

interaction with the remaining  $\text{Cl}^-$  ion to give incipient formation of a fifth  $\text{M}-\text{Cl}$  bond (Clegg, 1976). Spectroscopic and X-ray photographic data indicate that the Pd complex contains square-planar  $[\text{PdCl}_4]^{2-}$  and  $\text{Cl}^-$  anions with no significant bonding interaction (Greenhalgh, 1977; Clegg, 1977). With  $\text{MnCl}_2$ , the same method gives a complex initially formulated as  $[\text{Cr}(\text{NH}_3)_6][\text{MnCl}_5]$ , but the IR spectrum is inconsistent with this and suggests the possibility of bridged species  $[\text{Mn}_2\text{Cl}_x]^{(x-4)-}$  (Greenhalgh, 1977). The crystal structure was determined in order to resolve this difficulty.

The complex actually contains  $[\text{MnCl}_5(\text{H}_2\text{O})]^{3-}$  anions. These and the  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  cations have an essentially octahedral coordination geometry, *cis* angles

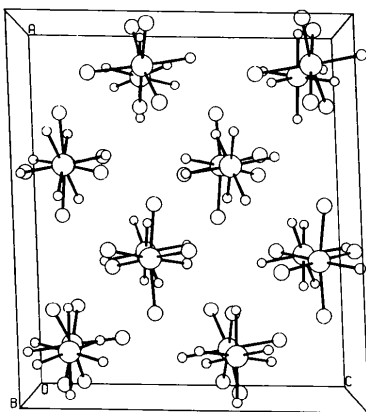


Fig. 2. The contents of one unit cell.

in the anions differing from  $90^\circ$  by rather more than is observed in the cations. The ions are held together by Coulombic forces and by a network of weak  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds.

The geometries of the two independent cations and two independent anions are shown in Fig. 1, and the contents of one unit cell in Fig. 2.

I thank Drs D. A. Greenhalgh and B. P. Straughan for providing the crystals. The structure was solved with the *SHELX* program system of Dr G. M. Sheldrick, and the figures were drawn with a local version of *PLUTO* by Dr W. D. S. Motherwell, implemented on the Newcastle IBM 370/168 computer.

#### References

- CHURCHILL, M. R. (1973). *Inorg. Chem.* **12**, 1213–1214.  
 CLEGG, W. (1976). *Acta Cryst.* **B32**, 2907–2909.  
 CLEGG, W. (1977). Unpublished results.  
 CLEGG, W., GREENHALGH, D. A. & STRAUGHAN, B. P. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2591–2593.  
 CROMER, D. T. & IBERS, J. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–150. Birmingham: Kynoch Press.  
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–102. Birmingham: Kynoch Press.  
 EPSTEIN, E. F. & BERNAL, I. (1971). *J. Chem. Soc. A*, pp. 3628–3631.  
 GREENHALGH, D. A. (1977). PhD thesis, Univ. of Newcastle upon Tyne.  
 RAYMOND, K. N., MEEK, D. W. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 1111–1117.

*Acta Cryst.* (1978). **B34**, 3330–3332

## An X-ray Diffraction Study of Nickel Thiosulphate Hexahydrate

BY Y. ELERMAN, A. AYDIN URAZ AND N. ARMAĞAN

*University of Ankara Faculty of Science, Department of Physics, Beşevler, Ankara, Turkey*

(Received 5 May 1978; accepted 31 May 1978)

**Abstract.**  $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ,  $M_r = 463.02$ , orthorhombic, *Pnma*,  $a = 9.282(5)$ ,  $b = 14.444(9)$ ,  $c = 6.803(3)$  Å,  $Z = 4$ ,  $V = 912.1$  Å<sup>3</sup>,  $D_x = 2.03$ ,  $D_m = 1.92$  g cm<sup>-3</sup> (floatation),  $\mu(\text{Cu } K\alpha) = 73.27$  cm<sup>-1</sup>. The title compound is isostructural with  $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ . The structure was refined by a full-matrix least-squares method to an *R* (excluding zero-weight data) of 0.056 for 248 reflexions and an *R* (including zero-weight data) of 0.072 for 266 reflexions. The S–S and S–O bond distances in the  $\text{S}_2\text{O}_3^{2-}$  anion are 2.015(7) and 1.465(10) Å respectively. The bond angle O–S–O is

110.2(6)°. The H atom positions were found from a difference Fourier synthesis.

**Introduction.** The first structural investigation of  $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  was made by Brunt (1946) who proposed that it was isomorphous with  $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ . In this study, which is based on the data collected at room temperature, Brunt's proposition is justified and the results are compared with those of the other ionic thiosulphates.

The diffraction data were collected employing a

needle crystal elongated along the [010] direction with dimensions  $0.52 \times 0.17$  mm. The crystals were found to be stable at room temperature. The crystal data of  $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  were obtained by Elerman, Uraz, Armağan & Aka (1977).

The lattice parameters, based on the data which were obtained employing an XDC Guinier–Hägg powder camera, were refined using the program *CELCIUS* (Tegenfeldt, 1967).

