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Synthesis, Crystal Structure, and IR Spectroscopic Characterization of 1,6-Hexanediammonium Dihydrogendecavanadate

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Summary. Anhydrous 1,6-hexanediammonium dihydrogendecavanadate ($(Hda H_2)_2H_2V_{10}O_{28}$, **1**) was prepared by reaction of V_2O_5 with 1,6-hexanediamine in aqueous solution. The crystal structure of **1** was determined, and the proton positions in the $H_2V_{10}O_{28}^{4-}$ anion were calculated by the bond length/bond number method. The protons are bound to the centrosymmetrically oriented μ–OV_3 groups of the decavanadate anion. Based on the analysis of IR spectra of **1** prepared from H_2O and D_2O, the absorption band at 871 cm^{-1} can be attributed to δ(V–O_b–H) vibrations.

Keywords. 1,6-Hexanediammonium dihydrogendecavanadate; IR spectroscopy; X-Ray structure determination; Protonation; Hydrogen bonds.

Introduction

All decavanadates with organic cations known so far contain $H_nV_{10}O_{28}^{(6-n)-}$ anions ($n = 0$–4). The majority of these decavanadates are dihydrogendecavanadates. The protons in the protonated decavanadates are always bonded to the bridging oxygens of the $V_{10}O_{28}^{6-}$ anion.

From crystal structure determinations of dihydrogendecavanadates it is known that there are three modes of proton bonding. The protons in $H_2V_{10}O_{28}^{4-}$ are mostly bonded to the centrosymmetrically arranged μ–OV_2 groups [1–3]. In two compounds, they are bonded to centrosymmetrically arranged μ–OV_3 groups [2, 4], and only in one dihydrogendecavanadate the protons are linked with the neighbouring μ–OV_2 and μ–OV_3 groups which, *via* hydrogen bonds with other $H_2V_{10}O_{28}^{4-}$ ions, form the $H_4V_{20}O_{56}^{8-}$ anions. [5]

According to some authors [1], IR spectra allow to distinguish between protonated and unprotonated decavanadates. In our study focused on isopolyvanadates we have prepared and structurally characterized anhydrous 1,6-hexanediammonium dihydrogendecavanadate (**1**) in which the protons are located on the

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centrosymmetrically arranged three-connective oxygens (OV_3) of the decavanadate anion; **1** is the third known dihydrogendecavanadate with this protonation mode. In a previous paper [3] we have structurally characterized the dihydrate of the same compound, $(Hda H_2)_2H_2V_{10}O_{28} \cdot 2H_2O$ (**2**). This compound, however, exhibits the most common bonding mode of protons to two-connective oxygens in centrosymmetrically arranged OV_2 groups [3]. We report here also the influence of different protonation modes in $H_2V_{10}O_{28}^{4-}$ on the IR spectra of **1** and **2**.

Results and Discussion

Infrared spectroscopy

The structures of polyvanadates are relatively rigid and only to a small extent influenced by the properties of the cation or hydrogen bond formation between anion and cation or between anion and crystal water molecules, respectively. Therefore, IR spectroscopy permits to identify the type of a polyvanadate anion.

Both IR spectra and chemical analysis of 1,6-hexanediammonium dihydrogendecavanadate (**1**) and its recently published dihydrate (**2** [6]) confirmed that both compounds are decavanadates. The IR spectra of **1** and **2** (Fig. 1) exhibit V–O stretching characteristics of a decavanadate anion in the 450–1000 cm^{-1} region. At 900–1000 cm^{-1} the bands corresponding to stretching of the short terminal $V–O_t$ bonds can be observed, whereas in the 450–900 cm^{-1} region the stretchings of the bridging $V–O_b$ bonds are found. Moreover, the IR spectra of both compounds exhibit a weak band at about 430 cm^{-1} which can be assigned to the deformation mode of the $V–O_b$ groups [1].

Although the global character of the IR spectra of **1** and **2** is similar, they differ by the presence of two absorption bands of medium intensity at 871 cm^{-1} in the spectrum of **1** and at 926 cm^{-1} in the spectrum of **2** (Fig. 1, bands annotated A). The fact that the protons in $H_2V_{10}O_{28}^{4-}$ are bonded in a different way, *i.e.* to the centrosymmetrically oriented μ–OV_3 groups in **1** and to the centrosymmetrically oriented μ–OV_2 groups in **2**, suggests that the IR spectra will differ with respect to bands corresponding to the deformation vibration $\delta(V–O_b–H)$.

