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Catalytical decomposition of L-glutamic acid and L-glutamine with vanadium species. Electronic spectra of ammonium–sodium oligovanadates isolated from the system [$NaVO_3(VOSO_4)$–Glu(Gln)]. Crystal structure of $Na_3(NH_4)_3[V_{10}O_{28}]\cdot 12H_2O$

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Abstract

Oligovanadates (tetra-, penta- and decamers) with the Na^+ and NH_4^+ cations have been isolated from systems [V(V)/V(IV)–L-glutamic acid (L-glutamine)]. Three basic processes: (i) the oxidation of the vanadium(IV) to vanadium(V); (ii) decomposition of Glu and Gln under the catalytic effect of V(V); (iii) the formation and precipitation of sodium ammonium oligovanadates have been observed. The polyoxovanadates have been studied with crystallographic (decavanadate–$Na_3(NH_4)_3[V_{10}O_{28}]\cdot 12H_2O$) and spectroscopic (absorbance UV–Vis, Ir) methods. Spectral analyses allowed the assignment of the electronic bands to particular transitions in the oligovanadate anions.

Keywords: Oligovanadates; L-Glutamic acid; L-Glutamine; Decomposition; Electronic spectra; Crystal structures

1. Introduction

Vanadium is an element which plays a variety of biochemical, pharmacological and physicochemical functions [1–6]. However, in the literature relatively few studies on the interaction between vanadium(V) (and V(IV)) and simple amino acid (AA) have been undertaken [7–12]. Moreover, the investigations on the interaction between V(V) and AA were devoted almost exclusively to the experiments in solution and, to the authors' best knowledge, only in one case, i.e. for the V(V) complex with the histidine derivative, has the structure been given [13]. This is in contrast to vanadium(V) peroxo complexes where many solid complexes were synthesised [14–16]. In our opinion, the lack of the solid complexes precipitating from the system: [vanadium(V)–amino acid] can be related to the chemistry of this metal ion. This chemistry is based on three most important variables: (1) total concentration of the reagents (usually, the concentration range being 10^{-4}–10^{-2} M is too low for isolation of the products) [17,18]; (2) acidity (physiological pH and a little lower prefers the complex formation due to the predominant presence of $VO_2(OH)_2^-$ and (indirectly) $H_2VO_4^-$ species interacting with an organic substrate) [17]; (3) metal:ligand ratio. The last parameter seems to be important as the competition between hydrolysis and oligomerization on the one hand and complexation on the other is taking place in the solution. Large excess (100x) of the ligand favorises the complex formation [18] although Fritzsche et al. [17] have found in solution a dinuclear V(V) complex at 'only' M:L = 1:4 ratio. Certainly, the low stability of formed V(V) and V(IV) complexes cannot be omitted [17].

Another important feature which influences the equilibria in solutions is the reversibility of the redox V(V)/V(IV) system: $H_2VO_4^- + 4H^+ + e \leftrightarrow VO^{2+} +$

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$3H_2O$ [9]. However, as a solid product the less soluble form existing in solution is obtained [19,20]. For example, the solid products containing the heteronuclear Cr(III)/V(IV) complexes with glutathione were obtained exclusively from V(V) as a substrate [21]. Moreover, this reversibility can be extended to V(III) [22].

In this work we have studied the precipitates obtained from the [V(V)/V(IV)–L-glutamic acid (L-glutamine)] systems at the condition of 'normal' (7×10^{-2} M) vanadium concentration but 'abnormally' low (1:1; 1:2 and 1:3) M:L ratio. L-glutamic acid (Glu) and L-glutamine (Gln) have been chosen as ligands. The [V(V)/V(IV)–Glu/Gln] systems were studied ealier in solutions [18,23]. The former studies showed that depending upon pH, the $[V^VO_2L]^-$ and $[V^VO_2L_2]^{n-}$ ($n = 1–3$) species had been formed [18].

Surprisingly enough in this work, instead of glutamate complexes, as in other transition metal ions [24], the oligovanadate salts with the NH_4^+ ion—one of the decomposition products of the organic ligand, have been obtained.

2. Experimental

2.1. Preparation of the compounds

Reagent grade commercially available chemicals (Aldrich) were used in all experiments. The system was studied with two different vanadium containing salts: $NaVO_3 \cdot H_2O$ and $VOSO_4 \cdot 5H_2O$ with the vanadium concentration $c = 7 \times 10^{-2}$ M and at three reagent ratios (M: L) 1:1, 1:2, 1:3.

2.2. General procedure

Vanadium salt (0.7 mol) and L-glutamic acid or L-glutamine (0.7, 1.4 or 2.1 mol) were dissolved in 100 cm^3 of water and warmed at 60 °C (30 min) with stirring. After 1 week the acidity was adjusted to pH 6–7 with solid NaOH. Each following week (totally 5–9 times depending upon the system) the solution was warmed at 60 °C for 2 h. The precipitates were filtered and washed with water. Table 1 presents the details.

