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STRUCTURAL CHARACTERIZATION OF A NEW DECAVANADATE COMPOUND WITH ORGANIC MOLECULES AND INORGANIC IONS

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A new decavanadate compound $V_{10}O_{28}[Co(H_2O)_6]_3(C_8H_{18}O_6N_2S_2)_2$ (**I**) is synthesized and characterized by single crystal X-ray diffraction, thermogravimetric analysis, FT—IR spectroscopy, and scanning electron microscopy. The sizes of the monoclinic unit cell are as follows: $a = 13.2851(16)$ Å, $b = 22.769(3)$ Å, $c = 13.1883(16)$ Å, $\beta = 117.555(2)°$, $V = 3536.7(7)$ Å^3, $C2/m$ space group, $Z = 2$. The studies revealed that different moieties in the compound show a three-dimensional framework structure, in which $\{CoO_6\}$, the decavandate cluster anions, and 1,4-piperazinediethanesulfonic acid (PIPES) interact with each other by intermolecular forces and strong hydrogen bonding. Bond valence calculations were used to calculate the valence states of the atoms.

Keywords: decavanadate cluster, three-dimensional array, crystal structure, single crystal X-ray analysis, metal-organic compounds.

INTRODUCTION

Vanadium cluster anions have been extensively studied for their potential effects [1], such as the electronic property [2], catalysis [3, 4], and biochemical function [5, 6]. Depending on the pH value and vanadium concentration, the aqueous solutions containing vanadium (V) will give rise to a large family of vanadium cluster anions, including monomers (H_2VO^{4-}, HVO_4^{2-}), dimers ($H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$), tetramer ($V_4O_{12}^{4-}$), pentamer ($V_5O_{15}^{5-}$), and decamer ($V_{10}O_{28}^{6-}$). Generally two kinds of chemical interaction have been employed between cations and cluster anions to assemble coordination compounds, one of which is the cluster anions acting as the bridging ligand coordinated to ions [7] and another is bonding through the ionic interaction [8, 9]. The predictable self-organization of molecules into one-two or three-dimensional frameworks is of great importance in crystal.

Polyoxometalates (POMs) have been investigated as compounds of pharmaceutical interest [10, 11], namely as antiviral [12] and anticancer [13] agents, and biological action [14]. Among these, vanadate oligomers have also been studied during the past decades in the biological area, namely, their interactions with peptides [15] and interaction with the action [16]. Therefore, the study of vanadium polyoxovanadates containing organic molecules is important, particularly the role of organic cations in the structure is of interest and how the organic moiety and decavanadate units interact.

Herein, a new decavanadate compound $V_{10}O_{28}[Co(H_2O)_6]_3(C_8H_{18}O_6N_2S_2)_2$ (**I**) has been synthesized. We focused our intention on the study of a decavanadate compound with inorganic ions and organic molecules, especially sulfonate that is rarely involved. The interaction of each moiety, the three-dimensional (3D) ordered structure, the surface morphology and thermal decomposition behaviors have subsequently been discussed in detail.

EXPERIMENTAL

Materials and methods. All chemicals used were purchased of analytical reagent grade and used directly without further purification. The IR spectrum was performed on an Alpha Centaurt FT—IR spectrometer in the region of 4000—400 cm^{-1} with KBr pellets. The thermogravimetric (TG) analysis was performed on a STA 409 PG/PC TG analyzer in the temperature range 30—550 °C with a heating rate of 10 °C/min under the air atmosphere. The surface morphologies were taken on a JSM-35CF scanning electron microscopy (SEM) and an Olympu-B060F5 microscope respectively.

Synthesis of $V_{10}O_{28}[Co(H_2O)_6]_3(C_8H_{18}O_6N_2S_2)_2$ (I). A mixture of $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), ammonium metavanadate (0.117 g, 1 mmol), 1,4-piperazinediethanesulfonic acid (PIPES) (0.604 g, 2 mmol), and 14.0 ml CH_3OH/H_2O (*v*/*v*, 1:1) was stirred for 30 min, the pH value was adjusted to 6.0 with NaOH (1 mol/l). Then it was stirred continuously for 60 min and the undissolved substance was filtered. The filtrate was kept at room temperature for slow evaporation until yellow crystals were separated from the solution after 20 days.

