

Acid Nickel Oxovanadate $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$: Synthesis, IR spectra, Thermal Analysis, and Crystal Structure

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Abstract—Acid nickel oxovanadate, $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ (**I**) was synthesized and studied by X-ray diffraction analysis, thermogravimetry, powder X-ray diffraction, and IR spectroscopy. The crystals are triclinic: space group $P\bar{1}$, $a = 8.869(2)$ Å, $b = 10.869(2)$ Å, $c = 11.116(2)$ Å, $\alpha = 65.14(3)^\circ$, $\beta = 74.11(3)^\circ$, $\gamma = 70.47(3)^\circ$, $V = 907.41$ Å³, $\rho(\text{calcd.}) = 2.56$ g/cm³, $Z = 1$.

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Heteropoly compounds (**HPC**) represent a class of complex coordination compounds with a unique structure [1]. If a central atom of the complex anion and the atoms of transition elements in the composition of a general ligand are identical, then isopoly compound (**IPC**) is realized. Different theories of IPC formation are considered in the literature [2–8]. The synthesis of novel compounds with the desired physicochemical properties and the establishment of regularities governing the changes in these properties with the changing compositions and structures are of great importance for the development of the HPC and IPC chemistry.

An interest in heteropolyvanadates is due to their use as catalysts in the selective oxidation of organic compounds, for example, methanol to formaldehyde, benzene to maleic anhydride, and as stabilizers of polymers and oils [9].

The data on vanadates and their use as catalysts in the methane oxidation reaction are reported in [10, 11].

The aim of this work was to synthesize and study the physicochemical properties of acid nickel oxovanadate, $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ (**I**).

EXPERIMENTAL

Synthesis of I was performed using the original procedure. To a hot solution of ammonium metavanadate acidified with nitric acid to pH 3, a hot solution of nickel sulfate and ammonium persulfate were added. The solution obtained was filtered and cooled in desiccator over an alkali. In a week, dark yellow crystals of **I** precipitated; these were filtered off, washed with distilled water and ethanol.

The chemical composition of synthesized compound **I** was established by mass-spectrometry; the water of crystallization was determined by TG method.

For $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$

anal. calcd., %: Ni, 8.38; V, 36.44; O, 32.02; H₂O, 23.16.

Found, %: Ni, 8.40; V, 35.96; O, 32.18; H₂O 23.46.

X-ray diffraction analysis was performed on an Enraf-Nonius CAD4 automated diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) at room temperature. The crystals are triclinic: $a = 8.869(2)$, $b = 10.869(2)$, $c = 11.116(2)$ Å, $\alpha = 65.14(3)^\circ$, $\beta = 74.11(3)^\circ$, $\gamma = 70.47(3)^\circ$, $V = 907.4$ Å³, $\rho(\text{calcd.}) = 2.56$ g/cm³, $Z = 1$, space group $P\bar{1}$. Yellow single crystal $0.24 \times 0.18 \times 0.15$ mm in size was used. Three control reflections measured every 100 min had unchanged intensities to within $\pm 0.6\%$. Of the total 4228 reflections, 3965 were independent reflections with $I > 2\sigma(I)$, the range of angles $\theta = 2/04^\circ$ – 26.99° ($R_{\text{int}} = 0.0157$).

The structure was solved by the direct method and refined by the full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms. An absorption correction was applied ($\mu = 3.599$ mm^{−1}) by ψ -scanning, $T_{\text{min}} = 0.6143$, $T_{\text{max}} = 0.4788$. The final values $R_1 = 0.0232$, $wR_2 = 0.0649$, GOOF = 1.106, extinction coefficient 0.0013(5). The calculations were carried out by the SHELX-97 program package [12].

The atomic coordinates and thermal parameters are given in Table 1, the bond lengths and bond angles are listed in Table 2.

Powder X-ray diffraction data were obtained on a XRD-6000 diffractometer ($\text{CuK}\alpha$ radiation, Ni filter) with silicon used as an external standard. The samples were preliminarily ground in a jasper mortar. The X-ray patterns obtained were interpreted in two steps. First, the position of the peak maximum was determined with the WinXpow program package. At the second step, the X-ray patterns were indexed using the Powder-2 program package. The phase identification was performed on the basis of the powder X-ray diffraction database JCPDS, 2001.

