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$MS_2O_6.6H_2O$ (M=Mg, Ni, Zn)

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Abstract. $MgS_2O_6.6H_2O$, $a=6{\cdot}819$ (2), $b=6{\cdot}747$ (2), $c=6{\cdot}506$ (2) Å, $\alpha=94{\cdot}23$ (2), $\beta=96{\cdot}76$ (2), $\gamma=101{\cdot}72$ (2)°, M.W. 292·5, $F(000)=152$, μ(Mo $K\alpha$)=5·6 $^{-1}$, $D_m=1{\cdot}8$ (1) (flotation), $D_x=1{\cdot}68$ g cm^{-3}. $NiS_2O_6.6H_2O$, $a=6{\cdot}751$ (3), $b=6{\cdot}699$ (3), $c=6{\cdot}451$ (3) Å, $\alpha=94{\cdot}53$ (4), $\beta=96{\cdot}30$ (4), $\gamma=101{\cdot}28$ (3)°, M.W. 326·9, $F(000)=168$, μ(Mo $K\alpha$)=21·1 cm^{-1}, $D_m=2{\cdot}0$ (1), $D_x=1{\cdot}92$ g cm^{-3}. $ZnS_2O_6.6H_2O$, $a=6{\cdot}799$ (2), $b=6{\cdot}752$ (3), $c=6{\cdot}491$ (4) Å, $\alpha=94{\cdot}58$ (4), $\beta=96{\cdot}20$ (2), $\gamma=101{\cdot}47$ (2)°, M.W. 333·6, $F(000)=170$, μ(Mo $K\alpha$)=25·7 cm^{-1}, $D_m=2{\cdot}0$ (1), $D_x=1{\cdot}91$ g cm^{-3}. $P\bar{1}$, $Z=1$. Average M–O bond lengths: for Mg 2·050 Å, for Ni 2·040 Å and for Zn 2·078 Å.

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Introduction. Crystals were supplied by Dr E. Stanley, formerly of this department. Their preparations were similar and have been described elsewhere (Chan & Stanley, 1970). Crystals of the magnesium and zinc compounds were white needles and those of the nickel compound were bluish-green needles. All crystals were mounted with the needle axis parallel to the fibre axis. Data were collected using a Picker-automated dif-

Table 1. *Data collection and refinement parameters*

	$MgS_2O_6.6H_2O$	$NiS_2O_6.6H_2O$	$ZnS_2O_6.6H_2O$
Crystal dimensions	0·30×0·14×0·15 mm	0·60×0·20×0·16 mm	0·48×0·2×0·2 mm
Base width	2·5°	3·6°	2·8°
Range of 2θ	3–62°	3–62°	3–65°
Scan rate	1° min^{-1}	2° min^{-1}	1° min^{-1}
Bgnd time	40 sec	40 sec	40 sec
Independent reflexions measured	1824	1816	2086
Independent reflexions refined	1393	1478	1573
§ (see text)	2·00	2·00	2·25
$F(000)$	152	168	170
R	0·036	0·077	0·031
R_ω	0·034	0·087	0·038
A_0	0·43302	0·44623	0·17650
A_1	−0·04648	−0·05757	0·02149
A_2	0·00255	0·00814	−0·00178
A_3	−0·00003	−0·00011	0·00005

Table 2. *Coordinates and thermal parameters with estimated standard deviations in parentheses*

(*a*) Fractional positional coordinates (×10^4)

	$MgS_2O_6.6H_2O$			$NiS_2O_6.6H_2O$			$ZnS_2O_6.6H_2O$		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
M	0	0	0	0	0	0	0	0	0
S	3597 (2)	5450 (2)	5014 (2)	3580 (1)	5452 (1)	5030 (1)	3589 (1)	5451 (1)	5016 (2)
O(1)	1285 (6)	2919 (5)	−435 (6)	1156 (6)	2967 (5)	−422 (5)	1211 (7)	2980 (5)	−428 (6)
O(2)	−702 (6)	970 (5)	2832 (5)	−701 (5)	842 (6)	2893 (5)	−717 (6)	882 (6)	2911 (5)
O(3)	2739 (5)	−365 (6)	1429 (6)	2795 (5)	−368 (6)	1273 (6)	2830 (6)	−370 (7)	1328 (7)
O(4)	2263 (5)	3693 (5)	5610 (5)	2229 (5)	3684 (6)	5603 (6)	2239 (6)	3695 (6)	5588 (6)
O(5)	4029 (5)	7213 (5)	6537 (6)	4011 (5)	7202 (6)	6612 (6)	4009 (6)	7204 (6)	6569 (7)
O(6)	3055 (5)	5888 (5)	2903 (5)	3038 (6)	5916 (5)	2915 (6)	3072 (7)	5907 (6)	2903 (6)

