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Synthesis and Properties of Dipropylammonium and 1,3-Propanediammonium Polyvanadates

Ľudmila Žúrková[1,*], **Jozef Tatiersky**[1], and **Pavel Fejdi**[2]

[1] Department of Inorganic Chemistry, Faculty of Sciences, Comenius University, SK-84215 Bratislava, Slovak Republic
[2] Department of Mineralogy and Petrology, Faculty of Sciences, Comenius University, SK-84215 Bratislava, Slovak Republic

Summary. Dipropylammonium (*DPA*H) decavanadates and 1,3-propanediammonium (*PDA*H_2) meta- and decavanadates of the composition $[PDAH_2](VO_3)_2$ (**1**), $[PDAH_2]_3V_{10}O_{28} \cdot 5H_2O$ (**2**), $[PDAH_2]_2H_2V_{10}O_{28}$ (**3**), $[DPAH]_5HV_{10}O_{28} \cdot 2H_2O$ (**4**), $[DPAH]_4H_2V_{10}O_{28} \cdot 2H_2O$ (**5**), and $[DPAH]_3H_3V_{10}O_{28}$ (**6**) were prepared from the reaction system *PDA*/*DPA*-V_2O_5-H_2O-HCl and characterized by X-ray powder diffraction and IR spectroscopy. The morphological and optical properties of **3** and **5** were studied.

Keywords. Dipropylammonium decavanadate; 1,3-Propanediammonium metavanadate; 1,3-Propanediammonium decavanadate.

Synthese und Eigenschaften von Dipropylammonium- und 1,3-Propandiammonium-polyvanadaten

Zusammenfassung. Dipropylammonium-(*DPA*H)-decavanadate und 1,3-Propandiammonium-(*PDA*H_2)-meta- und-decavanadate der Zusammensetzung $[PDAH_2](VO_3)_2$ (**1**), $[PDAH_2]_3V_{10}O_{28} \cdot 5H_2O$ (**2**), $[PDAH_2]_2H_2V_{10}O_{28}$ (**3**), $[DPAH]_5HV_{10}O_{28} \cdot 2H_2O$ (**4**), $[DPAH]_4H_2V_{10}O_{28} \cdot 2H_2O$ (**5**) und $[DPAH]_3H_3V_{10}O_{28}$ (**6**) wurden aus dem Reaktionssystem *PDA*/*DPA*–V_2O_5-H_2O-HCl gewonnen und mittels Pulverdiffraktometrie und Infrarotspektroskopie charakterisiert. **3** und **5** wurden auch bezüglich ihrer morphologischen und optischen Eigenshaften untersucht.

Introduction

The solid-state chemistry of vanadates(V) is characterized by a variety of anion species, ranging from monomers to clusters or polyanions with chain or layer structure. All these polyanions are formed by joined VO_x ($x = 4, 5, 6$) polyhedra. The results obtained so far indicate an influence of cation properties on the structure of the polyanions. That is the reason why after decades of studies of polyvanadates with inorganic cations, the interest now focuses mainly on polyvanadates with organic cations. Investigations of polyvanadates with organic cations have resulted either in the synthesis of new types of solid polyvanadates

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[*] Corresponding author

(dodecavanadates [1, 2], tridecavanadate [3], and pentadecavanadate [4]) or in the isolation of known types of polyvanadates with different polyanion structures (metavanadates [5–7], pentavanadate [8]). In all decavanadates, the isolated $V_{10}O_{28}^{6-}$ anion has the same structure, but the decavanadates with inorganic cations are all crystallohydrates [9], whereas decavanadates with organic cations are also known as anhydrous compounds [10].

We report here the synthesis and properties of a metavanadate and of decavanadates with different protonation degree, containing monovalent dipropylammonium and divalent 1,3-propanediammonium cations, respectively.

