O)_8] \cdot 2H_2O\}_n$ (**IV**). Its chain structure is more complicated than that of the cyclobutane-1,1-dicarboxylate analog (Fig. 4). The constitutional repeating unit (CRU) of polymeric structure **IV** consists of three independent dianions $[VO(BuMal)_2(H_2O)]^{2-}$ (containing three crystallographically nonequivalent V(1), V(2), and V(3) atoms), strontium cations (Sr(1), Sr(2), and Sr(3)), nine coordinated water molecules, and two solvate water molecules. The dianions $[VO(BuMal)_2(H_2O)]^{2-}$ in compound **IV** are structurally similar to the bis-chelate moieties of compounds **VI**, **I**, and **II**. As with the butylmalonates described in [24, 25], the metal bis-chelates $[VO(BuMal)_2(H_2O)]^{2-}$ in the crystal structure of **IV** form triangles with crystallographically nonequivalent V atoms as vertices (Figs. 4a, 4b). The metal-containing moieties in the crystal of compound **IV** are linked by the Sr^{2+} cations in such a way that each dianion $[VO(BuMal)_2(H_2O)]^{2-}$ is bound to three crystallographically nonequivalent Sr atoms. The shortest V···V distance (6.0778(14) Å) in the chain is found between the adjacent V(1) and V(2) atoms within the same CRU. The coordination polyhedra of the Sr atoms are completed with bridging and terminal water molecules. All strontium atoms form a chain, in which Sr(1) and Sr(3) are bridged by two water molecules (O(2*ws*) and O(5*ws*)). The Sr(1) and Sr(2) atoms are linked by a bridging water molecule (O(10*w*)), while Sr(2) and Sr(3) are bridged by the carboxylate O atoms of the butylmalonate dianions (Figs. 4a, 4c). The average Sr···Sr distance in this chain is 4.2330(7) Å.

The crystal packing formed by the chains of compound **IV** leaves through channels housing the butyl substituents of the ligand BuMal (Fig. 4d). The shortest V···V distance between the metal atoms in