(*b*) Fractional positional coordinates (×10^3) and isotropic temperatures factors (Å^2) for hydrogen atoms

	$MgS_2O_6.6H_2O$				$NiS_2O_6.6H_2O$				$ZnS_2O_6.6H_2O$			
	x/a	*y/b*	*z/c*	*B*	*x/a*	*y/b*	*z/c*	*B*	*x/a*	*y/b*	*z/c*	*B*
H(1)	174 (10)	372 (11)	40 (11)	5 (2)	184 (9)	394 (9)	59 (9)	2 (1)	176 (15)	381 (15)	31 (16)	7 (2)
H(2)	167 (8)	320 (8)	−141 (9)	3 (1)					181 (12)	323 (12)	−149 (14)	5 (2)
H(3)	−159 (10)	138 (10)	290 (10)	5 (2)					20 (13)	161 (13)	356 (13)	5 (2)
H(4)	5 (10)	149 (10)	358 (11)	5 (2)					−170 (12)	134 (11)	299 (11)	4 (2)
H(5)	293 (10)	−121 (10)	181 (10)	4 (2)	299 (12)	−128 (11)	125 (12)	4 (2)	294 (14)	−132 (16)	167 (14)	6 (2)
H(6)	353 (10)	48 (10)	190 (10)	5 (1)	370 (9)	55 (10)	159 (10)	3 (1)	356 (14)	48 (14)	191 (13)	5 (2)

Table 2 (*cont.*)

(*c*) Anisotropic thermal coefficients ($\times 10^3$) for non-hydrogen atoms. The temperature factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{12}hka^*b^*+\cdots)]$. The first, second and third numbers refer to $MgS_2O_6.6H_2O$, $NiS_2O_6.6H_2O$ and $ZnS_2O_6.6H_2O$ respectively.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	28 (1)	22 (1)	25 (1)	3 (1)	−2 (1)	−2 (1)
M	21 (1)	23 (1)	18 (1)	6 (1)	0 (1)	2 (1)
	28 (1)	22 (1)	25 (1)	3 (1)	−1 (1)	−2 (1)
	28 (1)	27 (1)	30 (1)	5 (1)	−2 (1)	−7 (1)
S	23 (1)	29 (1)	26 (1)	7 (1)	0 (1)	−3 (1)
	26 (1)	26 (1)	30 (1)	4 (1)	−2 (1)	−7 (1)
	63 (2)	29 (2)	30 (2)	−7 (1)	3 (2)	−1 (1)
O(1)	54 (2)	32 (1)	26 (1)	1 (1)	4 (1)	2 (1)
	67 (3)	27 (2)	31 (2)	−8 (2)	4 (2)	−2 (1)
	38 (2)	45 (2)	34 (2)	8 (2)	0 (1)	−11 (1)
O(2)	33 (3)	41 (2)	26 (1)	11 (1)	4 (1)	−2 (1)
	37 (2)	41 (2)	32 (2)	8 (1)	1 (1)	−9 (1)
	36 (2)	31 (2)	60 (2)	5 (1)	−16 (2)	2 (2)
O(3)	28 (1)	35 (2)	49 (2)	7 (1)	−10 (1)	8 (1)
	36 (2)	32 (2)	60 (2)	4 (1)	−15 (2)	4 (2)
	40 (2)	52 (2)	40 (2)	−14 (1)	8 (1)	−4 (1)
O(4)	33 (2)	62 (2)	35 (2)	−9 (1)	9 (1)	−1 (1)
	38 (2)	54 (2)	41 (2)	−16 (2)	9 (1)	−6 (2)
	38 (2)	46 (2)	58 (2)	12 (1)	−5 (1)	−30 (2)
O(5)	32 (1)	49 (2)	55 (2)	13 (1)	−5 (1)	−28 (2)
	37 (2)	48 (2)	60 (2)	12 (2)	−6 (2)	−32 (2)
	60 (2)	35 (2)	42 (2)	12 (1)	−19 (2)	4 (1)
O(6)	50 (2)	38 (2)	41 (2)	11 (1)	−18 (1)	9 (1)
	59 (2)	35 (2)	45 (2)	11 (2)	−20 (2)	5 (1)

