DOI: 10.1002/ejic.201001242

Synthesis, Spectroscopic and Structural Studies on Vanadium(V) Periodates

Andrew L. Hector*[a] and William Levason[a]

Keywords: Vanadium / Periodate / EXAFS spectroscopy

Reactions of V_2O_5 or NH_4VO_3 with periodic acid under basic conditions followed by acidification result in precipitates of general formula $M_5V_4I_2O_{19}(OH){\cdot}nH_2O$ (M = Na, n = 10; M = K, n = 5; M = Rb, n = 4; M = Cs, n = 3; M = NH_4, n = 11). These are amorphous, and attempts at crystallisation failed, but spectroscopic measurements and analysis show similar features and compositions throughout this series of compounds. V and I K-edge extended X-ray absorption fine structure (EXAFS) spectra show a polymeric structure containing edge-linked octahedral periodate and square-pyramidal vanadyl groups.

Introduction

The pseudo-octahedral orthoperiodate anions $[IO_6H_{5-x}]^{x-}$ are strongly coordinating ligands for many high-oxidation-state metal centres, particularly those of the later d block and p block.[1–5] Early transition metal complexes are less thoroughly explored, although we have reported examples with Sc, Y, La,[6] Ce^{IV},[7] and Ti, Zr, Hf and Th.[8] We have also shown that hydrothermal synthesis from H_5IO_6 and an appropriate metal salt is a convenient route to single crystals of lanthanide iodates, some of which have second harmonic generation (SHG) applications.[9,10] Recently, there has been interest in the SHG properties of vanadium iodates, including some very strong responses from $Na[VO_2(IO_3)_2(H_2O)]$.[11,12] In group 5, there is a single example of a vanadium periodate complex, $Na_6[V_2I_2H_2O_{16}]{\cdot}10H_2O$, whose structure has been independently reported twice,[13,14] which contains edge-sharing IO_5OH and VO_5 groups, although other data on this complex are limited. The only other report is on compounds with a 2:1 V/I ratio dating from 1923.[15] There is also a mixed metal periodate containing vanadium, $K_2[(UO_2)_2(VO_2)_2(IO_6)_2O]{\cdot}H_2O$, and several related tellurates are known including $[Th(VO_2)_2(TeO_6)(H_2O)_2]$, $[NH_4]_2[(VO_2)_2\{TeO_4(OH)_2\}]{\cdot}2H_2O$ and $[NH_4]_2[(VO_2)_2\{Te_2O_8(OH)_2\}]{\cdot}2H_2O$.[16–18] Here we report an investigation of the vanadium periodate compounds.

Results and Discussion

In contrast to Ti^{IV}, which forms $Ti_2O_2(HIO_6){\cdot}nH_2O$,[8] vanadium(V) does not seem to form a binary periodate in aqueous solution. Examination of solutions of V_2O_5 in H_5IO_6 by ^{51}V NMR spectroscopy revealed pH-dependent resonances in the region –500 to –580 ppm (relative to neat $VOCl_3$ at $\delta = 0$ ppm), which were also present in solutions of V_2O_5 in H_2SO_4 and hence are attributed to isopolyvanadates.[19]

$Na_6[V_2I_2H_2O_{16}]{\cdot}10H_2O$

The reaction of V_2O_5 with aqueous $NaHCO_3$, followed by the addition of sufficient H_5IO_6 to take the pH to approximately 7.5, gave a yellow solution from which pale yellow $Na_6[V_2I_2H_2O_{16}]{\cdot}10H_2O$ separated on standing.[13] The same product was also obtained by starting with $NaVO_3$ and H_5IO_6 and following a slightly modified literature procedure.[14] The powder X-ray diffraction patterns for the products obtained by the two methods were in excellent agreement and also agreed well with the pattern simulated from the single-crystal X-ray diffraction data.[14] The structure of this discrete complex anion (Figure 1) is based upon $IO_5(OH)$ octahedra [I–O 1.820(2)–1.961(3) Å] sharing vertices with two essentially square-pyramidal VO_5 groups [V–O 1.628(3)–2.109(2) Å] and a very long bond to a sixth oxygen [V–O 2.544(2) Å].[13,14] The IR spectrum shows bands at 3400 ν(OH), 1635 δ(HOH), 1174 δ(IOH), 939, 845 ν(VO), 756, 684 ν(IO) cm^{-1} and lower frequency bands due

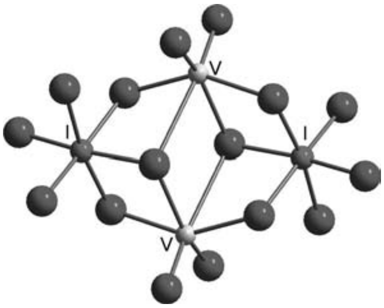

Figure 1. Structure of the $[V_2I_2H_2O_{16}]^{6-}$ ion in $Na_6[V_2I_2H_2O_{16}]{\cdot}10H_2O$.[14] H atom positions were not reported.