Thermogravimetric analysis (TGA) of **I** was carried out on a Paulik–Paulik–Erdey setup in the temperature range of 20–1000°C (heating rate 10 K/min, a 400 g sample) using calcined alumina as the reference.

IR spectra were recorded on a Perkin Elmer spectrophotometer at 400–4000 cm^{-1} (KBr pellets).

RESULTS AND DISCUSSION

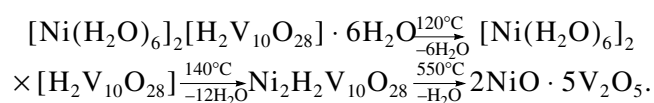
The structure of synthesized compound **I** (Fig. 1) consists of isopolyanions (**IPA**), crystallization water molecule, and hydrated complex cations $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

The Ni atom is coordinated at the vertices of an octahedron by six O atoms of water molecules. The Ni–O(*w*) bond length lies in the interval 2.048(2)–2.089 Å.

The $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ IPA consists of ten distorted VO_6 octahedra sharing common edges. The O atoms in octahedral surrounding of the vanadium cation have different nature of the bonds. The O(1) atom binds six V atoms of oxometallate sphere. The atoms O(4)–O(10) form double (V–O–V), while the atoms O(2) and O(3) form triple bridging bonds. The O(11)–O(14) atoms form multiple terminal bonds V=O.

The $[\text{V}_{10}\text{O}_{28}]^{6-}$ IPA can be schematically presented as duplication of the $[\text{V}_6\text{O}_{19}]^{8-}$ polyanions (Fig. 2a, 2b). The contacts between IPA, outer-sphere cations and water molecules are realized through electrostatic interactions and hydrogen bonds. The structure similar to **I** was described in [13, 14].

The TGA of **I** revealed three endotherms (Fig. 3). The first endotherms at 120 and 140°C correspond to the removal of the six crystallization and twelve coordinated water molecules, respectively, which results in crystal structure destruction. The endotherm at 550°C corresponds to the IPC decomposition and formation of the thermolysis products, i.e., oxides of vanadium(V) and nickel. The thermal decomposition of compound **I** can be represented as follows:



In order to confirm the thermal decomposition scheme, we performed powder X-ray diffraction analy-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters ($\times 10^3$) of $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
Ni	7797(1)	7324(1)	–2161(1)	18(1)
V(1)	6742(1)	5055(1)	5199(1)	14(1)
V(2)	6178(1)	2236(1)	5514(1)	16(1)
V(3)	6465(1)	4502(1)	2720(1)	15(1)
V(4)	6340(1)	2784(1)	8004(1)	19(1)
V(5)	3126(1)	2641(1)	600(1)	19(1)
O(1)	4868(2)	4015(2)	6216(2)	15(1)
O(2)	7406(2)	3664(2)	4418(2)	15(1)
O(3)	5198(2)	6432(2)	5903(2)	14(1)
O(4)	4918(2)	5591(2)	1630(2)	18(1)
O(5)	7655(2)	4097(2)	6584(2)	19(1)
O(6)	7748(2)	5707(2)	1994(2)	19(1)
O(7)	7919(2)	6112(2)	4105(2)	19(1)
O(8)	7222(2)	1694(2)	6930(2)	19(1)
O(9)	4614(2)	1990(2)	8732(2)	21(1)
O(10)	4404(2)	1610(2)	6568(2)	19(1)
O(11)	7429(2)	3332(2)	2079(2)	24(1)
O(12)	7106(2)	1075(2)	4850(2)	23(1)
O(13)	1787(2)	1790(2)	8456(2)	30(1)
O(14)	7438(3)	2019(2)	9163(2)	31(1)
O(1 _w)	6538(3)	8134(2)	–3755(2)	28(1)
O(2 _w)	6340(2)	8919(2)	–1467(2)	26(1)
O(3 _w)	6010(3)	6298(2)	–1062(2)	29(1)
O(4 _w)	9116(2)	6542(2)	–627(2)	32(1)
O(5 _w)	9417(3)	8498(3)	–3325(2)	40(1)
O(6 _w)	9099(3)	5663(3)	–2739(3)	43(1)
O(7 _w)	3201(3)	–824(2)	7661(3)	43(1)
O(8 _w)	10715(3)	1680(3)	5989(2)	41(1)
O(9 _w)	124(3)	612(3)	11145(2)	47(1)

