

**(NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·1.5H<sub>2</sub>O**Masato Hashimoto,<sup>a\*</sup> Michiru Kubata<sup>b</sup> and Atsushi Yagasaki<sup>c</sup><sup>a</sup>Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan, <sup>b</sup>Energy Storage System Development Group, Sumitomo Electric Industries Ltd, 1-1-3 Shimaya, Konohana, Osaka 554-0024, Japan, and <sup>c</sup>Department of Chemistry, School of Science, Kwansei Gakuin University, 1-155 Uegahara-Ichibancho, Nishinomiya 662-8501, Japan

Correspondence e-mail: mh1043@sys.wakayama-u.ac.jp

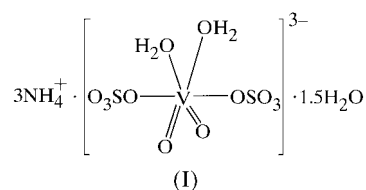
Received 19 June 2000

Accepted 5 September 2000

The title compound, triammonium *cis*-diaqua-*cis*-dioxo-*trans*-disulfatovanadate 1.5-hydrate, was obtained by oxidizing V<sup>IV</sup> to V<sup>V</sup> in a 2 M sulfuric acid solution of vanadyl sulfate and adding ammonium sulfate. Here, the V atom is sandwiched by two sulfate groups by corner-sharing to form a discrete [VO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>3-</sup> anion. The water molecules occupy *cis* positions in the equatorial plane of the vanadium octahedron.

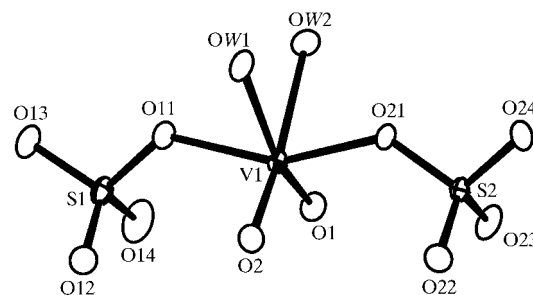
**Comment**

Vanadate solutions in concentrated sulfuric acid (2–6 M) are used commercially as electrolytes for redox-flow batteries (Kazacos *et al.*, 1990; Kumamoto *et al.*, 1999). However, the chemistry of vanadate in such concentrated and highly acidic solutions is still sketchy and the exact composition and structure of the species in solution is not yet known. During the study of such a solution, we isolated the title compound, (I).



The present compound (Fig. 1) consists of a discrete diaquadioxodisulfatovanadate anion, ammonium cations and water of crystallization. The anion shows a *trans* arrangement of the sulfate ligand about the V atom. A similar coordination mode has been observed for V(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>NH<sub>5</sub>)<sub>4</sub> (Ghosh *et al.*, 1995) and K[VO<sub>2</sub>(SO<sub>4</sub>)(OH<sub>2</sub>)<sub>2</sub>] (Richter & Mattes, 1991). Four additional O atoms bind to the metal

center to complete a distorted octahedral coordination; those four O atoms lie in a plane that contains the V atom [0.0161 (7) to −0.0141 (6) Å]. The V1–O distances for two of these O atoms are relatively long [V1–OW1 2.232 (1) and V1–OW2 2.259 (1) Å] and indicate that these two O atoms are those of the coordinated water molecules. The distances for the other two [V1–O1 1.634 (1) and V1–O2 1.620 (1) Å] are normal for terminal oxo ligands. Both terminal oxo ligands and both coordinated water molecules assume a *cis* arrangement. In other words, the coordination site *trans* to an oxo ligand is occupied by a water molecule. The coordination around the V atom is highly distorted and all the O–V–O angles deviate significantly from the ideal values of 90 and 180°. In addition, the V atom is displaced from the center of the octahedron towards two terminal oxo ligands. This kind of *cis*-dioxo octahedral unit is commonly found in polymolybdates and polytungstates (Pope, 1983). However, the current compound is to the best of our knowledge the first such example of a discrete inorganic vanadate. The sulfate tetrahedra, on the other hand, are quite normal. The bond lengths of S–O(–V1) [1.512 (1) Å for S1–O11 and 1.505 (1) Å for S2–O21] are longer than those of other S–O bonds [1.460 (2) to 1.468 (1) Å] due to the coordination to the V atom. The S1–V1–S2 angle is 162.60 (1)° and thus the anion is slightly bent. Hydrogen bonds formed in the crystal are listed in Table 2. There are two waters of crystallization; OW3 lies in a general position and OW4 lies on an inversion center with its H atoms disordered. These water molecules together with the ammonium cations (N1, N2 and N3) form a hydrogen-bond network through the crystal with each other and the disulfatovanadate anion. The slightly longer distance of V1–O1 compared with V1–O2 is probably caused by the rather short contact of OW3 to O1 [2.803 (2) Å].

**Figure 1**

The structure of the [VO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>3-</sup> anion. Displacement ellipsoids are plotted at the 30% probability level. H atoms have been omitted for clarity.

**Experimental**

An appropriate amount of vanadyl sulfate, VOSO<sub>4</sub>, was dissolved in sulfuric acid, and water was added to achieve a concentration of 2 M for both VOSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. Then, V<sup>IV</sup> was electrolytically oxidized to V<sup>V</sup>. To a 4 ml portion of this solution, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (3.3 g, 25 mmol) was added and the mixture was heated to 323 K to dissolve the ammonium sulfate. The resulting solution was kept at 301 K for 3 d after which time orange tabular crystals were obtained.