---

[a] School of Chemistry, University of Southampton,
Southampton SO17 1BJ, UK
E-mail: A.L.Hector@soton.ac.uk

to ν(V–O–I). The corresponding Raman bands are at 939 (vs), 917 (s), 838 (s), 757 (s), 704 (s) cm^{-1}. The diffuse reflectance UV/Vis spectrum shows broad features $>27\,000\ \text{cm}^{-1}$ attributable to O→V charge-transfer transitions. The crystals are poorly soluble in cold water, and examination of the solution by ^{51}V NMR (^{51}V 99.8%, I = 7/2, Ξ = 26.29 MHz, $Q = -0.052 \times 10^{-28}\ \text{m}^2$, D_c = 2150) showed resonances attributable only to isopolyvanadates formed by hydrolysis.[20]

Attempts to form analogues with the heavier alkali metal cations gave poor yields of the 2:1 V/I species described in the next section, and from LiOH, V_2O_5 and H_5IO_6 over a range of pH values, we obtained only white vanadium-free precipitates.

$M_5V_4I_2O_{19}(OH)\cdot nH_2O$ (M = Na, K, Rb, Cs or NH_4)

The very old work of Rosenheim and Yang reported yellow products with a 3:2:1 (Na or K or NH_4)/V/I ratio obtained by acidifying (HCl or H_2SO_4) aqueous solutions containing the appropriate periodate, V_2O_5 and MOH.[15] We explored a range of such reactions by varying the alkali metal (M = Na, K, Rb or Cs or NH_4), the V/I ratio present and the pH (the pH was adjusted with H_2SO_4, since HCl can reduce periodate to $[IO_3]^-$ under some conditions[6]). The reactions with Na^+ gave $Na_6[V_2I_2H_2O_{16}]\cdot 10H_2O$ at pH > 7 (see above), but if the yellow solution obtained from Na_3VO_4 and H_5IO_6 was acidified with H_2SO_4 to a pH of approximately 5, immediate precipitation of a yellow powder occurred, which had a 2.5:2.0:1.0 Na/V/I ratio as determined by energy dispersive X-ray (EDX) analysis. Obtaining pure samples of the sodium compound requires careful control of the conditions, especially the pH and thorough mixing during pH adjustment. Strongly acidified mixtures (pH ca. 1) cause formation of orange-red polyvanadates or V_2O_5. Similar reactions with V_2O_5/KOH, V_2O_5/RbOH, V_2O_5/CsOH or NH_4VO_3/NH_4OH with H_5IO_6 followed by addition of H_2SO_4 to give a final pH of approximately 5 as described in the Experimental Section, gave insoluble yellow products all with a V/I/M (M = alkali metal or NH_4) approximate ratio of 2:1:2.5. The samples were prepared several times, and EDX data and vibrational spectra (discussed below) showed very good reproducibility, indicating that the same single product formed for each metal. If very concentrated solutions are used, contamination with the modestly soluble MIO_4 can occur for the larger alkali metal systems. The compositions of the Na^+ and $[NH_4]^+$ salts were also determined by conventional wet analysis, and the water contents were estimated by thermogravimetric analysis (TGA). Similar reactions with $[n\text{Bu}_4\text{N}]^+$, $[\text{K(18-crown-6)}]^+$ or $[Ph_4P]^+$ as cations in attempts to obtain more soluble products were unsuccessful. Many reactions of $MOH/V_2O_5/H_5IO_6$ (M = K or Cs) mixtures in water under hydrothermal conditions (temperature ranges 110–175 °C) were also carried out in attempts to produce crystalline products, but only powders were obtained, and at higher temperatures decomposition occurred.

The solids are completely insoluble in water or aqueous alkali but dissolve with decomposition in concentrated mineral acids. The first mass loss in the TGA traces, which was complete by 150–200 °C, was attributed to loss of lattice water, and this was used to estimate the water content. The elemental analyses of $Na_5V_4I_2O_{19}(OH)\cdot 10H_2O$ and $(NH_4)_5V_4I_2O_{19}(OH)\cdot 11H_2O$ are consistent with these measured water contents. In the ammonium salt, water loss is closely followed by a fast mass loss at 160 °C, leaving 17.6% of the original mass by 180 °C. This is less than the vanadium content of $(NH_4)_5V_4I_2O_{19}(OH)\cdot 11H_2O$, suggesting some loss of all elements during the fast decomposition. The alkali metal salts underwent further mass losses in one or two steps that were complete by 800 °C. The residue at this point was slightly (1–2%) more than would be expected for the composition $A_5V_4O_{12.5}$ (A = Na, K, Rb or Cs), corresponding to loss of all iodine but no reduction of vanadium or loss of alkali metal.

