

SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NOVEL DECAVANADATE SALT, $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$

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ABSTRACT

A novel decavanadate salt, $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$, was obtained by the reaction of NH_4VO_3 with chinhydrone in an acidic medium. The title compound was characterized in the solid and solution phases by FT-IR, single crystal X-ray diffraction, voltammetry, UV-Vis., EPR and NMR measurements. The crystal data of the compound are: $H_{30}O_{42}V_{11}$, triclinic, $P\bar{1}$, $a = 8.4906$ (4) Å, $b = 10.4236$ (5) Å, $c = 11.2861$ (6) Å, $\alpha = 68.490$ (4)°, $\beta = 87.251$ (4)°, $\gamma = 67.145$ (4)°, $V = 851.11$ (8) Å³, and $Z = 1$. In the structure, $[H_2(V_{10}O_{28})]^{4-}$ anion is bound *via* hydrogen bonds to the dimer state of $[V_{0.50}(H_2O)_5]^{2+}$ cations and the water molecules. At this dimer moiety, it has been thought that the oxygen atoms of two water molecules form the bridges between two V(IV) center ions. The presence of high spin V(IV) ($I = 7/2$) in the compound was verified by EPR measurements. In addition, decavanadate unit gave a shoulder at about 400 nm on the UV-Vis. spectrum of the compound. Moreover, at the FT-IR spectrum, the symmetric and asymmetric stretching vibrations of the bridging V–O–V units were observed. On the cyclic voltammogram of the compound, two reduction peaks (V(V)-V(IV) and V(IV)-V(II) reduction steps, respectively) at -1.03 and -1.35 V were observed at the cathodic scan; however, one oxidation peak (V(II)-V(III) oxidation step) at -1.22 V showed at the anodic scan. NMR results also support that the synthesized salt includes the coordinated water molecules and hydroxo groups.

Keywords: Decavanadate, V(V) and V(IV) units, chinhydrone, single crystal, water-bridged dimer

INTRODUCTION

As a trace transition metal, vanadium has some biological, pharmacological and physicochemical properties.¹⁻⁷ In recent years, the interest to the chemistry of oxovanadates has grown considerably.⁸ The increasing interest is mainly owing to the role of vanadium in several biological processes such as the regulation of glucose level in the blood of diabetic animals and patients.^{3,4,9-17} Moreover, decavanadate and oxovanadates have many biological activities and been successfully used for the comprehension of several biochemical processes.¹⁸ Other interest for vanadium oxides is sourced from their potential uses as secondary cathode materials, both catalysis and electronics.¹⁹⁻²¹

Decavanadates, $[H_nV_{10}O_{28}]^{(6-n)-}$, are known as predominant polyoxovanadate species in the acidic pH range and also consist of three chemically different vanadium sites; the metal sites at the central junction correspond to two central VO_6 octahedra containing only bridging oxygen atoms, and two types of peripheral vanadium unit including a V=O bond are assembled around the central units.²² In aqueous medium, under some conditions, the vanadate oligomers may be in equilibrium with monomeric (V_1), dimeric (V_2) and tetrameric (V_4) vanadate species.²³

In the literature, the crystal structures of the decavanadate anion, $[V_{10}O_{28}]^{6-}$ ²⁴ and its many salts (e.g. $(NH_4)_2[Sr(H_2O)_6]_2[V_{10}O_{28}] \cdot 2H_2O$,²⁵ $K_2[Zn(H_2O)_6]_2[V_{10}O_{28}] \cdot 4H_2O$,²⁴ $K_2[Co(H_2O)_6]_2[V_{10}O_{28}] \cdot 4H_2O$,²⁶ $[Na(H_2O)_3]_2[Ni(H_2O)_6]_2[V_{10}O_{28}] \cdot 4H_2O$,²⁷), containing the different transition metal complex cations were characterized. The aim of this research was the synthesis, physicochemical characterization both in the aqueous solution and in the solid state, and the determination of molecular structure of a novel vanadium complex in the presence of chinhydrone.

EXPERIMENTAL

Chemicals and Solutions

NH_4VO_3 and chinhydrone were purchased from Merck and used as supplied. All the chemicals were of analytical-reagent grade. The solutions were prepared with ultra-pure water (specific resistivity: 18.2 MΩ cm). 0.1 M KBr solution was used as the supporting electrolyte for the voltammetric measurements.

