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Structure of Monoclinic Nickel Sulphate Hexadeuterate, $NiSO_4.6D_2O$

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Abstract. $M_r = 274{\cdot}92$, monoclinic, $C2/c$, $a = 9{\cdot}880$ (3), $b = 7{\cdot}248$ (4), $c = 24{\cdot}171$ (9) Å, $\beta = 98{\cdot}46$ (3)°, $V = 1712{\cdot}0$ Å^3, $Z = 8$. $D_x = 2{\cdot}133$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 25{\cdot}4$ cm^{-1}, $T = 295$ K, $F(000) = 1088$, final $R = 0{\cdot}061$ for 354 reflections. The structure was solved using constrained refinement of the orientations of the NiO_6 and SO_4 groups. Eleven of the twelve crystallographically independent hydrogen bonds are between water and sulphate O atoms; the twelfth is between two water O atoms.

Introduction. Tetragonal $NiSO_4.6D_2O$ is presently subject to a comparative study of the relative accuracy when collecting X-ray intensity data by conventional and extended-face techniques. In some attempts to grow small single crystals of this tetragonal phase a monoclinic phase appeared instead. A monoclinic phase of $NiSO_4.6H_2O$ was briefly studied by Sutor (1959), but only the unit-cell constants and possible space groups were determined at that time.

Experimental. Slow evaporation of a concentrated solution of nickel sulphate in heavy water in a closed flask at room temperature had earlier produced large deep-green crystals of the tetragonal phase. This flask was heated to about 313 K until all crystals had dissolved and was then rapidly agitated in a spray of liquid nitrogen for a few seconds. Well formed crystals were visible when the solution warmed to room temperature. To avoid exchange of the deuterium, the crystals were covered with a very thin layer of polystyrene. Cell parameters determined from three crystals by diffractometry all revealed a monoclinic, C-centred phase identical to that reported by Sutor (1959), although the crystallization procedure was quite different.

Intensity data collected at room temperature from an approximately spherical crystal with principal dimensions $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}20$ mm, PDP8/A-controlled Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ mode; cell dimensions determined by least-squares fitting of 25 centred reflections; systematic absences indicated space groups $C2/c$ or Cc; all reflections with $h + k = 2n$ recorded up to $\sin\theta/\lambda = 0{\cdot}36$ Å^{-1}; three standard reflections measured at regular intervals, standard deviations $\sigma(F^2)$ estimated from counting statistics; owing to the nearly spherical shape and relatively large transmission factor, no absorption correction made; averaging of equivalent reflections gave 685 or 354 independent reflections in Cc or $C2/c$, respectively.

Initially space group Cc was assumed which implies two independent Ni and two independent S atoms. S and possible O positions derived from a F_o synthesis based on Ni positions determined from vector maps. Structural model refined by least-squares methods with the program *UPALS* (Lundgren, 1979). $\sum w(|F_o| - |F_c|)^2$ minimized with $w^{-1} = \sigma^2(F^2) + (0{\cdot}01F^2)^2$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion corrections included (Cromer & Liberman, 1970). Several unsuccessful attempts to determine the O positions were made by conventional unconstrained refinements; the lowest R factor was 26%. Constraints were now introduced: in the first model (I) perfect octahedral NiO_6 and tetrahedral SO_4 groups were assumed. The orientation of each of the four groups was described by an orientation matrix defined by three Eulerian angles (Pawley, 1972). Starting with the same Ni and S positions as before, the coordinates of these four atoms, the 16 Eulerian angles and the two bond lengths (Ni—O and S—O) were refined. The isotropic temperature factors were fixed at the values observed in the tetragonal phase. After several cycles of refinement the R factor converged to 7% (refinement I). In a second model (II) the geometry of the NiO_6 groups was let free; only the SO_4 groups were constrained. The number of refined parameters was thus increased from 32 to 60. In model (III) no constraints were applied to either group. The statistical significance of the constraints on the NiO_6 and SO_4 groups was estimated from a comparison of the ratios R_w^c/R_w^u. The usual R-factor definitions are used.