Results and Discussion

From the reaction system *PDA*/*DPA*–V_2O_5–H_2O, six new polyvanadates, five decavanadates, and one metavanadate were isolated. From the viewpoint of protonation degree of the decavanadate anion, four types of compounds were prepared: $[PDAH_2]_3\ V_{10}O_{28}\cdot 5H_2O$ (**2**), $[DPAH]_5HV_{10}O_{28}\cdot 2H_2O$ (**4**), $[PDAH_2]_2H_2V_{10}O_{28}$ and $[DPAH]_4H_2V_{10}O_{28}\cdot 2H_2O$ (**3** and **5**), and $[DPAH]_3H_3V_{10}O_{28}$ (**6**). Which of the four types of decavanadates can be prepared depends on reaction conditions and cation properties. As in aqueous solutions, there is an equilibrium between decavanadate anions of different protonation degree $H_nV_{10}O_{28}^{(6-n)-}$ ($n = O$–4); the reaction conditions for the preparation of different types of decavanadates with the same cation depend also on their solubilities.

The new decavanadates are orange substances, soluble in water and almost insoluble in ethanol and common organic solvents. The optical and morphological properties of compounds **3** and **5** were studied. The other decavanadates prepared were isolated only in microcrystalline forms. The crystals of **3** occur in three morphological types: platy, pyramidal (Fig. 1), and exceptionally needle-like. In the transmitted polarized light the crystals are biaxial; oblique extinction in all orientations pointed to triclinic symmetry. Further morphological studies without informations about lattice parameters determined from X-ray data are irrelevant.

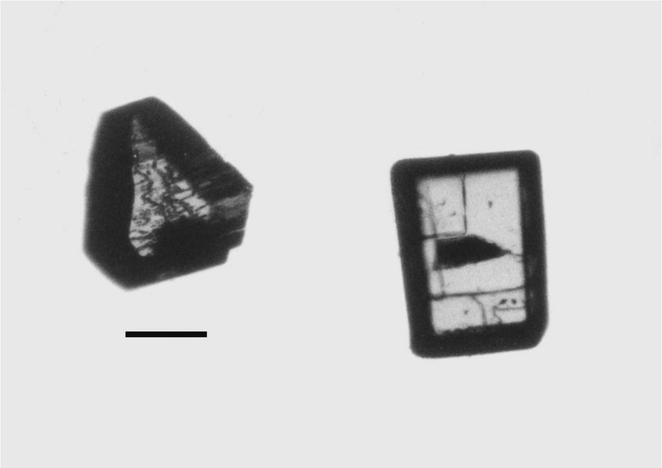

Fig. 1. Microphotograph of crystals of compound **3**; parallel polars, scale bar 0.125 mm; left: pyramidal, right: platy crystal

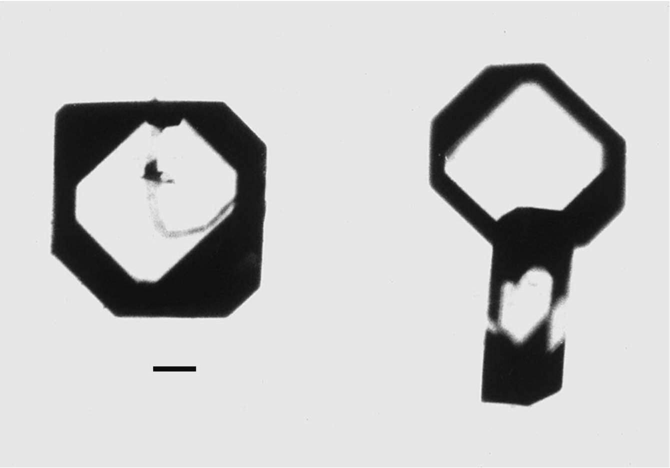

Fig. 2. Microphotograph of crystals of compound **5**; parallel polars, scale bar 0.125 mm; left: single crystals viewed down [010], the largest face is (010); right: twin of two crystals, twin plane (111), the largest face of crystal is (001)

Compound **5** forms two morphologically distinct crystal types: platy crystals with dominant {010} form and prismatic crystals, where {001} and {100} are the dominant crystal forms (Fig. 2). In transmitted polarized light, the crystals are biaxial with (001) as the plane of optical axes. The parallel extinction of crystal faces in the [010] zone and oblique extinction in direction perpendicular to [010] confirm that the crystals are monoclinic. As follows from goniometric measurements and subsequent stereographic projection, the point-group symmetry of the crystals (2/m) is consistent with the space group $P2_1/n$ determined in Ref. [11]. SEM morphological studies were not possible because of explosive crystal decomposition upon electron beam impact.

