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3D Coordination polymers with vanadyl fragments and alkaline earth metal ions*

E. S. Bazhina,★ M. E. Nikiforova, G. G. Aleksandrov, V. V. Minin,
N. N. Efimov, A. A. Sidorov, V. M. Novotortsev, and I. L. Eremenko

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 954 1279. E-mail: sidorov@igic.ras.ru

The reactions of vanadyl sulfate $VOSO_4 \cdot 3H_2O$ with barium or strontium cyclopropane-1,1-dicarboxylate (MCpdc, M = Ba, Sr, $H_2Cpdc = C_3H_4(COOH)_2$) afforded the polymeric heterometallic complexes $\{[(H_2O)_8Ba_2(VO)_2(Cpdc)_4] \cdot 2H_2O\}_n$ (**1**) and $\{[(H_2O)_6Sr(VO)(Cpdc)_2]\}_n$ (**2**), respectively. These complexes differ in the binding mode of mononuclear vanadyl fragments with alkaline earth metal ions. Coordination polymers **1** and **2** were characterized by ESR spectroscopy.

Key words: oxovanadium(IV), heterometallic complexes, cyclopropane-1,1-dicarboxylic acid, X-ray diffraction analysis, ESR spectroscopy.

Complexes containing the oxovanadium fragment VO^{2+} have attracted great interest among researchers due to their unique properties. Many of these compounds serve as models of biological systems that are present in the organism or have biological activity (biological clusters, metalloporphyrins, heterovalent and heteronuclear compounds).[1—3] Numerous examples of oxovanadium(IV) coordination compounds exhibiting high catalytic activity were reported.[4—7] In addition, due to the presence of one unpaired electron on the metal center in VO^{2+} complexes ($S = 1/2$), these compounds are convenient magnetic blocks for the synthesis of magnetically active complex structures, as well as for investigation of the nature of spin-spin exchange interactions.[8—10] In this respect, polynuclear compounds, particularly compounds containing two different types of metals (for example, an atom of transition metal, vanadium, and a p-block main-group element ion linked by bridging organic ligands) hold the most promise. In the present study, the dianion of cyclopropane-1,1-dicarboxylic acid ($H_2Cpdc = C_3H_4(COOH)_2$) was used as the bridging anion. This acid is similar in properties, in particular, in the geometric characteristics, to dimethylmalonic acid, but, as we have shown earlier, it not always forms analogous compounds.[11] The use of substituted malonic acids is determined primarily by the fact that they can form stable six-membered rings upon coordination to a metal ion, and these rings, in turn, stabilize vanadyl ions. At the same time, due to the presence of four O atoms of two carboxy groups, these vanadyl-containing chelates can be bound to Ba or Sr ions due to their high affinity for oxygen atoms.

The aims of the present study were to synthesize new framework heterometallic polymeric oxovanadium(IV) complexes containing alkaline earth metal (barium or strontium) atoms linked by bridging cyclopropane-1,1-dicarboxylate anions and to study these complexes by X-ray diffraction and ESR spectroscopy.

Results and Discussion

The heterometallic polymeric complexes $\{[(H_2O)_8Ba_2(VO)_2(Cpdc)_4] \cdot 2H_2O\}_n$ (**1**) and $\{[(H_2O)_6Sr(VO)(Cpdc)_2]\}_n$ (**2**) crystallized from an aqueous solution prepared by mixing barium or strontium cyclopropane-1,1-dicarboxylate, respectively, with an aqueous solution of vanadyl sulfate. Compounds **1** and **2** are 3D coordination polymers. They are characterized by the presence of mononuclear bis-chelate metal fragments containing a vanadium(IV) atom in the coordination environment formed by four O atoms of two chelate cyclopropane-1,1-dicarboxylate dianions and one O atom of a water molecule. The sixth coordination site is occupied by the vanadyl O atom, resulting in a distorted octahedral environment of the V atom (Figs 1—4, Table 1).