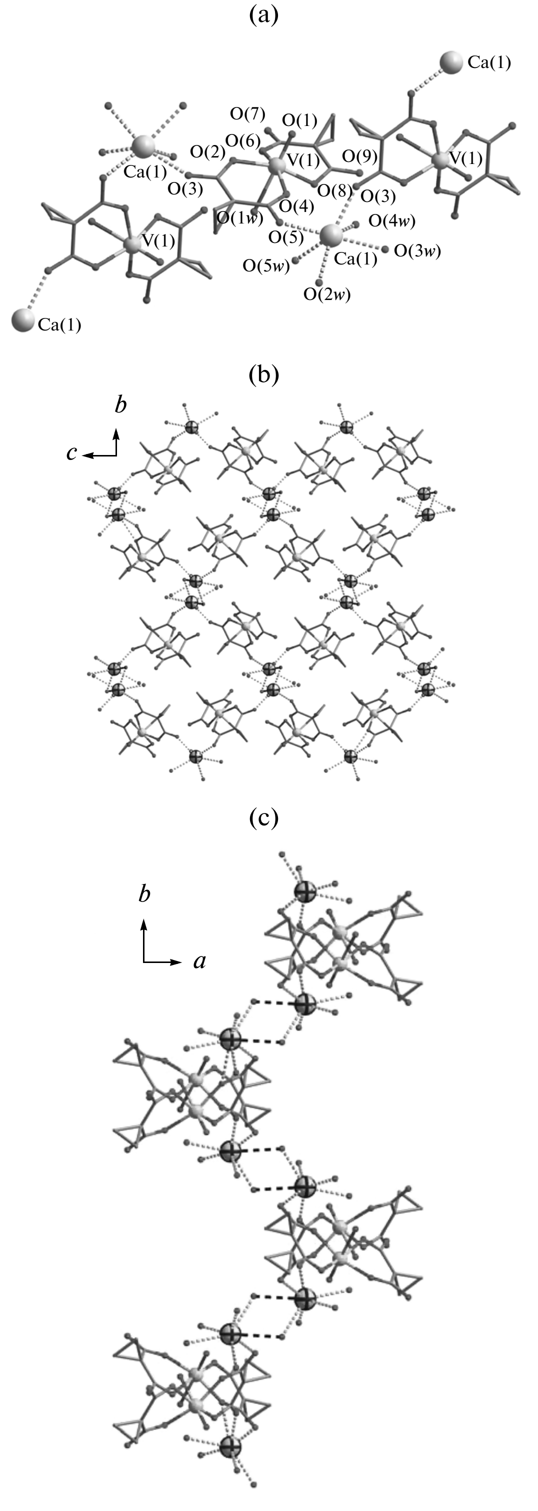

Fig. 1. Polymeric chain (a) and the crystal packing of compound **I**: a layer structure (b) and a combination of chains into a layer (c). The ionic Ca–O bonds (2.716(2) Å) are indicated with dark dashed lines. The hydrogen atoms are omitted.

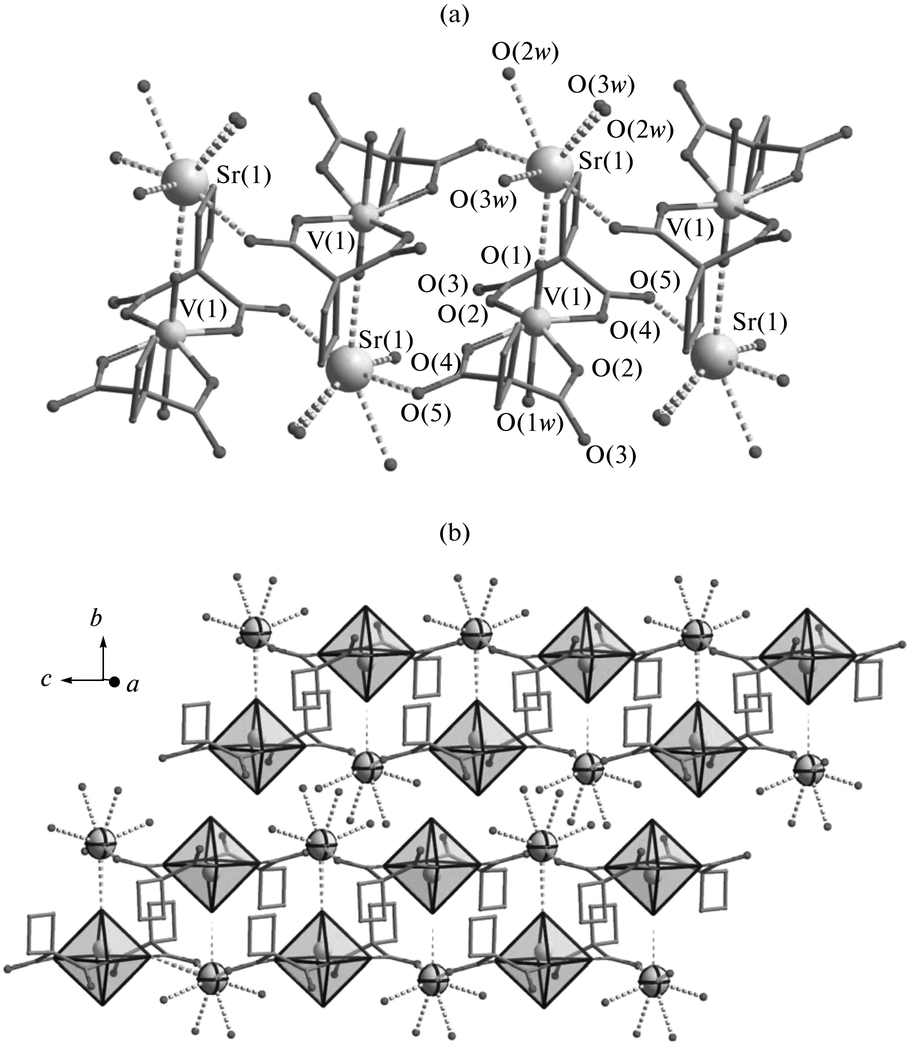

Fig. 2. Ribbon-type structure (a) and the crystal packing of compound **II** (b). The hydrogen atoms are omitted.

adjacent chains is 7.3355(15) Å. The six-membered vanadium-malonate rings V(2)–O(9)–C(15)–C(16)–C(17)–O(11) and V(2)–O(13)–C(22)–C(23)–C(24)–O(15) of the bis-chelate dianions $[(V(2))O(BuMal)_2(H_2O)]^{2-}$ adopt a half-chair conformation. The chelate rings formed by the butylmalonate dianions and the V(1) and V(3) atoms adopt a boat conformation.

