Oxovanadium(IV)–sulfite compounds: Synthesis and structural and physical studies*

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Abstract: Reaction of V⁴⁺Cl₂ in strongly acidic aqueous solution with either (NH₄)₂SO₃ or Na₂SO₃ and Bu₄NBr at ~70 °C in the pH range 2.5–4.5 gives the clusters (NH₄)₂[[V₄⁴⁺(μ₄-O)₂(μ₃-OH)₂(VIVO)₂(μ₃-SO₃)]₄O₄(H₂O)₂] and (n-Bu₄N)₂[[V₄⁴⁺(μ₄-O)₂(μ₃-OH)₂(VIVO)₂(μ₃-SO₃)]₄O₄(H₂O)₂], respectively. Reaction of NH₄VVO₃ with (NH₄)₂SO₃ resulted in the isolation of the first compound. When the latter reaction is carried out in the presence of MgO, compound (NH₄)[VIVO(SO₃)₁.₅H₂O]∞/H₂O was isolated instead. Compound (n-Bu₄N)₂[[V₄⁴⁺(μ₄-O)₂(μ₃-OH)₂(VIVO)₂(μ₃-SO₃)]₄O₄(H₂O)₂] and (NH₄)[VIVO(SO₃)₁.₅H₂O]∞/H₂O were characterized by X-ray structure analysis. The crystal structure of species (n-Bu₄N)₂[[V₄⁴⁺(μ₄-O)₂(μ₃-OH)₂(VIVO)₂(μ₃-SO₃)]₄O₄(H₂O)₂] revealed a unprecedented hexanuclear cluster consisting of a cubane core [M₄(μ₄-O)₂(μ₃-OH)] connected to two other metal atoms through the core oxo-groups and four μ₃-SO₃ bridges. Compound (NH₄)[VIVO(SO₃)₁.₅H₂O]∞/H₂O represents a rare example of an open-framework species prepared under mild conditions. Cyclic voltammetric examination of compound (n-Bu₄N)₂[[V₄⁴⁺(μ₄-O)₂(μ₃-OH)₂(VIVO)₂(μ₃-SO₃)]₄O₄(H₂O)₂] revealed a redox process which was assigned to the oxidation of one core of vanadium(IV) to vanadium(V).

Keywords: Oxovanadium; sulfite; vanadium clusters; vanadium(IV); electrochemistry.

INTRODUCTION

In the last two decades, polyoxometalate derivatives incorporating inorganic ligands [1] and, in particular, the tetrahedral phosphate [2] ion have been intensively investigated because this family of inorganic clusters has a wide variety of compositions and considerable structural versatility [3]. Also, inorganic clusters of this kind display important magnetic [4], optical [3], and catalytic properties [3]. In marked contrast, heteropolyanions containing the pyramidal sulfite anion as ligand are very limited [5]. The sulfite anion has C₃ᵥ symmetry and contains a nonbonding, but stereochemically active pair of electrons, and its metal-compounds may potentially display nonlinear optical (NLO) properties [6], which are observed in the metal–selenites [7] and metal–iodates [8]. Metal–sulfite chemistry is very
attractive in view of its potential for restricting the serious environmental problem of acid rain [9]. V₂O₅ is used as an industrial catalyst for the production of sulfuric acid, through oxidation of SO₂ to SO₃ at 400–600 °C. Crude oil may contain up to 4 % vanadium mainly in the form of VIVO²⁺-porphyrines [10], which are transformed to V₂O₅ on burning. The existence of V₂O₅ in the atmosphere may cause health hazards and the oxidation of SO₂ to SO₃ (acid rain). Thus, it is of vital importance to study the interaction of vanadium with the sulfite anion. Herein, we report the synthesis and structural and physicochemical characterisation of the oxovanadium(IV)–sulfite clusters (NH₄)₂[V₄(µ⁴-O)₂(µ³-OH)₂][V(IV)O]₃(µ₃-SO₃)₄O₄(H₂O)₂] 1, (n-Bu₄N)₂[V₄(µ⁴-O)₂(µ₃-OH)₂][V(IV)O]₃(µ₃-SO₃)₄O₄(H₂O)₂] 2, and (NH₄)[V(IV)O(SO₃)₁.₅H₂O]ₙ⁻.2.₅H₂O 3.

