

The Crystal and Molecular Structure of *meso*-Ethane-1,2-bis(methyl Sulphoxide), with Some Results from the Neglect of a Small Anomalous Dispersion Signal in a Centrosymmetric Case

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The structure of the title compound, crystallizing in space group $P\bar{1}$ with $Z=1$, was solved by Patterson methods. Full-matrix least-squares refinement was based on 579 counter-collected data corrected for absorption and anomalous dispersion. The final R is 0.021 ($R_w=0.030$). Bond lengths and angles in the sulphoxide group are compared with those of other organic sulphoxides. A short central C–C bond of 1.516 (2) Å can be explained qualitatively as a secondary rehybridization effect on C caused by the electron-withdrawing property of the O atoms. Neglect of anomalous dispersion corrections gives rise to significant changes in scale factor and vibrational parameters for the heavier atoms in good agreement with quantitative predictions by Gilli & Cruickshank [*Acta Cryst.* (1973). B29, 1983–1985]. The largest coordinate shift of an H atom corresponds to a change in the C–H length of 3σ . Dispersion effects in the final difference map are small and cannot explain the observed negative density regions near the S atoms.

Introduction

Some years ago Bruun, Hafnor & Sørensen (1950) reported the presence in sulphate turpentine of ethane-1,2-bis(methyl sulphoxide), presumably formed by the autoxidation of ethane-1,2-bis(methyl sulphide). The bis(sulphoxide) was later prepared in both α and β forms according to the procedure of Bell & Bennett (1927). These authors recognized that one of the crystal forms would be a *meso* form, the other racemic, but there was no means at that time to distinguish between the two.

An X-ray analysis of the two structures was initiated in order to resolve this problem. As we did not succeed in growing crystals of acceptable quality of the β form, only the structure of the higher-melting α form has been determined.

We also found this compound suitable for a study of errors in refined parameters due to neglect of the anomalous scattering by S of Cu $K\alpha$ radiation.

Experimental

The two forms of ethane-1,2-bis(methyl sulphoxide) were prepared as directed by Bell & Bennett (1927). Repeated and alternating crystallizations from acetone and ethyl acetate were necessary to obtain pure samples. Both forms were finally recrystallized from ethyl acetate and m.p.'s were 174–175° (α) and 132–133° (β). The α form crystallized either as prisms or, more commonly, as thin plates with \mathbf{b}^* normal to the plate. The crystals of the β form were invariably clusters of

interpenetrating needles that were easily shattered or deformed. Bell & Bennett described their α form from ethanol as monoclinic needles, m.p. 163–164° and the β form from ethanol or ethyl acetate as monoclinic bipyramids with m.p. 128–130°.

Preliminary photographs of the higher-melting crystals showed triclinic symmetry.

Crystal data

Ethane-1,2-bis(methyl sulphoxide), $C_4H_{10}(SO)_2$, F.W. 154.25, $a=5.305$ (4), $b=5.261$ (3), $c=7.280$ (8) Å, $\alpha=94.79$ (4), $\beta=98.87$ (7), $\gamma=116.22$ (2)°, $\lambda(\text{Cu } K\alpha)=1.5418$ Å, $V=177.4$ Å³, $D_x=1.44$ g cm⁻³ for $Z=1$, $\mu(\text{Cu } K\alpha)=59.0$ cm⁻¹. Space group: $P\bar{1}$ (from the analysis).

Cell dimensions were determined from the setting angles of 12 high-angle reflexions. The measurements were repeated on two occasions during and after data collection. The cell parameters a , c , α and β changed significantly during the 150 h X-ray exposure, a and c increasing almost linearly from 5.301 (1) and 7.272 (1) to 5.317 (1) and 7.301 (1) Å, respectively. The angles α and β changed by -0.1 and $+0.25^\circ$, respectively. The crystal was subsequently left on the diffractometer for another 150 h period and the cell constants were re-measured. As no significant changes were found this time we conclude that the crystal has suffered some kind of radiation damage, one possible explanation being enhanced autoxidation of sulphoxide to sulphone. Tabulated values of the cell constants are averages of the first two measurements which represent the part of the data used in the final refinement.

A plate-like crystal, $0.50 \times 0.38 \times 0.09$ mm, mounted with a nearly parallel to the goniometer φ axis was used for the data collection.