Table 2. Interatomic distances and bond angles in $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}^*$

Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$
Ni–O(6 w)	2.048(2)	V(1)–O(1)	2.1167(18)	V(2)–V(4)	3.1154(8)	V(4)–O(4A)	1.8918(18)
Ni–O(5 w)	2.048(2)	V(1)–V(5A)	3.0704(14)	V(3)–O(11)	1.6016(18)	V(4)–O(5)	2.027(2)
Ni–O(4 w)	2.052(2)	V(1)–V(4)	3.0767(14)	V(3)–O(6)	1.8100(18)	V(4)–O(1)	2.3370(19)
Ni–O(3 w)	2.057(2)	V(2)–O(12)	1.6055(18)	V(3)–O(4)	1.8357(19)	V(4)–V(5)	3.0668(9)
Ni–O(1 w)	2.067(2)	V(2)–O(8)	1.8258(18)	V(3)–O(2)	1.9989(18)	V(5)–O(13)	1.598(2)
Ni–O(2 w)	2.089(2)	V(2)–O(10)	1.8306(19)	V(3)–O(3A)	2.0031(18)	V(5)–O(9)	1.8328(19)
V(1)–O(7)	1.6810(18)	V(2)–O(2)	1.9753(18)	V(3)–O(1A)	2.2301(17)	V(5)–O(10)	1.8398(18)
V(1)–O(5)	1.6977(19)	V(2)–O(3A)	2.0058(19)	V(3)–V(5A)	3.1147(8)	V(5)–O(6A)	1.8977(17)
V(1)–O(2)	1.9046(17)	V(2)–O(1)	2.2331(17)	V(4)–O(14)	1.595(2)	V(5)–O(7A)	2.063(2)
V(1)–O(3)	1.9406(17)	V(2)–V(3)	3.0572(14)	V(4)–O(9)	1.834(2)	V(5)–O(1)	2.3023(19)
V(1)–O(1A)	2.1122(18)	V(2)–V(5)	3.0865(13)	V(4)–O(8)	1.8737(18)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(5W)NiO(6 w)	93.04(10)	O(12)V(2)O(8)	103.66(9)	O(14)V(4)O(8)	102.71(10)	V(1A)O(1)V(1)	101.98(7)
O(5W)NiO(4 w)	88.44(9)	O(12)V(2)O(10)	102.74(9)	O(9)V(4)O(8)	90.81(8)	V(1A)O(1)V(3A)	92.72(7)
O(6W)NiO(4 w)	89.63(10)	O(8)V(2)O(10)	94.00(8)	O(14)V(4)O(4A)	101.87(10)	V(1)O(1)V(3A)	93.91(6)
O(5W)NiO(3 w)	174.95(9)	O(12)V(2)O(2)	99.70(9)	O(9)V(4)O(4A)	90.69(8)	V(1A)O(1)V(2)	93.95(7)
O(6W)NiO(3 w)	90.36(9)	O(8)V(2)O(2)	91.12(8)	O(8)V(4)O(4A)	154.36(8)	V(1)O(1)V(2)	92.21(6)
O(4W)NiO(3 w)	95.31(9)	O(10)V(2)O(2)	155.06(7)	O(14)V(4)O(5)	101.24(10)	V(3A)O(1)V(2)	169.83(8)
O(5W)NiO(1 w)	89.62(9)	O(12)V(2)O(3A)	98.66(9)	O(9)V(4)O(5)	155.74(8)	V(1A)O(1)V(5)	88.03(7)
O(6W)NiO(1 w)	89.83(10)	O(8)V(2)O(3A)	156.14(7)	O(8)V(4)O(5)	84.57(8)	V(1)O(1)V(5)	169.91(8)
O(4W)NiO(1 w)	177.96(8)	O(10)V(2)O(3A)	89.15(8)	O(4A)V(4)O(5)	83.61(8)	V(3A)O(1)V(5)	86.80(6)