RESULTS AND DISCUSSION

Synthesis of compounds 1–3

The synthesis of the oxovanadium(IV)–sulfite compounds is summarized in Scheme 1. It is obvious from Scheme 1 that irrespective of the conditions used in the interaction of vanadium–SO₃²⁻ system, more specifically: (i) source of vanadium (VIVOCl₂ or NH₄VVO₃); (ii) temperature (room temperature or 70–80 °C); (iii) counterion (Na⁺, NH₄⁺, or n-Bu₄N⁺); and (iv) pH (pH range ~2.5–4.5) the same VIVSOST₂⁻ cluster, [{V₄(µ⁴-O)₂(µ³-OH)₂}[V(IV)O]₃(µ₃-SO₃)₄O₄(H₂O)₂]²⁻, was isolated. When NH₄VVO₃ was used as a vanadium source in the presence of Mg²⁺ as a counterion and (NH₄)₂SO₃ as a source of the sulfite anion a new oxovanadium(IV)–sulfite species, (NH₄)[VIVO(SO₃)₁.₅H₂O]ₙ⁻.2.₅H₂O 3, was isolated. The role of Mg²⁺ in the isolation of compound 3 is as yet unknown. Compounds 1 and 2 were prepared in a different way from that reported in the literature [5c], and the yield of compound 2 was almost quantitative (~90 %). When compounds 1 and 2 were prepared using a VIV compound as a vanadium source, the SO₃²⁻ plays a dual role as ligand and in raising the pH value of the solution, whereas the use of a VV compound as the vanadium source introduces an additional role for the sulfite anion, as a reducing agent.
Scheme 1 Synthetic routes leading to the isolation of compounds 1–3.
X-ray crystallography

Crystal data and details of data collection for compounds 2 and 3 are listed in Table 1. The core of the hexanuclear anion of 2, $[\text{V}^\text{IV}(\mu_4^\text{IV}O\text{)}_2(\mu_3^\text{III}O\text{)}_2(\text{V}^\text{IV}O\text{)}_2(\mu_3^\text{III}SO\text{)}_3O_4\text{)}(H_2O\text{)}_2]^{2^-}$ (Fig. 1), consists of a distorted cubane unit, $[\text{V}^\text{IV}O_2(O\text{)}_2]$, which is comprised of four, triply edge-sharing $\text{VIVO}_6$ octahedra, each having an oxo group (V=O 1.58 Å) in a position trans to a long V–O bond (2.36 Å). The four equatorial V–O bonds are similar in length, at approximately 2.2 Å. The two square-pyramidal $\text{O}_5\text{VIV}$ units are coordinated to the vanadium ions of the $[\text{V}^\text{IV}O_2(O\text{)}_2]_2$ fragment through one $\mu_4^\text{IV}O^2$ and two $\mu_3^\text{III}SO_3^{2^-}$ bridges. The two $\mu_4^\text{IV}$-oxygen atoms O(4) and O(4A) connect the network of six vanadium(IV) ions and possess almost a trigonal pyramidal geometry. The hexanuclear $\text{V}^\text{IV} \leftarrow [\text{V}^\text{IV}(\mu_4^\text{IV}O\text{)}_2(\mu_3^\text{III}O\text{)}_2] \rightarrow \text{V}^\text{IV}$ cluster represents a novel structural motif [11]. The temperature dependence of the susceptibility data for compound 2 revealed an overall ferromagnetic behavior [5b].