The structure of $[V_{10}O_{28}]^{6-}$ is well known [10–17]; it is formed by ten more or less distorted edge-sharing VO_6 octahedra. In the protonated anions, the hydrogen atoms are attached to double-linked or triple-linked oxygens [15], in $[HV_{10}O_{28}]^{5-}$ to triple-linked oxygen, and in $[H_2V_{10}O_{28}]^{4-}$ the hydrogen atoms are generally bonded to two symmetry-related double-linked oxygen atoms. Exceptions are $[NH_3(C_6H_{13})]_4H_2V_{10}O_{28}$ and $[\mathit{DPA}H]_4H_2V_{10}O_{28} \cdot 2H_2O$ (**5**). The hydrogen atoms in the first compound are attached to two symmetry-related triple-linked oxygens [16], and in latter one there are two non-symmetrical VO_b–H bonds: one of the hydrogen atoms is joined to a double- and the other to a triple-linked oxygen. These $[H_2V_{10}O_{28}]^{4-}$ anions are linked together in pairs by four hydrogen bonds, forming $[H_2V_{10}O_{28}]_2^{8-}$ dimers [11] (Fig. 3). In the $[H_3V_{10}O_{28}]^{3-}$ anion, there are three collinear protonated oxygens, two of them double- and one triple-linked [15]. In $[H_4V_{10}O_{28}]^{2-}$, the hydrogen atoms are joined to two double- and to two triple-linked oxygens [17].

As the structure of the decavanadate anion is relatively rigid, IR spectroscopy is able to identify these type of polyvanadates. In the region of V–O stretchings, the decavanadates prepared (Fig. 4) exhibit bands with slightly different positions and intensities. We can suppose that a certain deformation of the vanadium oxygen framework is affected not only by the protonation degree of $[V_{10}O_{28}]^{6-}$, but also by

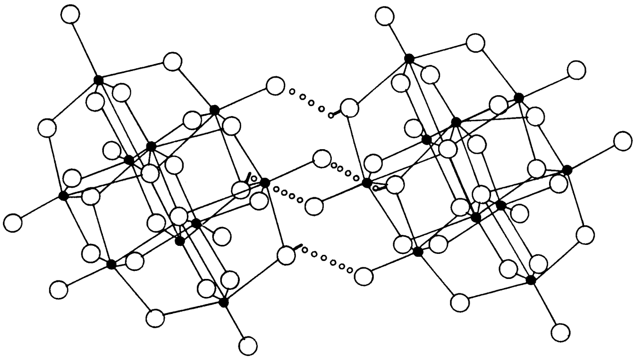

Fig. 3. The $[H_2V_{10}O_{28}]_2^{8-}$ dimer in crystal structure of **5** [11]; ●: vanadium, ○: oxygen, ○-: O_b-H, ∘∘∘: hydrogen bond