Using the procedure like that described for the synthesis of compound **III**, we obtained the crystals of compound $\{[Ca(VO)(\mu\text{-BuMal-}\kappa^2O,O')_2(H_2O\text{-}\kappa O)_5] \cdot H_2O\}_n$ (**V**). The resulting chain structure **V** retains the bis-chelate dianion $[VO(BuMal)_2(H_2O)]^{2-}$, in which the metal center has a distorted octahedral environment observed for compounds **I**, **II**, and **IV** (Table 2). The six-membered vanadium-malonate rings V(1)–O(3)–C(1)–C(2)–C(3)–O(5) and V(1)–O(7)–C(8)–C(9)–C(10)–O(9) adopt boat and half-chair conformations, respectively. Each malonate dianion, apart from chelating the V atom, links the bis-chelate moiety with a Ca atom completing its coordination polyhedron with four water molecules (Fig. 5a). The resulting chains run parallel to each other, but their crystal packing is much looser than that of compound **III** because of the steric hindrances presented by the butylmalonate ligands (Fig. 5b).

Unfortunately, we failed to select the proper conditions to obtain the single crystals of compound $[Ba(VO)(Cbdc)_2(H_2O)_x]_n$. Considering a structural similarity of the coordination polymerics $[Ba(Cu)(Cbdc)_2(H_2O)]_n$ and $[Ba(Cu)(Me_2Mal)_2(H_2O)_5]_n$ [33], one could assume that $[Ba(VO)(Cbdc)_2(H_2O)_x]_n$ would have a layered structure found in $\{[Ba(VO)(Me_2Mal)_2(H_2O)] \cdot H_2O\}_n$ [24]. However, it should be taken into account that strontium vanadyl dimethylmalonate, unlike the cyclobutane-1,1-dicarboxylate compound **II**, has a fundamentally different structure [34]. In its structure, the network polymeric dianions $[\{(VO)(Me_2Mal)_2\}_n]^{2n-}$ are constructed of the vanadyl cations $[V{=}O]^{2+}$ only