The IR spectra (Figure 2), which are only slightly sensitive to the cation present, show very strong and broad features at approximately 3400 and 1640 cm^{-1} due to the substantial amounts of lattice water indicated by the analytical data, a strong broad band at approximately 900 cm^{-1} with a high-energy shoulder (M = Na, K or Rb) or a weaker resolved band at 954 cm^{-1} (Cs) assigned as ν(V=O), and bands in the region 800–600 cm^{-1} due to IO_6 units. There is also a weak band in each complex at approximately 1120 cm^{-1}, which is tentatively assigned as δ(IOH),[1] but attempts to confirm this by deuteriation were inconclusive; the relative intensity of the band seemed to diminish after treatment of the solids with D_2O for 24 h, but the region where δ(IOD) was expected was obscured by other bands. The bands in the Raman spectra (Figure 3) are generally much sharper than those in the IR spectra, but they are also simple, which suggests a relatively symmetric core structure. The UV/Vis spectra show broad features at approximately 34 000 cm^{-1} with a low-energy shoulder confirming the presence of V^V.

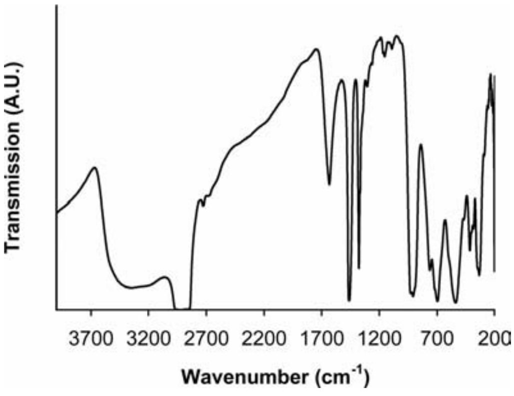

Figure 2. IR spectrum of $K_5V_4I_2O_{19}(OH)\cdot 5H_2O$ (Nujol mull).

Combining the analytical and spectroscopic data and charge balance requirements leads to the formulation of this series of compounds as $M_5V_4I_2O_{20}H\cdot nH_2O$, the amount of water varying with M. The spectroscopic data

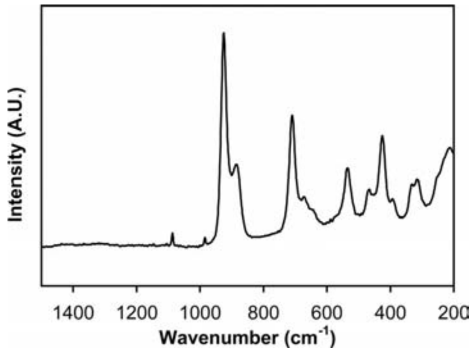

Figure 3. Raman spectrum of $K_5V_4I_2O_{19}(OH)\cdot 5H_2O$.

identify IO_6, probably $IO_5(OH)$, and VO_x groups, which are expected to be sharing vertices or edges (face sharing is rare[1]). Vanadium(V) has a rather flexible coordination geometry in oxide environments with 4-, 5- and 6-coordination well established[16–18,21,22] both in isopolyvanadates and in the few structurally characterised periodate or tellurate complexes. A tentative formulation of the complexes is $M_5[(VO_2)_4(IO_6)\{IO_5(OH)\}]\cdot nH_2O$. Unfortunately we have been unable to obtain crystals of any of the complexes, and they appear either amorphous or exhibit a few weak lines in the powder X-ray diffraction patterns, which prevents detailed structural characterisation. A combination of metal- and I/Te-edge extended X-ray absorption fine structure (EXAFS) data have proved to be able to provide structural characterisation of a range of metal periodate and tellurate complexes,[3,5,8,23] and hence we recorded similar data for this series of complexes.

Structure Investigation by X-ray Absorption Spectroscopy

The EXAFS data collected on $Na_6[V_2I_2H_2O_{16}]\cdot 10H_2O$ were fitted to the known crystal structure, as shown in Figure 1,[14] with reasonable fitting parameters. The I K-edge data needed to be modelled with two shells of 6O and 2V despite the splitting of these shells that the crystal structure would suggest (three shorter and three longer bonds to O, two bonds to V of different lengths). Splitting these shells significantly reduced the residuals associated with the EXAFS fitting but resulted in very highly correlated distances and negative Debye–Waller factors.

Fitting of the EXAFS data for the $M_5[V_4I_2O_{19}(OH)]\cdot nH_2O$ (M = Na, K, Rb, Cs or NH_4) phases initially used a series of periodate and tellurate structure types based on edge-sharing octahedra in small clusters.[1,23] These structures were excluded because of the higher numbers of scatterers than could be modelled in the EXAFS analysis (especially the first V···I or I···V shell) or incompatibility with the measured compositions.