Table 1 Summary of crystallographic data for compounds 2 and 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$M_r$</th>
<th>$\alpha$ [Å]</th>
<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
<th>$V$ [Å$^3$]</th>
<th>$Z$</th>
<th>$\rho$ calc’d [Mg m$^{-3}$]</th>
<th>Space group</th>
<th>$T$ [K]</th>
<th>$\mu$ [mm$^{-1}$]</th>
<th>$R_1$ (final)</th>
<th>WR2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\text{C}<em>{32}\text{H}</em>{78}\text{N}<em>{2}\text{O}</em>{24}\text{S}<em>{4}\text{V}</em>{6}$</td>
<td>1308.83</td>
<td>20.48910(10)</td>
<td>16.6679(4)</td>
<td>18.0218(3)</td>
<td>90</td>
<td>111.3460(10)</td>
<td>90</td>
<td>5732.42(17)</td>
<td>4</td>
<td>1.517</td>
<td>$I2/\alpha$</td>
<td>293(2)</td>
<td>1.156</td>
<td>0.0274</td>
<td>0.0693</td>
</tr>
<tr>
<td>3</td>
<td>$\text{H}_1\text{I}_1\text{NO}<em>9\text{S}</em>{1.5}\text{V}$</td>
<td>268.13</td>
<td>7.0680(17)</td>
<td>12.536(3)</td>
<td>8(5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1769.2(7)</td>
<td>8</td>
<td>2.013</td>
<td>$Pbcm$</td>
<td>293(2)</td>
<td>1.500</td>
<td>0.0586</td>
<td>0.1140</td>
</tr>
</tbody>
</table>

Fig. 1 Ball-and-stick representation of compound 2.
Compound 3 crystallizes in the orthorhombic space group *Pbcm* and exhibits a 2D open-framework structure. The crystallographically unique vanadium ion of 3 resides in a distorted octahedron comprised of four equatorial sulfite oxygen atoms, as well as an oxygen atom from a water molecule and an oxo group, which occupy the axial positions (Fig. 2). The 2D structure of compound 3 (Fig. 3) is a layered net of VO$_6$ octahedra, each sharing four corners with four adjacent sulfite trigonal pyramids. The connectivity between the VO$_6$ octahedra and the sulfite trigonal pyramids creates an open-framework compound with eight- and four-ring windows.

**Fig. 2** Ball-and-stick representation of compound 3.

**Fig. 3** 2D structure of compound 3.
In marked contrast to polyoxometalates (POMs) containing the tetrahedral phosphate group, the POM–SO$_3$$^{2-}$ chemistry is rather limited. More specifically, except of the POM–sulfite compounds reported in this paper the following molybdenum–sulfite species have been reported: [Mo$_{18}$O$_{54}$($\mu_9$SO$_3$)$_2$]$^{14/16-}$ 4 [5d], which is a M$_{18}$ Dawson structural-type species, [Mo$_{2}$O$_{15}$($\mu_5$SO$_3$)$_2$]$^{11-}$ 5 [5a], [(Mo$_2$O$_4$)$_6$($\mu_2$SO$_3$)$_{12}$($\mu_7$SO$_3$)$_4$]$^{20-}$ 6 [5b], {Na[[Mo$_2$O$_4$]$^3(\mu_2$SO$_3$)$_3$$^6(\mu_6$SO$_3$)]$^2$}]$^{15-}$ 7 [5b], and [(Mo$_2$O$_4$)$_4$(SO$_3$)$_4$($\mu_2$SO$_3$)]$^8$ 8 [5b]. For compounds 4, 5, and 7, their molybdenum–phosphate analogs have been reported in the literature [14]. Compound 6 is completely different from the Mo$_{12}$–PO$_4$$^{3-}$ Keggin analog [3a,14e]. The structural features of the vanadium–SO$_3$$^{2-}$ compounds 2 and 3 have no vanadium–PO$_4$$^{3-}$ precedents. No tungsten–SO$_3$$^{2-}$ or mixed-metal (V/Mo)–SO$_3$$^{2-}$ species have been reported thus far. From all these data, it is crystal clear that SO$_3$$^{2-}$ gives a very rich chemistry with unprecedented structural motifs, new sulfite bonding modes ($\mu_9$, $\mu_6$, $\mu_3$), and novel physical properties.

Electrochemistry

A cyclic voltammetric examination of compound 2 in acetonitrile at ~0 °C revealed an one electron quasi-reversible redox process at 0.67 V vs. NHE (Fig. 4) and two irreversible redox processes at 1.25 and 1.42 V vs. NHE the quasi-reversible redox process at 0.67 V was assigned to the oxidation of the V$^{IV}$ atom to V$^{V}$ and is summarized in Scheme 2. The irreversible redox processes are assigned to the oxidation of the sulfite groups, and this assignment is based on the fact that Na$_2$SO$_3$ gives two irreversible peaks at E/values very close to those observed for 2 (Table 2). When the switching potential is in the range, 0.3–1.4 V, the metal-based redox process is not influenced by the first oxidation of the sulfite groups as shown in Fig. 4b, and this of course means that the hexanuclear species retains its integrity in solution. In marked contrast, when the switching potential is in the range, 0.3–1.6 V, then the second oxidation of the sulfites results in the disappearance of V$^{IV}$/V$^{V}$ redox couple (Fig. 4c), presumably because of the decomposition of compound 2.