The control synthesis using all reagents except the organic ligand has been performed with the same conditions and no solid products have been obtained.

Anal. Found (no. of synthesis): (1) H, 1.6; N, 3.2; Na, 5.6; V, 45.7; (2) H, 2.5; N, 3.0; Na, 4.4; V, 38.0; (3) H, 2.6; N, 3.4; Na, 4.8; V, 40.4; (4) H, 2.3; N, 4.6; Na, 4.6; V, 46.4; (5) H, 2.1; N, 4.5; Na, 4.5; V, 46.6; (6) H, 2.1; N, 3.7; Na, 5.0; V, 44.2; (7) H, 1.9; N, 4.6; Na, 3.9; V, 46.8. Calc.: (no. of synthesis (compound)): 1(**1A**) $H_6NO_{12}V_4Na$: H, 1.4; N, 3.2; Na, 5.3; V, 46.3; 2(**1B**) $H_{16}NO_{17}V_4Na$: H, 3.0; N, 2.6; Na, 4.3; V, 38.5; 3(**3**) $H_{36}N_3O_{40}V_{10}Na_3$: H, 2.8; N, 3.2; Na, 5.3; V, 39.3; 4(**2**) $H_{10}N_2O_{15}V_5Na$: H, 1.8; N, 5.0; Na, 4.1; V, 45.8; 5(**2**) $H_{10}N_2O_{15}V_5Na$: H, 1.8; N, 5.0; Na, 4.1; V, 45.8; 6(**1C**) $H_8NO_{13}V_4Na$: H, 1.7; N, 3.1; Na, 5.0; V, 44.6; 7(**2**) $H_{10}N_2O_{15}V_5Na$: H, 1.8; N, 5.0; Na, 4.1; V, 45.8. IR (cm^{-1}): **1A**, **1B**, **1C** ν_{N-H} 3180–3200w, ν_{O-H} 1630–1636m, $\nu_{V=O}$ 985m; 955–945s, $\nu_{asV-O-V}$ 808m, 744s, ν_{sV-O-V} 595w, 530–539w; **2** ν_{N-H} 3178w, ν_{O-H} 1626m, $\nu_{V=O}$ 985m, 955s, $\nu_{asV-O-V}$ 809–828m, 742m, ν_{sV-O-V} 593w, 522w; **3** $\nu_{N-H} = 3178$w, ν_{O-H}1628m, $\nu_{V=O}$ 989m, $\nu_{asV-O-V}$ 743w, ν_{sV-O-V} 530s.

2.3. Physicochemical studies

The compounds were analysed by a modification of Kumpans' method (C, H, N, S) and the AES-ICP method and with an ARL 3410 emission spectrometer (V, K) using Aldrich standards.

2.4. X-ray measurements

Crystal data are given in Table 2 together with refinement details. All measurements of the crystal were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wroclaw) programs. The structure was solved by a direct method (program SHELXS-97 [25]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 [26] programs. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from the $\Delta\rho$ maps.

2.5. Spectroscopic studies

IR spectra were recorded on a Perkin–Elmer FTIR 1600 spectrophotometer (4000–400 cm^{-1}). The absorption spectra in solution ($c = 1 \times 10^{-4}$ M) were measured in the 7000–50000 cm^{-1} spectral range with a Cary 500 scan UV–Vis spectrophotometer. To obtain the band positions the analyses of the spectra were performed using variable digital filter method [27–29]. Filter parameters for absorption spectra: step = 100, $\alpha = 300$, $N = 30$[20]. An example of the resolution is shown in Fig. 3.

3. Results and discussion

By changing the M:L ratio (M = V(V), V(IV), L = L-glutamic acid or L-glutamine) seven precipitates forming three different compositions (including one (**1**) containing various amount of crystalline water molecules) and