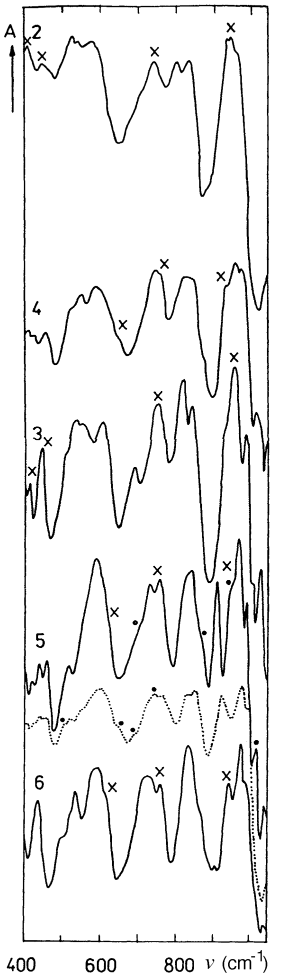

Fig. 4. IR spectra of decavanadates (labeling of compounds according to numbering in the summary); ····: IR spectrum of compound **5** prepared from D_2O, x: overlapping bands corresponding to ν(V–O) and vibrations of the cation, or vibrations of the cation only, •: deuteration effected bands

the nature of the cations, the number of hydrogen bonds between polyanion and cations, and the crystal water molecules.

The IR spectra of decavanadates are characterized by strong bands between 995–900 cm^{-1}, assignable to the stretchings of terminal V–O_t bonds, and by other strong bands in the interval 860–460 cm^{-1} corresponding to stretchings of V–O_b bonds. The bands in the 450–400 cm^{-1} region have been assigned to the deformation mode of the V–O_b group [18, 19]. According to Refs. [14, 16], there are two specific bands characteristic of protonated decavanadate anions: at about 995 cm^{-1} (assigned to V–O_t bonds in VO_5O–H octahedra, which are shortened owing to the elongation of the V–O_b–H bonds) and at about 630 cm^{-1} (assigned to V–O_b–H bonds). The IR spectra of hydrogendecavanadates **3**–**6** are not in agreement with this hypothesis. In the IR spectrum of **4**, the band at about 990 cm^{-1} is absent, and the spectra of hydrogendecavanadates **3**–**6** do not exhibit the band at about 630 cm^{-1}. On the other hand, the spectra of **4**–**6** exhibit a shoulder at 623 cm^{-1} which is present in the IR spectrum of [*DPA*H]Cl · H_2O, too.

As follows from Fig. 4, the IR spectrum of **5** differs from the other spectra by the presence of a sharp strong band at 914 cm^{-1}. This band is also absent in the IR spectrum of **3** which contains the same $[H_2V_{10}O_{28}]^{4-}$ polyanion. This fact we consider to be a consequence of the $[H_2V_{10}O_{28}]_2{}^{8-}$ dimer presence in the crystal structure of **5** [11]. In the IR spectrum of **5** prepared from D_2O, the sharp absorption band at 1018 cm^{-1} and the shoulders at 955, 874, and 700 cm^{-1} are markedly diminished or missing, and new shoulders at 740, 685, 650, and 512 cm^{-1} appear; also, a shift of the band from 914 to 921 cm^{-1} was observed. Therefore, we assign the band at 1018 cm^{-1} and the shoulder at 955 cm^{-1} to deformation vibrations of two structurally non-equivalent V–O_b–H groups, and the shoulders at 874 and 700 cm^{-1} to librations of water molecules. The absorption band at 914 cm^{-1} can be assigned to stretchings of the longest V–O_t bonds the existence of which is caused by presence of $[H_2V_{10}O_{28}]_2^{8-}$ pairs due to V–$O_t \cdots$H–O_b–V hydrogen bonds. Upon deuteration, the hydrogen bonds between $[D_2V_{10}O_{28}]^{4-}$ polyanions ($O_t \cdots$D) are elongated; as a consequence of this fact, a shortening of V–O_t bonds occurs. This is the reason of the band shift mentioned above.

In solid metavanadates with organic cations, the $(VO_3)_n^{n-}$ polyanion has a polymeric chain structure [20–22] or it forms isolated cyclic $[V_4O_{12}]^{4-}$ resp. $[HV_4O_{12}]^{3-}$ units [5–7], both originating from joined VO_4 tetrahedra. The structure of the metavanadate polyanion is only slightly influenced by the nature of the cation. Therefore, metavanadates can be identified by their IR spectra in the ν(V–O) region, and the type of the metavanadate anion structure can be proposed.

