

Fig. 3. The linkage of polyhedra about the cation sites; those in a slab bounded by $z=0$ and $z=\frac{1}{4}$ are shown. The hatched polyhedra are at $z=0$, the dotted ones at $z=\frac{1}{8}$ and those without patterns at $z=\frac{1}{4}$.

Regarding the silicate analogue (Fischer & Tillmanns, 1984), we find that the corresponding angles are 164.6 and 173.3° . The difference between this set of values and that of our structure may be rationalized by the differences in size of the rings and of the cation occupying the centres of the rings.

It is notable that the Ge—O bond length varies significantly according to the Ge—O—Ge angle; a plot of Ge—O versus Ge—O—Ge defines a slope as in the cases of Si—O (Brown, Gibbs & Ribbe, 1969) and Al—O (Takéuchi, Nishi & Maki, 1980). The slope of the regression line for $\text{Na}_{3.70}\text{Ca}_{1.15}\text{Ge}_3\text{O}_9$ (this study), $\text{Na}_{3.0}\text{Ca}_{1.5}\text{Ge}_3\text{O}_9$ and $\text{Na}_{2.50}\text{Ca}_{1.75}\text{Ge}_3\text{O}_9$ [$-0.0026 \text{ \AA deg}^{-1}$ (Nishi & Takéuchi, 1987)] is found to be much

steeper than those for silicates [$-0.0007 \text{ \AA deg}^{-1}$ (Brown, Gibbs & Ribbe, 1969)] and aluminates [$-0.0006 \text{ \AA deg}^{-1}$ (Takéuchi, Nishi & Maki, 1980)]. We have only calculated the slope for germanates having ring structures, but the slope only changed slightly (approximately $-0.0020 \text{ \AA deg}^{-1}$) even if some germanates having other structures were included. It would be desirable to refine the slope using more structural data for germanates in order to discuss in detail the difference in bonding character among these T—O bonds.

Fig. 3 illustrates the linkage of the metal polyhedra, including the octahedra about $M(5)$. The polyhedral sheets consisting of the $M(1)$, $M(2)$, $M(6)$ and $M(7)$ cations can be observed and the displacement vector has the horizontal component $a/2$ and the vertical component $a/4$.

In addition to this phase, we have derived the crystal structures of two Na Ca germanates having six-membered rings (Nishi & Takéuchi, 1987). The results will be published elsewhere.

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Polymorphism of Nickel Sulfate Hexahydrate

BY R. J. ANGEL AND L. W. FINGER

Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton St. NW, Washington, DC 20008, USA

(Received 10 March 1988; accepted 13 June 1988)

Abstract. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $M_r = 262.85$; data collections with Mo $K\alpha$ radiation, $\lambda = 0.7093 \text{ \AA}$, room temperature. Monoclinic polymorph: $C2/c$, $a = 9.880$ (3), $b = 7.228$ (2), $c = 24.130$ (3) \AA , $\beta = 98.38$ (2) $^\circ$, $V = 1704.7$ (6) \AA^3 , $Z = 8$, $D_x = 2.05 \text{ g cm}^{-3}$, $\mu = 25.54 \text{ cm}^{-1}$, $F(000) = 1088$, $R = 0.031$ ($wR = 0.038$)

for 2176 observed reflections. Tetragonal polymorph: $P4_2,2$, $a = 6.780$ (1), $c = 18.285$ (2) \AA , $V = 840.5$ (3) \AA^3 , $Z = 4$, $D_x = 2.07 \text{ g cm}^{-3}$, $\mu = 25.81 \text{ cm}^{-1}$, $F(000) = 544$, $R = 0.045$ ($wR = 0.050$) for 2102 observed reflections. The structure of the tetragonal polymorph originally determined (without H

positions) by Beevers & Lipson [*Z. Kristallogr.* (1932), **83**, 123–135], and refined by O'Connor & Dale [*Acta Cryst.* (1966), **21**, 705–709] and Stadnicka, Glazer & Koralewski [*Acta Cryst.* (1987), **B43**, 319–325], is confirmed by refinement of X-ray diffraction data. The structure of the monoclinic polymorph is confirmed as being isostructural with $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$ [Ptasiewicz-Bak, McIntyre & Olovsson (1983). *Acta Cryst.* **C39**, 966–968], and a number of other hexahydrate sulfates, e.g. $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ [Zalkin, Ruben & Templeton (1964). *Acta Cryst.* **17**, 235–240]. Both structures contain isolated $[\text{Ni}(\text{H}_2\text{O})_6]$ octahedra and $[\text{SO}_4]$ tetrahedra linked by hydrogen bonding.

