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# Hexaaquachromium(III) Trihydrogen Isopolyvanadate $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$: Synthesis and Study

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**Abstract**—Hexaaquachromium(III) trihydrogen isopolyvanadate $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$ (**I**) was obtained and examined by mass spectrometry, X-ray powder diffraction, thermogravimetry, and IR and NMR spectroscopy. The crystals are monoclinic, space group $P\bar{1}$, $a = 7.862(3)$, $b = 8.427(5)$, $c = 5.000(2)$ Å, $\beta = 96.46(4)°$, $V = 867.0(3)$ Å$^3$, $\rho_{calcd} = 5.83$ g/cm$^3$, $Z = 1$.

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## INTRODUCTION

Heteropoly compounds constitute an unusual class of coordination compounds with unique structures and various properties that are of theoretical interest [1, 2]. They are currently in wide use as catalysts. For instance, chromium and iron vanadates are employed as components of a catalyst for oxidation of alcohols into aldehydes. The properties and use of vanadates to catalyze the oxidation of methane are described in [3, 4].

Nickel hydrogen oxovanadate and sodium hydrogen oxovanadate have been obtained and examined in [5–7].

This work was devoted to the synthesis and physicochemical study of hexaaquachromium(III) trihydrogen isopolyvanadate of the formula $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$ (**I**).

## EXPERIMENTAL

**Synthesis of complex I.** A hot solution of chromium acetate and ammonium persulfate were added to a hot solution of ammonium metavanadate acidified to pH 3 with $HNO_3$. The reaction mixture was evaporated on a water bath to half of its initial volume. The resulting solution was filtered and cooled in a desiccator over alkali. After a week, the yellow crystals of complex **I** that formed were filtered off and washed with distilled water and ethanol.

The chemical formula of complex **I** was identified by mass spectrometry; the presence of crystallization water was determined by thermogravimetry.

For $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$

anal. calcd., %: Cr, 4.50; V, 44.05; O, 38.74; $H_2O$, 12.45.

Found, %: Cr, 4.94; V, 43.85; O, 38.81; $H_2O$, 12.28.

**X-ray powder diffraction study** was carried out on an EMMA diffractometer ($CuK_\alpha$ radiation, $2\theta = 6°–77°$, scan step 0.01°) at room temperature.

A $^{51}V$ NMR spectrum was recorded on an ECX-400 spectrometer (105.15 MHz; JEOL). The chemical shifts are referenced to $VOCl_3$.

IR spectra were recorded on a Perkin–Elmer spectrophotometer in the 200–4000 cm$^{-1}$ range (KBr pellets).

Thermogravimetric analysis of complex **I** was carried out on a Paulik–Paulik–Erdey instrument (sample weight 100 mg, temperature range 20–1000°C, heating rate 10°C/min). Calcined alumina was used as a standard.

## RESULTS AND DISCUSSION

To verify the purity and individuality of complex **I** and collect relevant crystallographic data, we performed X-ray powder diffraction. According to the data obtained (table), the crystals of complex **I** are monoclinic. The unit cell parameters are $a = 7.862(3)$, $b = 8.427(5)$, $c = 5.000(2)$ Å, $\beta = 96.46(4)°$, $V = 867.0(3)$ Å$^3$. The picnometric density determined using the Syromyatnikov method [7] is $\rho_{calcd} = 5.83$ g/cm$^3$. The number of formula units is $Z = 1$.

The poly anion $[V_{10}O_{28}]^{6-}$ in complex **I** is isostructural to that in cobalt isopolyvanadate [7]. The crystal unit cell consists of ten distorted $VO_6$ octahedra sharing common edges. The outer-sphere $Cr^{3+}$ cation is