Synthesis

NH_4VO_3 (0.01 mol) and chinhydrone (0.03 mol) were mixed in 100 mL of ethanol-water mixture (40:60, v/v) and refluxed at 60 °C with stirring for 2-hours. Then, the acidity was adjusted to pH 5-6 with glacial acetic acid. The generated solution was filtered and cooled to room temperature. After 1 day, the complex formation was observed. But, surprisingly, instead of vanadium-chinhydrone complex, a decavanadate salt which does not contain chinhydrone

has been obtained. The similar case was observed for glutamic acid or glutamine in a previous study.²⁸

Voltammetric Measurements

The voltammograms were recorded at room temperature using an EG&G PAR Model 384B polarographic analyzer controlled by a personal computer containing the ECDSOFT²⁹ software in conjunction with an EG&G PARC Model 303A SMDE stand, including a Hg working electrode, a Pt auxiliary electrode and an Ag |AgCl| KCl_{sat.} reference electrode.

Spectroscopic Measurements

The FT-IR spectrum was recorded with a Perkin Elmer Spectrum Two FT-IR spectrometer (4000-450 cm⁻¹) using KBr pellet. The electronic spectrum was carried out by using a Thermo Scientific Evolution Array EA-1301005 UV-Vis. spectrophotometer in the range of 200-800 nm with quartz cell of 1 cm length. The X-band EPR spectrum of compound was recorded on a Bruker EMX X-band spectrometer using 100 kHz magnetic field modulation, 9.751 GHz microwave frequency, 1 mT modulation amplitude and 20.02 mW microwave power. The ¹H NMR spectrum was recorded on a Mercury-300BB (300 MHz) spectrometer, using D₂O as a solvent and tetramethylsilane (TMS, δ 0 ppm) as an internal standard. The above spectroscopic measurements were carried out at ambient temperature.

X-ray Crystal Structure Determination

A suitable single crystal with dimensions 0.27×0.23×0.19 mm was chosen for the crystallographic study and then carefully mounted on goniometer of a STOE IPDS II diffractometer. Data collection of the title compound, $H_{30}O_{42}V_{11}$, was performed with STOE IPDS II single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature (296 K). Details of the data collection conditions and parameters of refinement process are given in Table I. Cell parameters were obtained by using X-AREA³⁰ and data reduction was achieved with X-RED32³⁰ software. The maximum peaks and deepest hole observed in the final $\Delta\rho$ map were 0.54 and -0.76 e Å⁻³, respectively. The scattering factors were taken from SHELXL-97.³¹ The molecular graphics were drawn using ORTEP-3 for Windows.³² All non-hydrogen atoms were refined anisotropically. The coordinates of the H atoms of the water molecules were determined from a difference Fourier map and refined isotropically subject to a restraint of O–H = 0.82(4) Å. The general-purpose crystallographic tool PLATON³³ was used for the structure analysis. WinGX³⁴ was used to prepare the data for publication.

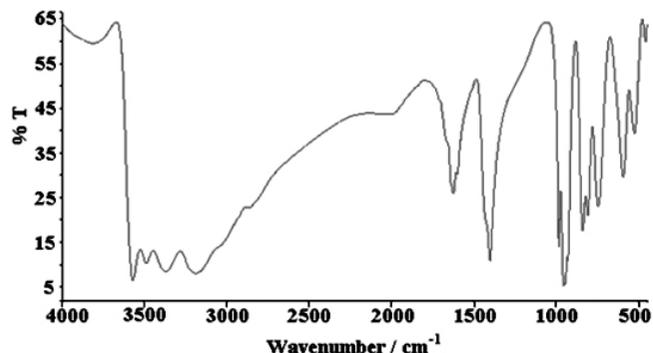
Table 1. Crystallographic data and refinement parameters for the compound.

