

A Reinvestigation of the Structure of Nickel Sulphite Hexahydrate, $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$

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A refinement of the crystal structure of $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$, $R3$, $a_{rh} = 5.898 \pm 0.008 \text{ \AA}$, $\alpha_{rh} = 95.4 \pm 0.1^\circ$, $Z_{rh} = 1$, $D_m = 2.03 \text{ g.cm}^{-3}$, $D_x = 2.04 \text{ g.cm}^{-3}$ (hexagonal, $a = 8.794 \text{ \AA}$, $c = 9.002 \text{ \AA}$), has been carried out by full-matrix least-squares methods with anisotropic temperature factors, by use of 383 independent reflexions of measurable intensity obtained from microdensitometer measurements of integrated precession and Weissenberg patterns. The discrepancy index R is 0.058 for all data. The pyramidal $(\text{SO}_3)^{2-}$ ion has S–O: $1.536 \pm 0.007 \text{ \AA}$ and O–S–O: $103.6 \pm 0.6^\circ$, in good agreement with values found for other sulphites. The $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ distorted octahedron has three equivalent Ni–O bonds of $2.043 \pm 0.008 \text{ \AA}$ and three of $2.076 \pm 0.008 \text{ \AA}$.

Introduction

The crystal structure of $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ was determined by Grand-Jean, Weiss & Kern (1962), and a detailed description of the structure was reported by Weiss, Grand-Jean & Wendling (1964). Their analysis used photographic data collected for the $[hk0]$ zone. The final coordinates and standard deviations were derived from a least-squares refinement with isotropic temperature factors. This refinement gave a residual of 0.16 for the 63 reflexions (of which 51 are independent) measured by these authors. In spite of the high residual they reported standard deviations (e.s.d.'s) of 0.010 \AA for the coordinates of S and 0.015 \AA for those of the O atoms. The length of the S–O bond and the O–S–O angle were found to be of $1.62 \pm 0.02 \text{ \AA}$ and of $95.4 \pm 1.8^\circ$ respectively. These dimensions differ significantly from those reported by Batelle & Trueblood (1965) in their paper on the crystal structure of ammonium sulphite monohydrate, in which they determined a S–O distance of $1.529 \pm 0.006 \text{ \AA}$ (average value, corrected for libration) and an O–S–O angle of $104.8 \pm 0.4^\circ$ (average value). The latter values are in accordance with expectation on the basis of: (1) an analysis of S–O stretching frequencies (Robinson, 1964), (2) a comparison with other third row oxyanions, and (3) a comparison with the structures of complex sulphites (Spinnler & Becka, 1967; Baggio & Becka, 1969; Nyberg & Kierkegaard, 1967; Kierkegaard & Nyberg, 1965). The only other reported structural study of the sulphite ion, that of Zachariasen & Buckley (1931) who studied the structure of sodium sulphite, is not very accurate owing to the presence of twinning. Thus, we undertook the present reinvestigation of the structure of $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ in order to provide additional information on the correct dimensions of the free sulphite ion, which are relevant to the discussions of π -bonding in compounds of second row elements (Cruickshank, 1961), and to the analysis of the bonding of the sulphite group in transition metal complexes (Spinnler & Becka, 1967; Baggio & Becka, 1969).

Experimental

Preparation

$\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ was prepared by the method reported by Klasens, Perdok & Terpstra (1936). Well developed crystals, many of which were star shaped interpenetrating twins, were obtained directly from the solution by slow evaporation in the absence of oxygen.

Crystal data

Nickel sulphite hexahydrate – $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$ – F.W. = 246.85. Rhombohedral – crystal faces: (100), (010), (001), (111). $R3$. Habit: pyramidal, many crystals are star shaped interpenetrating twins, law $(\bar{1}\bar{1}\bar{1})$; $a_{rh} = 5.898 \pm 0.008 \text{ \AA}$, $\alpha_{rh} = 95.4 \pm 0.1^\circ$ (hexagonal $a = 8.794 \text{ \AA}$, $c = 9.002 \text{ \AA}$); $V_{rh} = 201.0 \pm 0.1 \text{ \AA}^3$ (hexagonal, $V = 603.0 \text{ \AA}^3$); $D_m = 2.03 \text{ g.cm}^{-3}$ (by flotation); $D_x(Z = 1) = 2.04 \text{ g.cm}^{-3}$. The wavelength values $\lambda_{\text{Cu } K\alpha_1} = 1.54051 \text{ \AA}$, $\lambda_{\text{Cu } K\alpha_2} = 1.54433 \text{ \AA}$ were used for the cell dimension determinations; Zr-filtered Mo radiation was used for intensity measurements ($\mu = 27 \text{ cm}^{-1}$ for Mo $K\alpha$ radiation). The space group is $R3$ (No. 146), (Klasens, Perdok & Terpstra, 1936).

