

Hydrogen Bonding in Magnesium Thiosulphate Hexahydrate $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. A Neutron Diffraction Study

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Abstract. $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, orthorhombic, $Pnma$, $Z = 4$, $a = 9.405$ (4), $b = 14.449$ (4), $c = 6.866$ (4) Å, $V = 933.0$ Å³ (at 296 K) and $a = 9.304$ (3), $b = 14.447$ (3), $c = 6.847$, $V = 920.3$ Å³ (at 120 K). D_c (296 K) = 1.739, D_c (120 K) = 1.760 Mg m⁻³. 516 (296 K) and 706 (120 K) reflections measured by neutron diffraction. Refinement converged to $R_w(F) = 0.056$ (120 K) and 0.057 (296 K). The Mg–O distances range from 2.035 (3) (120 K) to 2.125 (5) (296 K) Å. The S–S and S–O bond lengths in the tetrahedron are 2.011 (14) and 1.457 (11)–1.469 (7) Å for the room-temperature and 2.047 (12) and 1.463 (5) and 1.471 (8) Å for the low-temperature data. Each water molecule is a donor for two hydrogen bonds of O–H...O and O–H...S type. The O–H...S hydrogen bonds are relatively short with H...S distances of 2.284 (11) (296 K), 2.340 (11) (296 K) Å and 2.268 (10) (120 K) and 2.291 (8) (120 K) Å.

Introduction. The X-ray structure of the title compound has been refined by Baggio, Amzel & Becka (1969). In the course of our current programme on the electron density of the thiosulphate group and related compounds (Elerman, Teng, Bats, Fuess & Joswig, 1981), we carried out a neutron diffraction study of the title compound. A prismatic crystal with dimensions 4 × 3 × 2 mm was used for data collection. Two data sets were collected at 296 (RT) and 120 K (LT) at the FR2 reactor of the Kernforschungszentrum, Karlsruhe, on a computer-controlled four-circle instrument by a θ – 2θ scan. Background corrections were made (Blessing, Coppens & Becker, 1974). Further experimental details are given in Table 1. Data was corrected for absorption by the Gauss integration method. Lorentz correction was applied with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The low-temperature data will be combined with X-ray data for an X – N deformation density study of the hydrogen bonds.

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Table 1. *Experimental conditions, refinement and anisotropic extinction parameters ($G_{ij} \times 10^3$)*

	Room temperature	Low temperature
$R(F) = \sum F_o - F_c / \sum F_o$	0.062	0.060
$R_w(F) = [\sum w(F_o - F_c)^2 / \sum F_o^2]^{1/2}$	0.057	0.056
Goodness of fit $S = [\sum (F_o - F_c)^2 / (No - Nv)]^{1/2}$	2.74	2.68
Number of reflections	720	1030
Number of variables	121	121
θ_{\max} (°)	32	45
$(\sin \theta / \lambda)_{\max}$ (Å ⁻¹)	0.60	0.70
G_{11}	1.8 (3)	1.5 (2)
G_{22}	3.0 (6)	2.3 (5)
G_{33}	0.1 (2)	0.03 (1)
G_{12}	-2.1 (4)	-1.6 (3)
G_{13}	0.4 (1)	0.21 (8)
G_{23}	-0.1 (1)	-0.19 (9)
λ (Å)	0.8952	1.021
μ (mm ⁻¹)	0.154	0.154

The structure was refined by full-matrix least-squares methods using the XRAY system and the ORXFLS 3 program (Busing *et al.*, 1971). The function minimized was $w\Delta^2$ with $\Delta = |F_o - F_c|$. The weights were based on counting statistics with $w = 1/\sigma^2(F_o)$, where $\sigma^2(F_o) = \sigma^2(\text{count}) + 0.02F_o^2$. The neutron scattering lengths were $b(\text{Mg}) = 5.39$, $b(\text{O}) = 5.80$, $b(\text{S}) = 2.85$ and $b(\text{H}) = -3.74$ (all in units of fm) (Koester, 1977). The refinement converged to $R_w(F) = 0.09$ and 0.08. In the last cycles, parameters for isotropic and anisotropic extinction (Coppens & Hamilton, 1970) were included in the refinement with ORXFLS 3 (Busing *et al.*, 1971).