The insolubility of the compounds suggested the possibility of a polymeric structure, and the first attempt at modelling this was based on $(NH_4)_2[(VO_2)_2\{Te_2O_8(OH)_2\}]\cdot 2H_2O$, which has edge-sharing $[Te_2O_8(OH)_2]^{6-}$ parallel to the chain direction and $[V_2O_{10}]^{10-}$ units (sharing many of the oxygen atoms) perpendicular to it,[18] and various modifications to this to achieve the correct stoichiometry including single periodate groups linking dinuclear $[V_2O_m]^{n-}$ units perpendicular to the chain direction. Figure 4 shows the only model that has been found to give a good fit to both the I and the V K-edge EXAFS data. The IR spectroscopic data support the presence of V=O, and this model is consistent with the measured compositions. Protons were not located, but on average every other iodine would be bound to an OH^- group.

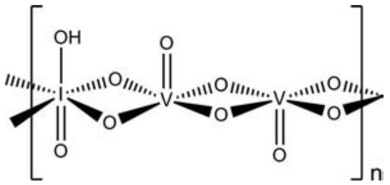

Figure 4. Structure of the polymeric unit used in modelling the EXAFS data for $M_5[V_4I_2O_{19}(OH)]\cdot nH_2O$ (M = Na, K, Rb, Cs or NH_4) samples.

The Fourier transformed EXAFS data for all of these samples followed similar profiles (Figure 5) and hence were all fitted with the same model. The V K-edge spectra (Table 1) were fitted with shells containing a short V=O, four V–O, one V···V, one V···I and three V···O interactions, the latter being attributed to the three terminal oxygen atoms attached to the neighbouring V and I. The I K-edge fits (Table 2) contained six I–O and two I···V interactions. Splitting the first shell is consistent with the model and results in an improvement in the refinement residuals. However, this also results in heavily correlated distances and negative Debye–Waller factors as observed with Na_6-

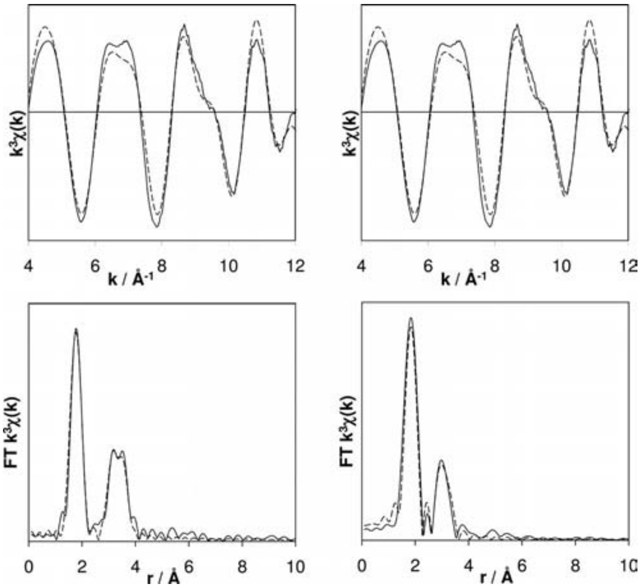

Figure 5. V (left) and I (right) K-edge EXAFS (top) and Fourier transformed EXAFS (bottom) data for $Na_5V_4I_2O_{19}(OH)\cdot 10H_2O$. Solid lines are the measured data, broken lines the fit as per the parameters in Tables 1 and 2.

Table 1. Refined parameters in fits to V K-edge EXAFS data for $M_5[V_4I_2O_{19}(OH)]\cdot nH_2O$ (M = Na, K, Rb or NH_4).

M	V=O r (Å) σ^2 N (ca. 1)	V–O r (Å) σ^2 N (ca. 4)	V···I r (Å) σ^2 N (ca. 1)	V···V r (Å) σ^2 N (ca. 1)	V···O r (Å) σ^2 N (ca. 3)	E_F	R (%)
NH_4	1.535(8)	1.865(6)	3.215(9)	3.30(3)	3.721(14)	38.7(17)	27.9
	0.064(6)	0.0064[a]	0.0041(10)	0.0013(6)	0.0015(19)		
	0.93(12)	3.83(19)	1.04(11)	1.2(3)	3.4(6)		
Na	1.531(7)	1.862(4)	3.221(6)	3.30(2)	3.707(11)	40.3(12)	20.0
	0.0053(4)	0.0064[a]	0.0026(15)	0.016(5)	0.0027(16)		
	0.80(9)	4.04(13)	1.01(7)	1.2(3)	3.5(6)		
K	1.548(12)	1.863(8)	3.237(10)	3.31(6)	3.71(2)	39(3)	29.1
	0.0049(7)	0.0049[a]	0.0022(8)	0.019(15)	0.002(3)		
	0.88(15)	4.0(3)	1.01(11)	1.0(8)	3.1(10)		
Rb	1.551(6)	1.887(5)	3.247(6)	3.37(3)	3.74(2)	30.9(5)	23.4
	0.0058(5)	0.0058[a]	0.0031(6)	0.019(7)	0.011(5)		
	1.13(10)	3.77(15)	1.03(8)	1.3(5)	3.2(8)		

[a] Debye–Waller factors for V=O and V–O constrained to the same value.