The cell dimensions and standard deviations thereof were determined from the $K\alpha_1$ – $K\alpha_2$ components of high angle reflexions, measured on a General Electric Single Crystal Orienter, and by use of the method of Main & Woolfson (1963).

Collection and reduction of intensity data

Intensity data were collected on single crystals of pyramidal shape having dimensions 0.1 mm along each of the three axes of the rhombohedral cell. The crystals were mounted along the threefold symmetry axis. Levels $h0l$ to $h5.l$ (referred to the hexagonal setting) were recorded on a precession camera and level $hk.0$ on a Weissenberg camera. A total of 383 independent reflexions, representing 100% of the reflexion sphere of $\sin \theta/\lambda = 0.70 \text{ \AA}$, were registered on these photographs. About 95% of these reflexions were of measurable intensity within a 1200:1 ratio of maximum to

minimum intensity; measurements were made with a microdensitometer on mechanically integrated spots. Lorentz and polarization corrections were applied. The effect of absorption was tested on a crystal of similar dimensions mounted on a General Electric Single Crystal Orienter with the [110] rhombohedral direction parallel to the spindle (φ) axis. The profile of intensity *versus* φ was plotted for several $hh0$ reflexions, which occurred at $\chi=90^\circ$, with the use of Mo $K\alpha$ radiation. The maximum variation of intensity for any of these reflexions was found to be $\pm 3\%$. Since at these orientations the variation of X-ray path is at least equal to that between the reflexions we recorded on the precession camera, we neglected the absorption correction. Reflexions from individual layer lines were put on the same intensity scale by use of the method of Hamilton, Rollett & Sparks (1965). The experimental uncertainty in the observed structure factors was estimated from the difference in intensity of equivalent reflexions measured on different layer lines, the discrepancy index being $R(F_o)=0.039$.

Least-squares refinement

The starting point of the refinement was the set of parameters given by Weiss, Grand-Jean & Wendling (1964). Referred to the rhombohedral axes, the Ni and S atoms are in special positions 1(*a*) of $R3$, Ni at the origin with $x=0$, and the three oxygen atoms (one sulphite and two water oxygens) are in the general positions 3(*b*). There are, therefore, ten positional parameters, plus the scale factor and temperature factors to be refined. The first structure factor calculation with these parameters and our data gave a residual R ($\Sigma |A|/\Sigma |F_o|$) of 0.28. In the following sequence of least-square refinements we assumed that the oxygen atoms of the sulphite group had a fractional charge of

$-\frac{2}{3}$ electron each, that the nickel atoms had a charge of +2, and that the other atoms were neutral. The form factors for Ni^{2+} and neutral S were taken from a paper by Cromer & Waber (1965), and those for oxygen from *International Tables for X-ray Crystallography* (1962), with the use of a linear interpolation to obtain the form factors of $O^{2/3}$. We have not included the imaginary component, $\Delta f''$, of the anomalous scattering in the form factors of the atoms. Ueki, Zalkin & Templeton (1966) pointed out that neglect of this component could lead to errors in the bond length, greater than estimated from the least-squares refinement, if the compound crystallizes in a polar space group. Cruickshank & McDonald (1967) analysed quantitatively these errors, and discussed cases in which the data will give no first order error in the coordinates even when $\Delta f''$ is neglected. By the use of the arguments put forward by the last mentioned authors we considered that our data could lead to correct coordinates, since we collected reflexions on the positive and negative hemispheres with respect to the threefold symmetry axis.