![Fig. 4 Cyclic voltammograms of 2 in CH$_3$CN at various switching potentials.](image-url)
Table 2 Redox potentials (vs. NHE) of compound 2 and Na₂SO₃ in CH₃CN (0 °C) measured from cyclic voltammograms (scan rate 100 mV/s).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{p,c}(V)$</th>
<th>$E_{p,a}(V)$</th>
<th>$\Delta E$(mV)</th>
<th>$E_{1/2}$</th>
<th>Number of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>+0.62</td>
<td>+0.72</td>
<td>100</td>
<td>+0.67</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>+1.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>+1.21</td>
<td></td>
<td></td>
<td>+1.39</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSION

In conclusion, we have prepared a series of oxovanadium(IV)–sulfite compounds by simply reacting VIVOCl₂ or NH₄VVO₃ with either (NH₄)₂SO₃ or Na₂SO₃. These VIVO²⁺–SO₃⁻² species represent the first examples of vanadium–sulfite compounds. The hexanuclear oxovanadium(IV)–sulfite cluster, \((n-Bu₄N)₂[V₄IVO₂(µ₄-O)₂(µ₃-OH)₂]$\((VIVO)₂(µ₃-SO₃)$_₄O₄(H₂O)$_₂\) 2, exhibits a unique structural motif, not only for vanadium but for any metal atom. The 2D structure of compound 3 represents a rare example of an open-framework compound isolated under mild conditions (~20 °C). The vanadium–sulfite chemistry is completely different from the vanadium–phosphate chemistry from the structural point of view. The temperature dependence of the magnetic susceptibility data for compound 2 revealed an overall ferromagnetic behavior, which is unexpected for VIVO clusters. The preparation of 1–3 and of the molybdenum(V/VI)–SO₃⁻₂ compounds further emphasizes the great ability of the seemingly pedestrian sulfite anion to act as a ligand in polyoxometalates. Taking into account the findings from the vanadium–SO₃⁻₂ and molybdenum–SO₃⁻₂ chemistry, it is certain that new metal–SO₃⁻₂ compounds would appear in the near future with novel structural features, new modes of coordination for the SO₃⁻₂ group, and unique physical properties. The synthesis of new vanadium(V)–SO₃⁻₂ and molybdenum(V/VI)–SO₃⁻₂ species by variation of temperature, pressure, counterions, and pH as well as of tungsten(VI)–SO₃⁻₂ and mixed-metal vanadium–molybdenum–SO₃⁻₂ compounds are future challenges. In addition, the NLO properties of the noncentrosymmetric metal–sulfite clusters should be studied.

EXPERIMENTAL SECTION

Physical measurements

IR spectra of the various compounds dispersed in KBr pellets were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrometer, CV measurements were carried out using a PAR model 273A elec-
trochemistry system. Platinum wire reference and auxiliary electrodes and a platinum disc working electrode were used in a three-electrode configuration. Ferrocene (0.665 V vs. NHE) [15] was used as internal reference. The supporting electrolyte was n-Bu4NCIO4 (~0.1 M), and the solute concentration was ~10^{-3} M. The half-wave potential \(E^{°}_{298}\) was set equal to \(0.5(E_{pa} + E_{pc})\), where \(E_{pa}\) and \(E_{pc}\) are anodic and cathodic cyclic voltammetric peak potentials, respectively. The number of electrons for each wave was calculated from rotating disk voltammograms and by comparing the height of the peaks in the rotating disk voltammograms. All experiments were carried out under a dinitrogen atmosphere in dry CH3CN; because compound 2 decomposes slowly in CH3CN, the solutions were cooled at 0 °C in order to reduce the decomposition rate. The decomposition of the complex was monitored by CV, and no decomposition was observed during the experiments, over a period of 30 min.