Table 1
Experimental conditions

No of synthesis	Substrates (mol)	Ratio M:L	pH_0	pH_f	Time of evaporation (weeks)	Formula	Compound (symbol)
1	$NaVO_3 \cdot H_2O_{0.7} + C_5H_9O_4N$ $(Glu)_{0.7}$	1:1	4.22	6.80	7	$NaNH_4[H_2V_4O_{12}]$	**1A**
2	$NaVO_3 \cdot H_2O_{0.7} + C_5H_9O_4N$ $(Glu)_{1.4}$	1:2	3.84	6.63	6	$NaNH_4[H_2V_4O_{12}] \cdot 5H_2O$	**1B**
3	$NaVO_3 \cdot H_2O_{0.7} + C_5H_9O_4N$ $(Glu)_{2.1}$	1:3	3.80	6.76	6	$Na_3(NH_4)_3[V_{10}O_{28}] \cdot 12H_2O$	**3**
4	$NaVO_3 \cdot H_2O_{0.7} + C_5H_{10}O_3N_2$ $(Gln)_{0.7}$	1:1	7.53	7.53	8	$Na(NH_4)_2[H_2V_5O_{15}]$	**2**
5	$NaVO_3 \cdot H_2O_{0.7} + C_5H_{10}O_3N_2$ $(Gln)_{1.4}$	1:2	7.24	7.24	8	$Na(NH_4)_2[H_2V_5O_{15}]$	**2**
6	$NaVO_3 \cdot H_2O_{0.7} + C_5H_{10}O_3N_2$ $(Gln)_{2.1}$	1:3	6.73	6.73	9	$NaNH_4[H_2V_4O_{12}] \cdot H_2O$	**1C**
7	$VOSO_4 \cdot 5H_2O_{0.7} + C_5H_{10}O_3N_2$ $(Gln)_{2.1}$	1:3	3.27	7.00	5	$Na(NH_4)_2[H_2V_5O_{15}]$	**2**

pH_0, acidity at the beginning of the reaction; pH_f, acidity adjusted with solid NaOH.

Table 2
Crystallographic data for compound **3**

Compound	**3**
Formula	$Na_3(NH_4)_3[V_{10}O_{28}] \cdot 12H_2O$
M_r	1296.7
Temperature (K)	100(1)
Wavelength (Å)	0.71073
System	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.992 (2)
b (Å)	17.100 (3)
c (Å)	18.038 (4)
β (°)	105.89
V (Å^3)	3557.6(12)
Z	4
D_{calc} (Mg m^{-3})	2.421
Absorption coefficient (mm^{-1})	2.668
$F(000)$	2560
θ Range for data collection (°)	3.35–25.00
Reflections collected/unique	19 870/6247 [$R_{int} = 0.0755$]
Refinement method	full-matrix least-squares on F^2
Data [$I > 2\sigma(I)$]/parameters	5091/505
Goodness-of-fit on F^2	1.132
Final R indices	$R_1 = 0.0481$, $wR_2 = 0.1132$
R indices (all data)	$R_1 = 0.0628$, $wR_2 = 0.1206$
Largest difference peak and hole (e Å^{-3})	0.686 and −0.734

belonging to the large family of polyoxovanadates(V) [30–34] have been isolated (Table 1). They appeared to be anionic tetra-, penta- and decamers with mixed sodium and ammonium cations. Elemental analysis and spectroscopic studies showed that irrespective of the oxidation state of vanadium and M:L ratios, the interaction with organic ligand resulted in the isolation of oligovanadates(V). It was found that the presence of both vanadium and organic ligands as substrates was a condition sine-qua-non to obtain precipitates. It was supported by the results of the control experiment (see the experimental part). Evidently, precipitating oligovanadates containing the ammonium group(s) as counter ion(s) must be the least soluble species in the system.

While discussing the chemistry of the final products, three basic processes must be taken into account, with atmospheric oxygen playing an active role in the first two: (i) the oxidation of the vanadium(IV) to vanadium(V) (see Table 1, compound **2** obtained from $VOSO_4$ system 7); (ii) the oxidation (decomposition) of Glu and Gln under the catalytic effect of V(V); (iii) the formation and precipitation of sodium ammonium oligovanadates. Stages (ii) and (iii) most probably take place simultaneously.

(i) The redox processes involving various vanadium oxidation states and also including atmospherical oxygen are well known in the literature [35–37]. Moreover, from the system [V(III)–guanine] under an inert atmosphere, the vanadium(V) decamer has been isolated with the organic species degradated to dimethylammonium ion [22].

(ii) Vanadium is a transition metal whose compounds play an important role as catalysts in a variety of oxidation reactions both in the technical processes (production of phthalic and sulfuric acids) and nature (e.g. vanadium haloperoxidases) [2,38,39]. Amino acids undergo decomposition forming various organic products, e.g. succinic acid and NH_4^+ group [40,41]. Formation of this group appears to be a predominant process over the conversion to, e.g. (NO_3^-) [41].

The analysis of the data presented in Table 1 shows that the final chemical formulae of isolated oligovanadates are governed by all parameters, i.e. organic ligand, M:L ratio, pH and time. Moreover, these factors seem to be interrelated. Evidently, additional studies including ^{51}V, ^1H and ^{13}C NMR spectroscopies must be carried out on the nature of the species in solution.

