

## Note on the Crystal Structure of VOSO<sub>4</sub>

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The crystal structure of vanadium oxide sulphate has been determined from single-crystal X-ray data using Fourier techniques. The parameters were refined using the least-squares method. The specimen was prepared according to Sieverts and Müller.<sup>1</sup>

The following data were obtained for the orthorhombic structure:

Unit cell dimensions (from a Guinier powder photograph taken with CuK $\alpha_1$  radiation):

$a = 7.371 \text{ \AA}$ ,  $b = 6.269 \text{ \AA}$ ,  $c = 7.082 \text{ \AA}$   
Cell content: 4 VOSO<sub>4</sub> (observed density 3.302, calculated density 3.308)

Space group: *Pnma* (No. 62)

Arrangements of atoms:

4 V, 4 S, 4 O<sub>2</sub>, 4 O<sub>3</sub>, 4 O<sub>4</sub> in 4(c);  $\pm(x, \frac{1}{4}, z)$ ;  $\pm(\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$   
8 O<sub>1</sub> in 8(d);  $\pm(x, y, z)$ ;  $\pm(\frac{1}{2}+x, y, \frac{1}{2}-z)$ ;  $\pm(x, \frac{1}{2}-y, z)$ ;  $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z)$

The discrepancy factor is 10.0 % (calculated for all reflections,  $h0l - h3l$ , registered with CuK $\alpha_1$  radiation).

| Atom           | $x \pm \sigma(x)$   | $y \pm \sigma(y)$   | $z \pm \sigma(z)$   | $B \pm \sigma(B) \text{ \AA}^2$ |
|----------------|---------------------|---------------------|---------------------|---------------------------------|
| V              | $0.1658 \pm 0.0005$ | 1/4                 | $0.2327 \pm 0.0005$ | $0.88 \pm 0.06$                 |
| S              | $0.8761 \pm 0.0006$ | 1/4                 | $0.8669 \pm 0.0006$ | $0.81 \pm 0.08$                 |
| O <sub>2</sub> | $0.7187 \pm 0.0018$ | 1/4                 | $0.9896 \pm 0.0020$ | $1.3 \pm 0.2$                   |
| O <sub>3</sub> | $0.0399 \pm 0.0018$ | 1/4                 | $0.9799 \pm 0.0017$ | $0.8 \pm 0.2$                   |
| O <sub>4</sub> | $0.3719 \pm 0.0022$ | 1/4                 | $0.1647 \pm 0.0025$ | $1.7 \pm 0.3$                   |
| O <sub>1</sub> | $0.1251 \pm 0.0015$ | $0.5733 \pm 0.0029$ | $0.2569 \pm 0.0016$ | $1.8 \pm 0.2$                   |