It is convenient to consider the structure of polymer **1** as composed of 2D polymeric fragments (layers) linked to each other. The barium ions lie in these planes and form zigzag chains, in which the Ba(1), Ba(1) and Ba(2), Ba(2) atoms are linked together by two bridging O atoms of water molecules, whereas the Ba(1) and Ba(2) atoms are

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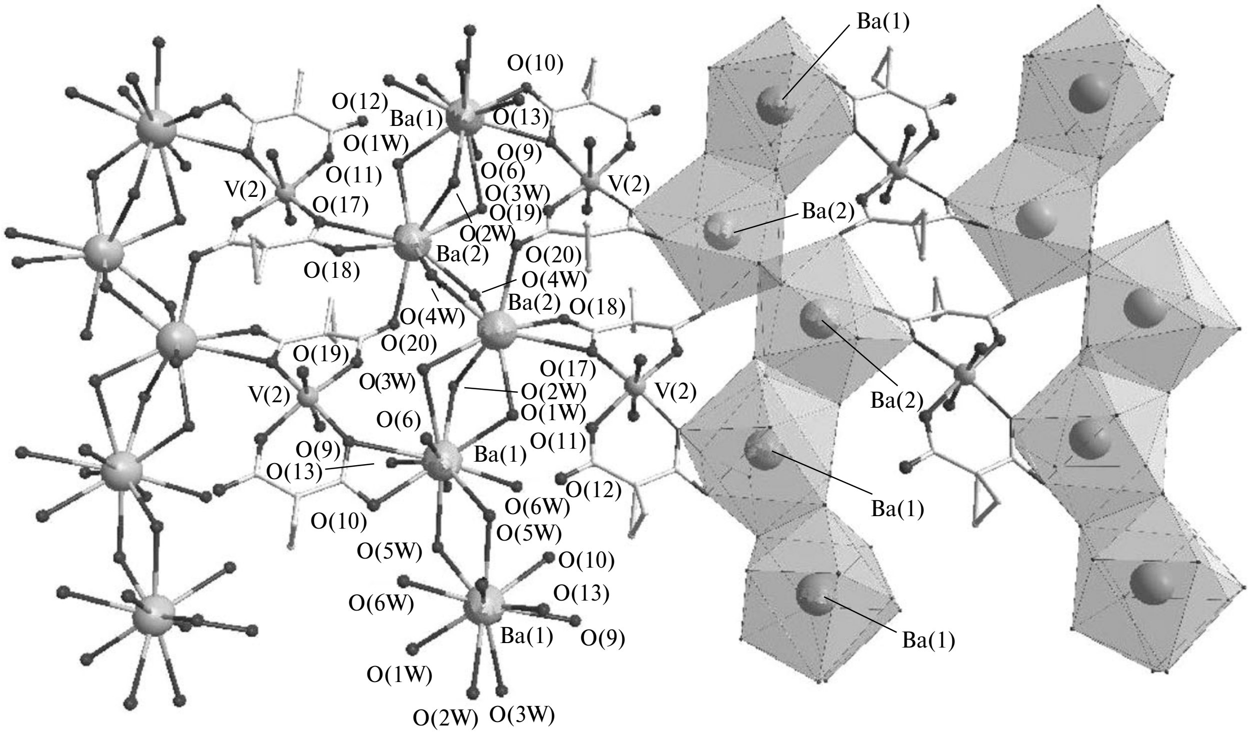

Fig. 1. Structure of the layer of 3D polymer **1** (hydrogen atoms are not shown).

triply bridged. The zigzag chains are linked to each other to form planes through the O atoms of the cyclopropane-1,1-dicarboxylate dianions of the bis-chelate vanadyl metal fragments. One of the cyclopropane-1,1-dicarboxylate anions has the η^2,μ_2-coordination mode and is involved in the binding of the vanadyl fragment to only one chain of barium ions, whereas another anion has the η^2,μ_3-coordination mode and links two adjacent chains of barium ions (see Fig. 1). The coordination environment of the Ba(1) atoms involves also monodentate water molecules.