Introduction. The majority of hydrated sulfates of the formula $\text{MSO}_4 \cdot 6\text{H}_2\text{O}$ ($M = \text{Mg}, \text{V}, \text{Co}, \text{Zn}, \text{Fe}$) crystallize with a monoclinic structure containing isolated $[\text{M}(\text{H}_2\text{O})_6]$ octahedra and $[\text{SO}_4]$ tetrahedra that are cross-linked by hydrogen bonding to form alternating layers of octahedra and tetrahedra (Zalkin, Ruben & Templeton, 1962, 1964; Cotton, Falvello, Llusar, Libby, Murillo & Schwotzer, 1986; Elerman, 1988). A number of hydrated selenates also crystallize with this structure (Groth, 1908; Zalkin *et al.*, 1962; Snyman & Pistorius, 1964). The structures of $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSeO}_4 \cdot 6\text{H}_2\text{O}$ also contain these two types of polyhedra, but in an arrangement with mixed layers and tetragonal symmetry (Groth, 1908; Snyman & Pistorius, 1964; Fuess, 1970; Palmer, Giles & Gross, 1978). $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ exhibits both structures, the tetragonal form occurring at low temperatures as the mineral retgersite, while the monoclinic polymorph is stable at temperatures above 326 K (Steele & Johnson, 1904). These two structure types differ only in the relative arrangement of the octahedra and tetrahedra (Fig. 1), and in the geometry of the linkages provided by the hydrogen bonding. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ provides an apparently unique opportunity to study these differences in polymorphic structures, and to elucidate the factors which determine the relative stability of the two structure types.

The structure of the tetragonal polymorph of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was originally determined by Beevers & Lipson (1932) using X-ray diffraction data, but they were unable to locate the H-atom positions. A partially deuterated crystal was used by O'Connor & Dale (1966) to locate H/D positions with two-dimensional neutron diffraction data, and a three-dimensional neutron diffraction study of a deuterium-free crystal was undertaken by Bargouth & Will (1981). More recently, the absolute configuration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was determined by Stadnicka, Glazer & Koralewski (1987). The deuterated monoclinic polymorph, $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$, has been shown to be isostructural with other monoclinic sulfate and selenate hexahydrates (Ptasiewicz-Bak, McIntyre & Olovsson, 1983), which have space-group symmetry $C2/c$. There is one report, however, of

diffraction patterns from monoclinic $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ exhibiting violations of the c -glide (Sutor, 1959), a discrepancy that we investigated during these experiments.

Experimental. Both datasets were collected with a Rigaku AFC-5 goniometer equipped with a rotating-anode generator. Unit-cell parameters were determined from the positions of 20 centered reflections in the range $45 < 2\theta < 60^\circ$. ψ scans indicated the presence of absorption and extinction effects in both crystals; corrections were made for absorption using the program of Burnham (1966). In the refinements a weight of $w = [\sigma^2(F_o) + kF_o^2]^{-1}$ was assigned to each reflection, where $\sigma(F_o)$ is the e.s.d. derived from counting statistics, and $k = 0.01$. The scale factor, extinction coefficient, and all variable positional and thermal parameters for each structure were refined by least squares [function minimized = $\sum w(|F_o| - |F_c|)^2$] using *RFINE88*, a development version of *RFINE4* (Finger & Prince, 1974). Extinction effects were corrected in both crystals with the Becker & Coppens (1974) formalism (isotropic Lorentzian type I distribution). Both refinements were terminated when the average least-squares shift/e.s.d. of all refined parameters was 0.005, with the maximum shift of any parameter being 0.02 e.s.d. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates and isotropic temperature factors for both structures are reported in Table 1.*