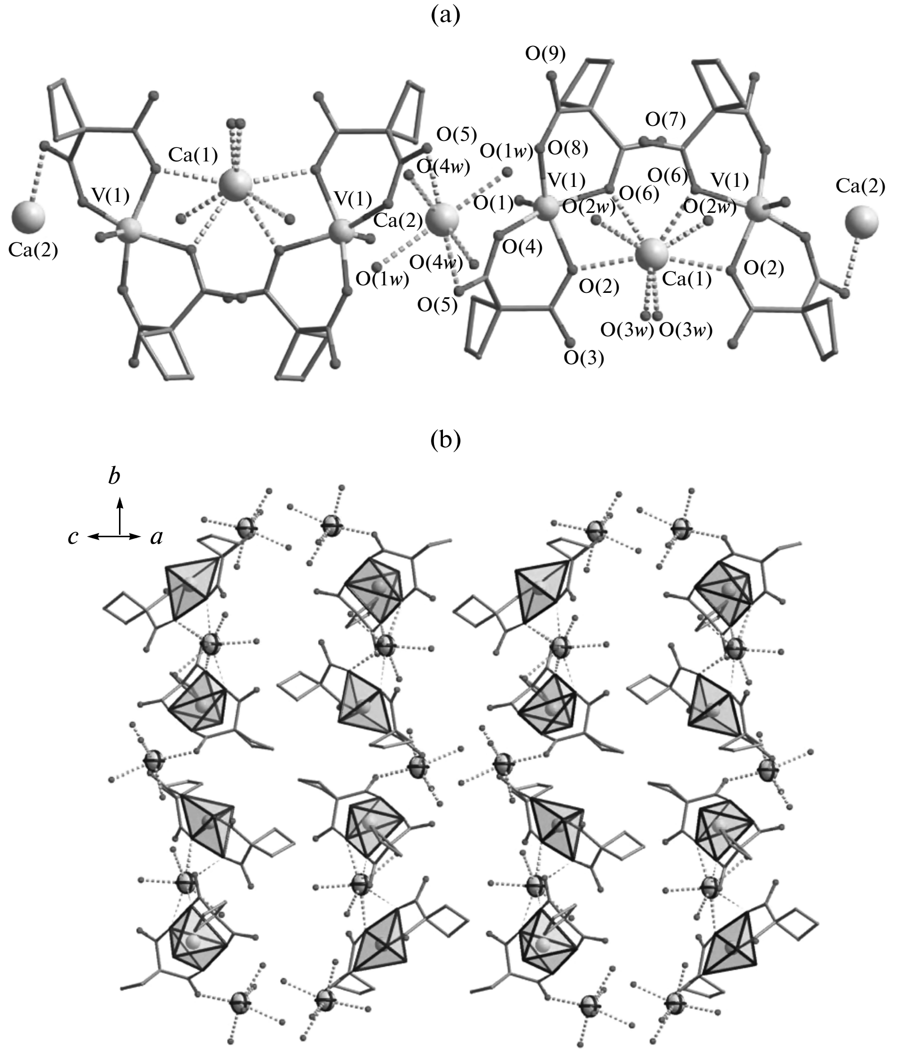

Fig. 3. Polymeric chain (a) and the crystal packing of compound **III** (b). The hydrogen atoms are omitted.

bridged by the Me_2Mal^{2-} anions. In this compound, the acid does not function as a chelating ligand.

Clearly, the preparation of new calcium vanadyl and strontium vanadyl compounds provides valuable information on how the steric hindrances affect the crystal structure formation in the systems $\{[M^{2+}(VO)(L)_2(H_2O)_x] \cdot yH_2O\}_n$. It is no wonder that the cyclopropane-1,1-dicarboxylate anion, which contains the most compact substituent, forms a 2D polymeric even with the calcium ion. Both the butylmalonate and cyclobutane-1,1-dicarboxylate anions yield chain structures. However, there is a considerable structural difference between such compounds with the Sr and Ca atoms. Because the Sr^{2+} cation is larger, the polymeric chain shows short contacts between the Sr atom and the carboxylate O atoms of the three nearest dianions $[VO(L)_2(H_2O)]^{2-}$, which gives rise to ribbon-type structures. In the Ca compounds, linkage only of two adjacent bis-chelate dianions is typical. Therefore, strontium compounds can be regarded as intermediate between chain and layered polymerics because of an increase in the number of vanadium-containing dianions bound by a Sr^{2+} ion. This increasingly strong trend results in the formation of layered structures in the systems $\{[M^{2+}(VO)(L)_2(H_2O)_x] \cdot yH_2O\}_n$, giving rise to 2D polymerics. One can believe that the correlations revealed for the effect of the substituent in substituted malonate dianions on the crystal architecture of the coordination polymerics obtained will be useful for further targeted chemical design of polymeric heteronuclear precursors containing vanadium and alkaline-earth metal ions that are promising for the thermal synthesis of mixed metal oxides having unusual physical and chemical properties.

ACKNOWLEDGMENTS

The X-ray diffraction studies were performed at the Joint Use Center of the Kurnakov Institute of General