Table 1. Selected geometric characteristics of compounds **1** and **2**

Parameter	**1** (M = Ba)	**2** (M = Sr)
Bond length	d/Å	
V(1)—O(1)	1.599(7)	1.596(4)
V(1)—O(2) (η^1-H_2O)	2.313(7)	2.320(4)
V(1)—O (Cpdc)	1.971(7)—2.007(7)	1.980(3)—2.007(3)
V...V	8.1504(2)—10.504(2)	7.135(3)—11.456(3)
M...M	4.5606(10)—4.5899(7)	4.3721(14)
M—O (η^1-H_2O)	2.783(7)—2.839(7)	2.657(3)—2.719(3)
M—O (μ_2-H_2O)	2.807(7)—2.929(7)	2.611(3)—2.727(3)
M—O (Cpdc)	2.710(7)—2.844(7)	2.488(3)—2.778(3)
Angle	ω/deg	
O(1)—V—O(2)	175.0(3)	179.41(16)

The 2D polymeric fragments of compound **1** are linked to each other by the carboxy O atoms of one cyclopropane-1,1-dicarboxylate dianion of the bis-chelate vanadyl fragment, which forms the four-membered chelate ring with the Ba atom. The carboxy group of another anion of the bis-chelate fragment forms the analogous chelate ring with the Ba atom lying in the adjacent plane (see Fig. 2).

Complex **2** can also be considered as layers linked together. The Sr atoms lying in these planes form zigzag chains and are linked to each other by two bridging O atoms of water molecules. The zigzag chains are linked together to form planes through O atoms of only one of the cyclopropane-1,1-dicarboxylate dianions of the bis-chelate vanadyl fragment. It should be noted that the cyclopropane-1,1-dicarboxylate anion involved in the binding of the V atoms and two Sr atoms of adjacent chains exhibits the η^2,μ_3-coordination mode. The coordination environment of the Sr atoms is completed by three monodentate water molecules (see Fig. 3).

Adjacent 2D polymeric fragments of compound **2** are linked together by the O atoms of both carboxy groups of only one of the cyclopropane-1,1-dicarboxylate dianions of the bis-chelate vanadyl fragment. Another carboxy dianion of each bis-chelate fragment of the polymer is not involved in the binding of the heteroatoms, exhibits the η^2-coordination mode, and forms a six-membered chelate ring with the V atom (see Fig. 4).

Both polymers are arranged in such a way that the V-containing mononuclear fragments are linked through