Single crystal X-ray diffraction analysis. A yellow rhombic crystal of compound **I** was selected to take crystal structure analyses. Crystal data were collected at room temperature (298 K) with a Bruker *SMART CCD* detector using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) in the φ and ω scan modes. A total of 6182 reflections ($4.88 \le 2\theta \le 55°$) were collected with 3565 unique ones, out of which 3191 reflections with $I > 2\sigma(I)$ were used for the structural elucidation. The structures were solved by direct methods using the SHELXS-97 program [17] and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques using the SHELXL-97 crystallographic software package [18]. The crystallographic data of **I** are given in Table 1, and the selected bond lengths and angles are in Table 2. Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC), CCDC No. 784510 for **I** (X-ray crystallographic files for compound **I** in CIF format). Copies of this data may be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail for inquiry: deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk).

Table 1

Crystal data and structure refinement for complex **I**

Chemical formula	$C_{16}H_{72}Co_3N_4O_{58}S_4V_{10}$
T, K	298
λ, Å	0.71073
Formula weight	2063.21
Crystal size, mm	0.16×0.12×0.10
Temperature, °C	298(2)
Crystal system	Monoclinic
Space group	*C*2/*m*
a, *b*, *c*, Å	13.2851(16), 22.769(3), 13.1883(16)
α, β, γ, deg.	90.00, 117.555(2), 90.00
Volume, $Å^3$	3536.7(7)
Z	2
F(000)	2070
μ, mm^{-1}	2.169
θ range for data collection, deg.	$4.88 \le 2\theta \le 55$
The number of reflections with $I > 2\sigma(I)$	3565
Data / restraints / parameters	3565 / 13 / 245
R-factor, $I > 2\sigma(I)$	$R_1 = 0.0459$, $wR_2 = 0.1260$
R-factor (all data)	$R_1 = 0.0492$, $wR_2 = 0.1284$
Largest diff. peak and hole, $e \cdot Å^{-3}$	1.723 and –0.623

Table 2

Selected bond distances (Å) *and angles* (deg.) *for complex* **I**

Co1(4h)—O2W(8j)^{i}	2.061(3)	Co2—O4W^{ii}	2.082(3)	V2—O7(8j)	1.842(2)
Co1—O2W	2.061(3)	Co2—O4W	2.082(3)	V2—O1^{v}	1.9919(18)
Co1—O1W(8j)	2.096(3)	V1(4i)—O2(8j)	1.688(2)	V2—O3	2.2492(6)
Co1—O1W^{i}	2.096(3)	V1—O2^{iii}	1.688(2)	V3(8j)—O9(8j)	1.597(2)
Co1—O3W(8j)	2.117(3)	V1—O4(4i)	1.924(3)	V3—O8(4g)	1.8357(17)
Co1—O3W^{i}	2.117(3)	V1—O1(4i)	1.935(3)	V3—O7	1.848(2)
Co2(2d)—O5W(4i)^{ii}	2.065(5)	V1—O3(4g)^{v}	2.1179(18)	V3—O6^{vi}	1.910(2)
Co2—O5W	2.065(5)	V1—O3	2.1180(18)	V3—O2(8j)	2.059(2)
Co2—O4W(8j)^{iii}	2.082(3)	V2(8j)—O5(8j)	1.600(2)	V3—O3	2.307(2)
Co2—O4W^{iv}	2.082(3)	V2—O6(8j)	1.821(2)		
O2W^{i}—Co1(4h)—O2W	91.63(19)	O2W^{i}—Co1—O3W	172.63(11)	O8—V3—V3^{vi}	33.57(8)
O2W^{i}—Co1—O1W	86.18(12)	O2W—Co1—O3W	91.32(12)	O7—V3—V3^{vi}	86.01(7)
O2W—Co1—O1W	93.69(13)	O6^{vi}—V3—O3	77.26(6)	O6^{vi}—V3—V3^{vi}	82.74(7)
O2W^{i}—Co1—O1W^{i}	93.69(13)	O2—V3—O3	74.68(8)	O2—V3—V3^{vi}	123.12(6)
O2W—Co1—O1W^{i}	86.18(12)	O9—V3—V3^{vi}	136.95(9)	O3—V3—V3^{vi}	48.48(5)
O1W—Co1—O1W^{i}	179.81(17)				