Monoclinic polymorph: The sample was grown from aqueous solution at 348 K. A clear green crystal of approximate dimensions $0.28 \times 0.28 \times 0.08$ mm encased in mounting medium (VYHH) to exclude air was used for data collection. No degradation of crystal quality was detectable during or after the data collection, although specimens exposed to the air develop pale-green crystals of $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ on their surfaces. Data were collected out to $(\sin\theta)/\lambda = 0.7 \text{ \AA}^{-1}$, with $0 < h < 13$, $0 < k < 10$, $-34 < l < 34$ (one asymmetric unit). The $\bar{4}25$, $\bar{4}\bar{2}5$ and $\bar{3}\bar{3}5$ reflections were monitored as intensity and orientation standards every 150 reflections; their intensities varied by less than 1% from the mean. Reflections that would violate the c -glide, as proposed by Sutor (1959), were collected, and none were observed with $I > 3\sigma_I$. Intensity statistics indicated the presence of a center of symmetry, so the space group is therefore $C2/c$. A total of 2442 symmetry-allowed reflections were measured, of which 31 were removed from the dataset because of uneven

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51184 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

backgrounds and 2176 of the remainder were observed at $I > 3\sigma_I$. Calculated transmission coefficients arising from absorption ranged from 55% to 82%. Atom coordinates for $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ from Zalkin *et al.* (1964) were used as an initial model for refinements. Correction for a small volume of a twin (twin matrix: $-1, 0, -0.1193/0, -1, 0/0, 0, 1$) was necessary, and the twin fraction refined to 8%. The secondary-extinction coefficient refined to $g = 0.00007$ (1). The final agreement indices for 2176 observed reflections are $R = 0.031$, $wR = 0.038$ and $S = 1.82$. The final difference electron density has maxima and minima of $\pm 0.25 \text{ e } \text{Å}^{-3}$.

Atom coordinates for the non-H atoms differ by 1–2 e.s.d.'s from those reported for the deuterated form by Ptasiewicz-Bak *et al.* (1983), and result in slightly shorter Ni–O bond distances than reported by these workers. These differences are probably not significant given the extremely limited dataset used for this previous work [$(\sin\theta)_{\text{max}}/\lambda = 0.36 \text{ Å}^{-1}$], their consequent use of only isotropic temperature factors, and their inability to locate the positions of the D atoms.

Tetragonal polymorph: The sample was selected from commercial analytical-grade material. A clear blue crystal of dimensions $0.15 \times 0.12 \times 0.06 \text{ mm}$ free from inclusions was selected for diffraction experiments. Data were collected out to $(\sin\theta)/\lambda = 1.0 \text{ Å}^{-1}$, with $0 < h < 13$, $0 < k < 13$, $0 < l < 36$ (two asymmetric units). The 519, 159 and 1,11,8 reflections were monitored as intensity and orientation standards every 150 reflections; their intensities varied by less than 2% from the mean. A total of 3948 reflections were measured, of which 2102 were observed at $I > 3\sigma_I$. Calculated transmission coefficients due to absorption ranged from 70% to 86%. Equivalent reflections were not averaged because of the presence of extinction effects. Atom coordinates from O'Connor & Dale (1966) were used as an initial model. Refinement in space group $P4_12_12$ gave final agreement indices on the two asymmetric units of observed reflections of $R = 0.045$, $wR = 0.050$ and $S = 1.19$. The final difference electron density has maxima and minima of $\pm 0.5 \text{ e } \text{Å}^{-3}$. The secondary-extinction coefficient refined to $g = 0.00009$ (1). Refinement in the alternative space group, $P4_23_12$, with inverted coordinates $(\bar{x}, \bar{y}, \bar{z})$ gave $R = 0.053$, $wR = 0.064$ and $S = 1.50$. Structure-factor calculations for models with $P4_12_12$ $(\bar{x}, \bar{y}, \bar{z})$ and $P4_23_12$ (x, y, z) gave $R \approx 0.16$, $wR \approx 0.37$. The space group is thus confirmed to be $P4_12_12$ as reported by Stadnicka *et al.* (1987). In addition, the bond distances and angles from the two studies differ by less than 1 e.s.d.