To verify this supposal, both compounds were prepared also from D_2O. The corresponding IR spectra (Fig. 1) show that the bands discussed almost disappear, and new bands caused by isotopic exchange are observed: at 623 cm^{-1} for **1** and as a shoulder at 690 cm^{-1} for **2**. The absorption bands at 871 cm^{-1} in **1** and at 926 cm^{-1} in **2** can thus be assigned to $\delta(V–O_b–H)$.

Román et al. [4] have published the structure and IR spectrum of *tetrakis*-(*n*-hexylammonium) dihydrogendecavanadate in which the protons of the $H_2V_{10}O_{28}^{4-}$ anion are bonded to the centrosymmetrically oriented μ–OV_3 groups. According to these authors, the IR spectrum of the protonated decavanadates exhibits characteristic bands at 630 and 995 cm^{-1}. The band at 995 cm^{-1} can be assigned to some $V–O_t$ bonds which are shortened due to the elongation of the $V–O_b$ bonds which involve the protonated oxygen atoms the stretching vibrations of which are seen as a band at 630 cm^{-1}. We found that this band is present in the spectrum of **1**, whereas the absorption band at 995 cm^{-1} is missing. Upon deuteration of **1**, a greater differentiation of the terminal $V–O_t$ bonds, manifested by splitting of the

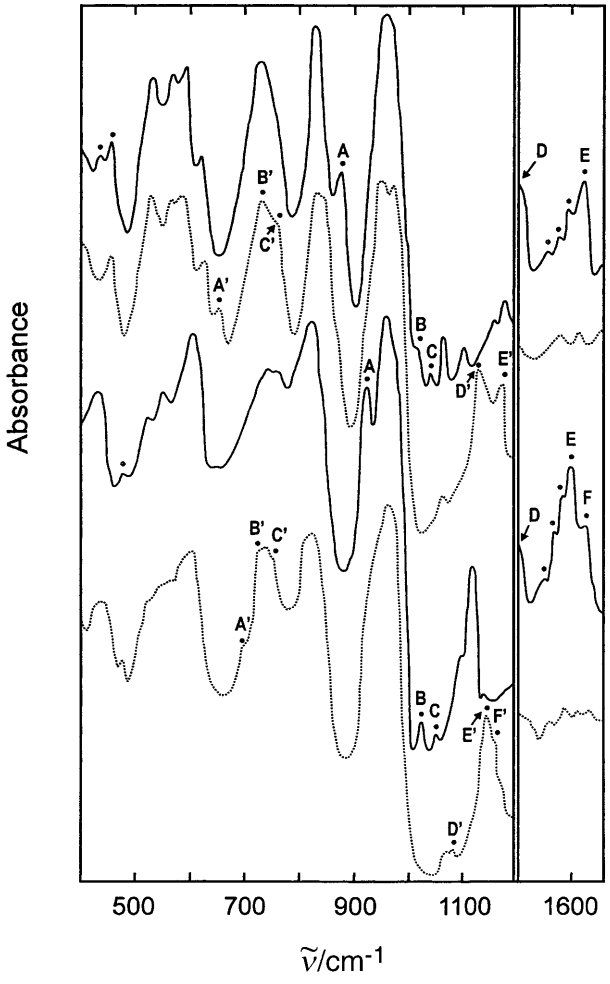

Fig. 1. IR spectra of compounds **1** and **2** and their deuterated forms **1-D** and **2-D**; all bands responsive to deuteration are marked with dots (•)

absorption band in the 900–1000 cm^{-1} region, takes place. In both compounds, two further bands (B and C) were also found to be sensitive to deuteration. This can be explained by hydrogen bond formation between $H_2V_{10}O_{28}^{4-}$ and $(HdaH_2)^{2+}$ in both compounds, in **2** also with water molecules.

As expected, deuteration also causes a shift of absorption bands corresponding to $\delta(NH_3)$ vibrations in the 1495–1610 cm^{-1} region (bands in the interval D–E, Fig. 1) and of the band at 1625 cm^{-1} (F) corresponding to $\delta(O–H_2)$ vibrations of crystal water molecules in **2**. All bands were shifted by a factor of 1.33–1.39 upon isotopic substitution, which is in good agreement with the theoretical value of 1.35.