Crystal data	
Chemical sum formula	$H_{30}O_{42}V_{11}$
Moiety formula	$[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$
M_r	1262.58
Crystal system, space group	Triclinic, P $\bar{1}$
Temperature (K)	296
a, b, c (Å)	8.4906 (4), 10.4236 (5), 11.2861 (6)
α, β, γ (°)	68.490 (4), 87.251 (4), 67.145 (4)
V (Å ³)	851.11 (8)
Z	1
Radiation type	Mo K α
μ (mm ⁻¹)	3.01
Crystal size (mm)	0.27 × 0.23 × 0.19
Data collection	
Diffractometer	STOE IPDS 2 diffractometer
Absorption correction	Integration
T_{min}, T_{max}	0.527, 0.689
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15542, 4765, 3557
R_{int}	0.088
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.100, 0.96
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.54, -0.76

RESULTS AND DISCUSSION

FT-IR Spectroscopy Measurements

For the characterization of this new vanadium salt, its infrared spectrum has also been taken (Fig. 1). Based on IR spectrum in Fig. 1 and the literature information,^{28,35-37} the proposed assignments for some important bands are presented in Table 2.

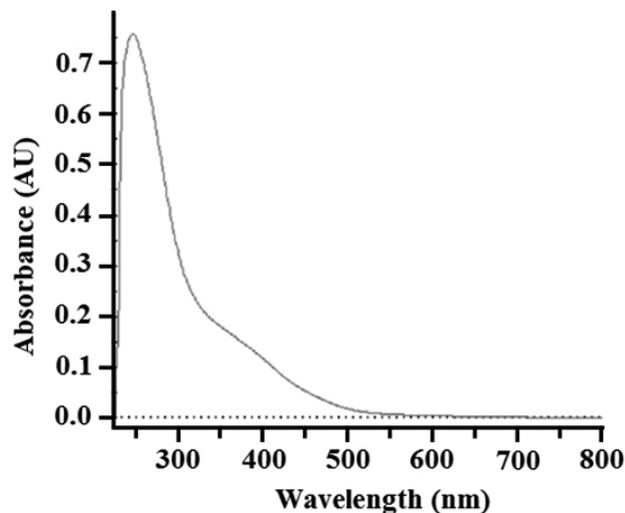
**Figure 1.** FT-IR spectrum of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$ **Table 2.** Assignments of the some important IR bands (cm⁻¹) of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$.

Infrared bands (cm ⁻¹)	Assignment
525.81	ν_s (V–O–V)
593.93	
745.31	ν_{as} (V–O–V)
808.46	
840.18	
984.19	ν (V=O)
955.27	
1626.81	ν (O–H)

It is well known that the symmetric and asymmetric stretching modes of the bridging V–O–V groups are between ~450 and ~850 cm⁻¹.³⁸ As can be seen in Fig. 1, the bands at 3188.64, 3368.48, 3488.80 and 3570.96 cm⁻¹ and the sharp band at 1626.81 cm⁻¹ are indicative of the presence of water molecules in the vanadium coordination sphere.³⁹⁻⁴¹ It has been seen that the water stretching bands (3188.64, 3368.48, 3488.80 and 3570.96 cm⁻¹) are very complex when compared with the water bending mode at 1626.81 cm⁻¹. Nevertheless, the bands at 3188.64 and 3368.48 cm⁻¹ can be resulted from the OH stretching vibration of strongly hydrogen bonded water rather than OH units.⁴² Other two bands 3488.80 and 3570.96 cm⁻¹ may be attributed to OH modes of hydroxyl units.⁴² Finally, the observed band at 1402.20 cm⁻¹ can be identified as due to O–H bending (δ OH in-plane).⁴³

UV-Vis. Spectroscopy Measurements

The electronic spectrum of this compound was recorded in KBr solution in the range of 200-800 nm (Fig. 2). Fig. 2 shows a relatively sharp band at 246.7 nm and one shoulder with very low intensity at about 400 nm, attributed to the charge transfer and $d_{xy} \rightarrow d_z^2$ transitions,⁴⁴⁻⁴⁷ respectively. However, it was reported that the binuclear V(III) complex with hydroxyl bridges exhibited a charge transfer band in 436 nm, having high absorptivity values.⁴⁸ Hence, the electronic spectrum of the synthesized compound is different from that of V(III)-hydroxo complexes.⁴⁸ Finally, it can be said that the structure of the compound does not include a binuclear V(III) complex-ion of di-ol type $[(H_2O)_4V(OH)_2V(H_2O)_4]^{4+}$. On the other hand, decavanadate, the decamer of monovanadate, can be distinguished by its absorbance at 400 nm.⁴⁹ Because this absorption band is characteristic of decameric vanadate.⁵⁰ Therefore, the shoulder at 400 nm may also contain the absorption additives from decavanadate moiety of the compound.