At a chosen level of the F distribution $F_{(N-n,M-N)}$, the quantity $S_{c/u}$ is:

$$S_{c/u} = [1 + \frac{N-n}{M-N} F_{(N-n,M-N)}]^{1/2}.$$

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M is the number of reflections used in the refinement, n and N are the number of parameters in the constrained (c) and unconstrained refinement (u), respectively. The various quantities are given in Table 1.

Pawley (1972) has empirically suggested the use of $R' = (R_w^c/R_w^u - 1)/(S_{c/u} - 1)$ when comparing the results of similar constrained refinements: if $R' \lesssim 3{\cdot}0$ the constraints are physically insignificant. The results in Table 1 indicate that the constrained refinement I is significantly poorer than both refinements II and III. In contrast, refinement II where only the SO_4 groups are constrained is not significantly poorer than refinement III. Thus, we conclude that there are, as expected, significant distortions from the idealized octahedral geometry of the NiO_6 groups but only small distortions from tetrahedral geometry for SO_4 groups.

The resulting atomic positions in Cc correspond very closely to a centrosymmetric structure, space group $C2/c$; the maximum individual deviation is 0·2 Å, *i.e.* less than 4σ. Subsequent refinement in $C2/c$ (refinement IV) led to atomic positions which were within 2σ of the corresponding positions in Cc. The R values are given in Table 1. Comparing the R_w values from the (unconstrained) refinements in $C2/c$ and Cc we find $R' = 3{\cdot}2$. We thus conclude that the noncentrosymmetric structure is not significantly different from the centrosymmetric one; the latter was therefore chosen.

Attempts to refine anisotropic thermal parameters gave unsatisfactory results. Prior to the final refinement in $C2/c$ (refinement V), Friedel pairs were averaged, resulting in 354 independent reflections. The B values of chemically equivalent atoms were constrained to be equal. R values are given in Table 1; final coordinates and thermal parameters in Table 2.*

The D atoms were not determined experimentally but from ordinary chemical considerations the assignment of hydrogen is straightforward and unambiguous (Fig. 1 and Table 3). Inclusion of the D atoms with fixed positional and thermal parameters did not significantly improve the results (the D atoms were then placed on the hydrogen bonds at normal distances from O). Attempts to refine the D positions gave unsatisfactory results.

Table 1. *Residuals for the refinements*

Level of F distribution: 99%; M: number of observations; N: number of parameters. The refinements are:

I: constrained NiO_6 and SO_4 groups in space group Cc;
II: constrained SO_4 groups in space group Cc;
III: unconstrained refinement in space group Cc;
IV: unconstrained refinement in space group $C2/c$ on the same reflections as III;
V: unconstrained refinement in space group $C2/c$ on an independent set of reflections.

	M	N	R	R_w	c:u	R_w^c/R_w^u	$S_{c/u}$	R'
I	683	32	0·068	0·116	I:III	1·38	1·06	6·3
II	683	60	0·053	0·086	II:III	1·02	1·03	0·7
III	683	76	0·050	0·084	—	—	—	—
IV	683	40	0·061	0·098	IV:III	1·16	1·05	3·2
V	354	40	0·061	0·101	—	—	—	—

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2)

	x	y	z	B
Ni(1)	0	0	0	1·81 (18)
Ni(2)	0	9493 (4)	2500	1·81 (18)
S	8717 (4)	4524 (6)	1235 (2)	1·96 (19)
OS(1)	7742 (10)	5913 (13)	1326 (4)	3·17 (21)
OS(2)	9813 (11)	4463 (14)	1716 (4)	3·17 (21)
OS(3)	9220 (11)	4926 (13)	712 (4)	3·17 (21)
OS(4)	8031 (10)	2742 (14)	1181 (4)	3·17 (21)
O(1)	5923 (8)	7229 (13)	429 (4)	2·69 (20)
O(2)	5302 (9)	3385 (14)	717 (4)	2·69 (20)
O(3)	3077 (9)	5627 (13)	192 (4)	2·69 (20)
O(4)	8861 (9)	1520 (13)	2836 (4)	2·69 (20)
O(5)	8862 (8)	7531 (13)	2835 (4)	2·69 (20)
O(6)	8573 (10)	9451 (14)	1785 (4)	2·69 (20)