The intensities of the strongest reflections were reduced by about 50% due to extinction. Refinement only converged for a type I crystal (Zachariasen, 1967). The parameters for anisotropic extinction are given with the experimental details in Table 1. The positional parameters are summarized in Table 2.‡

‡ Lists of structure factors and anisotropic temperature parameters and the details of the hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36699 (12pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters (estimated standard deviations in parentheses) and equivalent thermal parameters

		x	y	z	U_{eq} (Å ²)
Mg	RT	0.0	0.0	0.0	1.57
	LT	0.0	0.0	0.0	0.74
S(1)	RT	0.0424 (10)	0.25	0.4400 (15)	1.58
	LT	0.0400 (10)	0.25	0.4380 (11)	0.55
S(2)	RT	0.2174 (12)	0.25	0.6082 (14)	2.18
	LT	0.2178 (10)	0.25	0.6141 (12)	1.15
O(1)	RT	-0.0416 (4)	0.1662 (3)	0.4776 (6)	3.35
	LT	-0.0431 (3)	0.1660 (2)	0.4773 (4)	1.47
O(2)	RT	0.0908 (7)	0.25	0.2384 (8)	2.92
	LT	0.0914 (6)	0.25	0.2348 (6)	1.29
O(3)	RT	-0.1535 (4)	0.0816 (3)	0.1488 (5)	1.92
	LT	-0.1546 (4)	0.0815 (2)	0.1477 (5)	1.05
O(4)	RT	0.1263 (4)	0.1148 (3)	-0.0309 (5)	2.53
	LT	0.1277 (4)	0.1137 (2)	-0.0312 (4)	1.09
O(5)	RT	-0.0975 (5)	0.0272 (3)	-0.2612 (6)	2.50
	LT	-0.0982 (5)	0.0261 (2)	-0.2598 (5)	1.26
H(1)	RT	0.8798 (7)	0.1088 (5)	0.2650 (14)	3.55
	LT	0.8794 (7)	0.1111 (4)	0.2693 (9)	2.58
H(2)	RT	0.8096 (7)	0.1315 (5)	0.0679 (13)	3.88
	LT	0.8102 (7)	0.1324 (4)	0.0656 (9)	2.48
H(3)	RT	0.1200 (8)	0.1618 (6)	0.0671 (12)	3.75
	LT	0.1195 (7)	0.1618 (4)	0.0696 (9)	2.68
H(4)	RT	0.1533 (8)	0.1453 (6)	0.8566 (13)	4.31
	LT	0.1534 (8)	0.1465 (4)	0.8520 (9)	2.60
H(5)	RT	0.9214 (8)	0.0771 (7)	0.6542 (13)	4.60
	LT	0.9201 (7)	0.0778 (4)	0.6506 (8)	2.56
H(6)	RT	0.8206 (9)	0.9938 (6)	0.6948 (12)	4.04
	LT	0.8167 (8)	0.9936 (3)	0.6982 (9)	2.73

Discussion. The crystal structure of MgS₂O₃·6H₂O can be described as consisting of successive layers perpendicular to the **b** direction. The layers are built alternately by Mg(H₂O)₆²⁺ octahedra and S₂O₃²⁻ tetrahedra (Fig. 1). The environment of the Mg²⁺ ion is a slightly distorted octahedron. Mg–O distances are in good agreement with values for MgSO₄·4H₂O (Baur, 1964) (Table 3). The S–S distance (RT) is in agreement with those in Na₂S₂O₃ (Teng, Fuess & Bats, 1981) and in Na₂S₂O₃·5H₂O (Lisensky & Levy, 1978) which measure 2.005 and 2.024 Å respectively. It is,

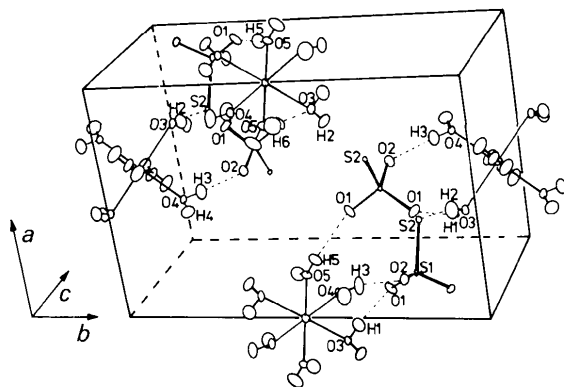


Fig. 1. The hydrogen bonding scheme in MgS₂O₃·6H₂O.