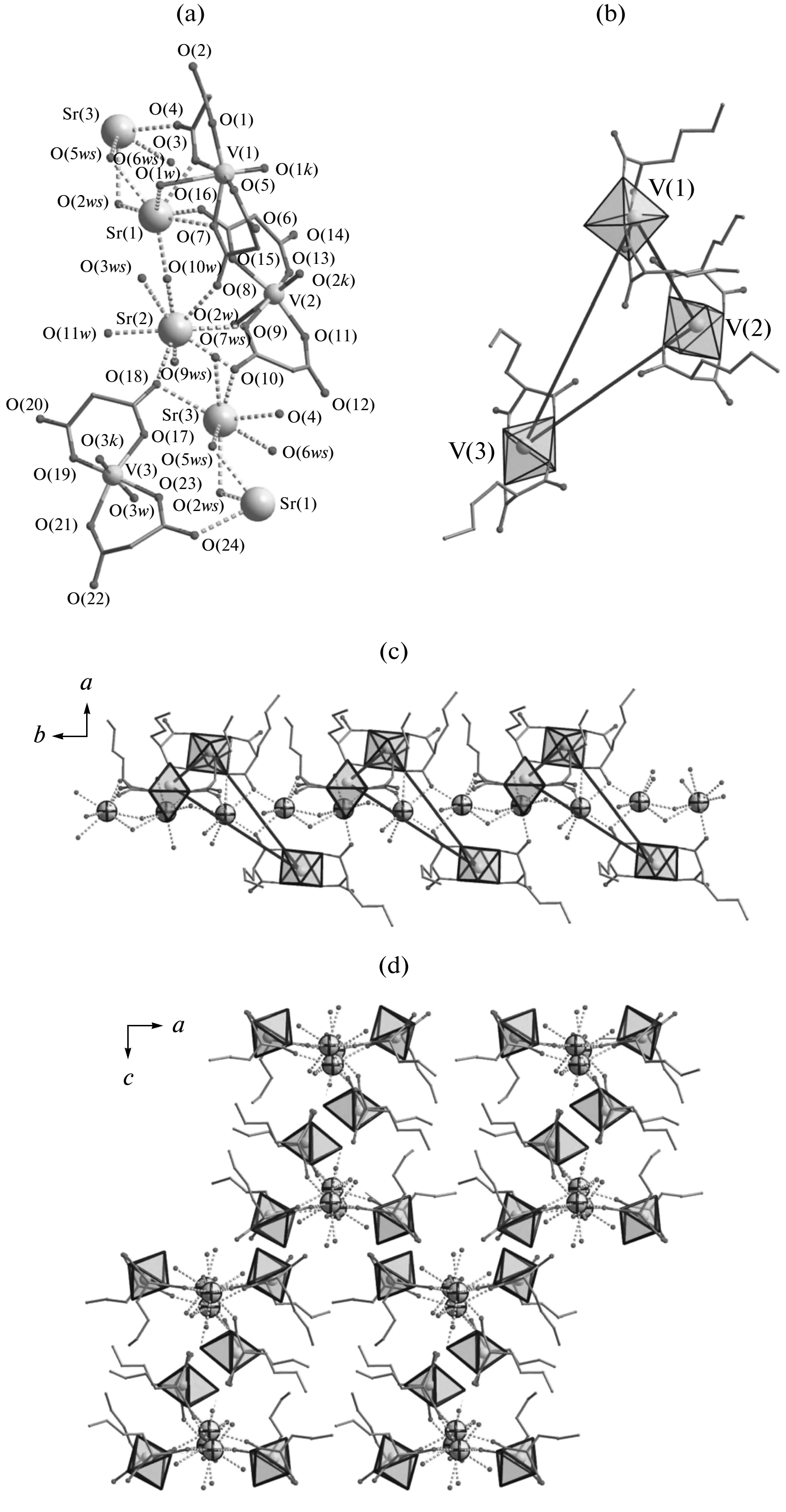

Fig. 4. (a) Strontium-linked mononuclear moieties $[VO(BuMal)_2(H_2O)]^{2-}$ in structure **IV** (the butyl substituents and the hydrogen atoms are omitted); (b) the triangular fragment of compound **IV**: the spatial arrangement of the dianions $[VO(BuMal)_2(H_2O)]^{2-}$ formed by the crystallographically nonequivalent vanadium atoms; (c) the polymeric chain of compound **IV**: the arrangement of the triangular fragments along a chain of strontium cations. The hydrogen atoms are omitted; (d) the crystal packing of compound **IV** (projection onto the *ac* plane). The hydrogen atoms are omitted.