O(3W)NiO(1 w)	86.66(8)	O(2)V(2)O(3A)	76.78(7)	O(14)V(4)O(1)	175.62(9)	V(2)O(1)V(5)	85.76(6)
O(5W)NiO(2 w)	91.59(9)	O(12)V(2)O(1)	173.94(8)	O(9)V(4)O(1)	81.35(7)	V(1A)O(1)V(4)	170.77(8)
O(6W)NiO(2 w)	175.36(9)	O(8)V(2)O(1)	81.21(7)	O(8)V(4)O(1)	77.49(7)	V(1)O(1)V(4)	87.24(7)
O(4W)NiO(2 w)	90.20(9)	O(10)V(2)O(1)	80.29(7)	O(4A)V(4)O(1)	77.44(7)	V(3A)O(1)V(4)	86.27(6)
O(3W)NiO(2 w)	85.03(8)	O(2)V(2)O(1)	76.40(7)	O(5)V(4)O(1)	74.39(7)	V(2)O(1)V(4)	85.92(6)
O(1W)NiO(2 w)	90.50(8)	O(3A)V(2)O(1)	76.02(7)	O(6)V(3)O(4)	95.56(8)	V(5)O(1)V(4)	82.76(6)
O(7)V(1)O(5)	106.93(9)	O(11)V(3)O(6)	102.12(9)	O(13)V(5)O(9)	103.44(10)	V(1)O(2)V(2)	107.82(8)
O(7)V(1)O(2)	98.40(8)	O(11)V(3)O(4)	102.20(9)	O(13)V(5)O(10)	102.46(9)	V(1)O(2)V(3)	107.26(8)
O(5)V(1)O(2)	97.82(8)	O(11)V(3)O(2)	99.76(9)	O(9)V(5)O(10)	93.25(8)	V(2)O(2)V(3)	100.57(8)
O(7)V(1)O(3)	96.43(8)	O(6)V(3)O(2)	89.96(8)	O(13)V(5)O(6A)	101.38(9)	V(1)O(3)V(3A)	107.35(8)
O(5)V(1)O(3)	96.29(8)	O(4)V(3)O(2)	155.65(7)	O(9)V(5)O(6A)	90.71(8)	V(1)O(3)V(2A)	107.25(8)
O(2)V(1)O(3)	155.57(7)	O(11)V(3)O(3A)	100.54(9)	O(10)V(5)O(6A)	154.18(8)	V(3A)O(3)V(2A)	99.39(8)
O(7)V(1)O(1A)	87.75(8)	O(6)V(3)O(3A)	155.19(7)	O(13)V(5)O(7A)	99.72(10)	V(3)O(4)V(4A)	113.85(9)
O(5)V(1)O(1A)	165.26(8)	O(4)V(3)O(3A)	89.40(8)	O(9)V(5)O(7A)	156.72(8)	V(1)O(5)V(4)	111.08(9)
O(2)V(1)O(1A)	81.00(7)	O(2)V(3)O(3A)	76.31(7)	O(10)V(5)O(7)	83.89(8)	V(3)O(6)V(5A)	114.27(9)
O(3)V(1)O(1A)	80.30(7)	O(11)V(3)O(1A)	175.12(8)	O(6A)V(5)O(7)	82.47(8)	V(1)O(7)V(5A)	109.78(9)
O(7)V(1)O(1)	165.71(8)	O(6)V(3)O(1A)	80.67(7)	O(13)V(5)O(1)	174.07(9)	V(2)O(8)V(4)	114.72(9)
O(5)V(1)O(1)	87.28(8)	O(4)V(3)O(1A)	81.40(7)	O(9)V(5)O(1)	82.35(7)	V(5)O(9)V(4)	113.51(9)
O(2)V(1)O(1)	80.77(7)	O(2)V(3)O(1A)	76.12(7)	O(10)V(5)O(1)	78.24(7)	V(5)O(10)V(5)	114.47(9)
O(3)V(1)O(1)	80.09(7)	O(3A)V(3)O(1A)	76.05(6)	O(6A)V(5)O(1)	77.03(7)		
O(1A)V(1)O(1)	78.02(7)	O(14)V(4)O(9)	103.01(10)	O(7A)V(5)O(1)	74.44(7)		