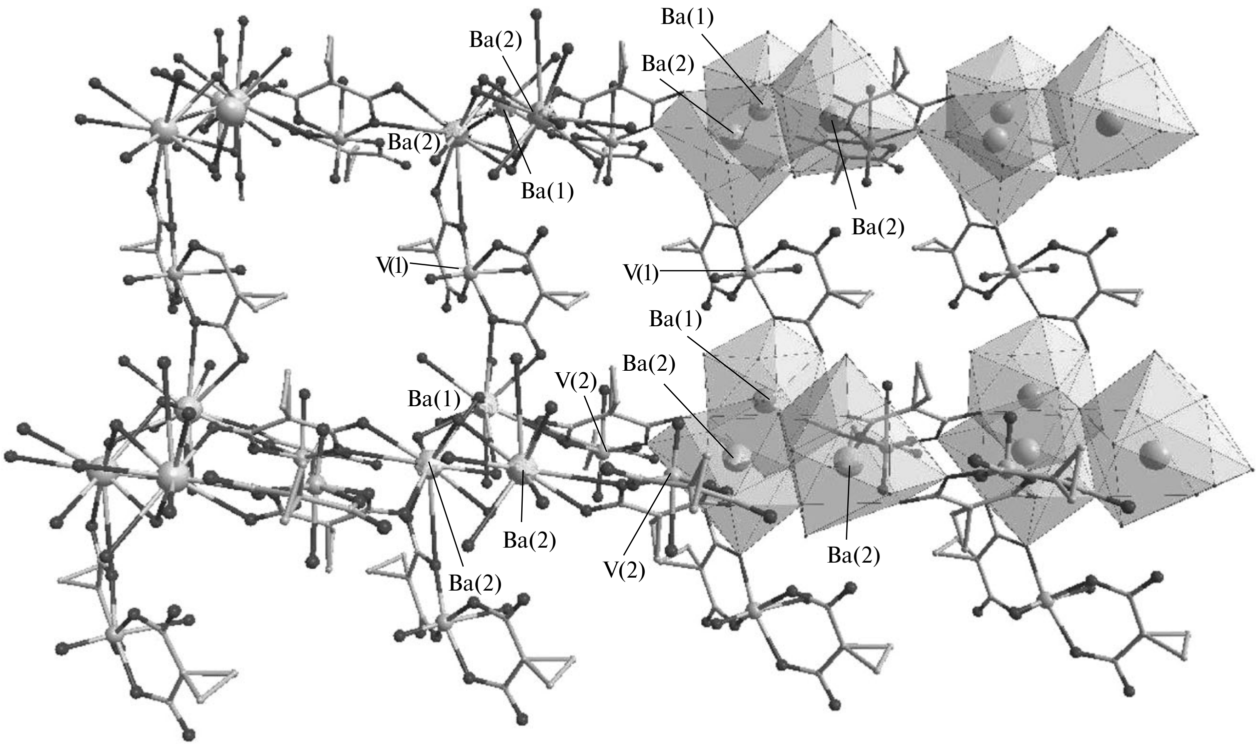

Fig. 2. Arrangement of the layers of compound **1** to form a framework structure (hydrogen atoms are not shown).