X-ray powder diffraction data for $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$

| No. of the peak | 2θ, deg | *d*, Å | *I*, % | *h* | *k* | *l* |
|---|---|---|---|---|---|---|
| 1 | 11.29 | 7.81 | 100 | 1 | 0 | 0 |
| 2 | 15.44 | 5.72 | 38 | 1 | 1 | 0 |
| 3 | 17.81 | 4.96 | 7 | 0 | 0 | 1 |
| 4 | 22.75 | 3.90 | 9 | 2 | 0 | 0 |
| 5 | 25.09 | 3.54 | 21 | 2 | 1 | 0 |
| 6 | 27.38 | 3.25 | 14 | 2 | 0 | −1 |
| 7 | 27.74 | 3.21 | 42 | 0 | 2 | 1 |
| 8 | 30.64 | 2.91 | 10 | 2 | 0 | 1 |
| 9 | 30.82 | 2.89 | 18 | 1 | 2 | 1 |
| 10 | 31.19 | 2.86 | 13 | 2 | 2 | 0 |
| 11 | 36.14 | 2.48 | 6 | 0 | 0 | 2 |
| 12 | 40.78 | 2.21 | 12 | 2 | 0 | −2 |
| 13 | 44.75 | 2.02 | 16 | 2 | 3 | 1 |
| 14 | 57.43 | 1.60 | 6 | 4 | 3 | 0 |

surrounded by six water molecules making up a distorted octahedron. The isopoly anion and the cation are linked by electrostatic attraction between the latter and the terminal O atoms of the isopoly anion $[V_{10}O_{28}]^{6-}$.

Structure **I** was examined by $^{51}V$ NMR spectroscopy. There are definite relationships between the parameters of a $^{51}V$ NMR spectrum (such as chemical shift and shift anisotropy) and the local (coordination) environment of the vanadium nucleus [7].

The decavanadate anion is found only for $V^{5+}$; its structure depends on the charge and size of the anion. In solution, this poly anion is stable in acidic media (at and below pH 6). This becomes evident when comparing the IR and $^{51}V$ NMR spectra of complex **I** in the solid state and in aqueous solution. The decavanadate anion can be represented as two isopoly anions $M_6O_{19}$ partially thrust into each other. The isopoly anion contains three types of vanadium atoms (Fig. 1). Four atoms (V(2), V(5), V(2*), and V(5*)) make the vertices of the isopoly anion, with two atoms above and two atoms below (in the plane *xy*) the median plane *xz* passing through six other vanadium atoms. Four of them (V(3), V(4), V(3*), and V(4*)) are peripheral and make the vertices of the poly anion, while the V(1) and V(1*) atoms lie in its central part. Note that the latter two atoms are more strongly shielded and have no terminal O atoms.

The $^{51}V$ NMR spectrum of the complex isopolyvanadate anion shows three singlets at δ ($^{51}V$) −424.16, −500.62, and −516.05 with a signal intensity ratio of 1 : 2 : 2 (Fig. 2), also revealing three structurally nonequivalent types of vanadium atoms. These data fully agree with the literature data [8, 9].

The bands in the IR spectrum of complex **I** (Fig. 3) can be assigned by comparing it with the spectra of structurally similar isopoly compounds studied in [6–10]. An intense doublet at 982.7 and 954.0 $cm^{-1}$ is due to the vibrations of the shortest terminal V=O double bonds (on average, 1.61 Å). The symmetrical ($\nu_s$) and antisymmetrical stretching vibrations ($\nu_{as}$) of the bridging V–O–V bonds (on average, 1.88 Å) are manifested as a triplet at 837.2, 807.0, and 745.6 $cm^{-1}$, respectively. Two O atoms in the isopoly anion obtained are both coordinated to six V atoms (on average, 2.22 Å). Four O atoms form a $\mu_3$-bridge V–O'$^V$–V (on average, 1.97 Å). The corresponding medium-intensity bands in the IR spectrum appear at 524.7–467.8 $cm^{-1}$. Weak bands at 423.9–408.7 $cm^{-1}$ can be assigned to the bending vibrations of the bridging metal–oxygen bonds.