X-Ray diffraction analysis of $(HdaH_2)_2H_2V_{10}O_{28}$

The dihydrogendecavanadate anions with usual C_i symmetry form a layered structure with an orientation parallel to the [001] plane (Fig. 2). However, the symmetry of the anion is very close to the ideal D_{2h} symmetry of a non-protonated

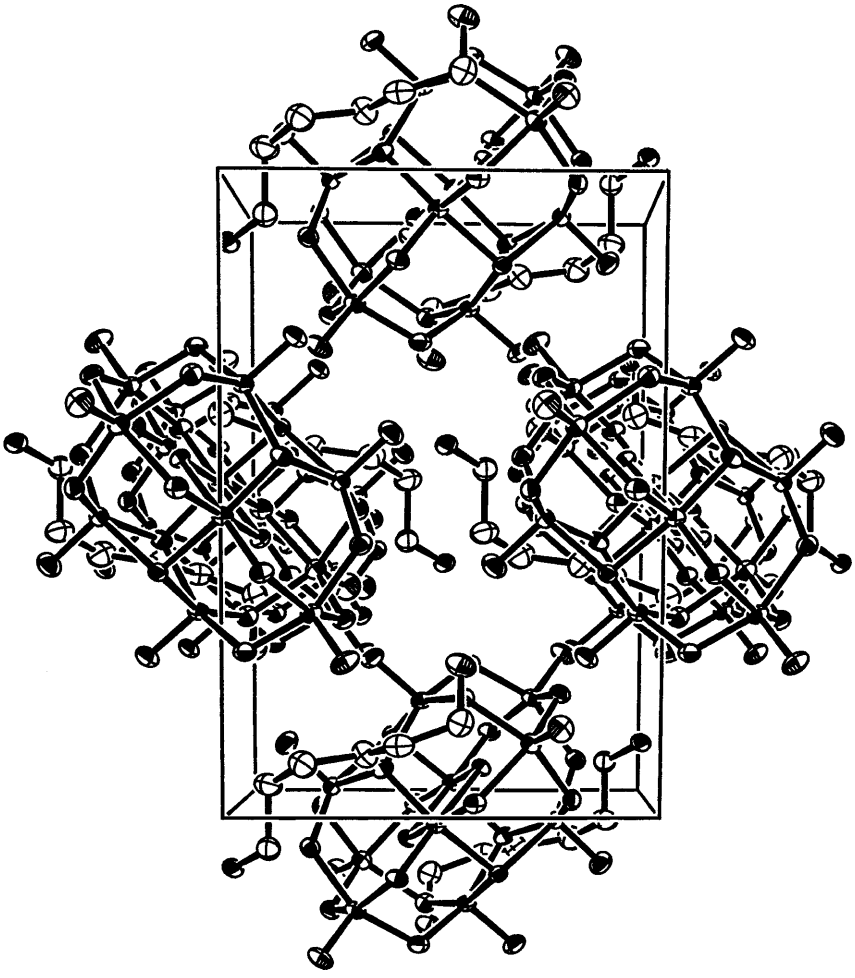

Fig. 2. ORTEP drawing of the unit cell of **1** (view parallel to the [010] plane) with the H atoms excluded for clarity (non-H atoms drawn as 50% probability ellipsoids)

decavanadate anion. The cation position is approximatelly parallel to the neighbouring anion in the same layer, but approximately perpendicular in adjoining layers. All ions in the unit cell are involved in a hydrogen bonding network.

The hydrogen atoms of the $H_2V_{10}O_{28}^{4-}$ anion could not be observed directly. In an attempt to investigate the H atoms of the polyanion we used the empirical bond length/bond number calculation in order to find the valence deficient O atoms using the power function $s = (R/1.791)^{-5.1}$ which relates the V–O distance R and the bond number s [7]. We obtained Σs values for O atoms in the range of 1.71 for O14 to 1.99 for O6 (which is unaccessible to protons) and O9, with an exception with $\Sigma s = 1.33$ (O10) indicating a H atom placement. This placement of H atoms onto centrosymmetrically arranged μ–OV_3 groups of the anion can be backed up by a possibility of an anion–anion hydrogen bond formation between O10 and O14 with an O–O distance of approximately 2.82 Å. Oxygen atom O14 has the lowest Σs (1.71) and suitable geometrical factors for hydrogen bonding as well. The hydrogen bond mentioned above is slightly weaker in comparison with anion–anion hydrogen bonds in other dihydrogendecavanadates with typical O–O lengths

between 2.6–2.8 Å. This hydrogen atom placement has been rarely observed in dihydrodecavanadate structures. Similar placements have been observed on O7 and O7′ atoms (onto centrosymmetrically arranged μ–OV_2 groups) [4] and on O7′ and O9 atoms (onto neighbouring μ–OV_2 and μ–OV_3 groups) [5].