* Symmetry transformations: (A) $-x + 1, -y + 1, -z + 1$.

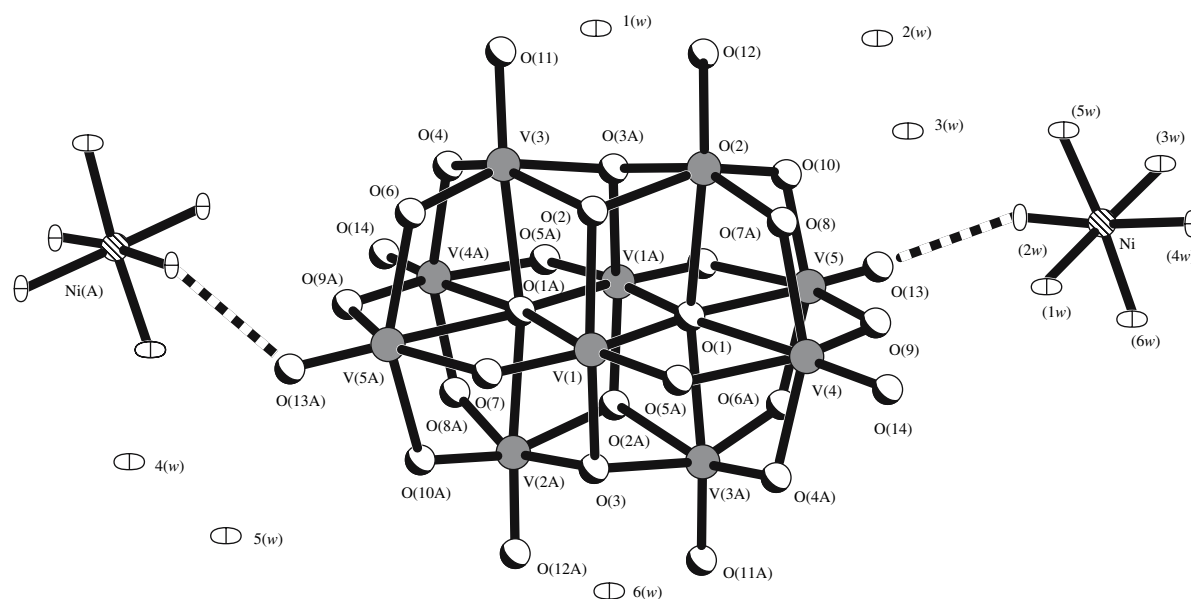


Fig. 1. Crystal structure of isopolyanion I.

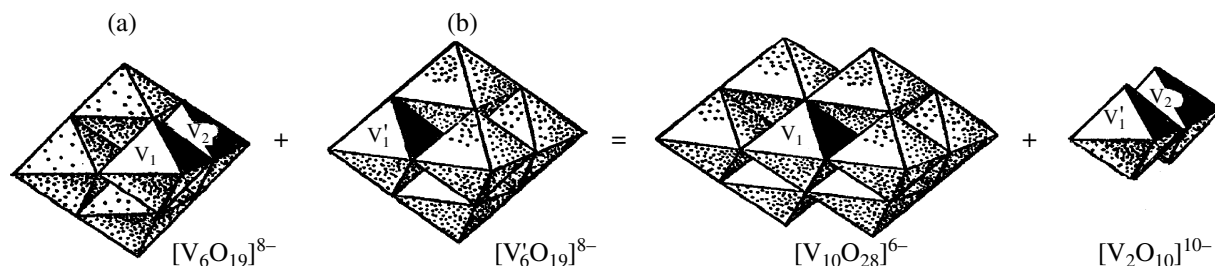


Fig. 2. Scheme of isopolyanion I formation.

sis of both **I** (Table 3) and of the thermolysis products using PCPDFWIN database. The X-ray diffraction patterns obtained at room temperature and after the first endotherm are identical, which indicates the retention of the IPC crystal structure. The X-ray diffraction pattern obtained after the third endotherm suggests the $\text{Ni}_2\text{H}_2\text{V}_{10}\text{O}_{28}$ decomposition and formation of the thermolysis products indicated in the scheme. The powder X-ray diffraction data of the thermal decomposition products are given in Table 4.