Discussion. The structure contains SO_4^{2-} and $Ni(D_2O)_6^{2+}$ groups, linked together by hydrogen bonds (Fig. 1). There are two crystallographically different $Ni(D_2O)_6^{2+}$ groups, with Ni in special positions with site symmetries $\bar{1}$ and 2, respectively. Interatomic distances and angles are given in Table 3. The mean Ni—O distance, 2·07 Å, agrees closely with the mean value of 2·06 Å in the tetragonal phase (O'Connor & Dale, 1966). The same applies to the S—O distances which are 1·45 and 1·47 Å, respectively. The relative arrangement of the constituent groups is rather different, however: each $Ni(D_2O)_6^{2+}$ group is surrounded by six SO_4^{2-} groups in the monoclinic phase (distance Ni—S = 4·39–5·23 Å) but by eight SO_4^{2-} groups in the tetragonal phase (Ni—S = 4·78–6·03 Å). The differences between the two structures clearly prohibit their interconversion. The fractional coordinates of corresponding atoms in $NiSO_4.6D_2O$ and the isomorphic compound $CoSO_4.6H_2O$ (Zalkin, Ruben & Templeton, 1962) differ by 0·014 or less.

All D atoms of the water molecules are involved in hydrogen bonds, with sulphate O atoms as acceptors except for the bond O(5)—H···O(4). The O atoms of water are only coordinated to Ni, except O(4) which

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38576 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

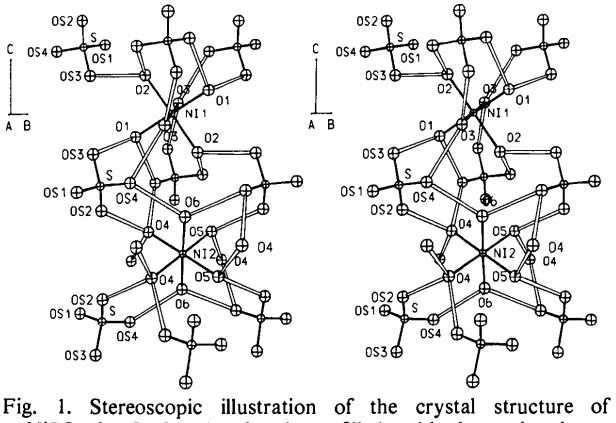

Fig. 1. Stereoscopic illustration of the crystal structure of $NiSO_4.6D_2O$. Covalent bonds are filled and hydrogen bonds are open.

Table 3. *Interatomic distances* (Å) *and angles* (°) *involving non-hydrogen atoms*

(*a*) Covalent bonds

Ni(1)—O(1)	2·059 (9)	S—OS(1)	1·433 (11)
Ni(1)—O(2)	2·075 (9)	S—OS(2)	1·468 (11)
Ni(1)—O(3)	2·072 (9)	S—OS(3)	1·454 (11)
Ni(2)—O(4)	2·086 (9)	S—OS(4)	1·456 (11)
Ni(2)—O(5)	2·051 (9)		
Ni(2)—O(6)	2·065 (9)		
O(1)—Ni(1)—O(2)	91·3 (4)	OS(2)—S—OS(4)	108·9 (6)
O(1)—Ni(1)—O(3)	93·9 (3)	OS(2)—S—OS(3)	112·9 (6)
O(3)—Ni(1)—O(2)	92·3 (4)	OS(2)—S—OS(1)	109·5 (6)
O(4)—Ni(2)—O(5)	88·7 (3)	OS(4)—S—OS(3)	108·3 (6)
O(4)—Ni(2)—O(6)	91·5 (4)	OS(4)—S—OS(1)	108·8 (6)
O(5)—Ni(2)—O(6)	90·3 (4)	OS(3)—S—OS(1)	108·5 (6)