With Cu  $K\alpha$  radiation and integrated Weissenberg equi-inclination techniques, multiple-film exposures were taken of the reciprocal layers  $0 \leq k \leq 5$ . Out of 1030 photographically recorded symmetry-related reflexions measured with the aid of Joyce–Loebl microdensitometer, 266 independent reflexions were obtained.

The maximum to minimum ratio of intensities measured photographically was 600:1. The intensities were corrected for Lorentz, polarization (Zalkin, 1967) and absorption (Alcock, 1975) effects with the IBM 360/40 computer.

The structure was refined by the full-matrix least-squares method with the computer program *LALS* (Zalkin, 1968). The function minimized was  $\sum_{hkl} W_{hkl} \Delta^2$ , where  $\Delta = |F_o| - |F_c|$  and  $F_o$  and  $F_c$  are the observed and calculated structure amplitudes. The weighting scheme used was  $W = 1/(\sigma F_o)^2$ , where  $\sigma F_o$  denotes the standard deviation of the observed structure factor determined from the symmetry-related reflexions.

The scattering factors used for the Ni, S and O atoms were taken from the data of Doyle & Turner (1968) and those used for H atoms were values calculated by Stewart, Davidson & Simpson (1965). The scattering factors were corrected for anomalous dispersion.

The refinement was started on the basis of the parameters of the initial structural model of Baggio, Amzel & Becka (1969). Three cycles of refinement of the positional and individual isotropic thermal parameters of all atoms (except H) led to an  $R$  (including zero-weight data) of 0.078 and  $R_w$  of 0.071 where  $R = \sum W\Delta / \sum |F_o|$  and  $R_w = (\sum W\Delta^2 / \sum WF_o^2)^{1/2}$ .

The reflexions 040 and 121 were corrected for extinction effects (Uraz & Armağan, 1975) as described by Zachariasen (1967) and Killean, Lawrence & Sharma (1972).

A three-dimensional difference Fourier synthesis with the parameters resulting from the refinement revealed the positions of the H atoms. The standard deviations of the H-atom positional parameters were calculated on the basis of a Fourier synthesis (Stout & Jensen, 1968).

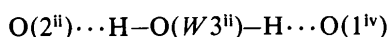
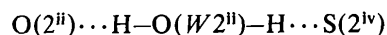
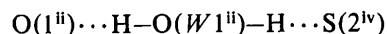
Isotropic temperature factors of  $3.5 \text{ \AA}^2$  were used for H atoms in the following six cycles of the refinement, where positional and anisotropic thermal parameters of

the atoms other than H were refined while all parameters of the H atoms were kept fixed. The refinement was terminated when no parameter shift was larger than one tenth of the estimated standard deviation of the parameter concerned. At this stage the refinement yielded  $R$  as 0.056 when zero-weight data were excluded (248 reflexions) and  $R$  as 0.072,  $R_w$  as 0.064 and  $S$  as 2.34 when zero-weight data were included (266 reflexions);  $S = [\sum W\Delta^2 / (n - m)]^{1/2}$ ,  $n$  and  $m$  denote number of reflexions and number of parameters refined, respectively.

An analysis of the distribution of  $\langle W\Delta^2 \rangle$  in intervals of  $\sin \theta$  and  $F_o$  confirmed that the weighting scheme adopted was appropriate to the data.

The positional parameters are given in Table 1.\*

**Discussion.** The crystal structure of  $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  can be described in terms of successive parallel layers. The layers, formed by either  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  octahedra or  $\text{S}_2\text{O}_3^{2-}$  tetrahedra, are found to be perpendicular to the  $b$  axis. Each octahedron is linked to the neighbouring four octahedra in the same layer and to the four tetrahedra in the next two layers, forming the following hydrogen bonds:



[(ii)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ ; (iv)  $-\frac{1}{2} - x, -y, \frac{1}{2} + z$ ].

Each Ni atom is surrounded by six water molecules whose O atoms are at the corners of a distorted octahedron. The Ni–O distances lie between 2.03 and 2.09

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33667 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final coordinates* ( $\times 10^3$  for hydrogen atoms and  $\times 10^4$  for the others) with standard deviations in parentheses

	$x$	$y$	$z$
Ni	0	0	0
S(1)	0428 (5)	2500	4367 (7)
S(2)	2177 (5)	2500	6123 (7)
O(1)	−0388 (9)	1667 (6)	4761 (10)
O(2)	0949 (9)	2500	2309 (13)
O( $W1$ )	−1555 (8)	0802 (5)	1450 (10)
O( $W2$ )	1318 (10)	1126 (5)	−0267 (12)
O( $W3$ )	−1016 (9)	0286 (5)	−2577 (11)
H(1)	891 (15)	096 (13)	230 (17)
H(2)	800 (15)	124 (13)	120 (17)
H(3)	084 (15)	130 (13)	022 (17)
H(4)	090 (15)	130 (13)	914 (17)
H(5)	935 (15)	010 (13)	690 (17)
H(6)	897 (15)	992 (13)	681 (17)

Å (see Table 2), in good agreement with distances in nickel ammonium sulphate hexahydrate (Montgomery & Lingafelter, 1964) and nickel sulphite hexahydrate (Baggio & Becka, 1969).