$[V_2I_2H_2O_{16}]\cdot 10H_2O$, and hence the different I–O distances are not resolvable from this data. Unfortunately, the V K-edge data for $Cs_5V_4I_2O_{19}(OH)\cdot 3H_2O$ were of very poor quality and could not be fitted due to the mass absorption of Cs combined with the fairly low-energy absorption edge, but the I K-edge data suggest that this compound may adopt the same basic structural motif.

Table 2. Refined parameters in fits to I K-edge EXAFS data for $M_5[V_4I_2O_{19}(OH)]\cdot nH_2O$ (M = Na, K, Rb, Cs or NH_4).

M	I–O r (Å) σ^2 N (ca. 6)	I···V r (Å) σ^2 N (ca. 2)	E_F	R (%)
NH_4	1.881(3)	3.106(6)	–13.7(7)	16.6
	0.0062(4)	0.0036(9)		
	6.02(15)	1.90(16)		
Na	1.878(3)	3.112(5)	–12.6(8)	18.8
	0.0047(5)	0.0002(8)		
	6.13(17)	2.02(15)		
K	1.902(6)	3.144(9)	–20.5(13)	32.7
	0.0041(8)	0.0007(15)		
	5.8(3)	2.0(3)		
Rb	1.876(7)	3.112(12)	–10.6(9)	31.8
	0.0030(8)	0.0010(19)		
	6.2(4)	2.1(4)		
Cs	1.871(6)	3.094(10)	–9.5(14)	28.0
	0.0044(7)	0.004(4)		
	6.1(3)	2.4(9)		

The V=O (ca. 1.54 Å) and V–O (ca. 1.87 Å) distances shown in Table 1 are slightly shorter than those associated with the six-coordinate V centres in $(NH_4)_2[(VO_2)_2\{Te_2O_8(OH)_2\}]\cdot 2H_2O$[18] or $Na_6[V_2I_2H_2O_{16}]\cdot 10H_2O$,[14] both of which contain distances of approximately 1.63 and 2.00 Å. The shorter distances support the five-coordinate model and are more comparable with the V=O distance of 1.57 Å in $[VOCl_4]^-$[24] or the V=O and V–O distances of 1.58 and 1.78–1.88 Å, respectively, in V_2O_5,[25] which contains square-pyramidal units with a further oxygen atom at a much longer distance. The I–O distances shown in Table 2 are typical of edge-linked $[IO_6]^{5-}$ ions.[1–8,14] The V···I distances measured by using V K-edge EXAFS analysis (3.21–3.24 Å) match the I···V from the I K-edge EXAFS analysis (3.09–3.11 Å) reasonably well, considering that the V···I and V···V shells in the V K-edge data are close together and hence have a degree of correlation.

The V K-edge XANES spectra should also be sensitive to the coordination environment of the vanadium atom; the spectra are shown in Figure 6. Square-pyramidal VO_5 units containing a V=O bond have been reported[26] to exhibit a pre-edge feature at 5468.6 to 5469.5 eV, and in our spectra this feature is observed at 5469 eV. In VO_4 units this feature was at lower energy, 5467.8 eV, though it was shifted to higher energy (5468.3 eV) if one of the bonds was a V=O.[26] Hence the position of this feature is more sensitive to the presence of a V=O double bond than to the coordination number, and the presence of a double bond is confirmed by IR and Raman spectroscopic evidence. The intensity of this feature is found to be sensitive to the coordination number: with VO_5 it was 0.51–0.74 times the edge jump, whereas with VO_4 it was 0.82–1.09 times the edge jump; with VO_4 containing a V=O this coefficient was 0.96.[26] The intensity of the pre-edge feature measured in this study was 0.55–0.63

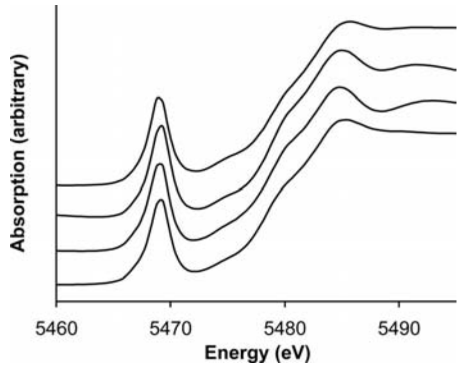

Figure 6. V K-edge XANES spectra of $M_5V_4I_2O_{19}(OH)\cdot nH_2O$ where M = Na (bottom), K, Rb and NH_4 (top).

times the edge jump. Hence, the XANES results support the fitting of the EXAFS data with five-coordinate VO_5 containing a V=O bond.