Metavanadate **1** exhibits a characteristic IR spectrum in the 400–1000 cm^{-1} region (Fig. 5). The assignments proposed are: $\nu_s + \nu_{as}$(V–O_t): 965*sh, 940* s, 915 m, 900 w, 883 s, 820 vs, and 800 sh cm^{-1}; $\nu_{as} + \nu_s$(V–O_b): 750* m, 742 sh, 710 m, 682 vs, 670 sh, 620 w, and 493 s cm^{-1}. The asterisk indicate cationic bands or overlaping bands corresponding to ν(V–O) and vibrations of the cation. The IR spectrum of **1** is very similar in its general spectral pattern to the IR spectra of metavanadates with a chain structure of the anion [23]. In [*PDA*H_2]$(VO_3)_2$, a pyroxene-like chain structure of the polyanion can thus be proposed.

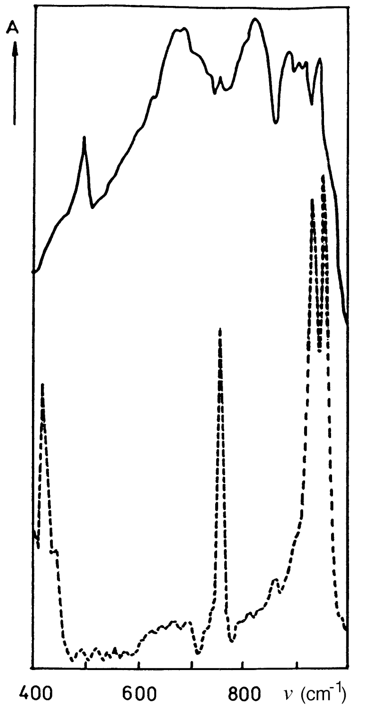

Fig. 5. IR spectra of [*PDA*H_2]$(VO_3)_2$ (—) and [*PDA*H_2]Cl_2 (- - - -)

Compound **1** is a white crystalline product, which is slightly soluble in water. It became dark upon exposure to sunlight because of photoreduction of vanadium(V) to vanadium(IV). The compound [*PDA*H_2]$_2V_2O_7 \cdot 3H_2O$ was also isolated from the reaction system *PDA*–V_2O_5–H_2O at $pH = 10$. The characterization and crystal structure of this compound have been published earlier [24].

Experimental

V_2O_5 was prepared by thermal decomposition of NH_4VO_3. The other chemicals used were of analytical grade. Vanadium(V) was determined by titration with $FeSO_4$ using diphenylamine as indicator or gravimetrically as V_2O_5. The elemental analysis was performed on a CHN analyzer 1106 (Carlo Erba). *pH* values were measured on a TTT-2 *pH*-meter (Radiometer, Copenhagen) using a GD 2401 C electrode. The IR spectra (nujol mull) were registered on a Specord M 80 spectrophotometer (Zeiss, Jena). The X-ray diffraction patterns were obtained on a Philips powder diffractometer, equipped with a PW 1050 goniometer using CuK_α radiation. The optical properties were studied using a polarizing microscope; detailed morphological observations were made using an optical two-circle goniometer.

Syntheses

The propanediammonium polyvanadates and dipropylammonium decavanadates were prepared by dissolving V_2O_5 in an aqueous solution of 1,3-propanediamine (*PDA*) or dipropylamine (*DPA*), respectively. The reaction mixtures were kept in the dark and were stirred at room temperature until complete dissolution of V_2O_5. After filtration, the *pH* of the solution was adjusted to the value required by addition of 4 *M* HCl. All decavanadates were washed with ethanol and air-dried in the dark.

$[PDAH_2](VO_3)_2$ (**1**)

Starting compounds: V_2O_5 (0.55 g, 3 mmol), *PDA* (1 cm^3, 12 mmol), H_2O (100 cm^3); *pH* = 9.0. The white crystalline product was formed within 35 d from the solution kept in a refrigerator. The crystals were washed with cold water and dried above silica gel in the dark. Calc.: V 37.18, C 13.15, N 10.22, H 4.41%; found: V 37.13, C 13.22, N 10.22, H 4.41%.

