

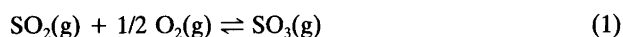
## The Crystal Structure of $\text{NaV}(\text{SO}_4)_2$

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This note forms part of our continuing studies on the chemistry of the widely used sulfuric acid catalyst, i.e. well modelled by the liquid–gas system  $\text{M}_2\text{S}_2\text{O}_7/\text{V}_2\text{O}_5\text{--SO}_2/\text{O}_2/\text{SO}_3/\text{N}_2$  (M = K, Na and/or Cs) which catalyses reaction (1) in the temperature range 400–600 °C. Below



about 420 °C the activity of the catalyst decreases sharply owing to the precipitation of V(IV) and V(III) compounds.<sup>1</sup>

Previously,<sup>2–4</sup>  $\text{KV}(\text{SO}_4)_2$ ,  $\text{K}_4(\text{VO})_3(\text{SO}_4)_5$  and  $\text{Na}_2\text{VO}(\text{SO}_4)_2$  have been isolated from molten vanadium pentoxide–pyrosulfate mixtures in  $\text{SO}_2$ -rich atmospheres, and these compounds have been recognized<sup>1</sup> as catalyst deactivation products. Here, by means of an X-ray crystal structure determination, we present the crystal structure of a new deactivation product, the V(III) compound  $\text{NaV}(\text{SO}_4)_2$ , formed in the  $\text{Na}_2\text{S}_2\text{O}_7/\text{V}_2\text{O}_5\text{--SO}_2/\text{O}_2/\text{N}_2$  liquid–gas system below a temperature of ca. 470 °C. As far as we are aware there is no previous report on the formation of sodium compounds containing vanadium in the +III oxidation state from commercial catalysts or model melts.

### Experimental

The experimental set-up presented briefly here has been described in more detail in Refs. 1 and 3.

**Reactor cell.** The crystals were prepared in a reactor flow cell of borosilicate glass. The melt was supported by a porous glass disc, thereby allowing the gas mixture to be bubbled through the melt. The reactor cell was placed in a tiltable double-walled transparent tube furnace of quartz. The crystals were isolated from the melt on the frit by reversing the gas flow, whereby the melt was filtered. The maximum temperature of the furnace was 500 °C, regulated to within  $\pm 0.5$  °C at the position of the melt.

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**Gas mixing unit.** The gas mixture used was prepared in a mixing unit utilising Brooks mass flowmeters with ranges 0–20 and 0–100 ml min<sup>-1</sup>, allowing any desired  $\text{SO}_2/\text{O}_2/\text{N}_2$  gas mixture to enter the reactor. Commercial gases in steel bottles were used:  $\text{SO}_2$  (> 99.9%),  $\text{O}_2$  (99.8%  $\text{O}_2$  + 0.2%  $\text{N}_2$  and Ar), and  $\text{N}_2$  (< 40 ppm  $\text{O}_2$  +  $\text{H}_2\text{O}$ ).

**Materials.** The  $\text{Na}_2\text{S}_2\text{O}_7$  used was synthesized by thermal decomposition of  $\text{Na}_2\text{S}_2\text{O}_8$  (Fluka, *pro analysi*) and stored in sealed ampules until used. The non-hygroscopic  $\text{V}_2\text{O}_5$  [Cerac, Pure (99.9%)] was used without further purification. All handling of solid chemicals, including the filling of the reactor cell, was performed in a glove box with a nitrogen atmosphere that was continuously dried to around 5 ppm  $\text{H}_2\text{O}$  through a column containing molecular sieves.