Data collection and processing

The intensities of 1110 reflexions were measured to a 2θ limit of 128° with Ni-filtered Cu $K\alpha$ radiation on a Picker FACS-1 four-circle instrument in the $\omega/2\theta$ scan mode. The scan rate in 2θ was 1° min^{-1} and the basic scan width was 1.8° . The counting rate was kept below ca. 9×10^3 counts s^{-1} by means of attenuators, and backgrounds were measured for 40 s at each end of the scan. Two standard reflexions were monitored every 30 reflexions. The data were collected in two sets, both of which were immediately preceded by a centring of the crystal and redetermination of the cell constants. Set I comprises all 590 reflexions $-h \pm k \pm l$ and in addition 90 $h \mp k \mp l$ reflexions. Set II comprises 705

reflexions, mainly $h \mp k \mp l$, and includes 275 reflexions also collected in set I. The two standard intensities showed a very similar rate of decay, 5.8% during collection of set I and another 6.0% during collection of set II. No single measurement of a standard intensity deviated by more than 0.2 times the statistical error from the normalized mean curve for the two which was used to scale the data.

The intensities were corrected for absorption with two different programs both based on the Gaussian integration method (Coppens, 1970). Weighted averages of F and $\sigma_s(F)$ were calculated for identical reflexions measured in both data sets. The last 65 measurements in set I were rejected because of increasing skewness in the peak scans due to changes in cell parameters. For the remaining 210 pairs the discrepancy $D = \sum |F_1 - F_{11}| / \sum F_{\text{ave}}$ was 0.010.

Of the 590 unique reflexions only three had

Table 1. Final atomic parameters ($\times 10^4$) of the S, C and O atoms with standard deviations

The table gives shifts in scale factor and atomic parameters at various levels of dispersion correction. Anisotropic thermal parameters, U_{ij} ($\times 10^4$), satisfy the equation: $U = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

	Parameters with full anomalous correction for S	Shifts without $\Delta f'_s$ but with $\Delta f''_s$ correction		Shifts with $\Delta f'_s$ but without $\Delta f''_s$ correction		Shifts without $\Delta f'_s$ and $\Delta f''_s$ correction	
		Exp.	Theor.†	Exp.	Theor.†	Exp.	
R (%)	2.1	2.1		2.1		2.2	
R_w (%)	3.0	2.8		3.1		2.9	
F_c scale factor	23.20 (8)	0.65	0.46	0.05	0.01	0.71	
S	x	2834.2 (7)	0.2	-0.4		-0.1	
	y	612.9 (7)	0.0	-0.9		-0.2	
	z	2677.9 (4)	0.2	-0.2		0.3	
U_{11}	346 (3)	-9	} -15	-1	} -1	-10	
	U_{22}	312 (3)		-9		0	-9
	U_{33}	352 (3)		-9		-1	-9
	U_{12}	149 (2)		-4		0	-4
	U_{13}	51 (2)		-2		0	-2
U_{23}	86 (2)	-1		0		-1	
O	x	3236 (3)	0	-1		1	
	y	-2011 (2)	1	1		2	
	z	2283 (2)	1	0		0	
U_{11}	531 (7)	20	} 16	1	} 0.5	24	
	U_{22}	328 (6)		20		3	22
	U_{33}	624 (7)		21		5	19
	U_{12}	236 (5)		10		-1	11
	U_{13}	25 (6)		3		1	4
U_{23}	130 (5)	4		3		0	
C(1)	x	6323 (4)	0	1		-1	
	y	3641 (4)	1	1		1	
	z	3128 (3)	0	-1		0	
U_{11}	390 (9)	15	} 16	2	} 0.5	20	
	U_{22}	353 (9)		20		-1	25
	U_{33}	512 (10)		19		5	17
	U_{12}	122 (7)		7		1	12
	U_{13}	1 (8)		4		-1	6
U_{23}	82 (7)	3		1		1	
C(2)	x	1483 (3)	1	2		1	
	y	1230 (3)	2	2		3	
	z	423 (2)	0	1		-1	
U_{11}	369 (8)	14	} 16	2	} 0.5	13	
	U_{22}	276 (7)		21		2	27
	U_{33}	367 (8)		13		2	13
	U_{12}	167 (7)		6		-1	7
	U_{13}	58 (6)		2		-1	3
U_{23}	89 (6)	5		1		6	

† Gilli & Cruickshank (1973).