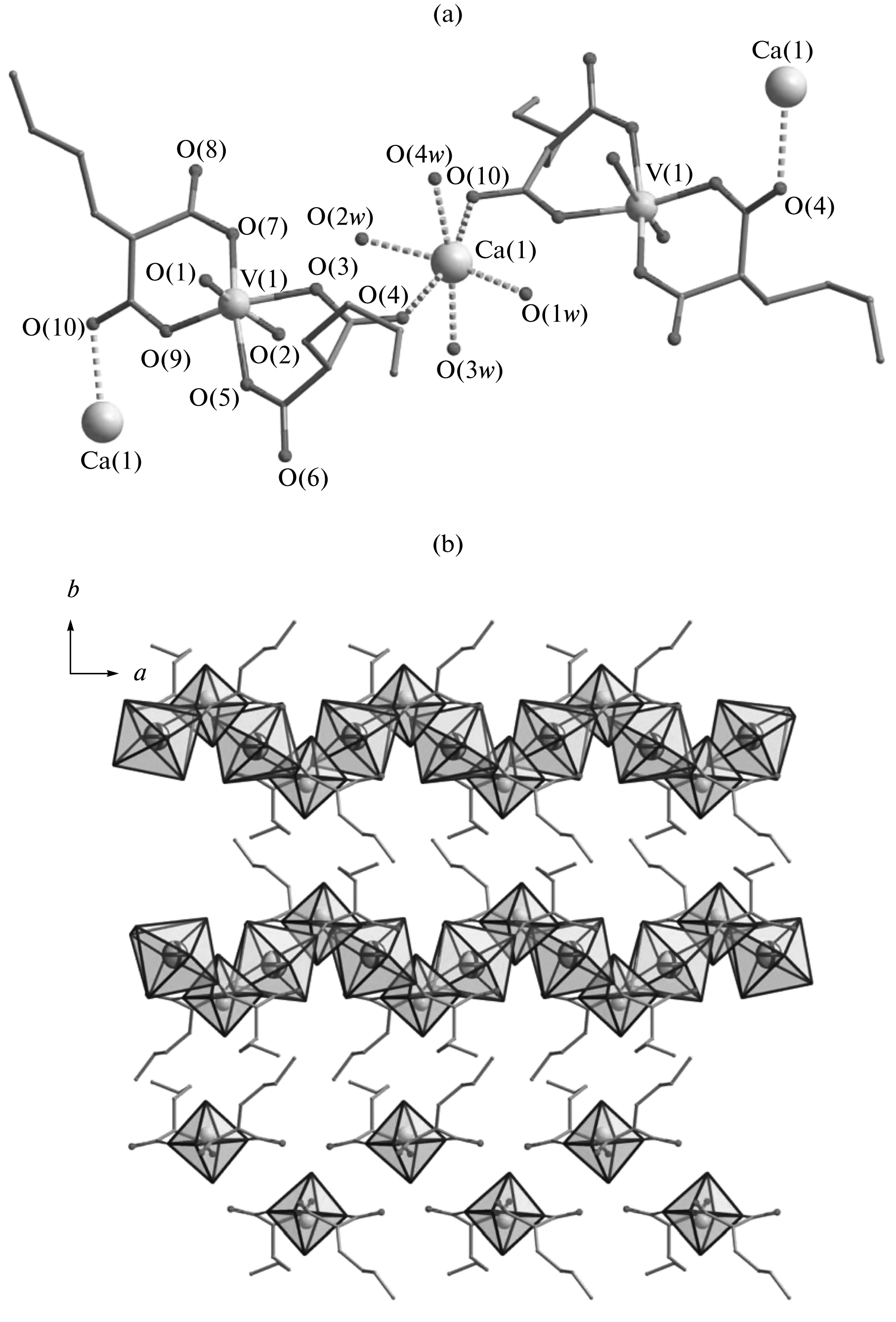

Fig. 5. Polymeric chain (a) and the crystal packing of compound **V** (b). The hydrogen atoms are omitted.

and Inorganic Chemistry of the Russian Academy of Sciences.

This work was supported by the Russian Foundation for Basic Research (project nos. 13-03-12430, 13-03-00682, 14-03-01116, and 14-03-31292), the Presidium of the Russian Academy of Sciences, and the Council on Grants at the President of the Russian Federation (grants MK-2917.2014.3 and NSh-4773.2014.3).

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Translated by D. Tolkachev