Discussion. As noted in the *Introduction*, this is the first time that structural data on the two structural types associated with the class of hexahydrates have been available for the same composition. The coordination

Table 1. *Atomic positions and equivalent isotropic temperature factors*

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{Å}^2)$
Monoclinic polymorph				
Ni(1)	0.0000	0.0000	0.0000	1.83
Ni(2)	0.5000	0.4504 (1)	0.2500	1.53
S	0.8711 (1)	0.4516 (1)	0.1241 (1)	1.83
O(1)	0.7737 (2)	0.5985 (3)	0.1337 (1)	2.53
O(2)	0.9836 (2)	0.4481 (3)	0.1703 (1)	3.59
O(3)	0.9212 (2)	0.4922 (3)	0.0705 (1)	3.09
O(4)	0.8017 (2)	0.2712 (2)	0.1186 (1)	2.66
O(5)	0.0926 (2)	0.2214 (3)	0.0427 (1)	2.55
O(6)	-0.0290 (2)	0.1600 (3)	-0.0705 (1)	3.39
O(7)	0.1897 (2)	-0.0593 (4)	-0.0204 (1)	3.69
O(8)	0.3834 (2)	0.6525 (3)	0.2811 (1)	2.13
O(9)	0.3859 (2)	0.2553 (3)	0.2828 (1)	2.56
O(10)	0.6441 (2)	0.4501 (3)	0.3200 (1)	2.63
H(51)	0.131 (3)	0.193 (5)	0.071 (1)	3.8 (8)*
H(52)	0.044 (3)	0.287 (5)	0.053 (1)	3.3 (8)
H(61)	0.007 (4)	0.254 (5)	-0.065 (1)	4.5 (9)
H(62)	-0.106 (4)	0.185 (6)	-0.082 (2)	5.6 (1.0)
H(71)	0.205 (4)	-0.122 (6)	-0.043 (2)	5.8 (1.1)
H(72)	0.258 (4)	-0.027 (5)	-0.004 (2)	5.2 (1.0)
H(81)	0.347 (4)	0.618 (5)	0.303 (1)	4.1 (9)
H(82)	0.436 (4)	0.724 (5)	0.294 (1)	4.4 (9)
H(91)	0.418 (4)	0.175 (5)	0.294 (2)	4.3 (9)
H(92)	0.308 (4)	0.241 (5)	0.270 (1)	4.4 (9)
H(101)	0.650 (4)	0.362 (6)	0.339 (2)	5.1 (1.0)
H(102)	0.647 (4)	0.527 (5)	0.339 (2)	4.8 (1.0)
Tetragonal polymorph				
Ni	0.2105 (1)	0.2105	0.0000	1.04
S	0.7093 (1)	0.7093	0.0000	1.26
O(1)	0.1727 (4)	-0.0475 (4)	0.0528 (1)	2.17
O(2)	0.4705 (3)	0.2451 (3)	0.0561 (1)	1.69
O(3)	0.0658 (3)	0.3559 (3)	0.0851 (1)	1.56
O(4)	0.6211 (4)	0.6204 (4)	0.0659 (1)	2.40
O(5)	0.9232 (3)	0.6733 (3)	0.0002 (1)	2.11
H(11)	0.110 (7)	-0.134 (7)	0.039 (2)	4.3 (1.2)*
H(12)	0.232 (6)	-0.065 (7)	0.088 (2)	3.2 (1.0)
H(21)	0.546 (7)	0.158 (6)	0.049 (2)	2.4 (0.9)
H(22)	0.525 (7)	0.352 (6)	0.063 (2)	3.3 (1.0)
H(31)	0.020 (7)	0.440 (6)	0.072 (2)	2.7 (1.0)
H(32)	-0.010 (6)	0.280 (6)	0.115 (2)	3.5 (1.0)

* Values are B_{iso} for H atoms.

polyhedra of both Ni and S show very little variation between the two polymorphs, although those in the lower symmetry monoclinic form show marginally greater distortion from ideal octahedral and tetrahedral geometries (Table 2). It seems unlikely, therefore, that the cation coordination is the factor that determines the relative stability of the two structure types. This conclusion is supported by the observation that the structure type displayed for a given composition does not vary systematically with the radius of either cation.