i) $-x, y, 1-z$; (ii) $1-x, -y, 1-z$; (iii) $x, -y, z$; (iv) $1-x, y, 1-z$; (v) $-x, -y, -z$; (vi) $-x, y, -z$; (vii) $0.5-x, 0.5-y, -z$.

RESULTS AND DISCUSSION

Structure description. Fig. 1 shows the molecular structure and labeling scheme for $V_{10}O_{28}[Co(H_2O)_6]_3(C_8H_{18}O_6N_2S_2)_2$ (ellipsoid probability 50 %). Each cobalt(II) is six-coordinated by six oxygen atoms from six water molecules. The Co1—O bond lengths are 2.061 Å, 2.096 Å, and 2.117 Å. The Co2—O bond lengths are 2.082 Å and 2.065 Å respectively, which are similar to those

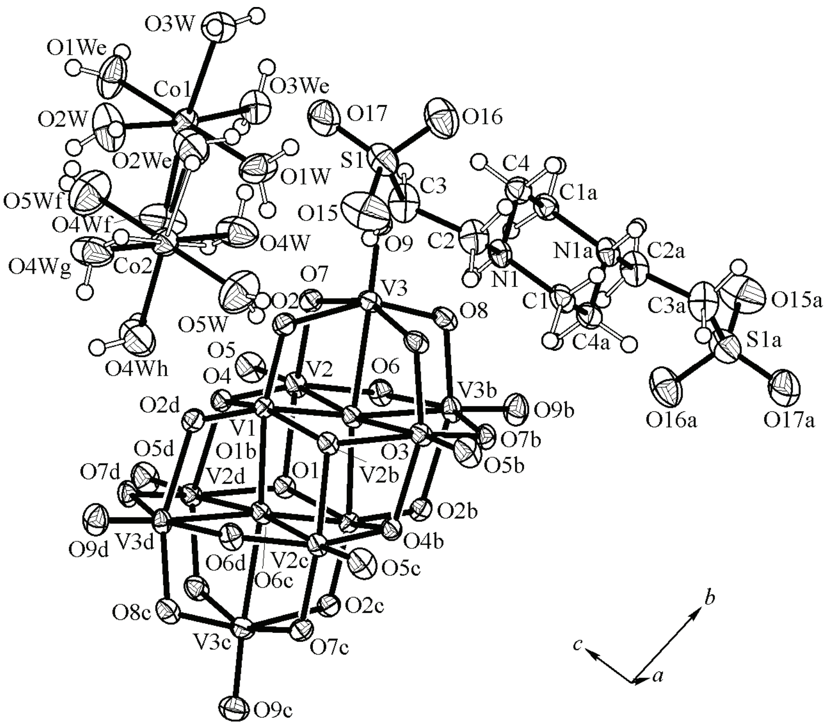

Fig. 1. Molecular structure and labeling scheme for compound **I**. Ellipsoid probability 50 %