We chose a weighting scheme of the form: $\omega^{-1} = (0.015|F_o| + 0.2)^2$ on the basis of an analysis of the discrepancies between equivalent reflexion measured on different layer lines, in ranges of F_o and $\sin \theta/\lambda$. Reflexions of unobservable intensity were excluded from the refinements, and the hydrogen atoms were not taken into account in the structure factor calculations.

After four cycles of full-matrix refinement of the coordinates, individual isotropic temperature factors and overall scale factor, the discrepancy factor R reduced to 0.075. At this stage the full matrix refinement was continued with individual anisotropic temperature factors. Convergence was now reached after three cycles, and R reduced to a value of 0.048. The significance of the anisotropic temperature factors was confirmed by use of Hamilton's (1965) test, with the

Table 1. *Final parameters*

Standard deviation, given in parentheses, are in units of the last decimal place. Parameters are referred to the rhombohedral axes
(a) Fractional coordinates and equivalent isotropic temperature factors*

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
Ni	0.0	0.0	0.0	1.13
S	0.5020 (7)	0.5020 (7)	0.5020 (7)	1.63
O(1)	0.5589 (10)	0.4786 (10)	0.2533 (10)	2.06
W(1)	0.0764 (14)	-0.3166 (14)	-0.1228 (13)	2.56
W(2)	0.3267 (13)	0.1401 (13)	-0.0506 (13)	1.78

* Equivalent isotropic temperature factors calculated with the expression:

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (\bar{a}_i \cdot \bar{a}_j) \quad (\text{Hamilton, 1959}).$$

(b) Anisotropic thermal parameters in \AA^2 ($\times 10^4$)†

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	152 (4)	152 (4)	152 (4)	47 (2)	47 (2)	47 (2)
S	208 (5)	208 (5)	208 (5)	24 (5)	24 (5)	24 (5)
O(1)	216 (24)	322 (25)	258 (24)	59 (18)	105 (17)	154 (17)
W(1)	450 (43)	280 (34)	318 (35)	162 (30)	100 (31)	148 (29)
W(2)	180 (26)	297 (32)	218 (27)	10 (21)	71 (21)	60 (24)

† The expression of the temperature factor in terms of the U_{ij} 's is:

$$\exp(-2\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* h_i h_j)$$

are included in the calculation of R with the parameters of the last anisotropic refinement. These parameters and their e.s.d.'s are given in Table 1, and the observed and calculated structure factors in Table 2.

With the final set of calculated structure factors we computed a three-dimensional difference Fourier synthesis on a mesh of $0.05 \times 0.05 \times 0.05 \text{ \AA}$, by use of all the observed reflexions. The highest positive and negative peaks were of $\pm 0.6 \text{ e.\AA}^{-3}$; they appeared along the symmetry axis and near the origin. All other peaks were of less than $\pm 0.4 \text{ e.\AA}^{-3}$. In order to locate the hydrogen atoms we computed another difference Fourier including only observed reflexions of $\sin \theta/\lambda < 0.45 \text{ \AA}^{-1}$. This map showed four peaks of 0.5 e.\AA^{-3} as the highest positive peaks in the asymmetric unit, located near to likely positions for the hydrogen atoms. These positions are given in Table 3. When hydrogen atoms with temperature factors of 3 \AA^2 were included in the structure factor calculation both R and R' increased. After two cycles of refinement of the heavy atoms the values of R and R' were the same as for the refinement without hydrogen atoms, and the new parameters differed by less than one e.s.d. from their previous values. The data were not sufficient quality to allow a refinement of the hydrogen parameters. When such a refinement was attempted allowing for the simultaneous variation of all parameters, including hydrogen atoms, the temperature factors of the latter became meaningless. Thus, we preferred to take the parameters derived from the anisotropic refinement without hydrogen atoms for the analysis of the structure.