The geometry and bonding in the  $S_2O_3^{2-}$  ion (Table 3) are similar to those observed in  $Na_2S_2O_3 \cdot 5H_2O$  (Uraz & Armağan, 1977),  $BaS_2O_3 \cdot H_2O$  (Manojlović-Muir, 1975),  $MgS_2O_3 \cdot 6H_2O$  (Baggio, Amzel & Becka, 1969). The bond angles for the central S atom are found to be between  $107.4(6)$  and  $110.2(6)^\circ$ . As can be seen from the values, the spread is less than those of the Na and Mg salts, and reveals smaller distortion from ideal tetrahedral symmetry. The S—O distances [ $1.447(10)$ ,  $1.482(12)$  Å] are in agreement with those in Na [ $1.455(5)$ – $1.490(4)$  Å], Ba [ $1.472(3)$ – $1.483(3)$  Å] and Mg [ $1.465(5)$ – $1.471(5)$  Å] salts. The S—S distance of  $2.015(7)$  Å is in excellent agreement with  $2.015(3)$  Å in Na and  $2.013(3)$  Å in Mg thio-sulphates, respectively.

The hydrogen-bonding scheme for  $MgS_2O_3 \cdot 6H_2O$  given by Baggio, Amzel & Becka (1969) and El Saffar (1969) is also found to be valid in this work for  $NiS_2O_3 \cdot 6H_2O$  (Table 4). O—H distances of

Table 2. *Interatomic distances and bond angles in the coordination polyhedron around a Ni ion*

Ni—O(W1)	$2.097 \pm 0.008$ Å	O(W1)—Ni—O(W2)	$90.8 \pm 0.3^\circ$
Ni—O(W2)	$2.043 \pm 0.009$	O(W1)—Ni—O(W3)	$91.4 \pm 0.3$
Ni—O(W3)	$2.034 \pm 0.009$	O(W2)—Ni—O(W3)	$87.8 \pm 0.4$

Table 3. *Geometry of the thiosulphate group*

S(1)—S(2)	$2.015 \pm 0.007$ Å	O(1)—S(1)—S(2)	$108.2 \pm 0.4^\circ$
S(1)—O(1)	$1.447 \pm 0.010$	S(2)—S(1)—O(2)	$107.4 \pm 0.6$
S(1)—O(2)	$1.482 \pm 0.012$	O(1)—S(1)—O(2)	$110.2 \pm 0.6$
O(1)—O(2)	$2.398 \pm 0.012$		

Table 4. *Hydrogen-bond distances (Å) for  $NiS_2O_3 \cdot 6H_2O$*

O(W1)···S(2)	$3.244(8)$	O(W2)···O(2)	$2.669(11)$
O(W1)···O(1)	$2.784(12)$	O(W3)···O(1)	$2.756(12)$
O(W2)···S(2)	$3.257(10)$	O(W3)···O(W2)	$2.826(12)$

$0.75(4)$ – $0.86(4)$  Å for H—O···H bonds and  $0.71(4)$ – $0.73(4)$  Å for H—O···S bonds were obtained in this work and considered as normal within the limitations of X-ray studies. The H—O—H bond angles are between  $103(2)$  and  $106(2)^\circ$ . This work revealed distances of  $2.53(3)$  and  $2.55(3)$  Å for H(2)···S(2) and H(4)···S(2), respectively, in agreement with the results of Baur (1972) ( $2.42$  Å) and Uraz & Armağan (1977) [ $2.42(2)$  Å].

## References

- ALCOCK, N. W. (1975). *ABSCOR. A Fortran Crystallographic Absorption Correction Program*. Private communication.
- BAGGIO, S., AMZEL, L. M. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 2650–2653.
- BAGGIO, S. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 1150–1155.
- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.
- BRUNT, N. A. (1946). Thesis, Leiden.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- ELERMAN, Y., URAZ, A. A., ARMAĞAN, N. & AKA, Y. (1977). *J. Appl. Cryst.* **10**, 362–363.
- EL SAFFAR, Z. M. (1969). *Acta Cryst.* **B25**, 1708–1711.
- KILLEAN, R. C. G., LAWRENCE, J. L. & SHARMA, V. C. (1972). *Acta Cryst.* **A28**, 405–407.
- MANOJLOVIĆ-MUIR, L. (1975). *Acta Cryst.* **B31**, 135–139.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 1478–1479.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 403. London: Macmillan.
- TEGENFELDT, J. (1967). *CELCIUS. A Fortran Crystallographic Least-Squares Program*. Uppsala, Sweden.
- URAZ, A. A. & ARMAĞAN, N. (1975). *A Fortran Crystallographic Extinction Program*. Univ. of Ankara, Dept. of Physics, Ankara, Turkey.
- URAZ, A. A. & ARMAĞAN, N. (1977). *Acta Cryst.* **B33**, 1396–1399.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
- ZALKIN, A. (1967). *DRF. A Fortran Crystallographic Data-Reduction and Fourier Program*. Berkeley, California.
- ZALKIN, A. (1968). *LALS. A Fortran Crystallographic Least-Squares Program*. Berkeley, California.