$F \leq 3\sigma_s(F)$. For a single measurement $\sigma_s(F) = \sigma(I)/2F$ where $\sigma(I)$ is the error from counting statistics.

Structure determination

The intensity distribution indicated space group $P1$. However, this molecule departs drastically from the assumption of a sufficiently large and random collection of approximately equal scatterers which is inherent in this test (Wilson, 1949). A structure in space group $P\bar{1}$ with a number of light atoms and one dominating heavy atom per asymmetric unit will have an intensity distribution shifted toward the acentric curve (Sim, 1958; Lipson & Cochran, 1965). We refined the structure in both space groups and found strong evidence for $P\bar{1}$.

The two S atoms were placed according to the S-S

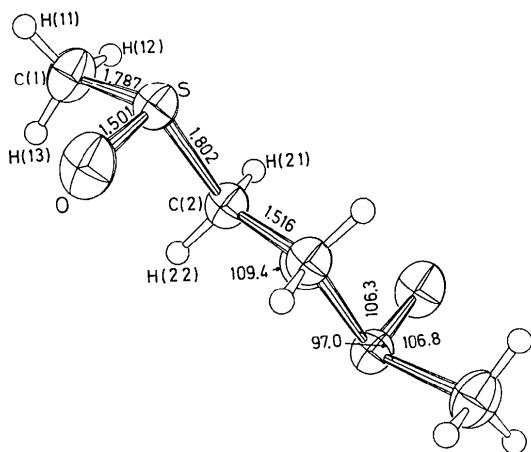


Fig. 1. Molecular conformation of *meso*-ethane-1,2-bis(methyl sulphoxide) with bond lengths (Å) and valency angles (°). E.s.d.'s in bonds are : 0.002 Å and in angles: 0.1°.

vector peak in the Patterson map. A ΔF map gave the positions of all C and O atoms. When the non-centrosymmetric refinement including H atoms converged there were many indications of refinement in a wrong space group, e.g. high correlation between pairs of corresponding variables, large deviations between chemically equivalent bonds, several unacceptable C-H lengths and residual peaks in the final ΔF map.

Anisotropic refinement in $P\bar{1}$ started with the properly shifted C, O and S atoms. H atoms from a ΔF map were treated isotropically. Refinements based on the unique reflexions in data set I and the averaged set of symmetry-equivalent reflexions in I and II gave nearly the same R . The goodness-of-fit was 2.72 with set I compared to 3.60 with the averaged set, indicating larger systematic errors in set II due to the radiation damage. Set I was therefore used in the final refinement.

Table 2. Final atomic parameters ($\times 10^3$) with standard deviations of the H atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
H(11)	610 (5)	531 (5)	317 (3)	60 (6)
H(12)	732 (5)	355 (5)	425 (4)	68 (6)
H(13)	718 (4)	348 (4)	212 (3)	46 (5)
H(21)	141 (4)	287 (4)	62 (3)	41 (5)
H(22)	278 (4)	132 (4)	-32 (3)	39 (4)

Table 3. Bond lengths and angles involving H atoms

Standard deviations are given in parentheses.

C(1)-H(11)	0.94 (3) Å	H(11)-C(1)-H(12)	113 (2)°
C(1)-H(12)	0.92 (3)	H(11)-C(1)-H(13)	109 (2)
C(1)-H(13)	0.94 (2)	H(12)-C(1)-H(13)	112 (2)
C(2)-H(21)	0.88 (2)	S-C(2)-H(21)	107 (1)
C(2)-H(22)	0.92 (2)	S-C(2)-H(22)	106 (1)
S-C(1)-H(11)	108 (1)°	C(2)-C(2)-H(21)	111 (1)
S-C(1)-H(12)	107 (1)	C(2)-C(2)-H(22)	111 (1)
S-C(1)-H(13)	107 (1)	H(21)-C(2)-H(22)	112 (2)

Table 4. Comparison of structure parameters of some organic sulphoxides

Uncorrected parameters in the table have been recalculated from published coordinates.