The intermolecular contacts are mainly based on a strong N–H···O interactions shown in Table 1 and on O–H···O anion–anion interactions discussed above. Less significant C–H···O interactions with H···O distances between 2.33–2.59 Å have been found, too. In comparison with **2** [3], the anion–anion interaction in this structure is much stronger (O–O distance 2.82 Å in **1** compared with 3.21 Å in **2**), and all significant N–H···O bonds are slightly shorter. This fact is caused by the absence of crystal water molecules in the structure of **1** which results in stronger interionic interactions. The obvious protonation sites are sterically prohibited from hydrogen bonding by the presence of cations; thus, the only possible protonation site is O10. The closer cell arrangement leads to a higher density ($\rho_{calc} = 2.339\ g \cdot cm^{-3}$ for **1** in comparison with $2.251\ g \cdot cm^{-3}$ for **2**) and a higher absorption coefficient ($\mu = 2.726\ mm^{-1}$ for **1** and $2.555\ mm^{-1}$ for **2**).

Table 1. Selected hydrogen bonds geometry: interatomic distances (Å) and bond angles (°)

D	H	*A*	D–H	H···A	D···A	D–H···*A*
N1	H1A	O12	0.8900	2.2806	3.0520	144.91
N1	H1A	O7	0.8900	2.5161	3.0101	115.64
N1	H1B	O3	0.8900	2.1997	3.0472	158.97
N1	H1C	O4	0.8900	2.0630	2.9303	164.50
N2	H2A	O13	0.8900	1.9218	2.7968	167.25
N2	H2B	O8	0.8900	1.8637	2.7033	156.50
N2	H2C	O2	0.8900	2.0000	2.8199	152.56

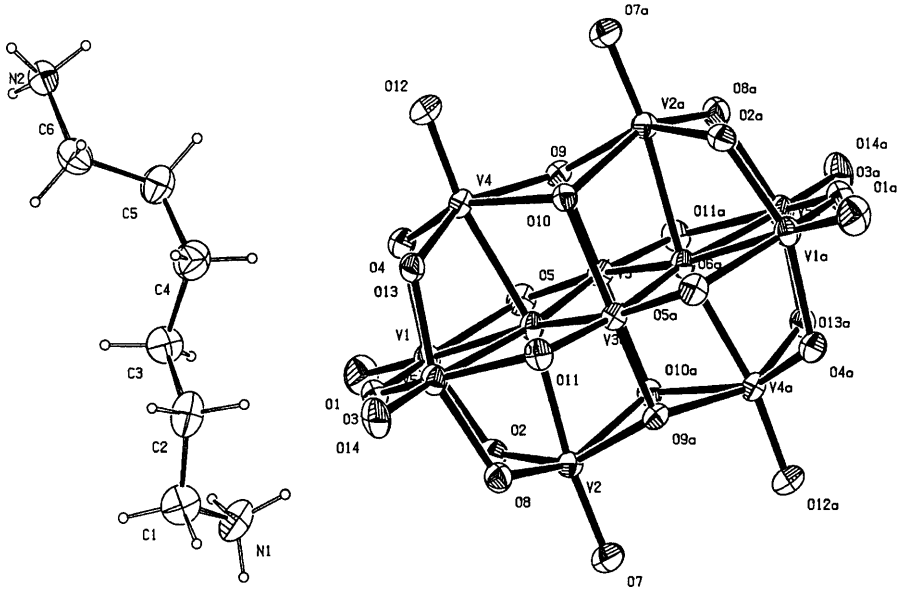

Fig. 3. ORTEP drawing of **1** with the non-H atoms drawn as 50% probability ellipsoids and numbering system

Experimental

V_2O_5 was prepared by thermal decomposition of previously purified NH_4VO_3. All other chemicals used were of standard grade. Vanadium was estimated by titration with $FeSO_4$ using diphenylamine as indicator. Carbon, hydrogen and nitrogen contents were determined on a 1006 CHN-analyzer (Carlo Erba, Milano). The results of elemental analyses agreed favourably with the calculated values. The IR spectra (nujol mull) were measured on a Specord M80 (Zeiss, Jena).