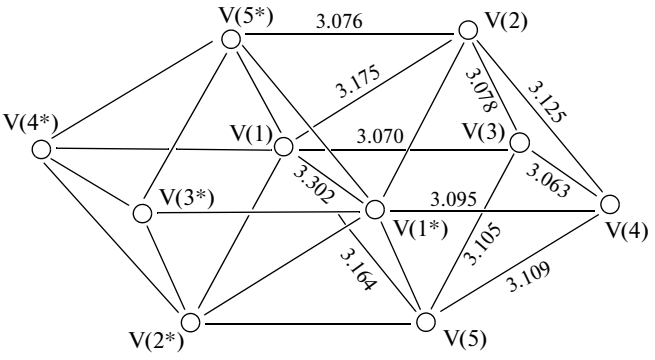


**Fig. 1.** Arrangement of the V atoms in the poly anion $[V_{10}O_{28}]^{6-}$

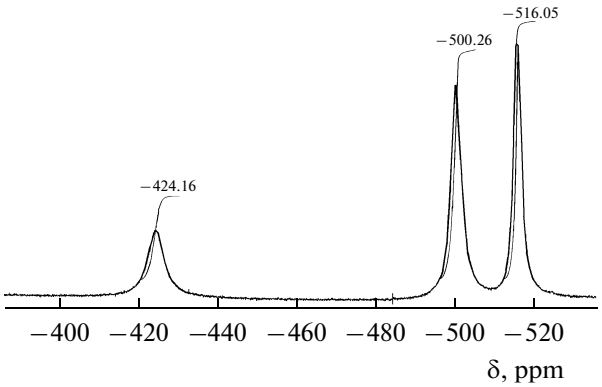


**Fig. 2.** $^{51}V$ NMR spectrum of $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$ in aqueous solution.

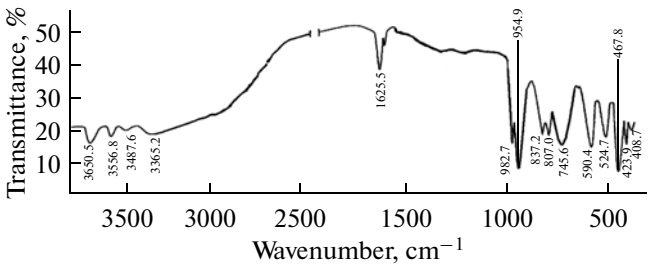


**Fig. 3.** IR spectrum of $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$.

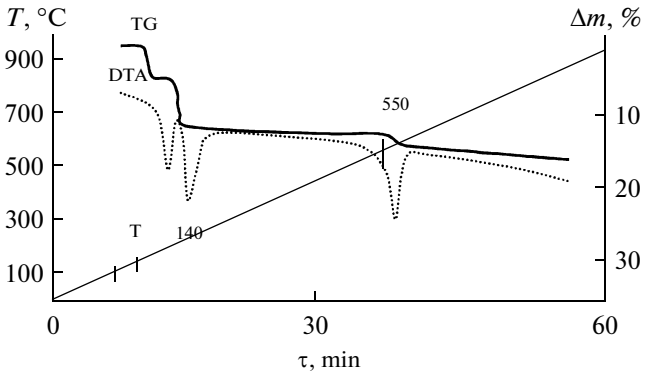


**Fig. 4.** TG and DTA curves of $[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$.

The fact that the IR spectrum of complex **I** is identical with those of the previously examined isopoly compounds confirms their structural similarity.

A thermogravimetric study of complex **I** revealed three endothermic transitions (Fig. 4). The first DTA peak (120°C) is due to elimination of two water molecules; the second DTA peak (140°C) is due to elimination of 7.5 water molecules and to the decomposition of the complex into a mixture of oxides. The third DTA peak involving no weight loss (550°C) corresponds to the melting of this mixture.

The thermolysis of complex **I** can schematically be represented as follows:

$$[Cr(H_2O)_6]H_3[V_{10}O_{28}] \cdot 2H_2O$$
$$\xrightarrow[-2H_2O]{120^\circ C} [Cr(H_2O)_6]H_3[V_{10}O_{28}]$$
$$\xrightarrow[-7.5H_2O]{140^\circ C} 1/2Cr_2O_3 \cdot 5V_2O_5 \xrightarrow[\text{Melting}]{550^\circ C}.$$

This thermolysis pattern was confirmed by IR spectroscopy and X-ray powder diffraction for both complex **I** and the thermolysis products.

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