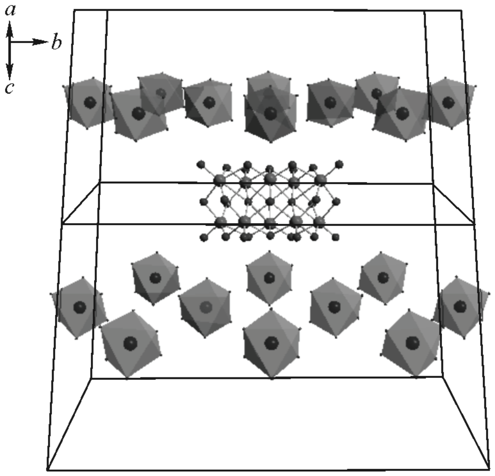

Fig. 2. View of the 2D layer structure of **I**

established for the $Co^{II}O_6$ [19, 20]. The two bonds parallel to *bc* are in the length of 2.082 Å. The bond lengths and angles indicate that the $\{CoO_6\}$ distorted octahedron is nearly a regular one. Compound **I** contains layers composed of 2D arrays of Co—O octahedra. Decavanadate cluster ions occupy inter-layer regions (Fig. 2). The bond distances of the decavanadate cluster are quite similar to the reported ones [21, 22], namely [V1—O2 1.688(2) Å, V1—O3 2.1180(18) Å, V2—O7 1.842(2) Å, V3—O3 2.307(2) Å, and V3—O8 1.8357(17) Å; Table 2]. The oxygen atoms on the cap were hydrogen bonded to water molecules and PIPES to afford a layered structure. There are three types of hydrogen bonds in this structure. The PIPES moieties are connected to the decavanadate cluster through N—H···O hydrogen bonds. The N1—H···O6 distance and the N1—H···O6 angle is 2.671 Å and 164° respectively. The water molecules are connected to the decavanadate cluster through O—H···O hydrogen bonds. The O1W···O7 distance and the O1W—H···O7 angle is 2.791 Å and 166° respectively. There are also strong hydrogen bonds between PIPES and water molecules. The acceptor in such O—H···O hydrogen bonds is the oxygen atom from the sulfonic group (O15, O16, O17), while the donor is the oxygen atom from a water molecule (Table 3). Two disordered water molecules are kept in the $[V_{10}O_{28}]^{6-}$ cluster, with a potential volume of 442.5 Å^3. The cluster anion, $\{CoO_6\}$, and PIPES show a 3D array in which the three moieties interact with each other via the van der Waals force and strong hydrogen bonding.

In order to evaluate the possibility of the protonation of sites in the decavanadate anion, we found the valence-deficiency for the O atoms in $[V_{10}O_{28}]^{6-}$. We used the function $s = (R/1.791)^{-5.1}$ supported by the bond valence model (BV model) [23], where R is the bond length and s is the bond valence. The valence sum rule is one of the basic assumptions of the BV model: $\sum s = V_i$, where V_i is the atomic valence of the atom under consideration. For all the oxygen atoms in $[V_{10}O_{28}]^{6-}$ the calculated $\sum s$ values are between 1.76 and 2.02. The exceptions are O6 (1.639076) and O7 (1.718913) that are connected with PIPES and $\{CoO_6\}$ with the hydrogen bond. It seems to be that the doubly and triply bonded oxygen atoms are expected to be more favorable for protonation, and therefore are easy to form hydrogen bonds to build a 3D array in the structure. The $\sum s$ values were also obtained for the vanadium atoms, which confirmed the oxidation state +5 with a slight deviation for all of them (the data included in Table 4).

Table 3

Selected hydrogen bond lengths and angles

D—H···A	D—H, Å	H···A, Å	D···A, Å	D—H···A, deg.
N1(8j)—H1AA(8j)—O6 I	0.85	1.84	2.671	164
O1W—H1WA(8j)—O7	0.82	1.99	2.791	166
O1W—HIWB(8j)—O16 II	0.81	2.16	2.954	167
O2W—H2WB(8j)—O15(8j) III	0.82	2.03	2.802	156
O3W—H3WB(8j)—O16 (8j) III	0.81	1.92	2.711	165
O3W—H3WA(8j)—O17(8j) II	0.82	1.95	2.746	164
O4W(8j)—H4WB—O17 III	0.83	1.84	2.658	169

Symmetry codes: I –*x*, *y*, –*z*; II: –1/2+*x*, 1/2–*y*, *z*; III: 1/2+*x*, 1/2–*y*, *z*.