fractometer equipped with a graphite monochromator and using a θ–2θ scan mode with Mo $K\alpha$ radiation. The integrated intensities were reduced to observed structure factors. Errors were calculated as $\sigma(F)=1{\cdot}0+0{\cdot}1|F|+\sigma'(F)$ where $\sigma'(F)$ was based on counting statistics. Non-hydrogen atoms were located from the Patterson function. Hydrogen atoms were located from difference maps. Three of the hydrogen atoms were not found in the case of $NiS_2O_6.H_2O$. The structures were refined by full-matrix least-squares calculations using the program *ORFLS* (Busing, Martin & Levy, 1962). Reflexions for which $\sigma/|F|>\S$ were excluded from the refinements. The value of § used in each refinement is given in Table 1. The weights were initially set as σ^{-2}. The weights in the last cycles of least-squares refinement were calculated from $\omega=(\sum_{n=0}^{3}A_n|F_o|^n)^{-2}$. The coefficients A_n were determined from a fit of $|F_o|-|F_c|$ to $|F_o|$. The scattering curves were taken from Cromer & Mann (1968) except those of the hydrogen atoms which were from Stewart, Davidson & Simpson (1965). Other pertinent data relating to the data collection and refinement are also listed in Table 1.

$$R=\sum||F_o|-|F_c||/\sum|F_o|,\ R_\omega=[\sum\omega(|F_o|-|F_c|)^2/\sum\omega|F_o|^2]^{1/2}.$$

Although the larger agreement factors for the Ni compound undoubtedly reflect the faster scan rate used to collect data for that compound, this would only be expected to increase the agreement factors by roughly a factor of $\sqrt{2}$. The crystal used for data collection in the case of the Ni compound may have exhibited larger anisotropic variations in the effects of absorption, thereby increasing the agreement factors further. The final coordinates and temperature factors are given in Table 2 with estimated standard deviations as determined by least-squares.*

Discussion. The nonlinear optical properties of dithionate crystals have been the subject of considerable interest (Hobden, Robertson, Davies, Hulme, Warner & Midwinter, 1966; Kovalchuk & Perekalina, 1972) but structural information for these compounds is limited. We originally undertook to compare the structures of $MgS_2O_6.6H_2O$ and $ZnS_2O_6.6H_2O$ with that of the transition metal dithionate $NiS_2O_6.6H_2O$ which had been reported earlier by Chan & Stanley (1970). It became apparent that a consistent transformation between the structures did not exist. For this reason the structure of $NiS_2O_6.6H_2O$ was redetermined and found to be isostructural with $MgS_2O_6.6H_2O$ and $ZnS_2O_6.6H_2O$ On closer inspection the two structure determinations describe the same crystals but the earlier determination does not arrive at the same reduced triclinic cell and some errors appear in the reported coordinates. Furthermore the reduced cell reported by Chan & Stanley is left-handed.

Each metal atom is surrounded by six water oxygen atoms forming a nearly regular octahedron. The water hydrogen atoms all form strong hydrogen bonds to the oxygen atoms on the dithionate groups, which are at the body centre of the unit cells. Each dithionate oxy-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30771 (27 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

	$MgS_2O_6.6H_2O$	$NiS_2O_6.6H_2O$	$ZnS_2O_6.6H_2O$
M—O(1)	2·042 (2)	2·040 (3)	2·069 (2)
M—O(2)	2·052 (2)	2·039 (3)	2·073 (2)
M—O(3)	2·055 (2)	2·042 (3)	2·092 (2)
O(1)–M–O(2)	90·5 (1)	91·6 (1)	91·4 (1)
O(1)–M–O(3)	90·2 (1)	91·2 (1)	90·7 (1)
O(2)–M–O(3)	90·3 (1)	91·0 (1)	90·8 (1)
S—S	2·123 (1)	2·123 (1)	2·127 (1)
S—O(4)	1·448 (2)	1·447 (4)	1·448 (2)
S—O(5)	1·449 (2)	1·454 (3)	1·453 (2)
S—O(6)	1·447 (2)	1·446 (3)	1·451 (2)
S—S–O(4)	104·2 (1)	104·7 (2)	104·5 (1)
S—S–O(5)	104·7 (1)	104·2 (2)	104·4 (1)
S—S–O(6)	104·6 (1)	104·7 (2)	104·6 (1)
O(4)–S–O(5)	114·2 (1)	113·8 (2)	114·1 (1)
O(4)–S–O(6)	113·6 (1)	113·2 (2)	113·6 (1)
O(5)–S–O(6)	114·1 (1)	114·8 (2)	114·3 (1)

