

Table 2. Atomic coordinates for  $\beta$ -CrOOD at 6 K. Standard deviations in parentheses.<sup>a</sup> (Refers to the chemical unit cell  $a$   $b$   $c$ ).

Atom	$x$	$y$	$z$
Cr	0.0	0.250(2)	0.0
O1	0.306(3)	0.486(2)	0.0
O2	0.616(3)	-0.009(2)	0.0
D	0.492(3)	0.178(2)	0.0

<sup>a</sup> Overall scale factor = 0.0188.  $R(F^2) = 11.0\%$ .  $R_{\text{nuc}} = 8.5\%$ .  $R_{\text{mag}} = 3.7\%$ . (For definition of these values see Ref. 3).

ously<sup>2</sup> were transformed to the magnetic cell and used as starting parameters. A non-collinear antiferromagnetic model for the magnetic structure was assumed with spin waves propagating in the direction of the  $y$ - and  $z$ -axis and with the spins in planes parallel to the  $xy$ -plane. Relative to the  $\text{CrO}_6$  coordination octahedra in the structure, the spins have directions from the chromium atoms towards oxygen atoms with same  $z$ -coordinates as the chromium atoms (see Fig. 1). This model of the magnetic structure refined to a magnetic  $R$ -value of 3.7% (see Table 1) and gave a magnetic moment  $\mu = 2.49(5) \mu_B$  for the chromium atom. The spin form angles of  $\pm 45(5)^\circ$  with the  $x$ -axis. The nuclear reflections gave an  $R$ -value of 8.5% (see Table 1). Additional scattering contributions to the powder pattern from the cryostat can account for the relatively high  $R$ -value. The atomic coordinates transformed to the chemical cell (Table 2) are within three standard deviations equal to those of  $\beta$ -CrOOD at 300 K.<sup>3</sup>

The magnetic structure of  $\beta$ -CrOOD has points of resemblance with that of  $\text{CrCl}_3$ .<sup>7</sup>

- Christensen, A. N. *Acta Chem. Scand. A* 30 (1976) 133.
- Christensen, A. N., Hansen, P. and Lehmann, M. S. *J. Solid State Chem.* 19 (1976) 299.
- Rietveld, H. M. *J. Appl. Crystallogr.* 2 (1969) 65.
- Rietveld, H. M. *Program F418 - Fortran IV Version*, Reactor Centrum Nederland, Petten, N. H., The Netherlands.
- Shull, C. G. *Coherent Neutron Scattering Amplitudes*, Massachusetts Institute of Technology, Cambridge, Mass. 1972.
- Delapalme, A. and Sivadriere, J. *Longeurs de Fermi, Facteurs de Forme Magnétiques, Rayons Ioniques*, Laboratoire de Diffraction Neutronique, C. E. N. G., Grenoble, France.
- Cable, J. W., Wilkinson, M. K. and Wollan, E. O. *Phys. Rev.* 118 (1960) 950.

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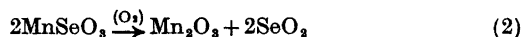
## The Crystal Structure of Manganese(II) Diselenite

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In our investigation of manganese(II) selenites,<sup>1</sup> we found that the equilibrium in aqueous solution shifts towards the diselenite ion when the pH of the solution decreases. Thus, a rose-coloured, crystalline precipitate was obtained from 1 mol/dm<sup>3</sup> selenous acid solution at 60°C. It was identified as  $\text{MnSe}_2\text{O}_5$  by chemical analyses and IR spectroscopy (cf. Table 1).

Thermal analysis (TG, DTG, DTA) of the compound was also carried out and the decomposition scheme in air was found to be as follows:



At a heating rate of 6°C/min the DTA peak temperatures for reactions 1 and 2 were found to be 420 and 525°C, respectively.

An X-ray crystallographic study of the crystals was initiated and rotation and Weissenberg photographs indicated orthorhombic symmetry. The accurate unit cell dimensions were obtained by least-squares refinement of Guinier powder data with KCl as the internal standard; cf. Table 2.

Table 1. Infrared absorption frequencies in the region 4000–250 cm<sup>-1</sup>.

Observed frequency	Assignment <sup>1</sup>
870 s, 845 m, 830 m, 760 vs, b	$\nu_{\text{Se-O}}$ (terminal)
585 s, 555 vs, 510 m	$\nu_{\text{Se-O}}$ (bridge)
445 m, 410 w, 380 m, 330 w, sh	$\delta_{\text{Se-O}}$ (terminal)

Table 2. Crystal data of  $\text{MnSe}_2\text{O}_5$ .

Space group $Pbcn$ (No. 60)
$a = 6.797(2) \text{ \AA}$ , $b = 10.617(3) \text{ \AA}$ , $c = 6.300(2) \text{ \AA}$ , $V = 454.6 \text{ \AA}^3$ , <sup>a</sup> $a = 6.822(3) \text{ \AA}$ , $b = 10.636(4) \text{ \AA}$ , $c = 6.323(3) \text{ \AA}$ , $V = 458.8 \text{ \AA}^3$ , <sup>b</sup> $Z = 4$ , $D_m = 4.2(1) \text{ g cm}^{-3}$ , $D_x = 4.28 \text{ g cm}^{-3}$ , <sup>a</sup> $\mu(\text{MoK}\alpha) = 168.8 \text{ cm}^{-1}$ .

<sup>a</sup> Powder data at 20°C [ $a$  (KCl) = 6.2927 Å].<sup>12</sup>

<sup>b</sup> Diffractometer data at 25°C.