$[PDAH_2]_3V_{10}O_{28} \cdot 5H_2O$ (**2**)

Starting compounds: V_2O_5 (0.55 g, 3 mmol), *PDA* (1 cm^3, 12 mmol), H_2O (100 cm^3). During adjusting the *pH* of the solution to 6.0, an orange precipitate was formed. Calc.: V 39.92, C 8.47, N 6.58, H 3.63%; found: V 39.56, C 8.37, N 6.50, H, 3.53%.

$[PDAH_2]_2H_2V_{10}O_{28}$ (**3**)

Starting compounds: V_2O_5 (1.1 g, 6 mmol), *PDA* (1 cm^3, 12 mmol), H_2O (100 cm^3); *pH* = 3.0. Orange crystals were formed within 24 h from the solution kept in a refrigerator. Calc.: V 45.82, C 6.48, N 5.04, H 2.35%; found: V 45.51, C 6.24, N 4.99, H 2.34%.

$[DPAH]_5HV_{10}O_{20} \cdot 2H_2O$ (**4**)

Starting compounds: V_2O_5 (0.5 g, 2.75 mmol), *DPA* (1.5 cm^3, 11 mmol), H_2O (40 cm^3); *pH* = 5.5. Dark orange crystals were obtained after 14 d. Calc.: V 33.58, C 23.94, N 4.65, H 5.69%, found: V 33.58, C 23.60, N 4.85, H 5.57%.

$[DPAH]_4H_2V_{10}O_{28} \cdot 2H_2O$ (**5**)

Starting compounds: V_2O_5 (0.5 g, 2.75 mmol), *DPA* (1.5 cm^3, 11 mmol), H_2O (40 cm^3); pH = 2.7. Large orange crystals were formed within 24 h. Calc.: V 36.24, C 20.53, N 3.99, H 5.00%; found: V 36.44, C 20.57, N 3.89, H 4.99%.

$[DPAH]_3H_3V_{10}O_{28}$ (**6**)

Starting compounds: V_2O_5 (0.67 g, 3.66 mmol), *DPA* (1.5 cm^3, 11 mmol), H_2O (40 cm^3). During adjusting the *pH* of the solution to 2.7, a yellow orange precipitate was formed. Calc.: V 40.21, C 17.06, N 3.32, H 4.06%; found: V 39.63, C 17.31, N 3.41, H 4.02%.

For identification purposes, the interplanar distances (nm) and the relative intensities (in parentheses) for the ten most intensive diffractions in **1**–**6** are given.

1: 0.2936 (100), 0.3243 (62), 0.536 (54), 0.3493 (50), 0.1789 (47), 0.1785 (43), 0.2655 (27), 0.3663 (26), 0.3732 (24), 0.2535 (23)

2: 0.868 (100), 0.912 (98), 0.2875 (67), 0.4575 (59), 0.725 (45), 0.703 (36), 0.4311 (36), 0.3281 (23), 0.3633 (19), 0.3243 (16)

3: 0.863 (100), 0.731 (75), 0.3738 (29), 0.3175 (28), 0.3576 (27), 0.3232 (24), 0.2171 (21), 0.2532 (16), 0.633 (13), 0.2652 (11)

4: 0.577 (100), 0.598 (18), 0.2788 (12), 0.4761 (8), 0.3760 (5), 0.2691 (5), 0.2755 (4), 0.3322 (3), 0.2940 (3), 0.2866 (3)

5: 0.672 (100), 0.2815 (17), 0.554 (10), 0.513 (10), 0.633 (9), 0.624 (8), 0.615 (8), 0.3533 (6), 0.1859 (6), 0.490 (5)
6: 0.587 (100); 0.504 (21), 0.2848 (14), 0.453 (10), 0.2931 (10), 0.2563 (10), 0.444 (5), 0.2592 (5), 0.537 (4), 0.3900 (4)

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