The control of the relative stability of these two structures must therefore lie with the nature of hydrogen bonding between the polyhedra (Fig. 1). Examination of Table 2 indicates that the Ni(2) octahedra of the monoclinic structure resemble the single Ni octahedra of the tetragonal form. The water molecules of both of these octahedra form ten hydrogen bonds to SO_4 groups, and participate in four hydrogen bonds (two as donor, two as acceptor) to O atoms of waters attached to adjacent Ni octahedra. By contrast, the Ni(1) octahedra in the monoclinic structure form hydrogen bonds only to sulfate groups.

Additional evidence for the importance of these Ni–O–H...O–Ni interoctahedral bonds in the stability

Table 2. *Interatomic distances (Å) and angles (°)*

	Monoclinic polymorph		Tetragonal polymorph		
Ni(1)—O(5)	2.045 (2) (×2)	Ni(2)—O(8)	2.068 (2) (×2)	Ni—O(1)	2.014 (2) (×2)
Ni(1)—O(6)	2.043 (2) (×2)	Ni(2)—O(9)	2.036 (2) (×2)	Ni—O(2)	2.053 (2) (×2)
Ni(1)—O(7)	2.051 (2) (×2)	Ni(2)—O(10)	2.045 (2) (×2)	Ni—O(3)	2.087 (2) (×2)
S—O(1)	1.474 (2)			S—O(4)	1.474 (2) (×2)
S—O(2)	1.455 (2)			S—O(5)	1.470 (2) (×2)
S—O(3)	1.479 (2)				
S—O(4)	1.470 (2)				
O(5)—H(51)	0.76 (3)	O(8)—H(81)	0.73 (4)	O(1)—H(11)	0.77 (5)
O(5)—H(52)	0.74 (3)	O(8)—H(82)	0.76 (4)	O(1)—H(12)	0.76 (4)
O(6)—H(61)	0.77 (4)	O(9)—H(91)	0.69 (4)	O(2)—H(21)	0.79 (4)
O(6)—H(62)	0.79 (4)	O(9)—H(92)	0.79 (4)	O(2)—H(22)	0.83 (4)
O(7)—H(71)	0.74 (4)	O(10)—H(101)	0.79 (4)	O(3)—H(31)	0.69 (4)
O(7)—H(72)	0.77 (4)	O(10)—H(102)	0.72 (4)	O(3)—H(32)	0.91 (4)
O(5)—Ni(1)—O(6)	88.5 (1)	O(8)—Ni(2)—O(8 ⁱⁱ)	90.1 (1)	O(1)—Ni—O(2)	88.2 (1)
O(5)—Ni(1)—O(6 ⁱ)	91.5 (1)	O(8)—Ni(2)—O(9)	88.8 (1)	O(1)—Ni—O(3)	89.6 (1)
O(5)—Ni(1)—O(7)	85.8 (1)	O(8)—Ni(2)—O(10)	93.4 (1)	O(1)—Ni—O(1 ⁱ)	90.5 (1)
O(5)—Ni(1)—O(7 ⁱ)	94.2 (1)	O(8)—Ni(2)—O(10 ⁱⁱ)	86.7 (1)	O(1)—Ni—O(3 ⁱ)	90.5 (1)
O(6)—Ni(1)—O(7)	86.6 (1)	O(9)—Ni(2)—O(9 ⁱⁱ)	92.4 (1)	O(2)—Ni—O(2 ⁱ)	93.1 (1)
O(6)—Ni(1)—O(7 ⁱ)	93.4 (1)	O(9)—Ni(2)—O(10)	92.1 (1)	O(2)—Ni—O(3)	88.7 (1)
O(5)—Ni(1)—O(5 ⁱ)	180.0	O(9)—Ni(2)—O(10 ⁱⁱ)	87.8 (1)	O(2)—Ni—O(3 ⁱ)	91.2 (1)
O(6)—Ni(1)—O(6 ⁱ)	180.0	O(8)—Ni(2)—O(9 ⁱⁱ)	178.3 (1)	O(1)—Ni—O(2 ⁱ)	178.5 (1)
O(7)—Ni(1)—O(7 ⁱ)	180.0	O(10)—Ni(2)—O(10 ⁱⁱ)	179.9 (1)	O(3)—Ni—O(3 ⁱ)	179.8 (1)
O(1)—S—O(2)	109.6 (1)			O(4)—S—O(5)	109.3 (2)
O(1)—S—O(3)	107.6 (1)			O(4)—S—O(4 ⁱ)	109.7 (2)
O(1)—S—O(4)	110.3 (1)			O(4)—S—O(5 ⁱ)	109.7 (1)
O(2)—S—O(3)	110.9 (1)			O(5)—S—O(5 ⁱ)	109.1 (2)
O(2)—S—O(4)	110.4 (1)				
O(3)—S—O(4)	107.9 (1)				
H(51)—O(5)—H(52)	98. (3.)	H(81)—O(8)—H(82)	108. (4.)	H(11)—O(1)—H(12)	117. (4.)
H(61)—O(6)—H(62)	104. (4.)	H(91)—O(9)—H(92)	114. (4.)	H(21)—O(2)—H(22)	113. (4.)
H(71)—O(7)—H(72)	108. (4.)	H(101)—O(10)—H(102)	105. (4.)	H(31)—O(3)—H(32)	114. (4.)