**Synthesis of green crystalline  $\text{NaV}(\text{SO}_4)_2$ .** In general, blue or green crystals or mixtures of these were obtained when the molten  $\text{Na}_2\text{S}_2\text{O}_7/\text{V}_2\text{O}_5$  system (molar ratios Na/V = 3, 4, 4.7 or 10) was contacted with an  $\text{SO}_2$ -rich atmosphere. The preparation was performed in the reactor cell. The cell, loaded with chemicals, was transferred from the glove box, mounted in the furnace, quickly connected to the gas supply and vent tubes and heated.<sup>4</sup> The volume of the melt did not exceed 1.5 ml. The melt was purged gently with the desired gas mixture overnight. Independent of whether the gas mixture consisted of 10%  $\text{SO}_2$  in  $\text{N}_2$  or 10%  $\text{SO}_2$ , 11%  $\text{O}_2$  and 79%  $\text{N}_2$ , blue and/or green crystals were formed slowly at temperatures in the range 400–470 °C. The lower the temperature the larger the crop of crystals that was isolated on the porous disc. Bluish and green compounds were also isolated<sup>4</sup> from  $\text{NaHSO}_4/\text{V}_2\text{O}_5$  molten mixtures in an  $\text{SO}_2$  atmosphere. After filtration and cooling, the reactor cell was opened and flushed gently with water for several hours to dissolve the residual crystallized  $\text{Na}_2\text{S}_2\text{O}_7$  solvent on the disc, leaving the non-hygroscopic blue and green crystalline product. Blue crystals isolated from the melt with molar ratio Na/V = 10 at 400 °C have previously been identified as the V(IV) compound  $\text{Na}_2\text{VO}(\text{SO}_4)_2$ , and

its crystal structure was reported recently.<sup>4</sup>  $\text{Na}_2\text{VO}(\text{SO}_4)_2$  crystals are easily recognizable by means of their needle shape.

Only green crystals were obtained from the  $\text{V}_2\text{O}_5/\text{Na}_2\text{S}_2\text{O}_7$  molten mixtures with the molar ratio  $\text{Na}/\text{V} = 4$  treated with a 10%  $\text{SO}_2$ , 90%  $\text{N}_2$  gas mixture at 467°C. Surprisingly these crystals, consisting mainly of a V(IV) compound, were green. [(V(IV) compounds are usually blue.)] The formula of the compound was found to be  $\text{Na}_8(\text{VO})_2(\text{SO}_4)_6$  (identified by a single-crystal X-ray investigation in progress). A minor amount of the product consisted of the green V(III) compound  $\text{NaV}(\text{SO}_4)_2$ , the subject of the X-ray investigation presented here. A suitable single crystal was selected in a polarization microscope.

### X-ray single crystal investigation

The crystal symmetry and space group were determined from Weissenberg photographs. Crystal data and other experimental results, including previous data on  $\text{NaV}(\text{SO}_4)_2$ , are given in Table 1. Intensity data were collected at room temperature on an Enraf-Nonius CAD-4F four-circle diffractometer with monochromated  $\text{Mo-K}\alpha$  radiation (0.71069 Å). The cell dimensions were determined by least-squares refinement based on the settings of 24 high-order reflections. The intensities were corrected for Lorentz and polarization effects, but because of the irregular shape of the crystal no correction for absorption was attempted. The structure was solved and refined in space group  $C2/m$ . The calculations were made using the SHELX program,<sup>5</sup> and included full-matrix least-squares refinements of positional and anisotropic thermal parameters.

The atomic scattering factors and anomalous dispersion corrections used were those given by Cromer and Mann.<sup>6</sup> Reflections with  $I < 2\sigma(I)$  were omitted from the refinement. The weight function [ $w^{-1} = \sigma^2(F) + 0.01 F^2$ ] gave a uniform distribution of  $w|\Delta F|^2$ . Atomic coordinates, equivalent isotropic thermal parameters, bond lengths and angles are listed in Tables 2 and 3.  $R$  and  $R_w$ -values are given in Table 1. A list of observed and calculated structure factors as well as anisotropic thermal parameters ( $U_{ij}$ ) may be obtained from the authors. The packing of the structure is shown in Fig. 1.