	S-C (Å)		S-O (Å)		C-S-O (°)		C-S-C (°)
	Terminal C				Terminal C		
Dimethyl sulphoxide (a)	{ 1.775 (8)† 1.821 (11)†		1.531 (5)†		{ 106.7 (4) 106.8 (4)		97.4 (4)
(+)-Methyl <i>p</i> -tolyl sulphoxide (b)	1.809 (3-6)†	1.804 (3-6)†	1.505 (3-6)†		105.5 (3)	106.6 (3)	97.6 (3)
Methyl [2-phenyl-(3',4'-dimethyl-2-phenyl)]vinyl sulphoxide (c)	1.814 (5)	1.775 (7)§	1.514 (4)		104.0 (2)	104.1 (2)	96.1 (3)
Methyl [2-hydroxyl-2-phenyl-2-(2',4'-dimethylphenyl)]ethyl sulphoxide (d)	1.791 (5)	1.817 (5)	1.530 (5)		105.7 (2)	104.8 (2)	97.8 (2)
<i>o</i> -Carboxyphenyl methyl sulphoxide (e)	1.788 (5)	1.800 (3)	1.517 (3)		104.6 (2)	103.1 (1)	97.8 (2)
(-)- <i>o</i> -Carboxyphenyl methyl sulphoxide (f)	1.783 (6)	1.800 (5)	1.517 (4)		104.4 (2)	103.7 (2)	98.8 (2)
Ethane-1,2-bis(methyl sulphoxide) (g)	1.788 (2)‡ 1.794 (2)*	1.802 (2)	1.501 (2)‡ 1.515 (2)*		106.8 (1) 106.3 (1)	106.3 (1)	97.0 (1)

* 'riding' correction (Busing & Levy, 1964).

† corrected for librational motion (Cruickshank, 1961).

‡ 'minimum' correction (Busing & Levy, 1964).

§ S-C(*sp*²) bond.

(a) Thomas, Shoemaker & Eriks (1966), (b) de la Camp & Hope (1970), (c) Tranqui & Fillion (1972), (d) Tranqui, Richard, Vicat & Fillion (1974), (e) Dahlén (1973), (f) Dahlén (1974), (g) present work.

Weights were applied in the form $w = [\sigma_S^2(F) + cF^2]^{-1}$; c was 3.0×10^{-4} from an analysis of $w(F_o - KF_c)^2$ with groups of increasing F_o . The two most intense reflexions, $\bar{1}11$ and $\bar{1}01$, being impaired by the use of attenuators, were weighted zero together with three reflexions below the $3\sigma(F)$ threshold. Another six low-order reflexions were given zero weight owing to excessive streaking in the ω direction on the Weissenberg films. Full-matrix least-squares refinement of the 57 parameters based on 579 F_o converged at an R of 0.021 and $R_w = [\sum w(|F_o| - K|F_c|)^2 / \sum w F_o^2]^{1/2}$ was 0.030. All final parameter shifts were less than 0.01σ . Refinement including the six reflexions with ΔF in the range 1.5 to 3.5 increased R to 0.025. Except for the temperature factors of S, which shifted *ca.* 2σ , all parameters remained unchanged within σ . Coordinates and thermal parameters are given in Tables 1 and 2.*

A ΔF map calculated after the refinement shows residual density in the range -0.20 to $0.19 \text{ e } \text{\AA}^{-3}$. The highest density is in the bonds between non-hydrogen atoms ranging from $0.05 \text{ e } \text{\AA}^{-3}$ in the S-O bond to $0.19 \text{ e } \text{\AA}^{-3}$ in the S-C bonds. Final atomic positions are on zero or slightly negative density. There are two elongated negative regions of strength -0.12 to $-0.20 \text{ e } \text{\AA}^{-3}$ almost symmetrically disposed on either side and close to the S atom position.

Scattering factors for S, C and O were those of Doyle & Turner (1968); the values of Stewart, Davidson & Simpson (1965) were used for H. Anomalous dispersion corrections (Cromer & Liberman, 1970) were applied for S and O.

Thermal motion

The thermal parameters of the atoms do not conform to a rigid-body model of the motion. The terminal O atoms have larger and also more anisotropic movements. Corrections have been calculated for the bonds S-O(l_1) and S-C(1) (l_2). With the minimum correction (Busing & Levy, 1964) these are $l_1 + 0.002$ and $l_2 + 0.001 \text{ \AA}$. The corresponding values assuming riding motion (Busing & Levy, 1964) are $l_1 + 0.016$ and $l_2 + 0.007 \text{ \AA}$. Minimum-corrected bond lengths are given in Fig. 1.

Results and discussion

The α form of ethane-1,2-bis(methyl sulphoxide) is the *meso* form of the molecule shown in Fig. 1. Bond lengths and angles involving the H atoms are listed in Table 3.