**Figure 2.** Electronic spectrum of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$.

EPR Measurements

The X-band EPR spectrum of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$ is given in Fig. 3. As can be seen in Fig. 3, an eight-line pattern was obtained as a

result of an unpaired electron being coupled with a vanadium nuclear spin ($I = 7/2$).⁴⁴ This spectrum also supports the presence of V(IV) unit in the structure of complex.

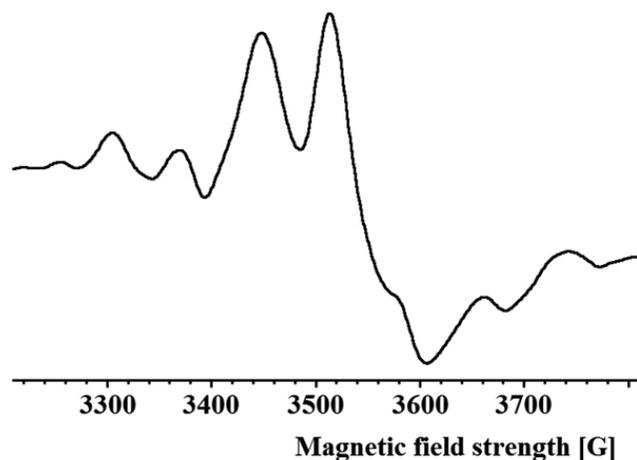


Figure 3. X-band EPR spectrum of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$.

The calculated parameters from the epr spectrum of the complex are given as follows: $g_{\perp} = 1.997$, $A_{\perp} = 23$ G, $H_{\perp} = 3488$ G, $g_{\parallel} = 1.963$, $A_{\parallel} = 66$ G and $H_{\parallel} = 3549$ G. From these data, $g_{\parallel} < g_{\perp}$ and $A_{\parallel} > A_{\perp}$ relationships were obtained. This case is characteristic for an axially compressed d^1_{xy} configuration.^{51,52}

Cyclic Voltammetry (CV) Study

The electrochemical redox properties of the compound in 0.1 M KBr solution have been investigated using CV technique. The compound gave two cathodic waves at -1.03 and -1.35 V, respectively (Fig. 4).

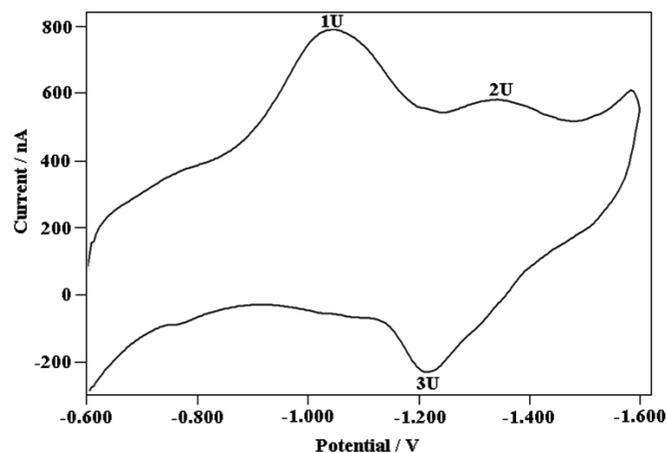


Figure 4. Cyclic voltammogram of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$ in 0.1 M KBr solution (Experimental conditions: scan rate of 800 mV/s, equilibrium time of 5 s, medium drop size of 0.0154 cm² and hanging mercury drop electrode as working electrode).

It was reported that V(V) characteristically gives two cathodic waves in acidic, neutral, and some complex-forming media. The first wave represents the reduction to V(IV), while the second wave has properties identical with those of the cathodic wave of V(IV).⁵³ At potentials more negative than about -0.6 V, the reduction of V(IV) proceeds directly to V(II). In the case of V(II), the reduction to the elemental vanadium is never observed; only anodic waves are obtained. The first step of oxidation gives V(III).⁵³

In Fig. 4, the first cathodic wave can be assigned to the reduction of V(V) to V(IV) in agreement with previous reports,⁵³ while the second wave at more negative potential may be attributed to the reduction of V(IV) to V(II). In addition, the anodic wave at -1.22 V may be ascribed to the oxidation of V(II) to V(III).