(iii) Oligovanadates are forming under the processes of hydrolysis and oligomerisation [19,20,42]. Dimers (V2), tetramers (V4), pentamers (V5), hexamers (V6), decamers (V10) and even species containing more than ten vanadium atoms are known in the literature [43–45]. The size of the polyvanadium centres is important for the sake of physiological and pharmacological relevance [3,46]. For example, enzyme inhibition or activation is dependent upon the size of polyoxovanadates [46]. The literature studies indicate that the easiest isolatable crystal form of oligovanadates was found to be a

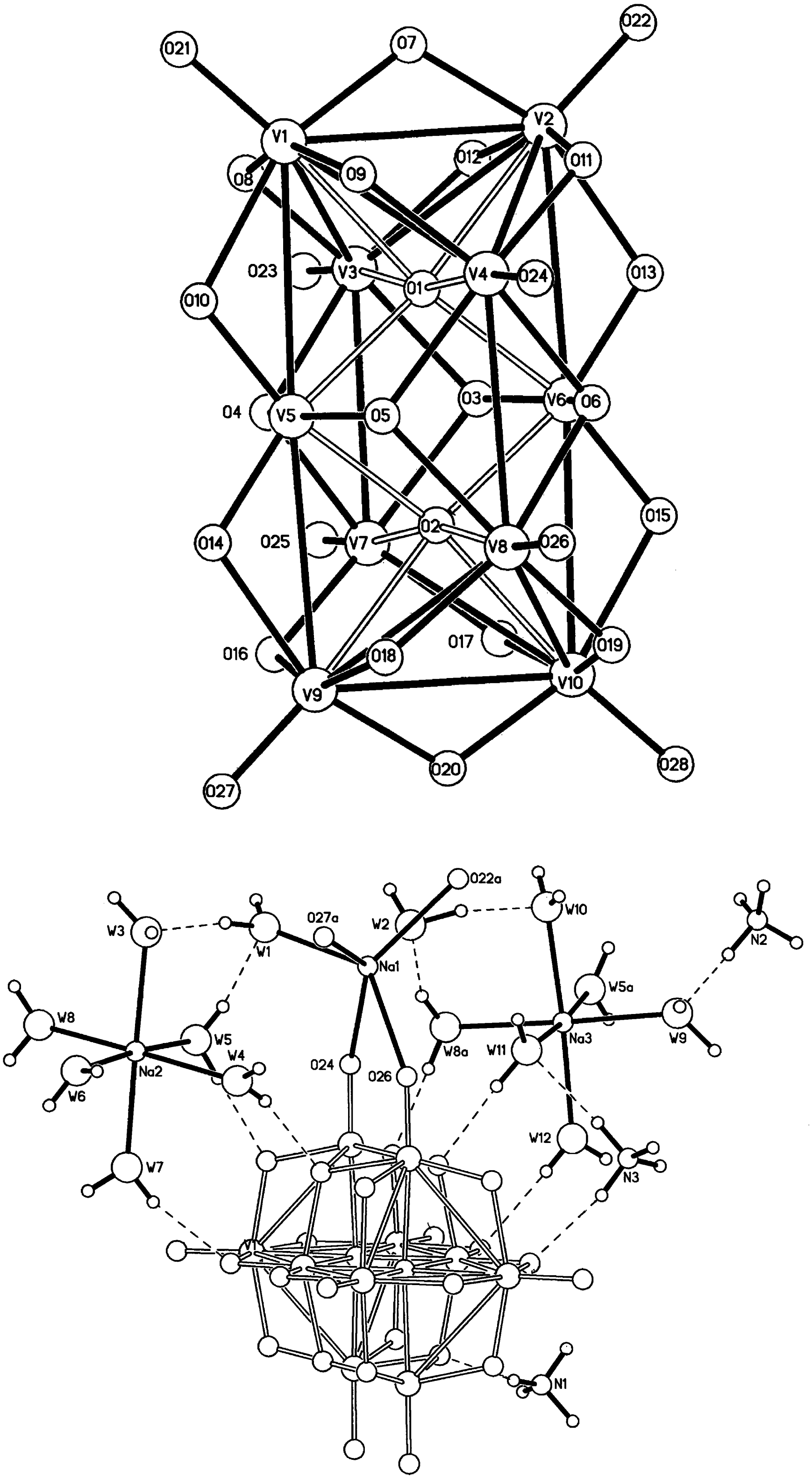

Fig. 1. Crystal structure of obtained decavanadate.

combination of polyanion and organic cation, with an additional inorganic component (Na^+, NH_4^+) [30–34]. The typical inorganic form of decavanadate $Na_6V_{10}O_{28}$ is also known [47]. However, in contrast to the results obtained in this work, the organic part of the isolated species in most cases does not change in the reaction.