*Discussion of the structure.* The asymmetric unit contains one hexaoxocoordinated vanadium(III) ion, a sodium ion and two sulfate ions. All the oxygen atoms coordinated to vanadium are sulfate oxygens (O1 and O3), but there are also oxygens (O2) which are bound to sulfur but not to vanadium. In this way a basically two-dimensional layer of linked octahedra ( $\text{VO}_6$ ) and tetrahedra ( $\text{SO}_4$ ) is formed, separated from the next layer by sodium ions in the  $ab$  plane. The vanadium is located in the centre of a nearly perfect octahedron, distorted towards a  $2/m$  ( $C2_v$ ) symmetry, and consisting of four O3 atoms in the mirror plane and two O1 atoms on the local twofold axis (Fig. 1). The bond distances and angles of the octahedron are given in Table 3, and have values typical of vanadium(III) compounds.<sup>7</sup>

The length of the bond between sulfur and the non-coordinated oxygen, O2, is relatively short [1.433(2) Å] in comparison with the sulfur–oxygen bonds (S–O1 and S–O3) found in the vanadium–oxygen–sulfur coordination bridges [1.475(2) and 1.490(1) Å, respectively].

Around the sulfur atoms, nearly tetrahedral angles are

Table 1. Crystal data of  $\text{NaV}(\text{SO}_4)_2$  and, for comparison, yavapaiite,  $\text{KFe}(\text{SO}_4)_2$ .

| Formula   | $\text{NaV}(\text{SO}_4)_2$ ,<br>This work | $\text{NaV}(\text{SO}_4)_2$ ,<br>Ref. 9 | Yavapaiite,<br>$\text{KFe}(\text{SO}_4)_2$ ,<br>Ref. 12 |
|---|--|---|---|
| $M_w/\text{g mol}^{-1}$                               | 266.055                                    |   |   |
| Crystal system  | Monoclinic                                 |   |   |
| $V/\text{Å}^3$  | 295.11                                     | 295                                     | 329.7   |
| Space group   | $C2/m$ (No. 12)                            |   |   |
| $a/\text{Å}$  | 8.020(1)                                   | 8.014                                   | 8.152(5)  |
| $b/\text{Å}$  | 5.160(1)                                   | 5.163                                   | 5.153(4)  |
| $c/\text{Å}$  | 7.135(2)                                   | 7.142                                   | 7.877(5)  |
| $\beta/^\circ$  | 91.87(2)                                   | 91°53'                                  | 94.90(7)  |
| $D_c/\text{g cm}^{-3}$                                | 2.99                                       | 2.98                                    | 2.891   |
| $D_x/\text{g cm}^{-3}$                                |  | 2.9                                     | 2.88 <sup>11</sup>                                      |
| $Z$   | 2  |   |   |
| $\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$               | 47.66                                      |   |   |
| $\theta_{\text{max}}/^\circ$                          | 40   |   |   |
| Total no. of reflections                              | 1038                                       |   | 530   |
| Reflections with $I > 2\sigma(I)$                     | 830  |   |   |
| No. of parameters                                     | 36   |   |   |
| Crystal size/mm                                       | ca. 0.13×0.20×0.013                        |   | ca. 0.22×0.26×0.30                                      |
| $R_1 = \sum  F_o  -  F_c  /\sum F_o $                 | 0.0284                                     |   | 0.032   |
| $R_2 = [\sum w( F_o  -  F_c )^2/\sum w F_o ^2]^{1/2}$ | 0.0312                                     |   |   |
| Residual charge density/ $\text{e}^- \text{Å}^{-3}$   | -0.83 < $\rho$ < 0.98                      |   |   |

Table 2. Fractional coordinates and equivalent isotropic thermal parameters for the atoms in NaV(SO<sub>4</sub>)<sub>2</sub>. (For comparison the corresponding values for yavapaiite KFe(SO<sub>4</sub>)<sub>2</sub> are given in italics.<sup>11</sup>)