Crystal Structure Description of the Compound

The ORTEP diagram of the title compound, a decavanadate salt, $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$ with thermal ellipsoids pictured at a 30% probability is shown in Fig. 5. The crystallographic data and hydrogen bonding are given in Tables 1 and 3, respectively. The selected bond lengths and angles of the title compound are listed in Table 4. Single crystal X-ray diffractions confirm the molecular structure of the title molecule, $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$, decavanadate salt. The molecular structure of compound is shown in Fig. 6(a). Its structure consists of a diprotonated decavanadate unit, a binuclear V(IV) moiety with two water bridges and four water molecules of crystallization Fig. 6(b). The structures of $[H_2(V_{10}O_{28})]^{4-}$ and $[V_{10}O_{28}]^{6-}$ were already reported in detail.^{24,54,55} In the present study, the bond lengths and angles of $[H_2(V_{10}O_{28})]^{4-}$ anion are similar to data given in the literature.^{24,54,55} The dihydrogen decavanadate anion contains ten edge-sharing VO_6 octahedra as reported in the literature.²⁴ The crystal structure of the compound is mainly stabilized by electrostatic attraction forces of $[H_2(V_{10}O_{28})]^{4-}$ with the V(IV) cations, $[V_{0.50}(H_2O)_5]^{4+}$. At the cationic V(IV) dimer, each of the hydrated V(IV) ions of 0.5 mole is coordinated by five water molecules (Fig. 6). The V(IV)–O bond length distances are ranging from 2.337 (3) to 2.378 (3) Å (Table 4). Besides, there are O–H...O hydrogen bonding interactions (Fig. 6a) which play an important role in the structural stabilization, and the O...O distances vary between 2.803 - 3.037 Å (Table 3). The angles which correspond to these interactions are between 142° - 178° (Table 3) that fit well with the previous predictions.^{56,57}

Table 3. Hydrogen-bond geometries (Å, °) for $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$

D—H...A	D—H	H...A	D...A	D—H...A
O15—H15B...O5 ⁱ	0.81 (1)	2.17 (2)	2.953 (3)	163 (4)
O17—H17B...O10 ⁱ	0.82 (1)	2.04 (1)	2.852 (3)	170 (4)
O17—H17A...O2 ⁱⁱ	0.82 (1)	2.23 (1)	3.037 (3)	168 (4)
O15—H15A...O7 ⁱⁱⁱ	0.81 (1)	2.13 (2)	2.873 (3)	152 (4)
O16—H16A...O6	0.81 (1)	2.04 (2)	2.828 (3)	165 (5)
O16—H16B...O9 ⁱ	0.81 (1)	2.06 (2)	2.864 (3)	168 (5)
O20—H20B...O2	0.82 (1)	2.14 (2)	2.941 (4)	165 (5)
O18—H18B...O11 ^{iv}	0.82 (1)	1.99 (1)	2.804 (3)	171 (4)
O19—H19A...O12 ^{iv}	0.82 (1)	1.98 (1)	2.803 (3)	178 (4)
O21—H21A...O9	0.82 (1)	2.34 (6)	3.031 (3)	142 (8)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+2$; (iii) $x, y+1, z$; (iv) $-x+1, -y+2, -z+1$.