3.1. Crystal structure analysis

The $Na_3(NH_4)_3[V_{10}O_{28}]\cdot 12H_2O$ crystals have a monoclinic symmetry with space group $P2_1/n$. The crystal structure of compound **3** consists of a decavanadate anion, three Na^+ and three NH_4^+ cations and water molecules. The decavanadate anion can be described as a section of close-packed cubic oxygen atoms with vanadium atoms in the octahedral centres [48]. There are three types of VO_6 octahedra in the decavanadate polyanion [30,49] (see Fig. 1(a)). In type I, characteristic of V1, V2, V9, V10, the vanadium atom occupies the central plane of decavanadate. In type II (V3, V4, V7, V8) the vanadium is above and below the plane. All vanadium atoms in type I and II are bound to one terminal oxygen atom with the V–O bond length ca. 1.601–1.612 and ca. 1.610–1.631 Å, for types I and II, respectively. Type III (V5 and V6) occupies a central position in the polyanion, and the vanadium atoms are not linked to the terminal oxygen atoms. In many known decavanadates all three types of VO_6 octahedra can be found. The differences between the respective V–O bond lenghts in decavanadates are related to cation effects [22,35,42,46].

Additionally, in compound **3** each Na^+ atom interacts electrostatically with the decavanadate anion. Moreover, Na2 and Na3 are surrounded with six water molecules while Na1 with two water molecules and two terminal oxygen atoms of one polyanion and two terminal oxygen atoms form a second one. In each compound the hydrogen bonding network is developed between ammonium, water molecules and the polyanion. Both cations are bound to the terminal and doubly bridging oxygen atoms of decavanadate (Fig. 1(b)). Table 3 shows interatomic distances involving hydrogen bonded atoms in crystals of $Na_3(NH_4)_3[V_{10}O_{28}]\cdot 12H_2O$. The system of hydrogen bonding among NH_4^+, H_2O and decavanadate anion allows multiplying of decamers in three directions.

Table 3
Hydrogen contacts (Å) in the crystal structure of compound **3**

Bond type	*d* (D–H)	*d* (H···A)	*d* (D···A)	∠ (DHA)
N(1)–H(1)···W(4)#6	0.96	1.90	2.854(3)	167.8
N(1)–H(2)···O(14)#6	0.89	1.99	2.857(3)	164.7
N(1)–H(3)···O(26)#1	0.91	2.05	2.914(3)	159.1
N(1)–H(4)···O(3)	0.85	2.05	2.889(3)	168.9
W(1)–H(11)···W(3)	0.98	1.84	2.796(3)	167.5
W(1)–H(12)···O(16)#7	0.81	1.99	2.799(3)	173.3
W(2)–H(21)···W(10)	1.04	1.77	2.774(3)	162.8
W(2)–H(22)···O(17)#7	0.92	1.90	2.770(3)	158.6
W(3)–H(31)···O(22)#4	0.93	2.03	2.955(3)	171.1
W(3)–H(32)···O(20)#2	0.76	1.99	2.720(3)	160.4
W(4)–H(41)···O(18)#2	0.87	1.96	2.815(3)	166.3
W(4)–H(42)···O(5)	0.80	2.00	2.774(3)	165.5
W(5)–H(51)···O(9)	0.90	1.94	2.837(3)	176.1
W(5)–H(52)···W(1)	0.87	1.99	2.831(3)	161.6
W(6)–H(61)···O(19)#2	0.92	2.08	2.961(3)	160.3
W(6)–H(62)···O(25)#8	0.91	2.21	2.899(3)	132.0
W(6)–H(62)···O(23)#8	0.91	2.44	3.172(3)	137.9
W(7)–H(71)···O(10)	0.90	2.00	2.878(3)	165.5
W(7)–H(72)···O(17)#8	0.92	1.93	2.838(3)	169.8
W(8)–H(81)···O(11)#4	0.92	1.87	2.788(3)	176.4
W(8)–H(82)···W(2)#4	0.92	1.95	2.814(3)	155.3
W(9)–H(91)···O(8)#3	0.72	2.10	2.793(3)	162.5
W(9)–H(92)···O(23)#6	1.05	2.18	3.123(3)	147.1
W(9)–H(92)···O(25)#6	1.05	2.21	2.879(3)	119.3
W(10)–H(101)···O(7)#3	0.81	1.91	2.716(3)	176.1
W(10)–H(102)···O(21)#5	0.88	2.28	2.922(3)	129.7
W(11)–H(111)···O(6)	0.95	1.96	2.890(3)	168.1
W(11)–H(112)···O(12)#3	1.00	1.93	2.827(3)	146.8
W(12)–H(121)···O(13)	0.85	2.06	2.910(3)	178.2
W(12)–H(122)···O(16)#6	0.84	2.05	2.826(3)	153.8
W(12)–H(122)···O(14)#6	0.84	2.58	3.213(3)	133.3
N(2)–H(5)···W(9)	0.95	2.04	2.937(4)	158.0
N(2)–H(6)···W(6)#9	0.91	2.14	3.019(4)	162.1
N(2)–H(7)···O(9)#5	0.97	2.30	3.137(4)	144.0
N(2)–H(7)···O(11)#5	0.97	2.31	3.148(4)	144.5
N(2)–H(8)···O(21)#3	0.97	2.23	3.014(3)	137.6
N(2)–H(8)···O(28)#10	0.97	2.41	2.975(3)	117.0
N(3)–H(9)···W(11)	0.96	2.02	2.965(4)	168.0
N(3)–H(10)···O(15)	0.91	1.97	2.868(3)	168.7
N(3)–H(11′)···O(4)#6	0.97	1.96	2.928(3)	173.2
N(3)–H(12′)···O(23)#3	0.97	2.17	2.929(3)	134.9