Table 4

Bond valence calculations of the decavanadate anions

Atom	∑s	Atom	∑s	Atom	∑s	Atom	∑s
O1	1.837	O4	1.814	O7	1.719	V1	4.924
O2	1.844	O5	1.777	O8	1.764	V2	5.017
O3	2.026	O6	1.639	O9	1.794	V3	5.015

Spectral analysis. Fig. 3 shows the IR spectrum of compound **1**. The terminal V=O stretching bands are displayed within 1000—930 cm^{-1} [9]. The asymmetric and symmetric vibrations of the bridging V—O—V fragments appeared in the ranges 850—730 cm^{-1} and 600—450 cm^{-1} respectively [22]. A strong bond at 3368.13 cm^{-1} is attributed to water molecules that are in unprotonated states. The bonds at 1184.61 cm^{-1} and 1047.52 cm^{-1} can be assigned to asymmetric stretching bands of the sulfonic group in PIPES.

Thermal analysis. The thermal decomposition behavior of compound **I** in its solid state was assessed by the TG analysis. The TG curve of **I** can be divided into three stages (Fig. 4). It suggests that the first weight loss of 11.83 % (calc. 11.81 %) in the temperature range 66—150 °C is associated with the loss of coordinated water molecules that come from $Co(H_2O)_6^{2+}$. The second stage in the temperature range 150—500 °C with the cumulative weight loss of 29.77 % (calc. 29.06 %) corresponds to the loss of two disordered water molecules and two PIPES. At the last stage in the temperature range 500—600 °C, the weight loss of 2.33 % (calc. 2.25 %) is attributed to the framework decomposition of the polyanion. The final products are Co_2O_3 and V_2O_5 with a total weight loss of 43.13 %, similar to calculated 43.86 %.

Hence, we have obtained and structurally characterized the new decavanadate compound with the composition $V_{10}O_{28}[CO(H_2O)_6]_3(C_8H_{18}O_6N_2S_2)_2$ (**I**). Three types of hydrogen bonds lead to the formation of the decavanadate compound with a 3D network structure. The research may be helpful to further study the interaction between the organic moiety and decavanadate units in the biological function. The TG analysis indicates the proper thermal stability of the compound.

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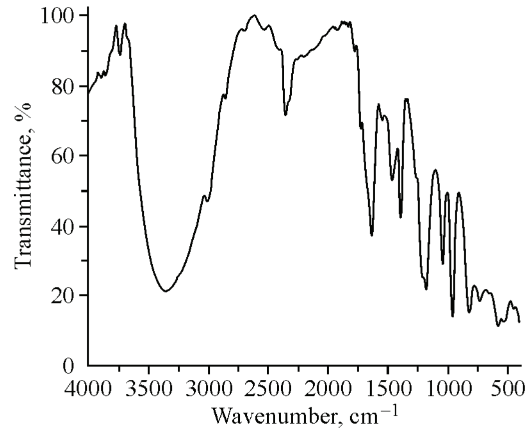

Fig. 3. IR spectrum of compound **I**

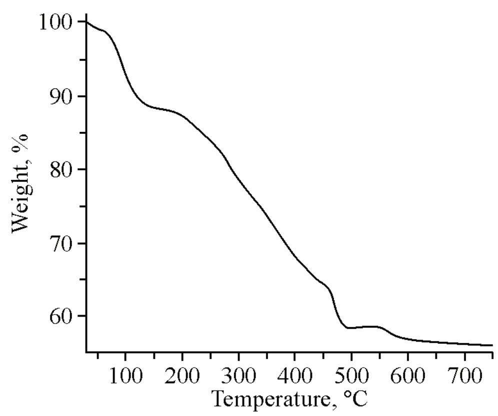

Fig. 4. TG curve of compound **I**

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