Conclusions

Dissolution of V_2O_5 in alkali metal hydroxides followed by addition of periodic acid and acidification by H_2SO_4 results in insoluble precipitates of formula $[M_5V_4I_2O_{19}(OH)]\cdot nH_2O$ (M = Na, K, Rb, Cs). The analogous ammonium salt can be produced from NH_4VO_3 in aqueous ammonia by a similar route. V and I K-edge EXAFS analyses indicate polymeric structures formed from edge-linked periodate octahedra and square-pyramidal vanadyl units.

Experimental Section

Vanadium pentoxide, metal vanadates and periodic acid were obtained from Aldrich, BDH or Alfa and used as received. Physical measurements were made as described previously.[2–8]

$Na_6[V_2I_2H_2O_{16}]\cdot 10H_2O$

Method 1: Using the method of Mattes et al.,[13] a slurry of $NaHCO_3$ (7.6 g, 90 mmol) in water (125 mL) and V_2O_5 (2.75 g, 15 mmol) was heated until a clear pale yellow solution was formed. The solution was cooled to room temperature and filtered. Then, a solution of H_5IO_6 (1.15 g, 5 mmol) in water (25 mL) was added dropwise to the filtrate. The addition was stopped when the pH had reached 7.5. The orange-yellow solution was decanted from any precipitate and allowed to stand. The pale yellow crystals, which deposited over the course of 48 h, were filtered off and dried in vacuo. Yield 0.3 g, 2.1%.

Method 2: In a modification of the method of Michiue et al.,[14] sodium metavanadate ($NaVO_3\cdot xH_2O$; 1.0 g, ca. 7 mmol) was dissolved in an aqueous solution (40 mL) of NaOH (0.8 g, 20 mmol) with heating. The solution was filtered and treated with a solution of H_5IO_6 (1.36 g, 1.0 mmol) in water (15 mL). The pH was adjusted to 7.5 by dropwise addition of sulfuric acid (5 M) to the vigorously stirred solution. The yellow solution formed was decanted from any precipitate and allowed to stand. Yellow crystals deposited over the course of 24 h. These were collected after 48 h and dried in vacuo. Yield 0.25 g, 7.7%.

The products obtained by the two methods were identified as the same material by IR spectroscopy. EDX: Na/V/I = 3.1:1.2:1.0. IR (Nujol): $\tilde{\nu}$ = ca. 34 00 (vbr), 1635 (s), 1302 (w), 1174 (s), 939 (s), 845 (s), 756 (s), 684 (m), 590 (m), 560 (m), 420 (w), 342 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 939 (vs), 917 (s), 838 (s), 757 (s), 704 (s), 509 (m), 424 (m), 286 (w), 248 (w) cm^{-1}. UV/Vis (diffuse reflectance): E_{max} = 25600(sh), 29000, 34250 (sh), 38000 cm^{-1}.

$K_5V_4I_2O_{19}(OH)\cdot 5H_2O$: A suspension of V_2O_5 (0.54 g, 3 mmol) in aqueous potassium hydroxide (1.01 g, 18 mmol in 50 mL water) was heated until a clear solution was obtained, then H_5IO_6 (0.23 g, 1 mmol) was added. The solution was allowed to cool, and then dilute H_2SO_4 (3 M) was added with stirring to the yellow-orange solution until a pale yellow precipitate formed (pH ca. 5). The mixture was allowed to stand for 4 h and then filtered. The precipitate was rinsed with cold water (20 mL) and dried in vacuo. Yield 0.45 g, 14%. EDX: K/V/I = 2.4:1.9:1.0. TGA: 12% H_2O. IR (Nujol): $\tilde{\nu}$ = 3450 (s,br), 1636 (s), 1304 (w), 1172 (sh), 1122 (m), 897 (vs), 710 (s), 541 (m), 410 (m), 349 (m) cm^{-1}. Raman: $\tilde{\nu}$ = 3300 (br), 1074 (vw), 925 (vs), 883 (s), 709 (s), 669 (m), 534 (m), 464 (w), 438 (m), 391 (w), 311 (w) cm^{-1}. UV/Vis (diffuse reflectance): E_{max} = 31000(sh), 34400 cm^{-1}.