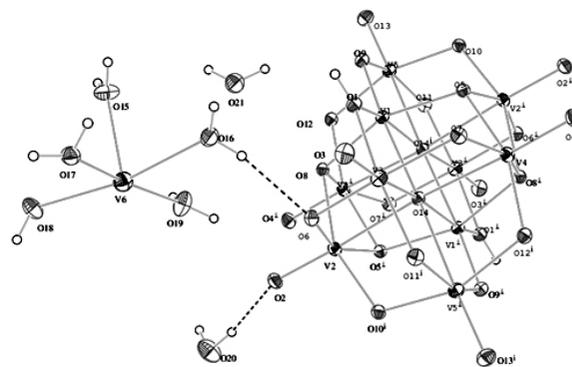
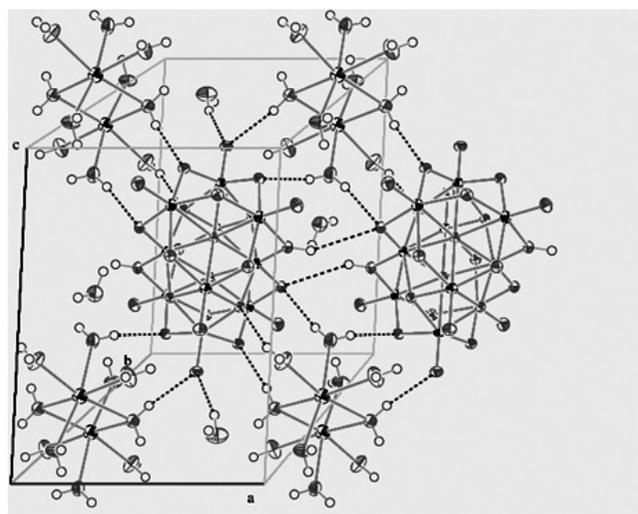
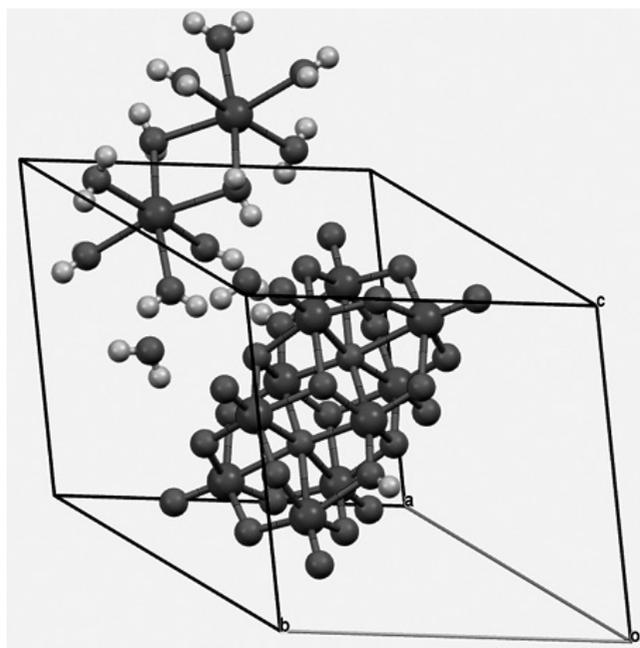


Figure 5. ORTEP plot of the $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$ compound, showing the atom-numbering scheme and 30% probability displacement ellipsoids for the non-hydrogen atoms. The hydrogen bonds are shown as dashed lines.



(a)



(b)

Figure 6. (a) Crystal-packing diagram of the title compound, $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$, along b axis. Hydrogen bonds are shown as dashed lines. (b) Perspective view of the unit cell of decavanadate salt. Two vanadium atoms, V(IV), formed bridge *via* two water molecules.

Zhang and Chen⁵⁸ investigated magnetic exchange interaction in the μ -hydroxo bridged V(IV) dimers. They reported that the distances between the V(IV) site and the oxygen atom of the bridging aqua ligand (2.332 and 2.500 Å) are much longer than the distances between the V(IV) site and the oxygen atom of the bridging hydroxo ligand (1.959 and 1.967 Å). At the bridging V(IV) moiety of the title compound, the distance of V6–O17 is 2.409 (3) Å (Table 4). This result may support the presence of the bridging aqua ligand instead of the bridging hydroxo ligand.