**Synthesis of (NH4)2\{[V4IV(\mu_4-O)2(\mu_3-OH)2](VIVO)2(\mu_3-SO3)4O4(H2O)2}\}, 1**

**First method**
To a stirred aqueous solution (20 mL, pH = 9) of (NH4)2SO3 (2.0 g, 14.7 mmol) was added dropwise an acidic aqueous solution (5.5 mL, pH = 0) of VIVOCl2 [13] (0.68 g, 4.95 mmol). Upon addition of VIVOCl2, a sequence of color changes [from deep brown–black (pH ≈ 7–8), through deep green (pH ≈ 5–7) and green–blue (pH = 4) to blue (pH = 3)] was induced as the pH of the solution was gradually falling. The solution was heated to =70 °C, without magnetic stirring, for almost 6 h, and then it was cooled to room temperature (=20 °C) and filtered to obtain light blue crystals of 1. Yield: 0.55 g (50 %, based on vanadium). Elemental analysis calc’d. (%) for H14NO24S4V6 (860.01): H 1.64, N 3.26, S 14.92, V 35.54; found: H 1.75, N 3.10, S 15.10, V 25.85. [IR(cm−1): \(\nu(SO): 1015(m), 995(s), 985(s), 923(m), 880(w), 825(m); \nu(V=O): 952(vs)\].

**Second method**
NH4VVO3 (0.60 g, 5.1 mmol) was dissolved in aqueous hydrochloric acid (37 % HCl in water, 1:4 v/v, 20 mL, pH = 0). A solution (15 mL, pH = 9) of (NH4)2SO3 (2.0 g, 14.7 mmol) was added to it. Upon addition of (NH4)2SO3, the yellow color of NH4VVO3 changed to blue and the pH of the solution was ≈3. The solution was heated to =70 °C, without magnetic stirring, for 6 h, and then it was cooled to room temperature and filtered to get light blue crystals of 1. Yield: 0.49 g (68 %, based on vanadium).

**Synthesis of (n-Bu4N)2\{[V4IV(\mu_4-O)2(\mu_3-OH)2](VIVO)2(\mu_3-SO3)4O4(H2O)2}\}, 2**
Compound 2 was prepared in a fashion similar to that used for 1 (first method) except that Na2SO3 was used instead of (NH4)2SO3. n-Bu4NBBr (vanadium: n-Bu4NBBr = 1:5) was added to the solution just prior to heating it. Yield: 0.95 g (88 %, based on vanadium). Elemental analysis calc’d. (%) for C32H78N2O24S4V6 (1308.83): C 29.37, H 6.00, N 2.14, S 9.80, V 23.35; found: C 29.68, H 6.04, N 2.17, S 9.63, V 23.50. [IR(cm−1); \(\nu(SO): 1022(m), 997(s), 987(s), 926(m), 881(w), 823(m); \nu(V=O): 951(s)\].

**Synthesis of NH4[VIVO(SO3)1.5(H2O)]2.5H2O, 3**
To a stirred aqueous hydrochloric acid (37 % HCl in water, 1:4 v/v, 2.0 mL, pH = 0) solution of NH4VVO3 (0.60 g, 5.1 mmol), solid magnesium oxide (0.59 g, 14.6 mmol) was added in one portion. Then, addition of solution of (NH4)2SO3 (4.50 g, 45.9 mmol) in water (15 mL, pH = 9) to it resulted in a color change from yellow to blue–green. The final pH value of the solution was 4. The solution was filtered and the filtrate was left for crystallization in an open vessel at ambient temperature (~20 °C). After two days, blue hexagonal crystals were formed, which were filtered and dried in air to get (1.1 g, 30 % based on vanadium) of compound 3. Elemental analysis calc’d. (%) for H11NO9S1.5V (268.13):
H 4.13, N 5.22, S 17.94, V 19.00; found: H 4.20, N 5.10, S 18.05, V 18.80. [IR(cm⁻¹): ν(SO): 1018(s), 993(sh), 987(s), 966(sh), 903(s), 841(m); ν(V=O): 952(s)].

REFERENCES