Syntheses

1,6-Hexanediammonium dihydrogendecavanadate ($Hda H_2)_2H_2V_{10}O_{28}$, **1**; $C_{12}H_{38}N_4V_{10}O_{28}$)

1 was prepared by dissolution of V_2O_5 (0.45 g, 2.5 mmol) in an aqueous solution of 1,6-hexanediamine (0.3 g, 2.5 mmol). After dissolution of the V_2O_5, the resulting solution was diluted with water to 100 cm^3, and the *pH* was adjusted to 3.1 by addition of 4 *M* HCl. After 42 days, yellow–orange crystals were obtained.

IR (nujol): $\tilde{\nu} = 1610$ w, 1590 w, 1565 vw, 1550 vw, 1070 w, 1040 vw, 1020 w, 960 vs, 871 m, 830 vs, 730 s, 630 m, 595 s, 575 m, 530 s, 459 w, 430 w cm^{-1}.

1,6-Hexanediammonium dihydrogendecavanadate (($Hda H_2)_2H_2V_{10}O_{28} \cdot 2H_2O$, **2**; $C_{12}H_{42}N_4V_{10}O_{30}$)

The synthesis of **2** proceeded similarly to that of **1**; the *pH* value of the resulting solution was set to 3.5. The orange crystalline product was obtained after 6 days. Preparation, analytical, and IR spectroscopic characterization of **2** has already been published [6].

X-Ray crystallography

The X-ray measurement on a selected crystal was performed on a Kuma KM-4 four-circle κ-axis diffractometer equipped with an Oxford Cryostream Cooler [8] at 298 K. MoK_α radiation ($\lambda =$ 0.71073 Å), a graphite monochromator, and a CCD detector under a nitrogen atmosphere were used. The θ range for data collection was 3.43 to 26.92°, the corresponding index ranges $-8 \le h \le 14$, $-12 \le k \le 11$, and $-17 \le l \le 14$. The data set was corrected for *Lorentz* and polarization effects as well as for absorption employing the ψ-scan procedure (range of transmission factors: 0.2513 to 0.4085). All data collection, cell refinement, data reduction, and correction procedures were done with the Kuma KM-4 CCD and Kuma KM-4 Datared software. The crystal data and refinement details are given in Table 2.

The phase problem was solved by direct methods using the SHELX97 package [9, 10] which was also used to refine the structure full-matrix least-squares on F^2. All atoms other than hydrogens were refined using the anisotropic thermal parameters. Hydrogen atoms on the carbon and nitrogen atoms of the cation were placed in idealized positions with $U_{iso} = 1.2U_{eq}$ (C atoms) and $U_{iso} = 1.5U_{eq}$ (N atoms) for the non-hydrogen atoms; the NH_3^+ group was treated as an idealized rigid rotor in the final stages of the least-squares refinement. The final residual values are: $R_{wF2} = 13.23\%$, $R_F = 8.30\%$, and $S = 1.120$ for all 3167 reflections with the weight defined as $w = 1/(\sigma^2(F_o^2) + (0.0335P)^2 + 12.7847P)$ where $P = (F_o^2 + 2F_c^2)/3$. A restriction of the reflections used in the refinement to the condition $I > 2\sigma$ resulted in 2228 unique reflections and $R_{wF2} = 9.90\%$, $R_F = 4.45\%$. The largest difference electron density (peak and hole) was 0.745 and -0.813 e/Å^3 after the final refinement.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-164367. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystal data and structure refinement

Compound	$(H_3N–(CH_2)_6–NH_3)_2H_2V_{10}O_{28}$
CCDC No.	164367
Color/shape	orange prism
Crystal dimensions (mm)	$0.7 \times 0.5 \times 0.4$
Chemical formula	$C_{12}H_{38}N_4O_{28}V_{10}$
Formula weight	1195.86
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 11.4338(10)$ Å, $b = 10.1090(7)$ Å, $c = 14.9684(1)$ Å, $\beta = 101.00(4)^\circ$
Volume	1698.32(19) Å^3
Z	2
Density (calculated)	2.339 g · cm^{-3}
Absorption coefficient	2.726 mm^{-1}
Reflections measured	11360
Independent/observed reflections	3189/2228 ($I \geq 2\sigma(I)$)
Refined parameters/restraints	244/0
Absolute structure parameter	$F(000) = 1184$
Goodness of fit on F^2	1.120
Final R indices ($I > 2\sigma(I)$)	$R_{wF2} = 9.90\%$, $R_F = 4.45\%$
R indices (all data)	$R_{wF2} = 13.23\%$, $R_F = 8.30\%$

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