Symmetry transformations used to generate equivalent atoms: #1, $x+1/2$, $-y+1/2$, $z+1/2$; #2, $-x$, $-y+1$, $-z$; #3, $x-1/2$, $-y+1/2$, $z-1/2$; #4, $-x-1/2$, $y+1/2$, $-z+1/2$; #5, $-x-1/2$, $y-1/2$, $-z+1/2$; #6, $-x+1/2$, $y-1/2$, $-z+1/2$; #7, $x-1$, y, z; #8, $-x+1/2$, $y+1/2$, $-z+1/2$; #9, x, $y-1$, z; #10, $-x$, $-y$, $-z$.

3.2. Electronic spectra

The absorption spectra in solution are shown in Figs. 2 and 3 whereas Table 4 presents their analysis. Additionally, Fig. 2 shows the spectrum of an aqueous solution of freshly prepared $NaVO_3$ which contains VO_4 units (T_d). The analysis of Fig. 2 and Table 4 shows clearly that the solution spectra of various oligovanadates (**1**–**3**) are almost identical and substantially different from that of monovanadate. The similarity of the band positions of **1**–**3** implies the structural identity of the absorbing units (i.e. $\{VO_6\}$, see the crystallographic part) of all studied oligovanadates. The octahedral coordination of vanadium in tetra- and pentavanadates does not exist in monovanadates and oligovanadates up to four vanadium centres which usually exhibit a tetrahedral structure [50–52]. The coordination number 6 for both decavanadates and vanadium complexes with O-donor ligands is well known [35,36,48,53]. Therefore, we can suppose that in solution of tetra- and pentavanadates the decavanadate is the predominant species. The difference of the absorption spectra of oligovanadates from that of monovanadate is related to the difference in the symmetry of the absorbing chromophores, i.e. $\{VO_6\}$ versus $\{VO_4\}$. Generally, the band positions in the ML_6