The single crystal intensity data in the interval  $5^\circ < \theta < 35^\circ$  were collected with a Syntex P2<sub>1</sub> automatic diffractometer using the  $\omega$ -scan technique and graphite monochromatized MoK $\alpha$  radiation. The scan speed was 1°/min. A total of 599 reflections satisfying the criterion  $I > 4\sigma(I)$  were used in the subsequent calculations; the intensities were corrected for Lorentz and polarization effects as well as for absorption from the  $\phi$ -scan data. The structure was solved by direct methods and refined to an  $R$ -value of 0.074. In the refinement scattering factors for neutral atoms were used.<sup>2</sup>

The compound MnSe<sub>2</sub>O<sub>5</sub> was found to be isostructural with ZnSe<sub>2</sub>O<sub>5</sub>, recently prepared by a solid-state synthesis and characterized by single crystal methods.<sup>3</sup> However, as ZnSe<sub>2</sub>O<sub>5</sub> seems to be the only diselenite whose structure has been reported in the literature, we present, for comparison, the structural data for the manganese compound.

The final positional parameters are given in Table 3. A listing of structure factors and

Table 3. Final positional parameters of MnSe<sub>2</sub>O<sub>5</sub>. Standard deviations are given in parentheses.

Atom	$x$	$y$	$z$
Se	0.3717(2)	0.1556(1)	0.5386(2)
Mn	1/2	0.5580(3)	1/4
O(1)	0.3324(16)	0.4317(11)	0.0479(24)
O(2)	0.3045(17)	0.7133(11)	0.1558(23)
O(3)	1/2	0.9283(13)	1/4

Table 4. Selected distances (Å) and angles (°) involving the Se<sub>2</sub>O<sub>5</sub> group and MnO<sub>6</sub>-octahedron. Estimated standard deviations are given in parentheses. The values are uncorrected for thermal motion.

(a) Se <sub>2</sub> O <sub>5</sub> -group			
Se—O(1)	1.675(11)	O(3)—Se—O(1)	95.8(5)
—O(2)	1.644(13)	O(3)—Se—O(2)	102.6(6)
—O(3)	1.830(7)	O(1)—Se—O(2)	102.9(6)
		Se—O(3)—Se'	121.6(9)
(b) MnO <sub>6</sub> -octahedron			
Mn <sup>Ia</sup> —O(1) <sup>I,II</sup>	2.178(13)		
—O(2) <sup>I,II</sup>	2.206(12)		
—O(2) <sup>III,IV</sup>	2.206(14)		

<sup>a</sup> The superscript denotes the symmetry transformation:

I  $x, y, z$                       III  $\bar{x}, \bar{y}, \bar{z}$   
 II  $\bar{x}, y, 1/2 - z$             IV  $x, \bar{y}, 1/2 + z$

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anisotropic thermal parameters is available from the authors upon request. Table 4 lists selected distances and angles for the basic building units of the structure: the diselenite group and the MnO<sub>6</sub>-octahedron.

The geometry of the Se<sub>2</sub>O<sub>5</sub> group in MnSe<sub>2</sub>O<sub>5</sub> is in good agreement with the values reported for ZnSe<sub>2</sub>O<sub>5</sub>. The MnO<sub>6</sub>-octahedron is almost regular, with Mn—O distances ranging from 2.18 to 2.21 Å, in accordance with literature values.<sup>4</sup> The mean metal-oxygen distances in MnO<sub>6</sub> and ZnO<sub>6</sub> octahedra are 2.20 and 2.11 Å, respectively; the difference (0.09 Å) corresponds rather well to the ionic radii difference of the six-coordinated divalent metals (0.07 Å).<sup>5</sup>

On the basis of IR and Raman spectra, a molecular symmetry of  $C_{2v}$  was predicted for both the diselenite<sup>6</sup> and the disulfite<sup>7,8</sup> anion. The structures of ZnSe<sub>2</sub>O<sub>5</sub> and MnSe<sub>2</sub>O<sub>5</sub> confirm the symmetry prediction for the diselenite group, but crystal structure determinations<sup>9,10</sup> have shown that the disulfite group is asymmetric with an S—S bond and a  $C_s$  symmetry. In vibrational spectroscopy the large number of fundamentals of these compounds makes exact assignment difficult, but different symmetries should be distinguishable through careful analysis, as shown by Herlinger and Long for the disulfite anion.<sup>11</sup>

Regarding the IR spectrum of MnSe<sub>2</sub>O<sub>5</sub> (cf. Table 1), it may be noted that it resembles the spectra of CaSe<sub>2</sub>O<sub>5</sub> and BaSe<sub>2</sub>O<sub>5</sub>,<sup>8</sup> which may indicate a structural relationship.

1. Koskenlinna, M., Niinistö, L. and Valkonen, J. *Cryst. Struct. Commun.* 5 (1976) 663.
2. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, p. 72.
3. Meunier, P. and Bertand, M. *Acta Crystallogr. B* 30 (1974) 2840.
4. Popov, D., Herak, R., Prelesnik, B. and Ribár, B. *Z. Kristallogr.* 137 (1973) 280, and references therein.
5. Shannon, R. D. and Prewitt, C. I. *Acta Crystallogr. B* 25 (1969) 925.
6. Simon, A. and Paetzold, R. *Z. Anorg. Allg. Chem.* 303 (1960) 39.
7. Simon, A., Waldmann, K. and Steger, E. *Z. Anorg. Allg. Chem.* 288 (1956) 131.
8. Rocchiccioli, C. *C. R. Acad. Sci. Ser. C* 250 (1960) 2347.
9. Lindqvist, I. and Mörtzell, M. *Acta Crystallogr.* 10 (1957) 406.
10. Baggio, S. *Acta Crystallogr. B* 27 (1971) 517.
11. Herlinger, A. W. and Long, T. V. *Inorg. Chem.* 8 (1969) 2661.
12. Hambling, P. G. *Acta Crystallogr.* 6 (1953) 98.

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