Table 4. Selected bond lengths (Å) and angles (°) for $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$

V6—O18	2.337 (3)	V6—O19	2.378 (3)
V6—O15	2.339 (3)	V6—O17	2.409 (3)
V6—O16	2.339 (3)		
O18—V6—O15	84.19 (11)	O16—V6—O19	88.49 (11)
O18—V6—O16	169.87 (12)	O18—V6—O17	91.06 (10)
O15—V6—O16	88.10 (12)	O15—V6—O17	97.11 (11)
O18—V6—O19	97.51 (10)	O16—V6—O17	83.37 (11)
O15—V6—O19	86.07 (11)	O19—V6—O17	171.14 (10)
O4—V4—O7—V3	−175.16 (11)	O2—V2—O6—V3	175.05 (11)
O3—V3—O7—V4	177.91 (11)	O3—V3—O6—V2	−178.33 (11)

When vanadium compounds with high oxidation states are dissolved in water, various hydrolytic, acid/base, condensation and redox reactions can be observed. In addition, it is well known that an inter-conversion between V(IV) and V(V) oxidation states exists.^{59,60} In some circumstances, vanadate (+5) is readily reduced to V(IV) or V(III) with the formation of an oxidized product. The V(IV) oxidation state can be also maintained by the appropriate reducing agents.⁶⁰

Crystal structure determination, especially, the obtaining signals from the epr measurements for the title compound have revealed that a dynamic redox process is involved between V(V) species (NH_4VO_3) and chinhydrone during its synthesis, as similar to the overall reaction being represented by the following equation:



where H_2Q = hydroquinone and Q = para-benzoquinone.⁶¹ It is also well known that chinhydrone consists of para-benzoquinone with hydroquinone, 1:1 redox couple.⁶² Finally, the synthesized complex includes not only V(V) but also V(IV) units.

NMR Spectroscopy Study

¹H NMR spectrum of the title compound dissolved in D_2O is shown in Fig. 7. The residual solvent (hydrogen-deuterium-oxygen, HD₂O) peak appears at 4.65 ppm (Fig. 7). The signals at about 2.01 ppm are attributed to the coordinated H_2O at $[V_{0.50}(H_2O)_5]^{4+}$ cation.⁶³ The chemical shift at 5.24 ppm can be assigned to the bridging hydroxyl groups^{64,65} at $[H_2(V_{10}O_{28})]^{4-}$ anion. Unfortunately, other signals could not be assigned.

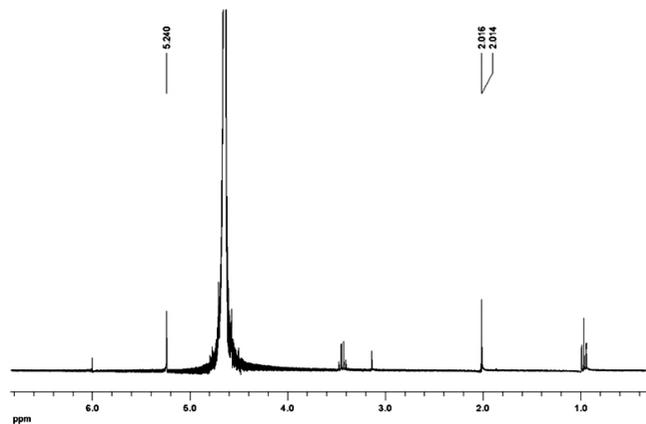


Figure 7. ¹H NMR spectrum of $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$ dissolved in D_2O .

CONCLUSIONS

In conclusion, the study concentrates on the synthesis and characterization of a novel decavanadate salt, $[V_{0.50}(H_2O)_5]_2[H_2(V_{10}O_{28})] \cdot 4(H_2O)$. This salt was

clearly characterized by means of the single crystal X-ray analysis. It has been found that there are electrostatic forces between diprotonated decavanadate anion, $[H_2(V_{10}O_{28})]^{4-}$, and the aqua bridged V(IV) cation, along with O–H···O hydrogen bonds in the unit cell.

The presence of V(IV) in the structure has been supported by the EPR study. The electrochemical results have signified that the complex has two irreversible V(V)/V(IV), V(IV)/V(II) reduction processes and a V(II)/V(III) oxidation process. Furthermore, the bridging V–O–V groups and decameric vanadate units were also characterized by FT-IR and UV-Vis. spectroscopy techniques. In addition, the presence of the coordinated water molecules and hydroxo groups supported by NMR analysis.

As a result, the structure of the decavanadate salt synthesized in this study is different from its other salts²⁴⁻²⁷ according to the arrangement of cations and transition metal species. An exciting part of this study is that the mentioned synthesis method may play an important role in the synthesis of different decavanadate compounds in the future.

Supplementary Materials. – CCDC 1472918 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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