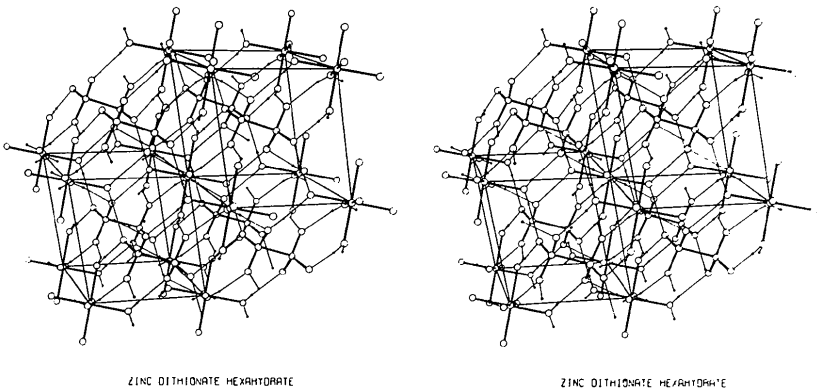

Fig. 1. Stereoscopic view of the molecular packing. Bonds to hydrogen atoms are drawn with lighter lines. The *a* axis points to the right, the *b* axis is vertical and the *c* axis points out of the page.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

The first, second and third numbers refer to $MgS_2O_6.6H_2O$, $NiS_2O_6.6H_2O$ and $ZnS_2O_6.6H_2O$ respectively.

	D–H	H···*A*	*D*···H	*D*–H···*A*
O(1)–H(1)···O(6)	0·73 (4)	2·09 (4)	2·818 (2)	176 (4)
	0·90 (6)	1·91 (6)	2·810 (5)	173 (5)
	0·72 (5)	2·10 (5)	2·814 (3)	169 (5)
O(1)–H(2)···O(4)	0·73 (3)	2·07 (3)	2·792 (3)	170 (3)
			2·793 (5)	
	0·85 (5)	1·99 (5)	2·804 (3)	160 (4)
O(2)–H(3)···O(4)	0·68 (3)	2·13 (4)	2·806 (2)	167 (4)
			2·800 (5)	
	0·77 (4)	2·04 (4)	2·804 (3)	169 (4)
O(2)–H(4)···O(5)	0·72 (3)	2·13 (4)	2·844 (3)	173 (4)
			2·837 (5)	
	0·80 (4)	2·04 (4)	2·844 (3)	173 (4)
O(3)–H(5)···O(6)	0·67 (3)	2·14 (3)	2·809 (3)	171 (4)
	0·65 (8)	2·23 (8)	2·808 (5)	149 (9)
	0·71 (5)	2·11 (5)	2·816 (3)	174 (5)
O(3)–H(6)···O(5)	0·72 (4)	2·13 (3)	2·851 (2)	174 (3)
	0·77 (6)	2·10 (6)	2·849 (5)	166 (7)
	0·73 (5)	2·13 (5)	2·850 (3)	172 (5)

gen atom is the acceptor for hydrogen bonds from two water molecules, one forming part of the octahedron at the origin and one at a lattice point removed by the translation **a**, **b** or **c**. Each of the three cell edges is therefore parallel to similar infinite chains formed by M–O bonds and O–H···O hydrogen bonds with the result that all three cell edges have a similar length.

The bonds and angles of the $M(H_2O)_6^{2+}$ groups and the $S_2O_6^{2-}$ ions are given in Table 3. The details of the hydrogen bonded network are given in Table 4. The hydrogen bonded network is also shown in Fig. 1, which was prepared with the program *ORTEP* (Johnson, 1965).

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