The molecular chain is not planar. C(1), S and C(2) deviate from the best plane through these atoms by -0.016 , 0.012 and 0.043 \AA , respectively. The plane equation $-0.758x + 0.550y + 0.351z = 0$ refers to orthogonal axes as defined for the triclinic case in the

X-RAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Table 4 is a survey of the structural parameters from some recent X-ray studies of organic sulphoxides. Most of the compounds listed in this table deteriorated to some extent during exposure to X-rays. Absorption corrections were applied only in (b) and (g). Averages of the angles C-S-O and C-S-C are 105.2 (range 103.1 - 106.8) and 97.5° (range 96.1 - 98.8°), respectively. Presumably, bond lengths are affected more than bond angles by thermal motion. In these sulphoxides the largest effects and individual variations would appear in the S-O and the terminal S-C bonds and corrections for rigid or non-rigid thermal motion are only approximate. The average for the innermost S-C bond is 1.805 \AA calculated from the most precisely determined structures in the table.

The central C-C bond in ethane-1,2-bis(methyl sulphoxide) is significantly shorter than a normal C(sp^3)-C(sp^3) bond of 1.534 \AA . Low and fairly isotropic thermal motion of the bonded atoms indicates that thermal effects are of minor importance in this case. A similar contraction has been observed in organic sulphides; for example, 1.515 (5) and 1.523 (4) \AA for the two C β -C γ bonds in L-methionyl-L-methionine (Stenkamp & Jensen, 1975). These authors list parameters for several methionine structures determined by X-ray methods. The C-C bonds in the atomic sequence $\ddot{\text{S}}-\text{C}-\text{C}$ are in general short, even when allowing for a reasonable thermal correction. Another related example is the very short central C-C bond of 1.506 (7) \AA in dioxonium ethane-1,2-disulphonate

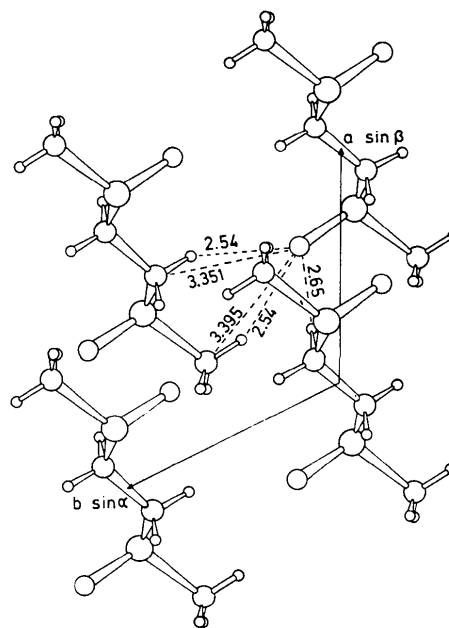


Fig. 2. Packing of the molecules as seen down c . The shortest intermolecular distances are given.

* The structure factor table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31271 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(Mootz & Wunderlich, 1970) in which the S atom is in its highest oxidation state. The shortened C–C bonds in all these structures can be explained qualitatively in terms of a rehybridization of the C atoms induced by the electron-withdrawing properties of the S–O group. The correlation between properties of carbon bonds and the degree of orbital hybridization has been rationalized by Walsh (1947) in a set of rules. Bent (1961) has further substantiated the validity of the rules and demonstrated that they can be applied also to second-row elements. In the sulphoxide there will be a concentration of *p* character in the S σ -bonding orbital toward O and consequently an increase in *s* character of the other σ orbitals pointing toward the C atoms. This induces a rehybridization of the C atoms, increasing the *p* character of the C(2) orbital toward S and the *s* character of its orbital toward C(2)'. Increase in *s* character of a σ orbital implies a shortening of that bond. Shortening of the C–C bond next to S therefore should occur and with increasing magnitude in the series sulphide, sulphoxide, sulphone.

The packing of the molecules is shown in Fig. 2. The O atom is involved in two normal van der Waals contacts with C(1) and C(2) of the molecule at $x, y-1, z$ and in a third contact with H(22) at $1-x, -y, -z$. The weak intermolecular forces explain the rather poor mechanical properties of these crystals.