| Atom | Site<br>(multiplicity,<br>symmetry) | <i>x/a</i>                    | <i>y/b</i>                    | <i>z/c</i>                    | <i>B</i> <sub>eq</sub> /Å <sup>2</sup> <sup>a</sup> |
|------|-------------------------------------|-------------------------------|-------------------------------|-------------------------------|---|
| V    | <i>a</i> (2, $\bar{2}$ )            | 0                             | 0                             | 0                             | 0.60(1)<br><i>0.67</i>                              |
| Na   | <i>b</i> (2, $\bar{2}$ )            | 0                             | 0                             | 0.5                           | 2.15(6)<br><i>1.69</i>                              |
| S    | <i>i</i> (4, <i>m</i> )             | 0.3619(1)<br><i>0.3701(1)</i> | 0                             | 0.2216(1)<br><i>0.2020(1)</i> | 0.63(2)<br><i>0.56</i>                              |
| O1   | <i>i</i> (4, <i>m</i> )             | 0.2401(2)<br><i>0.2371(3)</i> | 0                             | 0.0622(2)<br><i>0.0626(4)</i> | 0.93(4)<br><i>1.08</i>                              |
| O2   | <i>i</i> (4, <i>m</i> )             | 0.2886(2)<br><i>0.3128(4)</i> | 0                             | 0.4021(2)<br><i>0.3702(4)</i> | 1.56(6)<br><i>1.76</i>                              |
| O3   | <i>j</i> (8, 1)                     | 0.4694(1)<br><i>0.4741(3)</i> | 0.2334(2)<br><i>0.2325(4)</i> | 0.2026(1)<br><i>0.1807(3)</i> | 1.15(3)<br><i>1.22</i>                              |

<sup>a</sup>*B*<sub>eq</sub> is defined as  $(8\pi^2/3) \sum_{i=3}^3 \sum_{j=3}^3 U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$ . The anisotropic temperature parameters *U*<sub>*ij*</sub> can be obtained from the authors.

Table 3. Bond and contact lengths (in Å), and angles (in °) for NaV(SO<sub>4</sub>)<sub>2</sub>.

|       |                              |         |                |
|-------|------------------------------|---------|----------------|
| V–O1  | 1.962(2) (2×)                | O1–V–O1 | 180            |
| V–O3  | 2.016(1) (4×)                | O1–V–O3 | 91.18(4) (4×)  |
| S–O2  | 1.433(2)                     |         | 88.82(5) (4×)  |
| S–O1  | 1.475(2)                     | O3–V–O3 | 180 (2×)       |
| S–O3  | 1.490(1) (2×)                |         | 93.96(4) (2×)  |
| Na–O2 | 2.439(2) (2×), 3.153(1) (4×) |         | 86.04(4) (2×)  |
| Na–O3 | 2.534(1) (2×)                |         |                |
| Na–O1 | 4.393(2)                     | O3–S–O1 | 107.49(6) (2×) |
| V–Na  | 3.568(1)                     | O3–S–O3 | 107.87(6)      |
| V–S   | 3.240(1), 3.260(1)           | O3–S–O2 | 109.72(5) (2×) |
| S–Na  | 3.418(1), 3.570(1)           | O1–S–O2 | 114.34(9)      |
| V–O2  | 3.627(2)                     |         |                |

found, deformed in such a way that the O–S–O angles involving oxygen atoms bridging to vanadium (i.e. angles O1–S–O3 and O3–S–O3) are smaller [107.40(6) and 107.87(6)°] than the ideal tetrahedral angle of 109.47°. This is probably due to repulsion from the short-bonded oxygens.

The O–S–O angles not involving oxygen atoms bridging to vanadium (i.e. angles O1–S–O3 and O3–S–O3) are enlarged to values above 109.47°. The S–O distances (Table 3) depend on the angles in such a way that the larger the average of the three possible O–S–O angles involving a

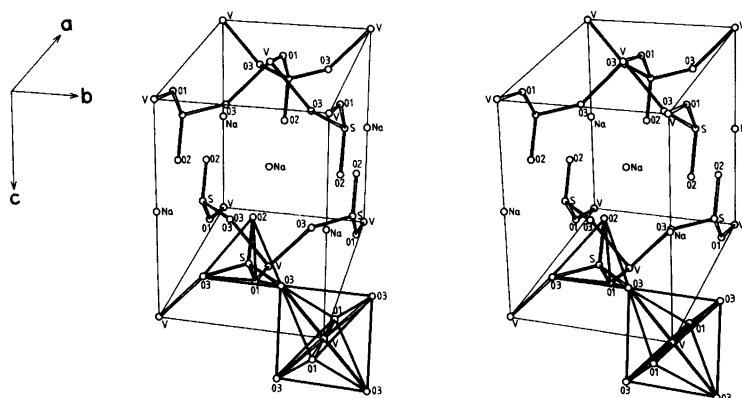


Fig. 1. Stereo-plot of the unit cell of NaV(SO<sub>4</sub>)<sub>2</sub>, seen along the *a*-axis.