Table 3. Bond distances (Å) and angles (°) for Mg(H₂O)₆²⁺ octahedra and S₂O₃²⁻ tetrahedra

	296 K	120 K
Mg–O(3)	2.125 (5)	2.114 (3)
Mg–O(4)	2.051 (5)	2.037 (3)
Mg–O(5)	2.052 (5)	2.035 (3)
O(3)–Mg–O(4)	89.7 (2)	89.9 (1)
O(3)–Mg–O(5)	90.6 (2)	90.5 (1)
O(4)–Mg–O(5)	90.8 (2)	90.9 (1)
S(1)–S(2)	2.011 (14)	2.047 (12)
S(1)–O(1)	1.469 (7)	1.463 (5)
S(1)–O(2)	1.457 (11)	1.471 (8)
S(2)–S(1)–O(1)	109.5 (5)	108.5 (3)
S(2)–S(1)–O(2)	106.8 (6)	107.0 (4)
O(1)–S(1)–O(2)	109.5 (6)	110.2 (3)

however, significantly longer than the distances in BaS₂O₃·H₂O (Manojlović-Muir, 1975) and (NH₄)₂S₂O₃ (Teng, Fuess & Bats, 1979), where values of 1.979 (3) and 1.979 (1) Å were observed.

The three independent water molecules are involved in hydrogen bonds where the oxygen and the sulphur atoms of the thiosulphate group act as acceptors. The O–H bonds [mean 0.954 (8) Å (RT) and 0.977 (6) Å (LT)] and H–O–H angles [mean 106.1 (7)° (RT) and 106.4 (4)° (LT)] vary in the usual range (Ferraris & Franchini-Angela, 1972). All O–H...O bonds [O...O distances between 2.711 (7) and 2.940 (7) Å (RT) and 2.702 (5) and 2.949 (5) Å (LT)] may be classified as medium to weak.

Only very few neutron diffraction studies of O–H...S bonds are reported in the literature (Mereiter, Preisinger & Guth, 1979; Van Roey & Kerr, 1981). All of them show O–H...S bonds which are almost linear with deviations between 2 and 15° from linearity. An average value of 3.32 Å for the oxygen–sulphur distance is given from several X-ray studies (Mereiter *et al.*, 1979).

The O...S distances (RT) of 3.242 (7) and 3.252 (7) Å and (LT) of 3.248 (6) and 3.237 (5) Å are shorter than the sum of the van der Waals radii, which is given by Bondi (1964) as $r_O + r_S = 1.52 + 1.80 = 3.32$ Å. Similarly, the H...S distances (RT) of 2.284 (11) and 2.340 (11) Å and (LT) of 2.268 (10) and 2.291 (8) Å are considerably smaller than the radii sum of $r_H + r_S = 2.80$ Å according to the values $r_H = 1.0$ Å (Baur, 1972) and $r_S = 1.80$ Å. The O–H...S hydrogen bonds are therefore stronger than those observed in Schlippe's salt Na₃SbS₄·9H₂O (Mereiter, Preisinger & Guth, 1979) where H...S distances in the range from 2.343 and 2.407 Å were found. A shorter H...S distance was observed by Van Roey & Kerr (1981) for 1-(2-hydroxythiobenzoyl)piperidine in a 20 K neutron diffraction study where values of 2.262 (6) Å for H...S and of 3.214 (5) Å for O...S were found.

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Dineptunium Sodium Nonfluoride

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Abstract. NaNp₂F₉, orthorhombic, *Pnma*, *a* = 8·617 (5), *b* = 11·274 (9), *c* = 6·955 (4) Å, *V* = 676 Å³, *d*_{calc} = 6·56 Mg m⁻³, *Z* = 4. The Np atoms are surrounded by nine F atoms at distances between 2·260 (5) and 2·371 (5) Å. Na atoms are surrounded by ten F atoms at distances between 2·552 (6) and 3·171 (6) Å. This compound, prepared by hydrothermal synthesis, is isostructural with KU₂F₉. The crystal structure was refined to *R* = 0·030 for 1816 independent reflexions.

Introduction. NaTh₂F₉ was reported to be cubic (Zachariasen, 1948). NaU₂F₉ is orthorhombic and was thought probably to be isomorphous with KU₂F₉ by Thoma, Insley, Herbert, Friedman & Weaver (1963). Since this type of compound was unknown for Np, we decided to synthesize NaNp₂F₉ as single crystals in

order to establish its crystal structure and to compare it with the existing Th and U compounds.

In our laboratory we recently introduced an apparatus that enables us to prepare single crystals of transuranium fluoride complexes: hydrothermal synthesis under hydrofluoric acid atmosphere. In fact, the flux-growth method, previously used successfully for the preparation of single crystals containing actinide elements, presented some drawbacks which do not appear with this new method. In particular, cation exchange between the chloride flux and the fluoride compound to be synthesized do not occur (Cousson, Tabuteau, Pagès & Gasperin, 1979). A major advantage is that single crystals can be grown using very small quantities of transuranium tetrafluoride.

NaNp₂F₉ is the first neptunium fluoride obtained as single crystals using hydrothermal synthesis. 20 mg of