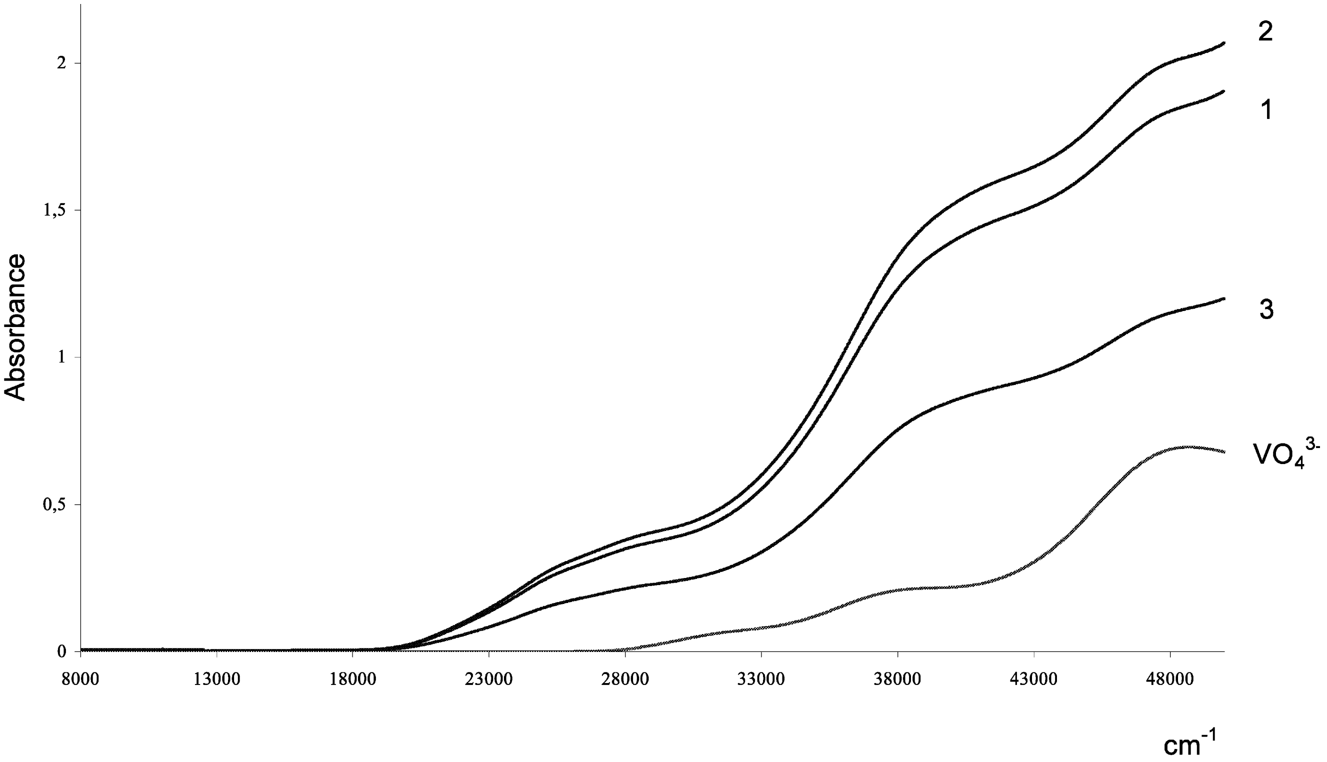

Fig. 2. The absorption spectra of polyvanadates **1**–**3** and $[VO_4]^{3-}$ ion in water solution (for **1**, **2** and $[VO_4]^{3-}$ $C = 1 \times 10^{-4}$ M, for **3** $C = 2.5 \times 10^{-5}$ M).

Table 4
Band resolution in charge transfer spectra of polyoxovanadates in solution (in cm^{-1})

Compound	$\pi_L - t_{2g}$			$\pi_L - 2_{eg}$		$\sigma_L - 2_{eg}$
	$\pi 1t_{2g}$ **1**	$(\pi+\sigma)2t_{1u}$ **2**	$\pi 1t_{2u}$ **3**	$(\pi+\sigma)2t_{1u}$ **4**	$(\pi+\sigma)1t_{1u}$ **5**	$\sigma 1t_{1u}$ **6**
1A	22 000	25 200	28 100	38 400	41 400	47 400
1B	22 000	25 200	28 100	38 400	41 400	47 400
1C	22 000	25 200	28 100	38 400	41 400	47 400
2	22 000	25 200	28 100	38 400	41 400	47 400
2	22 000	25 200	28 100	38 400	41 400	47 400
2	22 000	25 200	28 100	38 400	41 400	47 400
3	22 000	25 200	28 100	38 400	41 400	47 400

are bathochromically shifted reflecting less covalent character of the single M–L bond in the former due to more oxygen ligands being coordinated to the metal centre [54].

Table 4 and Fig. 3 show the deconvolution of the spectra under digital filtration process. For assignment of each band to a particular electronic transition in the VO_6 unit the molecular diagram for metal hexahalides MX_6^{n-} has been adopted [54]. However, it must be stressed that oxide ligands perturb metal orbitals significantly and the sequence of the energy levels must be taken with caution. Moreover, the intensity of the bands (probability of the particular transition) was found to be ca. 10 times higher than expected for the intensity of the mononuclear MX_6 species, presumably due to the coupling of the VO_6 chromophores linked with the oxide bridges (Fig. 1).

Generally, two types of LMCT transitions may be expected in the single MO_6 octahedron: L-t_{2g} and L-e_g (Table 4). Particularly, taking into account oxygen π and σ orbitals and assuming the analogy of VO_6 with MX_6, the LMCT energy levels may be arranged in the