Finally, we tested our weighting scheme and the validity of the form factor choice, performing two new sequences of refinements. The first with a unit weighting scheme, and the other with form factors for neutral atoms. The unit weighting scheme gave higher

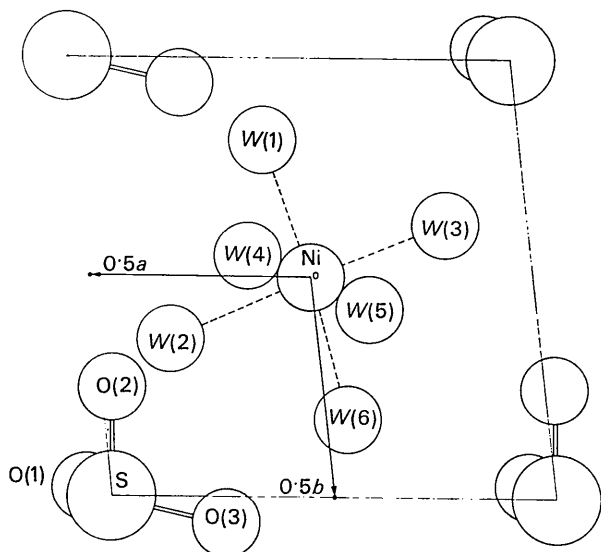


Fig. 1. Projection along [001].

Table 3. Coordinates of hydrogen atoms

This table gives assigned fractional coordinates of the hydrogen atoms. These atoms were not included in the structure factor calculation.

		x	y	z
$W(1)$	H(1)	0.032	-0.440	-0.031
	H(2)	0.144	-0.367	-0.269
$W(2)$	H(3)	0.414	0.267	0.064
	H(4)	0.383	0.180	-0.191

R and R' values, and the plot of $\omega\Delta^2$ versus F_o reproduced our previous weighting scheme. The alternate choice of form factors converged to the same R and R' values, the coordinates differing by less than one e.s.d. and the temperature factors by less than two e.s.d.'s. Since the previous form factors seem more reasonable from a chemical point of view we will present the results obtained with them.

The coordinates and isotropic temperature factors obtained from the refinement of our data differed from the corresponding values reported by Weiss, Grand-Jean & Wendling (1964) by more than three e.s.d.'s. However, when we calculated a sequence of refinements with their data, we obtained e.s.d.'s which were about six times larger than those reported by these authors. After two cycles of refinement, that data gave $R=0.138$ and e.s.d.'s of the order of eight times larger than those obtained with our data. Taking into account the new e.s.d.'s, the difference between the coordinates fitted by our data and those obtained from the previous data is not significant. The following programs were used and are gratefully acknowledged:

1. A. Zalkin & B. Foxman: General Fourier synthesis, *FORDAP* (IBM 360).
2. C. T. Prewitt, B. Foxman & L. Becka: Full matrix least-squares, *SFLSO* (IBM 360).
3. D. P. Shoemaker & S. R. Srivastava: Anisotropic Temperature factor interpreting program, *VIBELL* (IBM 360).
4. M. E. Pippy & F. R. Ahmed: Mean plane calculation (IBM 360).
5. M. E. Pippy & F. R. Ahmed: Scan of interatomic distances and angles (IBM 360).
6. L. M. Amzel & S. Baggio: Photographich data processing and layer correlation program, *PHOTO* (IBM 360).

Discussion of the structure

A projection of the structure down [001] is shown in Fig. 1, and the disposition of atoms around the three-fold symmetry axis in Figs. 2 and 3. The crystal can be considered as composed of two separate crystallographic entities, namely the sulphite ion and the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion, the S atom lying along the symmetry axis, so that the SO_3^- group has C_3 symmetry, and the coordination around Ni^{2+} is that of a deformed octahedron. The two groups are one atop the other when viewed along the symmetry axis. The distances

between planes perpendicular to the threefold axis and containing the various atoms of the cell are given in Table 4; these distances correspond to the z coordinate of these atoms when referred to a hexagonal cell having the Ni^{2+} ion at the origin. The distances of closest approach between neighbouring $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ octahedra and between SO_3^{2-} and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ are indicated in Figs. 2 and 3 and in Table 5. The latter gives the environment, at less than 3.0 Å, around each of the atoms in the asymmetric unit.

Table 4. *Interplanar spacings*

This table gives the distances from the origin of relevant planes perpendicular to the symmetry axis. The distances are given in Å taking Ni^{2+} at the origin. Each plane is identified by three equivalent atoms. Plane 4 is equivalent to plane 1 by a $[100]$ translation and plane 5 is equivalent to plane 2 by a $[110]$ translation.