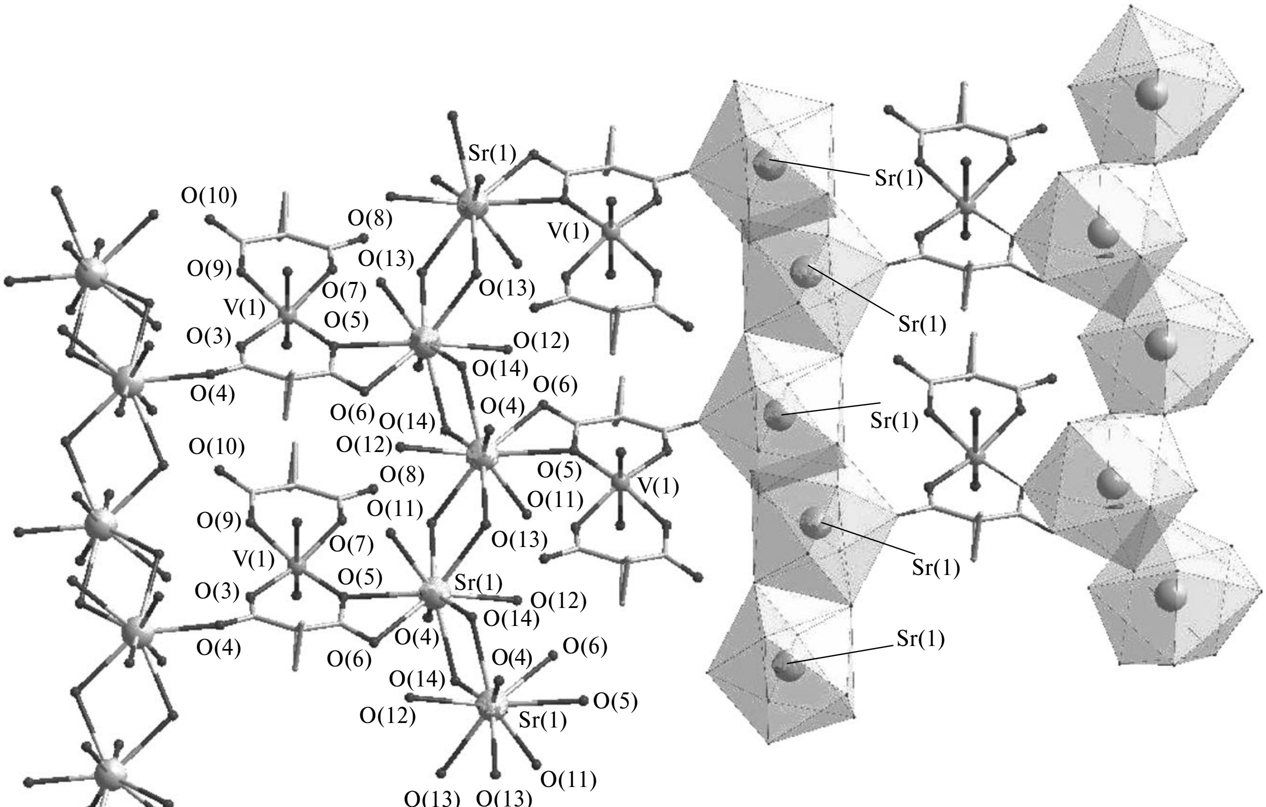

Fig. 3. Structure of the layer of 3D polymer **2** (hydrogen atoms are not shown).

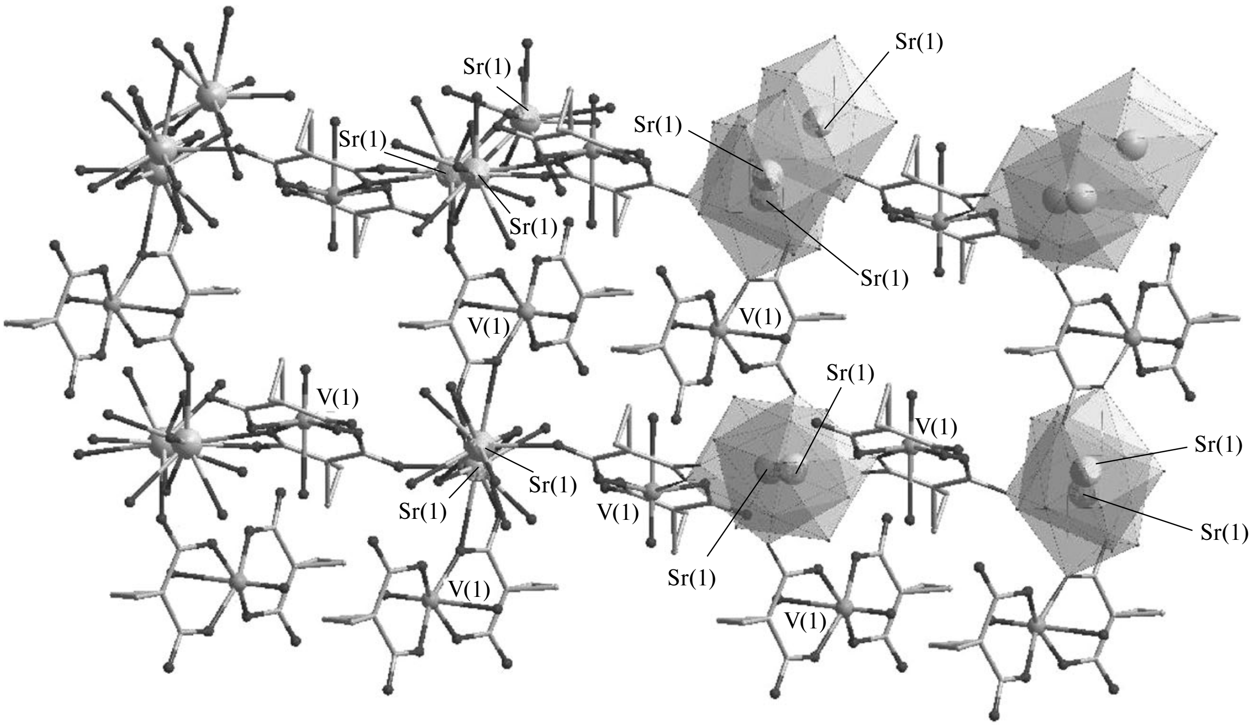

Fig. 4. Arrangement of the layers of compound **2** to form a framework structure (hydrogen atoms are not shown).