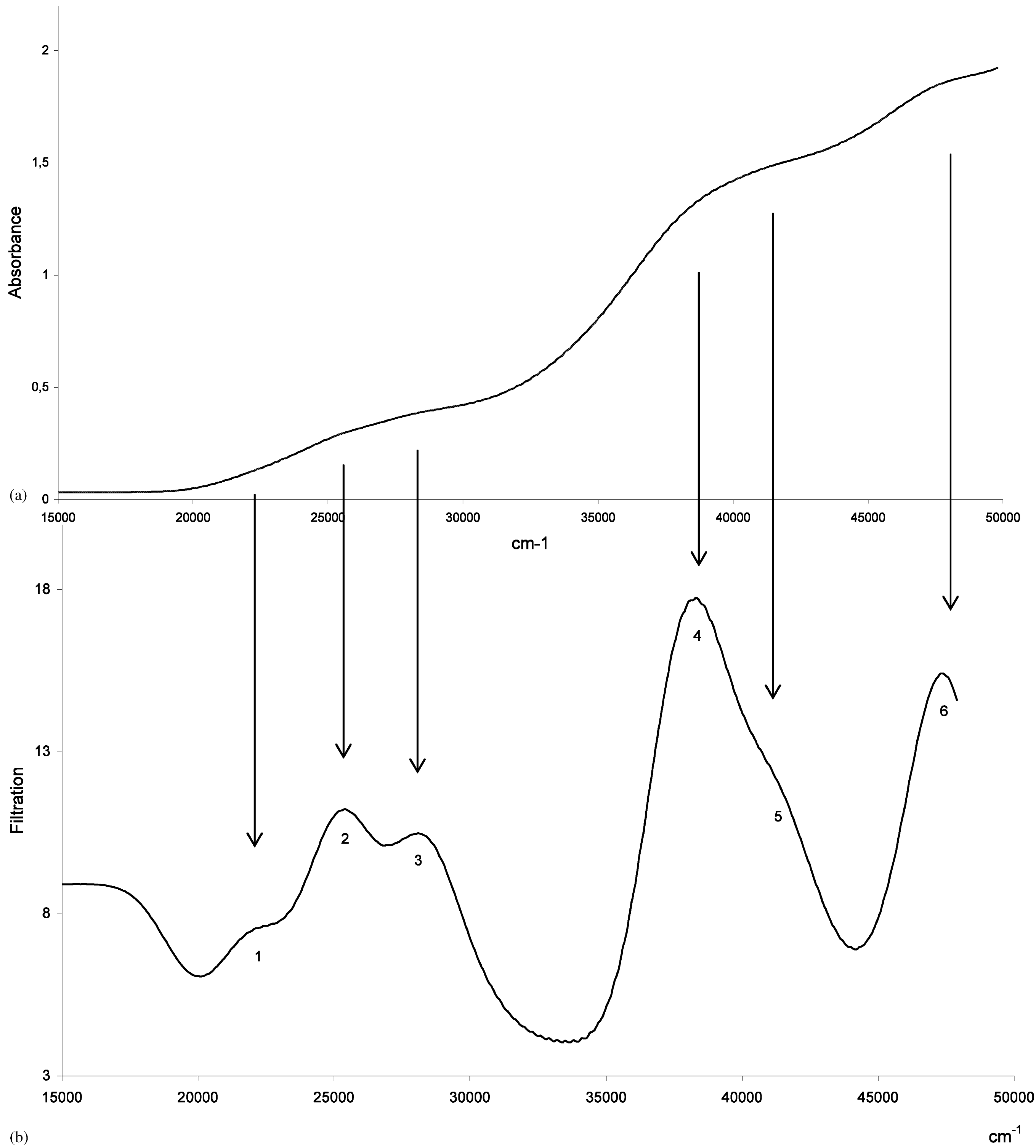

Fig. 3. (a) The absorption spectrum of $Na_3(NH_4)_3[V_{10}O_{28}]\cdot 12H_2O$, (b) the result of filtration analysis (for band numbering and assignment see Table 4).

following sequence:

$$\pi 1t_{1g} > (\pi+\sigma)2t_{1u} > \pi 1t_{2u} > (\pi+\sigma)2t_{1u} > (\sigma+\pi)1t_{1u} > \sigma 1t_{1u}$$

The absorption bands in the spectra of **1**–**3** were assigned accordingly and are shown in Table 4.

Having analysed particular transitions one can obtain characteristic values related to the spectral properties of a given system: Jørgensen optical electronegativity for vanadium(V) ($\chi_{V(v)}$) and Δ, i.e. the differences between metal t_{2g} and e_g levels. For d^0 configuration in O_h complexes the differences between $\pi(O)t_{2g}$ and $\pi(M)t_{2g}$ are equal to $30\,000(\chi(L)-\chi(M))$ [54]. From the above expression, taking the position of the lowest energy transition = 22 000 cm^{-1} and assuming $\chi_O = 3.5$, $\chi_{V(v)}$ can be calculated. The value of $\chi_{V(v)}$ being 2.76 is in line with the reported values for V(IV) = 2.6 [54].

Based on the transition to the e_g level (i.e. 38 400cm^{-1}) $10Dq$ values = 16200 cm^{-1} can be obtained from the following relation: $e_g = 30(\chi(L)-\chi(M)) + 10Dq$ [54].

4. Summary and conclusions

A series of polyoxovanadates(V) have been isolated from the [vanadium(IV/V)–glutamic acid (glutamine)] systems. The NH_4^+ group found as a counter ion indicated organic ligand decomposition. It shows also that its presence influences (decreases) the solubility of a particular species present in solution, i.e. oligovanadates. Moreover, the crystal data indicated that the presence of ammonium ions influences the geometry of the polyanion through the non covalent (hydrogen bonding network) cation–anion interactions. It can be important in the synthetic strategy when a oligovanadate of defined properties, e.g. with selective affinity towards proteins, is needed [34].

The electronic spectra analysis supports the VO_6 unit as a building element in solution in all studied polyoxovanadates. Assuming a molecular orbital sequence analogous to the metal hexahalides an attempt to assign the electronic bands to particular transitions in oligovanadates has been given.

5. Supplementary material

Supplementary data are available from the Inorganic Crystallographic Database—FIZ Karlsruhe No. CDS 412811.

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