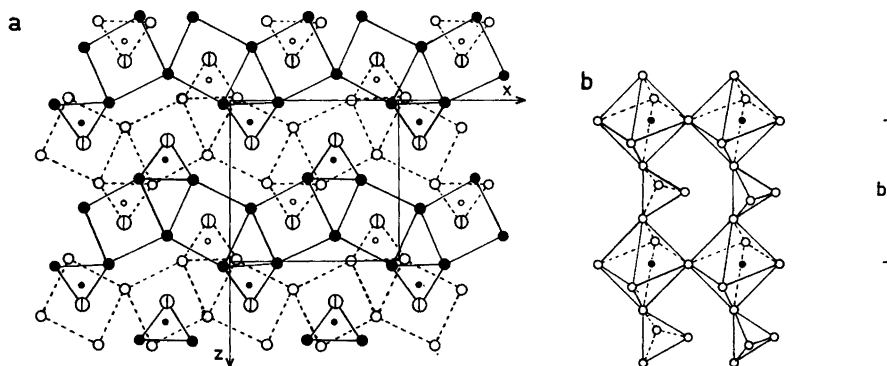


Fig. 1. Schematic drawings showing the structure of VOSO<sub>4</sub>. a) The structure viewed along [010] showing the zigzag-chains formed by VO<sub>6</sub> octahedra linked together by sharing corners and also showing the links between the SO<sub>4</sub> tetrahedra and VO<sub>6</sub> octahedra. Open and full circles denote atoms (large circles oxygen and small ones sulphur) situated in two separate planes  $b/2 = 3.13 \text{ \AA}$  apart. Lined open circles denote oxygen atoms shared between VO<sub>6</sub> octahedra and SO<sub>4</sub> tetrahedra as shown in Fig. 1b. The vanadium atoms have not been indicated. b) The linking in the  $y$ -direction between VO<sub>6</sub> octahedra and SO<sub>4</sub> tetrahedra. Only two VO<sub>6</sub> octahedra in each chain (cf. 1a) have been indicated. Full circles denote vanadium atoms and open ones oxygen atoms. The sulphur atoms have not been indicated.

Interatomic distances:

$$V - O = \begin{cases} 1.59 \\ 2.00 - 2.06 \text{ (4 distances)} \\ 2.28 \end{cases}$$

$$S - O = 1.43 \text{ \AA (mean length within tetrahedron)}$$

$$O - O = 2.34 \text{ \AA (mean length within tetrahedron)}$$

$$O - O = 2.81 \text{ \AA (mean length within octahedron)}$$

The structure may be described as consisting of zig-zag chains running parallel to the *a*-axis and formed from distorted  $VO_6$  octahedra linked together by sharing corners. The chains are coupled together by  $SO_4$  groups, so that every  $VO_6$  octahedron shares corners with four sulphate tetrahedra, each one of which shares corners with four octahedra, giving a three dimensional framework. A schematic drawing, showing the linking of octahedra and tetrahedra is given in Fig. 1.

Full details of this investigation and a discussion of the structure will be given elsewhere.

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1. Sieverts, A. and Müller, F. L. *Z. anorg. allgem. Chem.* **173** (1928) 313.

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## The Synthesis of Some Seleninic Acids

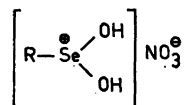
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The interest in organo-selenium compounds was greatly increased by the discovery of their nutritional importance.<sup>1</sup> A great many compounds have been tested in biological experiments during recent

years to investigate their Factor 3-activity and it was found that some diseleno-dicarboxylic acids have a comparatively high activity. For comparison, it was important to test some seleninic acids, analogous to these diselenides, and the synthesis of a series of such selenino-carboxylic acids was begun. The results from this synthetic work are given in this note.

Seleninic acids have been prepared from diselenides by two principal methods. Fredga<sup>2</sup> oxidized diselenides in acetone solution with hydrogen peroxide and Backer and van Dam<sup>3</sup> frequently used concentrated nitric acid as an oxidizing agent. In both cases it was possible to isolate the seleninic acids in good yields. However seleninic acids are comparatively unstable substances tending to decompose and liberate selenium when isolated. This complication can be avoided by isolating them as their heavy metal salts which are usually easily prepared. Besides, because of the amphoteric character of seleninic acids, they form salts with strong acids. Thus, it is possible to prepare, *e.g.*, their hydrochlorides and hydronitrates. The structure of such salts has been widely discussed. By infrared spectroscopy, Paetzold *et al.*<sup>5</sup> could prove the structure of seleninic acid hydrochlorides, and quite analogously the structure of their hydronitrates should be as follows:



It was found suitable for many reasons to isolate the present seleninic acids as such hydronitrates and a direct method of preparation of these compounds is communicated in this note. The method is on the whole that of Backer and van Dam. Thus, the diselenides were treated with an excess of fuming nitric acid with cooling. The reaction mixture was evaporated to dryness in a vacuum desiccator at room temperature and the residual crystals were, if found necessary, recrystallized from concentrated nitric acid. In this way the hydronitrates of the seleninic acids were isolated in almost quantitative yields. These compounds are fairly stable and can be stored for a long period without decomposition.