the alkaline earth metal atoms to form a framework structure, and the cyclopropane fragments of the dicarboxylate anions are buried inside small cavities (channels) in the framework. As a result, the crystal packings of the compounds synthesized in the present study differ in the way, in which the mononuclear vanadyl fragments are linked to each other through the alkaline earth metal ions. In compound **1**, the metal atoms are linked together through the O atoms of both carboxylate dianions of the bis-chelate vanadyl fragment, whereas the metal atoms in compound **2** are linked together through the O atoms of only one of the dianions. This is attributed to the fact that barium forms a larger number of bonds in the 3D polymeric structure, because its coordination number is 10, whereas the coordination number of strontium is 9.

Since both compounds contain "magnetic" vanadium(IV) atoms ($S = 1/2$), it was reasonable to study these compounds by ESR spectroscopy. The ESR spectrum of a polycrystalline sample of polymer **1** at room temperature (Fig. 5) shows a single broad line ($g = 1.995$, $\Delta H = 52.3$ mT) with a poorly resolved hyperfine structure (HFS). The second-derivative ESR spectrum displays HFS components from the magnetic interaction between the unpaired electron spin and the nuclear spin of vanadium ($I = 7/2$). A considerable width of the spectrum is apparently attributed to the intermolecular interaction and hindered vibrations of the metal atoms in the polycrystalline matrix. The ESR spectrum of polymer **2** (Fig. 6) is similar to that of polymer **1** ($g = 1.999$, $\Delta H = 58.0$ mT). The better resolution of HFS for **2** (the second-derivative spectrum) is apparently due to the smaller weight of the architectural motif containing lighter Sr atoms compared with barium-containing polymer **1**. The parameters of the spectra of compounds **1** and **2** remain virtually unchanged upon a decrease in the temperature. The g factors for both compounds are similar to those observed for mononuclear vanadium(IV) complexes.[12] The absence of low-temperature transitions characteristic of vanadium dimers, including the half-field transition (175 mT) corresponding to $\Delta m_S = \pm 2$,[13] is indicative of a very weak exchange interaction between V^{IV} atoms or its complete absence.

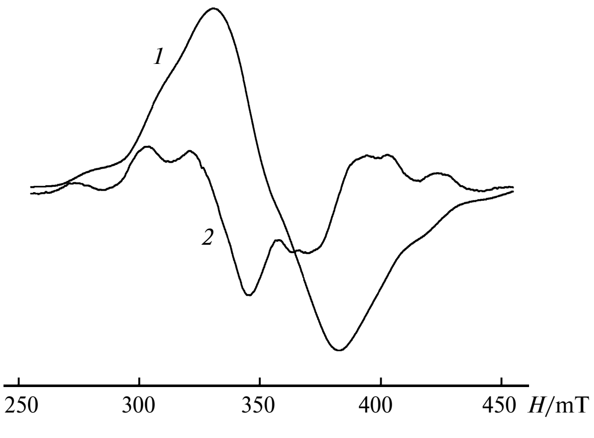

Fig. 5. ESR spectrum of a polycrystalline sample of compound **1** (*1*) and its second derivative (*2*) at $T = 293$ K.