Plane	Distances
1 $W(2), W(4), W(6)$	1.27
2 $W(1), W(3), W(5)$	-1.11
3 $O(1), O(2), O(3)$	3.95
4 $W(2'), W(4'), W(6')$	-1.73
5 $W(1'), W(3'), W(5')$	4.89

The structure can be envisaged as being derived from that of cesium chloride, the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ octahedra being at the nodes of the rhombohedral cell and the SO_3^{2-} ion approximately at the center. When the structure is viewed looking down the symmetry axis one can imagine that all the oxygen atoms are on parallel infinite sheets perpendicular to this axis. On each sheet every oxygen atom of each SO_3^{2-} group might be hydrogen bonded to $W(2)$ and $W(1)$ type water molecules be-

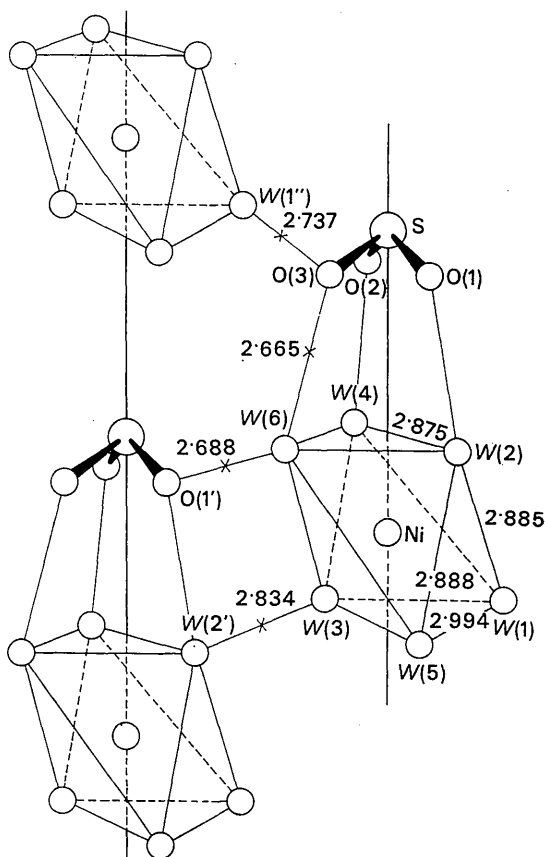


Fig. 2. A view of part of the structure seen along the symmetry axis, showing the distance (Å) between atoms in close contact. Likely hydrogen bonds are indicated by crosses.

Table 5. *Distances and angles*

Interatomic distances (Å), not corrected for libration, and angles ($^\circ$) in $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$. Estimated standard deviations shown in parentheses, are in units of the last place. The Table shows the environment of each of the atoms in the asymmetric unit.

Distances		Angles	
Ni---W(1)	2.043 (8)	W(1)---Ni---W(3)	94.2 (3)
Ni---W(2)	2.076 (8)	W(1)---Ni---W(2)	88.9 (3)
S---O(1)	1.536 (7)	W(1)---Ni---W(4)	89.0 (3)
S---Plane O(1), O(2), O(3)	0.668 (4)	W(1)---Ni---W(6)	175.2 (6)
O(1)---O(2)	2.414 (8)	W(2)---Ni---W(4)	87.6 (3)
O(1)---W(2)	2.665 (10)	O(1)---S---O(2)	103.6 (6)
O(1)---W(3')	2.737 (10)	W(2) --- O(1)---W(3')	114.9 (3)
O(1)---W(6')	2.688 (10)	W(2) --- O(1)---W(6')	88.1 (3)
W(1)---W(3)	2.994 (11)	W(3')---O(1)---W(6')	88.9 (3)
W(1)---W(5)	2.885 (11)	W(4) --- W(1)---W(5)	58.7 (3)
W(1)---W(2)	2.885 (11)	O(3')---W(1)---W(6)	116.7 (3)
W(1)---W(4)	2.888 (1)		
W(1)---W(6')	2.834 (11)	O(2)---W(2)---W(3')	96.5 (3)
W(1)---O(3')	2.737 (10)	O(2)---W(2)---O(1')	100.6 (3)
W(2)---W(4)	2.875 (11)		
W(2)---W(6)	2.885 (11)		
W(2)---W(1)	2.885 (11)		
W(2)---W(5)	2.888 (11)		
W(2)---O(1)	2.665 (10)		
W(2)---O(2')	2.688 (10)		

Table 6. Averaged S-O distances (Å) and O-S-O angles (°) in sulphites

The values given for distances and angles are not corrected for libration; e.s.d.'s are in brackets as units of the last decimal place.