$Na_5V_4I_2O_{19}(OH)\cdot 10H_2O$: Prepared as described for the K salt. Yield 1.31 g, 45%. EDX: Na/V/I = 2.4:2.0:1.0. $Na_5V_4I_2O_{30}H_{21}$ (1073.7): calcd. I 23.6, Na 10.7, V 19.0, H_2O 16.8; found I 23.6, Na 11.0, V 18.9, H_2O 18.1 (water measured by TGA). IR (Nujol): $\tilde{\nu}$ = ca. 3300 (vbr), 1620 (s), 1304 (w), 1143 (w), 1070 (w), 887 (vs), 720 (s), 693 (s), 560 (m, br), 410 (m), 345 (m) cm^{-1}. Raman $\tilde{\nu}$ = 3300 (br), 1620 (w), 936 (sh), 917 (vs), 892 (sh), 708 (s), 663 (m), 530 (m), 457 (sh), 424 (m), 387 (w), 314 (w) cm^{-1}. UV/Vis (diffuse reflectance): E_{max} = 31000(sh), 35000 cm^{-1}.

$Rb_5V_4I_2O_{19}(OH)\cdot 4H_2O$: Prepared by a method analogous to that for the K salt. Yield 1.65 g, 43%. EDX: Rb/V/I = 2.4:2.0:1.0. TGA: 7.1% H_2O. IR (Nujol): $\tilde{\nu}$ = 3450 (s,br), 1640 (s), 1310 (w), 1172 (sh), 1144 (m), 1114 (m), 893 (vs), 774 (m), 719 (s), 553 (m), 511 (m), 408 (m), 346 (m) cm^{-1}. Raman $\tilde{\nu}$ = 3300 (br), 1087 (vw), 956 (sh), 927 (vs), 890 (s), 811 (w), 709 (s), 663 (m), 518 (m), 463 (m), 422 (m), 321 (m) cm^{-1}. UV/Vis (diffuse reflectance): E_{max} = 31000(sh), 34400 cm^{-1}.

$Cs_5V_4I_2O_{19}(OH)\cdot 3H_2O$: Prepared by a method similar to that for the Rb salt. Yield 1.93 g, 58%. EDX: Cs/V/I = 2.4:2.1:1.0. TGA: 4.7% H_2O. IR (Nujol): $\tilde{\nu}$ = 3400 (s,br), 1620 (s), 1304 (w), 1122 (m), 954 (sh), 893 (vs), 808 (m), 719 (s), 553 (m), 439 (m), 346 (m) cm^{-1}. Raman $\tilde{\nu}$ = 3300 (br), 1087 (w), 968 (vs), 928 (vs), 810 (s), 719 (s), 710 (sh), 695 (sh), 499 (m), 420 (m), 321 (m) cm^{-1}. UV/Vis (diffuse reflectance): E_{max} = 31000(sh), 34400 cm^{-1}.

$[NH_4]_5V_4I_2O_{19}(OH)\cdot 11H_2O$: NH_4VO_3 (1.1 g, 9 mmol) was dissolved in a mixture of water (20 mL) and “0.88” ammonia (2 mL) with gentle heating. H_5IO_6 (3.5 g, 1.5 mmol) in water (20 mL) was added, which produced an orange solution, and the pH was adjusted to approximately 5 by addition of H_2SO_4. The very pale yellow precipitate was filtered off, rinsed with cold water (5 mL) and dried in vacuo. Yield 1.3 g, 27%. EDX: V/I = 1.8:1.0. $V_4I_2N_5O_{31}H_{43}$ (1066.9): calcd. H 4.0, I 23.8, N 6.6, V 19.2; found H 3.6, I 23.3, N 7.3, V 19.3. IR (Nujol): $\tilde{\nu}$ = 3400–2600 (s,vbr), 1640 (s), 1146 (m), 930 (s), 880 (vs), 692 (vs), 569 (m), 518 (s), 433 (m), 395 (m), 360 (m), 293 (m) cm^{-1}. Raman (some decomposition in the laser beam) $\tilde{\nu}$ = 3300–3000 (br), 1660 (m), 917 (vs), 868 (s), 722 (s), 529 (m), 492 (m), 395 (m), 293 (br) cm^{-1}. UV/Vis (diffuse reflectance) E_{max} = 31 000, 36 000 cm^{-1}.

EXAFS Studies: EXAFS data were collected by using stations 7.1 (V K-edge with Si 111 monochromator) and 9.3 (I K-edge, Si 220) at the SRS, Daresbury. Samples were diluted with dry boron nitride powder pressed into approximately 1 mm thick pellets before measurement of their X-ray absorption spectra in transmission mode. At least two data sets were collected for each sample and averaged. Background subtraction was achieved with the PAXAS program,[27] and K^3-weighted EXAFS data were fitted by using the single scattering, curved wave formalism[28] in Excurve.[29] The EXAFS fitting protocols have previously been extensively tested against periodate compounds of known (single-crystal) X-ray structures,[23] and similar procedures are applied in this paper. Initial fitting of the spectra of $Na_6[V_2I_2H_2O_{16}]\cdot 10H_2O$ showed that no amplitude reduction factor needed to be employed in order to obtain accurate coordination numbers. The coordination numbers quoted in Tables 1 and 2 were initially varied manually in integer units and the visual effect on the fit and fit statistics were monitored in order to obtain reasonable fits. They were then refined in final cycles to obtain esd values. The statistically justified number of free parameters according to the Nyqvist theorem[30] is 32 from the V K-edge data and 27 from the I K-edge data; in fitting the data the number of parameters used were 16 and 7, respectively.