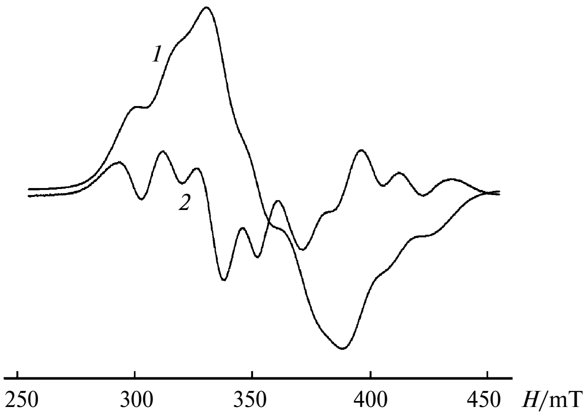

Fig. 6. ESR spectrum of a polycrystalline sample of compound **2** (*1*) and its second derivative (*2*) at $T = 293$ K.

To conclude, let us mention that the new magnetically active heteronuclear carboxylate coordination polymers $\{[(H_2O)_8Ba_2(VO)_2(Cpdc)_4]\cdot 2H_2O\}_n$ (**1**) and $\{[(H_2O)_6Sr(VO)(Cpdc)_2]\}_n$ (**2**) are rare examples of a combination of transition (vanadium(IV)) and main-group (Ba or Sr) metal ions having sharply different acidic properties. It should be noted that the nature of an alkaline earth metal introduced into such systems has no effect on the dimensionality of the resulting polymer but influences the structure and the crystal packing. Cyclopropane-1,1-dicarboxylic acid that is involved in compounds **1** and **2** as a bridge in different coordination modes proved to be a convenient ligand for the binding of metal atoms of different nature and the formation of stable compounds having an unusual crystal structure.

Experimental

The complexes were synthesized at room temperature in aqueous solutions in the presence of atmospheric oxygen with the use of $VOSO_4\cdot 3H_2O$ (analytical grade), $Ba(OH)_2\cdot 8H_2O$ (reagent grade), $Sr(OH)_2\cdot 8H_2O$ (Sigma Aldrich), and 1,1-cyclopropanedicarboxylic acid (Acros Organics). The attenuated total internal reflection (ATR) infrared spectra were recorded on a Thermo Nicolet NEXUS Fourier transform infrared spectrometer in the frequency range of 4000—400 cm^{-1}. The ESR spectra were measured on an ELEXSYS E-680X radiofrequency spectrometer (Bruker). The measurements were performed at $T = 293$ and 120 K. The elemental analysis was carried out on a Carlo Erba automated CHN analyzer.

X-ray diffraction study was performed on a Bruker APEX II diffractometer equipped with a CCD detector and a monochromated radiation source (Mo-Kα, $\lambda = 0.71073$ Å) with the use of the standard procedure.[14] For both complexes, semiempirical absorption corrections were applied.[15] The structures of the complexes were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were positioned geometrically and refined using a riding model. The calculations were carried out with the use of the SHELXS-97 and SHELXL-97 program packages.[16] The crystallographic parameters of the complexes are given in Table 2.

Poly[(η²,μ₃-cyclopropane-1,1-dicarboxylato-*O,O,O′,O″,O‴*)-tris(η²,μ₂-cyclopropane-1,1-dicarboxylato-*O,O,O′*,O″)penta-(μ₂-aqua)triaquadioxovanadium(IV)dibarium(II)] dihydrate (1). To a solution of cyclopropane-1,1-dicarboxylic acid (0.18 g, 1.38 mmol) in distilled water (25 mL), $Ba(OH)_2\cdot 8H_2O$ (0.436 g, 1.38 mmol) was added, and the reaction mixture was stirred at ~20 °C for 15—20 min. Then a solution of $VOSO_4\cdot 3H_2O$ (0.15 g, 0.69 mmol) in distilled water (10 mL) was added with vigorous stirring to the reaction mixture, and the stirring was continued for 15 min. The bright blue-violet solution and the white fine-crystalline precipitate of barium sulfate were kept at ~20 °C for ~5 h. Then the precipitate was filtered off using a blue ribbon paper filter, and the filtrate was kept at ~20 °C. After slow evaporation for several days, blue-violet crystals suitable for X-ray diffraction were obtained. The crystals were washed with ethanol and dried in air. The yield of compound **1** was 0.448 g (58.9% based on the initial amount of vanadium). Found (%): C, 22.62; H, 2.68. $C_{20}H_{32}Ba_2O_{26}V_2$ (without taking into account solvent water molecules). Calculated (%): C, 22.55; H, 3.03. IR (ATR), ν/cm^{-1}: 3380.38 m.b, 3238.28 m.b, 1658.97 w, 1641.58 w, 1554.86 v.s, 1390.43 v.s, 1235.95 m, 1207.20 m, 1082.08 w, 971.67 m, 955.30 m, 937.91 s, 869.04 m, 807.66 w, 754.94 m, 740.40 m, 584.10 w.