O—H...O

Monoclinic polymorph

O—H...O	H...O	O...O	∠OHO
O(5)—H(51)...O(1 ⁱⁱⁱ)	2.02 (3)	2.769 (3)	164. (3.)
O(5)—H(52)...O(3 ^{iv})	2.00 (3)	2.736 (3)	170. (4.)
O(6)—H(61)...O(3 ^v)	1.98 (4)	2.730 (3)	166. (4.)
O(6)—H(62)...O(4 ^{vi})	2.03 (4)	2.818 (3)	174. (4.)
O(7)—H(71)...O(4 ^{vii})	2.12 (4)	2.833 (3)	164. (4.)
O(7)—H(72)...O(3 ^{viii})	2.23 (5)	2.953 (3)	156. (4.)
O(8)—H(81)...O(1 ^{ix})	2.07 (4)	2.780 (3)	164. (4.)
O(8)—H(82)...O(2 ^x)	1.95 (4)	2.687 (3)	162. (4.)
O(9)—H(91)...O(2 ^{xi})	2.04 (4)	2.729 (3)	177. (4.)
O(9)—H(92)...O(8 ^{xii})	2.19 (4)	2.968 (3)	165. (3.)
O(10)—H(101)...O(1 ^{xiii})	2.11 (4)	2.847 (3)	155. (4.)
O(10)—H(102)...O(4 ^{xiiii})	2.06 (4)	2.764 (3)	164. (4.)

Tetragonal polymorph

O(1)—H(11)...O(5 ⁱ)	1.95 (5)	2.714 (3)	172. (5.)
O(1)—H(12)...O(3 ⁱⁱ)	2.04 (4)	2.789 (3)	167. (4.)
O(2)—H(21)...O(5 ⁱⁱⁱ)	2.02 (4)	2.777 (3)	160. (4.)
O(2)—H(22)...O(4)	1.93 (4)	2.747 (3)	170. (4.)
O(3)—H(31)...O(5 ^{iv})	2.16 (4)	2.824 (3)	161. (5.)
O(3)—H(32)...O(4 ^v)	1.83 (4)	2.726 (3)	169. (4.)