(*b*) Hydrogen bonds

O(1)—D···OS(1)	2·775 (13)	O(4)—D···OS(2)	2·651 (13)
O(1)—D···OS(3)	2·730 (13)	O(4)—D···OS(1)	2·783 (13)
O(2)—D···OS(4)	2·804 (13)	O(5)—D···OS(2)	2·724 (13)
O(2)—D···OS(3)	2·755 (14)	O(5)—D···O(4)	2·891 (13)
O(3)—D···OS(4)	2·846 (13)	O(6)—D···OS(4)	2·806 (14)
O(3)—D···OS(3)	2·938 (14)	O(6)—D···OS(1)	2·866 (14)
OS(3)···O(1)···OS(1)	113·8 (4)	OS(1)···O(4)···OS(2)	97·5 (4)
OS(3)···O(2)···OS(4)	101·7 (4)	O(4)···O(5)···OS(2)	110·7 (4)
OS(3)···O(3)···OS(4)	126·3 (4)	OS(1)···O(6)···OS(4)	122·5 (4)

(*c*) α = angle between Ni—O_i and the projection of Ni—O_i on the $O_j\cdots O_i\cdots O_k$ plane; β = angle between Ni—O_i and the bisector of the angle $O_j\cdots O_i\cdots O_k$ (e.s.d.'s for α and β are ~0·6°)

Plane	α(°)	β(°)
OS(1), O(1), OS(3)	45·9	94·1
OS(4), O(2), OS(3)	52·3	138·5
OS(4), O(3), OS(3)	15·0	164·9
OS(2), O(4), OS(1)	38·2	141·6
OS(2), O(5), O(4)	43·9	143·5
OS(4), O(6), OS(1)	55·4	89·4

also accepts the hydrogen bond from O(5). All water molecules are thus trigonally surrounded, except O(4) which has a tetrahedral environment. The trigonal arrangements show, however, considerable deviations from planarity (Fig. 1 and Table 3*c*). Note that also in tetragonal $NiSO_4.6H_2O$ (O'Connor & Dale, 1966) and orthorhombic $FeSO_4.7H_2O$ (Baur, 1964*a*), $NiSO_4.7H_2O$ and $MgSO_4.7H_2O$ (Baur, 1964*b*) two of the water O atoms coordinated to the metal ion accept hydrogen bonds to form tetrahedral water environments instead of the predominant trigonal arrangment.

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Structure de la Phase Ordonnée du Sesquiséléniure de Gallium, Ga_2Se_3

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Abstract. $M_r = 376{\cdot}32$, monoclinic, *Bb*, $a = b = 6{\cdot}66$ (1), $c = 11{\cdot}65$ (1) Å, $\gamma = 108{\cdot}12$ (1)°, $V = 491{\cdot}1$ Å^3, $Z = 4$, D_m(flotation) = 4·95 (2), $D_x = 5{\cdot}09$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, μ(Mo $K\bar{\alpha}$) = 328 cm^{-1}, $F(000) = 656$, room temperature. The entirely ordered monoclinic phase of Ga_2Se_3 is a superstructure of the basic distorted sphalerite-type. The structure has been solved by Fourier methods and refined by full-matrix least-squares calculations, to a final $R = 0{\cdot}067$, for 804 observed reflexions collected with a four-circle diffractometer. Ordering of metal vacancies involves two different Se-atom surroundings, infinite chains of vacancies, running in the **b** direction, and the particular stacking sequence *abca'b'c'* derived from *ABC* cubic close packing, for Ga atoms.

Introduction. Le sesquiséléniure de gallium Ga_2Se_3, dont la structure dérive du type de la blende, se présente sous différentes formes, suivant le traitement thermique subi par l'échantillon considéré (Palatnik & Belova, 1965; Eholié, 1971). En reprenant cette étude, nous avons observé soit un désordre total entre les sites lacunaires et les sites occupés par le gallium, dans le réseau cubique de la blende, soit une mise en ordre des sites lacunaires dans une maille de surstructure de symétrie monoclinique. La maille du sous-réseau de la blende subit une déformation qui augmente avec le degré d'ordre, tout en restant peu accentuée: le sous-réseau devient quadratique, avec $1 < c/a < 1{,}015$. Parallèlement, il se produit une augmentation des intensités des réflexions de structure complémentaire,

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