Acknowledgments

The authors thank the Science and Technology Facilities Council for provision of beam time under reference number 46043 at the Synchrotron Radiation Source (Daresbury), Drs S. Fiddy and I. Harvey for their assistance with data collection and the Royal Society for a University Research Fellowship (to A. L. H.).

---

[1] W. Levason, *Coord. Chem. Rev.* **1997**, *161*, 33–79.

[2] D. B. Currie, A. L. Hector, W. Levason, M. Thomas, *J. Mater. Chem.* **1997**, *7*, 1871–1875.

[3] A. L. Hector, W. Levason, M. Webster, *J. Chem. Soc., Dalton Trans.* **1998**, 3463–3471.

[4] A. L. Hector, W. Levason, M. Webster, *Inorg. Chim. Acta* **2003**, *343*, 90–94.

[5] N. Binsted, A. L. Hector, W. Levason, *Inorg. Chim. Acta* **2000**, *298*, 116–119.

[6] A. L. Hector, W. Levason, M. Webster, *Inorg. Chim. Acta* **2000**, *298*, 43–49.

[7] W. Levason, R. D. Oldroyd, *Polyhedron* **1996**, *15*, 409–413.

[8] A. L. Hector, W. Levason, *Eur. J. Inorg. Chem.* **2005**, 3365–3370.

[9] P. Douglas, A. L. Hector, W. Levason, M. E. Light, M. L. Matthews, M. Webster, *Z. Anorg. Allg. Chem.* **2004**, *630*, 479–483.

[10] A. L. Hector, S. J. Henderson, W. Levason, M. Webster, *Z. Anorg. Allg. Chem.* **2002**, *628*, 198–202.

[11] C.-F. Sun, T. Hu, X. Xu, J.-G. Mao, *Dalton Trans.* **2010**, *39*, 7960–7967.

[12] B.-P. Yang, C.-L. Hu, X. Xu, C.-F. Sun, J.-H. Zhang, J.-G. Mao, *Chem. Mater.* **2010**, *22*, 1545–1550.

[13] R. Mattes, K.-L. Richter, *Z. Naturforsch., Teil B* **1982**, *37*, 1241–1244.

[14] Y. Michiue, H. Ichida, Y. Sasaki, *Acta Crystallogr., Sect. C* **1987**, *43*, 175–177.

[15] A. Rosenheim, K. H. Yang, *Z. Anorg. Allg. Chem.* **1923**, *129*, 181–195.

[16] R. E. Sykora, A. E. Albrecht-Schmitt, *Inorg. Chem.* **2003**, *42*, 2179–2181.

[17] T. A. Sullens, A. E. Albrecht-Schmitt, *Inorg. Chem.* **2005**, *44*, 2282–2286.

[18] H. Kim, Y. Cho, H. Yun, J. Do, *Z. Anorg. Allg. Chem.* **2007**, *633*, 473–477.

[19] O. W. Howarth, *Prog. Nucl. Magn. Reson. Spectrosc.* **1990**, *22*, 453–485.

[20] D. Rehder in *Transition Metal NMR* (Ed.: P. S. Pregosin), Elsevier, New York, **1991**, p. 18.

[21] G. Yun, Y. Hwang, H. Yun, J. Do, A. Jacobsen, *Inorg. Chem.* **2010**, *49*, 229–233.

[22] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed, Wiley, New York, **1999**., p. 717.

[23] W. Levason, R. D. Oldroyd, M. Webster, *J. Chem. Soc., Dalton Trans.* **1994**, 2983–2988.

[24] CIF access: D. Wulff-Molder, M. Meisel, *Acta Crystallogr., Sect. C* **1998**, *54*, IUC9800068 (DOI: 10.1107/S010827019809917X).

[25] H. G. Bachmann, F. R. Ahmed, W. H. Barnes, *Z. Kristallogr.* **1961**, *115*, 110–131.

[26] M. Nabavi, F. Taulelle, C. Sanchez, M. Verdaguer, *J. Phys. Chem. Solids* **1990**, *51*, 1375–1382.

[27] N. Binsted, *Program for the Analysis of X-ray Absorption Spectra*, version 3.33, University of Southampton, UK, **1998**.

[28] S. J. Gurman, N. Binsted, I. Ross, *J. Phys. C* **1984**, *17*, 143–151.

[29] N. Binsted, *Excurve 9.271*, University of Southampton, UK, **2003**.

[30] E. A. Stern, *Phys. Rev. B* **1993**, *48*, 9825–9827.

Received: November 26, 2010