Compound	r(S-O)	O-S-O	References
NiSO ₃ ·6H ₂ O	1.53 (6)	105 (4)	This work, data from Weiss <i>et al.</i> (1964).
NiSO ₃ ·6H ₂ O	1.536 (7)	103.6 (6)	This work.
(NH ₄) ₂ SO ₃ ·H ₂ O	1.524 (6)	104.8 (4)	Battelle & Trueblood (1965).
Cu ₂ SO ₃ ·CuSO ₃ ·2H ₂ O	1.509 (16)	106.9 (8)	Kierkegaard & Nyberg (1965).
NH ₄ CuSO ₃	1.506 (12)	105.3 (7)	Nyberg & Kierkegaard (1967).
PdSO ₃ (NH ₃) ₃	1.49 (2)	108.6 (1.1)	Spinnler & Becka (1967).
Pd(SO ₃) ₂ (NH ₃) ₂ Na ₂ ·6H ₂ O	1.478 (16)	108.6 (9)	Capparelli & Becka (1968).
Co(en) ₂ SO ₃ NCS·2H ₂ O	1.485 (12)	110.3 (7)	Baggio & Becka (1968).

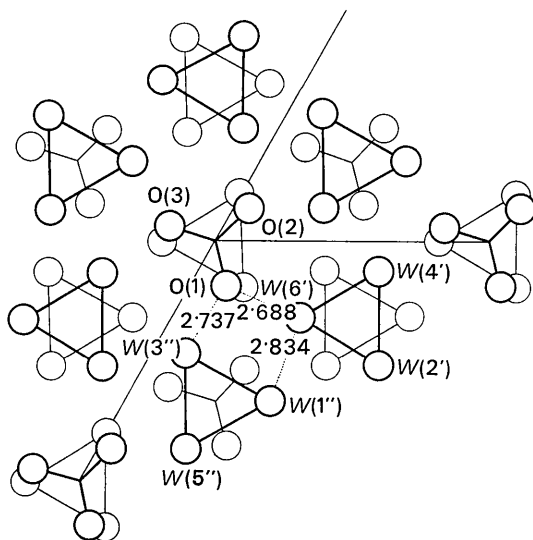


Fig. 3. Projection along [111] of part of the structure showing distances (Å) between atoms in close contact.

longing to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ octahedra located at a (100) and at a (110) type node of the rhombohedral cell, respectively. In addition to these hydrogen bonds, there are others between each $W(2)$ and each $W(1)$ type water molecule on the same sheet, and it is also likely that two neighbouring sheets are linked together by hydrogen bonds between each $W(2)$ type water molecule and an oxygen atom of the SO_3^- group on top of it. The location of hydrogen atoms given in Table 3 correspond to the hydrogen bonding scheme proposed in this discussion.

The geometry of the SO_3^- ion is summarized in Table 6, where the dimensions obtained with the data of Weiss *et al.* (1964) and those of SO_3 groups in other sulphites are also given. It seems certain that the dimensions obtained with our refinements of the structure of $\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$, as well as those obtained by Battelle & Trueblood (1965) in their study of $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, are probably correct. We are prompted to this conclusion by the consistency between the above mentioned results, as well as by the fact that these dimensions correlate well with the expected shortening of the S-O bond and the opening of the O-S-O angle when SO_3^- becomes coordinated through its S atom to an electronegative atom or ion. The S-O length of

1.536 ± 0.007 Å and the O-S-O angle of $103.6 \pm 0.6^\circ$ we obtained in this investigation are as predicted by Robinson (1964) from his studies of the correlation of S-O stretching frequencies with bond order and bond length. For a discussion of the interpretation of these dimensions in relation to bonding we refer to Battelle & Trueblood (1965).

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