Poly[(η²,μ₃-cyclopropane-1,1-dicarboxylato-*O,O,O′,O″*,O‴)-(η²-cyclopropane-1,1′-dicarboxylato-*O,O″*)bis(μ₂-aqua)tetra-aquaoxovanadium(IV)strontium(II)] (2). To a solution of cyclopropane-1,1-dicarboxylic acid (0.18 g, 1.38 mmol) in distilled water (25 mL), $Sr(OH)_2\cdot 8H_2O$ (0.37 g, 1.38 mmol) was added. The reaction mixture was stirred at ~20 °C for 15—20 min. Then

Table 2. Crystallographic parameters for compounds **1** and **2**

Parameter	1	2
Molecular formula	$V_2C_{20}H_{36}Ba_2O_{28}$	$VC_{10}H_{18}SrO_{15}$
Molecular weight	1101.05	516.80
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P*2₁/c
a/Å	10.5040(5)	8.073(3)
b/Å	12.7797(6)	15.372(5)
c/Å	13.3883(6)	13.948(4)
α/deg	76.3133(6)	90
β/deg	83.8683(6)	101.075(6)
γ/deg	85.5495(7)	90
V/Å	1733.62	1698.8(9)
Z	2	4
ρ_{calc}/g cm^{-3}	2.109	2.021
μ/cm^{-3}	2.87	3.77
Scan range, θ_{min}—θ_{max}/deg	1.6—27.5	2.0—29.0
Number of measured reflections	16568	13867
Number of reflections with $I > 2\sigma(I)$	6920	3715
R_1 ($I > 2\sigma(I)$)	0.060	0.05
wR_2 ($I > 2\sigma(I)$)	0.198	0.144
$T_{min/max}$	0.451/0.782	0.369/0.660

a solution of $VOSO_4 \cdot 3H_2O$ (0.15 g, 0.69 mmol) in distilled water (10 mL) was added with vigorous stirring to the reaction mixture, and the stirring was continued for 15 min. The bright blue solution and the white fine-crystalline precipitate of strontium sulfate were kept at ~20 °C for ~5 h. Then the precipitate was filtered off using a blue ribbon paper filter, and the filtrate was kept at ~20 °C. After slow evaporation for several days, blue crystals suitable for X-ray diffraction were obtained. The crystals were washed with ethanol and dried in air. The yield of compound **2** was 0.198 g (55.4% based on the initial amount of vanadium). Found (%): C, 23.53; H, 3.74. $C_{10}H_{18}O_{15}SrV$. Calculated (%): C, 23.24; H, 3.51. IR (ATR), ν/cm^{-1}: 3396.13 m.b, 3105.43 m.b, 1639.07 w, 1562.64 v.s, 1394.75 v.s, 1380.77 v.s, 1237.05 m, 1213.05 m, 1095.16 w, 1056.54 w, 1012.71 w, 985.71 m, 967.62 s, 945.84 m, 933.56 m, 866.03 m, 809.92 w, 793.01 m, 744.80 m, 586.30 w.

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