IR spectrum of compound **I** contains three groups of absorption bands at $400\text{--}1000\text{ cm}^{-1}$ corresponding to vibrations of different vanadium–oxygen bonds of the complex IPA [15, 16]. The intense band in a range of $900\text{--}1100\text{ cm}^{-1}$ belongs to the terminal *cis*-V=O bonds. The stretching vibrations of the bridging bonds $\nu_s(\text{V}\text{--}\text{O}\text{--}\text{V})$ and $\nu_{as}(\text{V}\text{--}\text{O}\text{--}\text{V})$ appear as a doublet at 685 and 420 cm^{-1} , respectively. The bands at 589 and

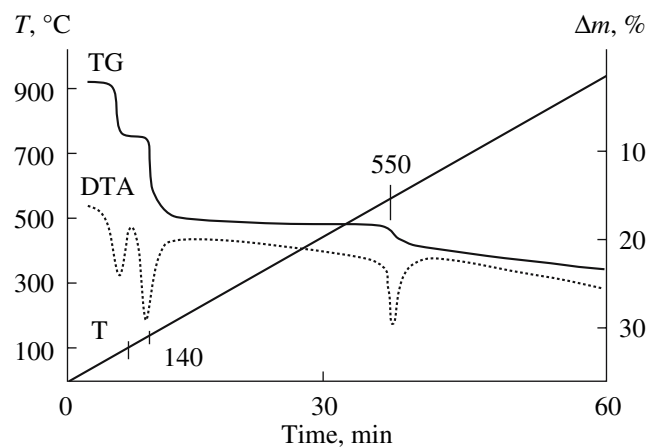


Fig. 3. Thermoderivatogram of compound I.

Table 3. Powder X-ray diffraction data for $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$

Peak no.	2 θ , deg	<i>d</i> , Å	<i>I</i> , %	<i>h</i>	<i>k</i>	<i>l</i>
1	17.52	5.87	41.54	0	2	0
2	21.03	4.90	70.61	2	0	–1
3	24.97	4.13	39.41	2	2	0
4	27.49	3.76	44.71	2	2	–1
5	29.50	3.51	16.40	2	2	1
6	30.86	3.36	6.73	2	0	–2
7	32.88	3.15	100	1	2	–2
8	35.84	2.90	76.50	4	0	0
9	37.19	2.80	10.00	3	1	–2
10	38.55	2.70	13.86	1	3	–2
11	39.82	2.62	11.59	2	4	0
12	42.86	2.44	23.67	4	0	–2
13	46.59	2.26	2.48	4	2	–2
14	47.62	2.21	4.43	2	4	–2
15	49.84	2.12	14.04	2	5	–1
16	50.22	2.10	10.80	2	4	2
17	51.15	2.07	5.76	2	5	1
18	57.03	1.87	5.88	2	4	–3
19	57.68	1.85	9.84	2	5	2
20	58.11	1.84	5.80	1	0	4

Table 4. Powder X-ray diffraction data for the products of $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ thermal decomposition*

Peak no.	2 θ , deg	<i>d</i> , Å	<i>I</i> , %
1	17.51	5.47	9.12
2	22.31	5.26	23.12
3	24.67	5.10	14.34
4	26.11	4.97	13.21
5	28.65	3.64	26.54
6	30.12	3.52	23.45
7	32.64	3.39	100
8	33.56	3.34	21.43
9	35.13	3.12	41.45
10	36.12	3.05	15.45
11	38.45	2.79	11.33
12	40.12	2.70	16.08
13	41.46	2.65	15.87
14	43.14	2.45	12.59
15	44.23	2.39	18.76
16	45.63	2.27	10.99
17	46.86	2.21	19.87
18	46.43	2.18	20.14
19	48.64	2.11	8.56
20	50.31	2.06	16.44
21	53.12	1.98	12.34
22	55.23	1.87	11.23
23	56.12	1.81	10.21

* Peaks no. 2, 5, 9, 14, 16, and 20 belong to NiO, the remaining peaks refer to V_2O_5 .

806 cm^{-1} are due to different types of the vanadium–oxygen bridging bonds, i.e., V(3)–O, V(4)–O. The band at 850 cm^{-1} is produced by the Ni–O bond vibrations. The absorption bands observed in IR spectrum in the regions of 1632 and 3439 cm^{-1} correspond to the vibrations of water molecules.

The identity of IR spectrum of $[\text{Ni}(\text{H}_2\text{O})_6]_2[\text{H}_2\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ to the spectra of the previously studied IPC confirms our suggestion on their similar structures.

The X-ray diffraction patterns and IR spectra obtained at room temperature and after every endotherm confirm the proposed scheme of the thermal decomposition of the title compound.

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