**Table 1**  
Selected geometric parameters (Å, °).

V1—O2	1.6206 (11)	S1—O13	1.4608 (11)
V1—O1	1.6352 (10)	S1—O12	1.4725 (14)
V1—O21	2.0026 (10)	S1—O11	1.5107 (11)
V1—O11	2.0103 (10)	S2—O22	1.4622 (11)
V1—OW1	2.2296 (11)	S2—O24	1.4665 (11)
V1—OW2	2.2551 (12)	S2—O23	1.4672 (10)
S1—O14	1.4591 (13)	S2—O21	1.5045 (9)
O2—V1—O1	103.80 (6)	O21—V1—OW1	78.73 (4)
O2—V1—O21	97.41 (5)	O11—V1—OW1	79.56 (4)
O1—V1—O21	97.72 (5)	O2—V1—OW2	170.71 (5)
O2—V1—O11	97.06 (5)	O1—V1—OW2	85.45 (5)
O1—V1—O11	98.77 (5)	O21—V1—OW2	81.85 (5)
O21—V1—O11	154.76 (4)	O11—V1—OW2	80.55 (5)
O2—V1—OW1	94.74 (6)	OW1—V1—OW2	76.02 (4)
O1—V1—OW1	161.43 (5)		

### Crystal data

(NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].1.5H<sub>2</sub>O  
*M<sub>r</sub>* = 392.24  
 Triclinic,  $\bar{P}1$   
*a* = 7.748 (2) Å  
*b* = 14.164 (3) Å  
*c* = 6.268 (2) Å  
 $\alpha$  = 91.54 (2)°  
 $\beta$  = 95.30 (2)°  
 $\gamma$  = 88.25 (2)°  
*V* = 684.4 (3) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.903 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 17.35–17.50°  
 $\mu$  = 1.103 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Plate, orange  
 0.60 × 0.50 × 0.20 mm

### Data collection

Rigaku AFC-5R automated four-circle diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction:  $\psi$  scan (TEXSAN; Molecular Structure Corporation, 1995)  
*T<sub>min</sub>* = 0.576, *T<sub>max</sub>* = 0.802  
 7201 measured reflections

7201 independent reflections  
 $\theta_{\max}$  = 37.50°  
*h* = -13 → 13  
*k* = -23 → 23  
*l* = -10 → 0  
 200 standard reflections  
 intensity decay: 1.9%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.100  
*S* = 1.053  
 7201 reflections  
 179 parameters  
 H-atom parameters not refined  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0539*P*)<sup>2</sup> + 0.2450*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

( $\Delta$ /σ)<sub>max</sub> = 0.001  
 $\Delta\rho_{\max}$  = 0.90 Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.81 e Å<sup>-3</sup>  
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.0052 (17)

All H atoms were fixed at the positions obtained from difference Fourier maps.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1993); cell refinement: MSC/AFC

**Table 2**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
OW1—H11...O22 <sup>i</sup>	0.77	1.94	2.7103 (15)	172
OW1—H12...O23 <sup>ii</sup>	0.80	1.99	2.7939 (15)	177
OW2—H21...O12 <sup>iii</sup>	0.80	1.98	2.7620 (17)	165
OW2—H22...OW3 <sup>iii</sup>	0.84	1.96	2.8015 (19)	173
OW3—H31...O1	0.84	1.98	2.803 (2)	167
OW3—H32...O13 <sup>iv</sup>	0.95	2.22	3.171 (2)	175
OW4—H41...O22	0.89	2.05	2.9263 (14)	167
OW4—H42...O24 <sup>v</sup>	0.88	2.13	2.9740 (13)	159
N1—H51...O24 <sup>vi</sup>	0.77	2.14	2.8994 (18)	169
N1—H52...O12	0.79	2.16	2.923 (2)	161
N1—H53...O24 <sup>i</sup>	0.84	2.05	2.8536 (17)	160
N1—H54...O23 <sup>ii</sup>	0.83	2.27	3.074 (2)	161
N2—H61...O14 <sup>vii</sup>	0.79	2.08	2.857 (2)	172
N2—H62...O12 <sup>viii</sup>	0.83	2.04	2.862 (2)	171
N2—H63...O23	0.72	2.19	2.8450 (18)	152
N2—H64...O13 <sup>iv</sup>	0.87	2.08	2.899 (2)	157
N3—H71...O13 <sup>iv</sup>	0.89	2.09	2.923 (2)	153
N3—H72...O14	0.87	2.05	2.805 (2)	143
N3—H74...OW2 <sup>vii</sup>	0.97	2.09	2.825 (2)	131

Symmetry codes: (i) 1 - *x*, -*y*, 1 - *z*; (ii) *x* - 1, *y*, *z*; (iii) *x*, *y*, 1 + *z*; (iv) 1 + *x*, *y*, *z*; (v) *x*, *y*, *z* - 1; (vi) *x* - 1, *y*, *z* - 1; (vii) 1 - *x*, 1 - *y*, 1 - *z*; (viii) 1 + *x*, *y*, 1 + *z*; (ix) 1 - *x*, 1 - *y*, -*z*.

*Diffractometer Control Software*; data reduction: TEXSAN (Molecular Structure Corporation, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1299). Services for accessing these data are described at the back of the journal.

### References

- Ghosh, P., Taube, H., Hasegawa, T. & Kuroda, R. (1995). *Inorg. Chem.* **34**, 5761–5775.  
 Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Kazacos, M., Cheng, M. & Skyllas-Kazacos, M. (1990). *J. Appl. Electrochem.* **20**, 463–467.  
 Kumamoto, T., Shigematsu, T., Ito, T. & Tokuda, N. (1999). Japanese Patent 2994210.  
 Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Molecular Structure Corporation (1995). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Pope, M. T. (1983). In *Heteropoly and Isopoly Oxometalates*. Berlin: Springer-Verlag.  
 Richter, K.-L. & Mattes, R. (1991). *Inorg. Chem.* **30**, 4367–4369.  
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.