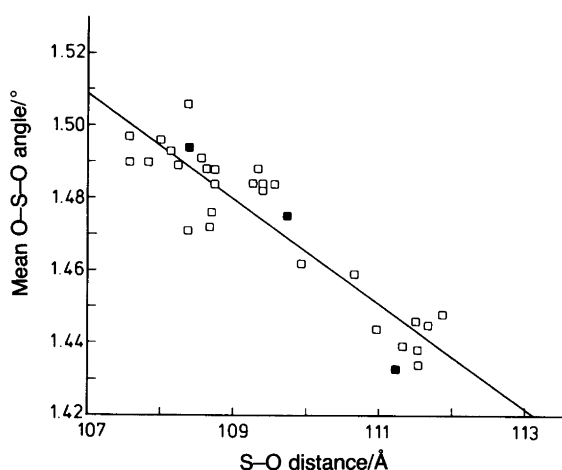


Fig. 2. Plot of S-O distances for a particular bond versus the average of the three angles involving this bond and the other S-O bonds of the sulfate tetrahedron (three solid points). Also shown are 28 points taken from the literature.<sup>3,4</sup> The line is a regression line of all 31 points:  $S-O \text{ distance}/\text{\AA} = 3.05310$  minus  $0.014434$  times the average O-S-O angle/ $^{\circ}$ . The correlation coefficient  $r^2$  is 0.843 and the standard error on the estimated distance is 0.0087.

particular bond, the smaller is the S-O distance. This is shown in Fig. 2, in which an approximately linear relationship (shown as a line) is found which is similar to that observed for the seven different sulfate ions in the  $K_4(VO)_3(SO_4)_5$  and  $Na_2VO(SO_4)_2$  structures.<sup>3,4</sup> The connection indicates a general relationship between S-O bond distances and hybridization of the sulfur atom in sulfate groups, at least in these cases, as pointed out previously.<sup>3,4</sup> The bond lengths and bond angles of the sulfate tetrahedra (Table 3) are generally close to the usual values of  $1.474 \text{ \AA}$ <sup>8</sup> and  $109.47^{\circ}$  for the sulfate group.

*Comparison with other related structures.* It is known that monoclinic crystals of  $NaV(SO_4)_2$ ,<sup>9</sup> as well as of  $KV(SO_4)_2$ ,<sup>10</sup> and  $AgV(SO_4)_2$ ,<sup>9</sup> can be synthesized directly, by fusing together the component salts [ $V_2(SO_4)_3$  and  $Na_2SO_4$ ,  $K_2SO_4$  or  $Ag_2SO_4$ ]. The double salts obtained in this way crystallize in the so-called yavapaiite structure,\* space group  $C2/m$ , found first for an anhydrous  $KFe(SO_4)_2$  sample from Jerome, Arizona.<sup>11</sup> In the crystal structure of

yavapaiite,<sup>11-13</sup> ferric sulfate sheets of composition  $n[Fe(SO_4)_2]^-$  are linked to coplanar potassium ions, thereby accounting for a perfect {001} cleavage.<sup>12</sup> Only results for the  $KFe(SO_4)_2$  structure obtained by Graeber and Rosenzweig<sup>12</sup> are included in Tables 1 and 2, because the other results are virtually the same.

*Note added in proof.* In Ref. 2 the description of the  $KV(SO_4)_2$  structure is not entirely correct:  $VO_6$  octahedra are said to be corner- or edge-connected to the  $SO_4^{2-}$  tetrahedra, although only corner-connected ones exist. In Fig. 1 the projection also implies edge-connected  $SO_4^{2-}$  groups. However, the stereo-plot (Fig. 2) shows the correct structure.

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\* The name yavapaiite refers to the Indian tribe which inhabited the area where the mineral was first found.<sup>11</sup>