Monoclinic symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (iv) $-1+x, y, z$; (v) $1-x, y, -z$; (vi) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (vii) $-1+x, -y, -z$; (viii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ix) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (x) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

Tetragonal symmetry codes: (i) $y, x, -z$; (ii) $-1+x, -1+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $y, -1+x, -z$; (v) $-1+x, y, z$.

of these phases can be found by examining the structures of two other nickel sulfate hydrates. The first of these is $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Baur, 1964) with 8% of the hydrogen bonds of interoctahedral nature. This phase breaks down to the tetragonal form of the hexahydrate with 17% of interoctahedral hydrogen bonds. The monoclinic form of this study with 9% transforms to $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ with 25% of this type of hydrogen bond (Baur, 1962). In both instances the fraction of interoctahedral hydrogen bonds more than doubles.

We would like to thank Tom Hoering for his help with this project. The work was supported by NSF grants EAR86-18602 and EAR86-18649 (to Charles Prewitt and LWF) and EAR84-19982 (to LWF), and by the Carnegie Institution of Washington.

Note added in proof: A determination of the structure of the monoclinic polymorph of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was recently reported [Gerkin & Reppart (1988), *Acta Cryst. C* **44**, 1486–1488]. With an origin shift the

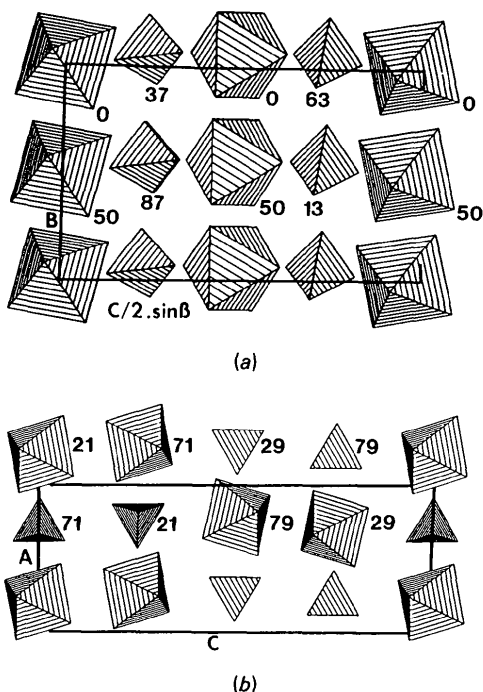


Fig. 1. Polyhedral representations drawn with *STRUPLO* (Fischer, 1985) of the (a) monoclinic and (b) tetragonal polymorphs of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Unit-cell edges are indicated by the heavy lines, and heights of the cations central to each polyhedron are given in hundredths of the cell repeat in the projection direction.

positional parameters of non-H atoms do not differ significantly from those reported here, but Gerkin & Reppart were unable to refine the positions of the H atoms. Their smaller reported unit-cell parameters have resulted in shorter bond distances.

Acta Cryst. (1988). **C44**, 1873–1876

Structure of Barium Perchlorate Trihydrate

BY JUDITH C. GALLUCCI AND ROGER E. GERKIN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

(Received 19 May 1988; accepted 28 June 1988)

Abstract. $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, $M_r = 390.28$, hexagonal, $P6_3/m$, $a = 7.277(2)$, $c = 9.656(1) \text{ \AA}$, $V = 442.9(1) \text{ \AA}^3$, $Z = 2$, $F(000) = 368$, $D_x = 2.93 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $T = 295 \text{ K}$, $\mu = 52.60 \text{ cm}^{-1}$, 456 unique reflections, $R = 0.023$. The barium atoms in this structure are coordinated by six water oxygens, O(3), at $2.919(1) \text{ \AA}$ and by six perchlorate oxygens, O(2), at $3.026(2) \text{ \AA}$ in a slightly distorted icosahedral

The readers attention is also drawn to the recent determination of the absolute configuration of $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ by Stadnicka, Glazer & Koralewski [*Acta Cryst.* (1988), **B44**, 356–361].

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