Dispersion errors in refined parameters

As pointed out by Templeton (1955), neglect of the dispersion corrections will perturb the final electron density distribution. For centrosymmetric structures significant errors may be deposited in scale factor and vibrational parameters and the positional parameters of the lighter atoms may also be affected depending on the magnitude of the anomalous signal of the heavy atoms (Parthasarathy, Sabesan & Venkatesan, 1970). Gilli & Cruickshank (1973), hereinafter GC, have calculated approximate shifts in scale factor and thermal parameters due to neglect of $\Delta f'$ or $\Delta f''$ in the centrosymmetric case and found good agreement with experimental results from refinements of OsO₄. We have carried out a similar analysis for a case in which the anomalous corrections for the heavy atom are moderate; $\Delta f' = 0.319$ and $\Delta f'' = 0.557$ e for S with Cu *K* α radiation (Cromer & Liberman, 1970). The present structure also contains H atoms for which the positional parameters should be more sensitive to possible effects due to the lack of dispersion corrections.

Various full-matrix least-squares refinements were made with full, partial or no corrections for $\Delta f'$ and $\Delta f''$ as described by GC. The results are set out in Table 1 with the theoretical shifts in the F_c scale factor and the U_{ij} 's calculated according to GC. In general, the theoretical shifts are in good agreement with shifts from the refinements. It is noted, however, that the theoretical shifts are somewhat underestimated for the scale factor and overestimated for the vibrational parameters of S ($\Delta f'$ correction omitted). There are no

significant coordinate shifts of the heavier atoms when dispersion corrections are omitted. The largest coordinate shifts of two H atoms were *ca.* 2.5σ . The maximum change in one C–H length was $+0.07$ Å, approximately 3σ , but shifts in the other C–H lengths correspond to 2σ or less.

The fractional contribution of S to the mean intensity, σ_1^2 , is 0.80 and the ratio $\Delta f''/(f^0 + \Delta f')$ ≈ 0.07 . The expectation value of the phase error from neglect of the $\Delta f''$ correction is then approximately 6.0° according to Parthasarathy *et al.* (1970). Comparison of ΔF maps after refinements with and without $\Delta f''$ correction shows that the effects of phase error are small, of magnitude similar to differences appearing with different least-squares weighting schemes. In particular, the negative regions near S are preserved with only minor modifications in all ΔF maps calculated at various levels of correction for anomalous dispersion. These features therefore must be largely due to other errors in the scattering factor curve for S and errors in the absorption correction.

Crystallographic programs from the X-RAY 72 system (Stewart *et al.*, 1972) were used for structure solution and all subsequent computations. Fig. 1 was made with ORTEP (Johnson, 1965).

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Structure Refinement of $H\text{-Nb}_2\text{O}_5$

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The crystal structure of the high-temperature modification of Nb_2O_5 ($H\text{-Nb}_2\text{O}_5$) was refined by the least-squares method based on 10140 observed intensities. The crystal data are $a=21.153$ (7), $b=3.8233$ (5), $c=19.356$ (5) Å, $\beta=119.80$ (2)°, $Z=14$, $D_x=4.548$ g cm⁻³. The results agree generally with those of the previous structure determination except for the position of one tetrahedrally coordinated Nb atom, which is distributed equally over $2(i) 0, \pm y, 0$ of $P2/m$ with $y=0.2285$ (3). The final R is 0.052. $H\text{-Nb}_2\text{O}_5$ crystallizes in the space group $P2/m$ instead of $P2$ which was assumed in the earlier work.

Introduction

$H\text{-Nb}_2\text{O}_5$ was first described by Brauer (1941) as the high-temperature modification of niobium pentoxide. Gatehouse & Wadsley (1964) determined its crystal structure by means of Patterson and difference syntheses using $h0l$, $h1l$ and $h2l$ intensities recorded on integrated Weissenberg photographs taken with Cu $K\alpha$ radiation; their final R was 0.118. With respect to the space group symmetry, they examined both $P2$ and $P2/m$ and chose the former. The difference between the two consists solely in the position of one tetrahedrally coordinated Nb atom. While in $P2/m$ this Nb atom must be distributed equally over two equivalent positions, in $P2$ it can occupy a definite position $1(a)$. The arrangement of the other atoms conforms to the symmetry of $P2/m$. In order to shed light on the details of the structure including the question of the space-group assignment, a least-squares refinement based on a large number of observed intensities has been carried out.

Experimental

The single-crystal samples of $H\text{-Nb}_2\text{O}_5$ were taken from the product of a crystal-growth experiment, according to Bridgman's method, performed in air using the spec-pure grade Nb_2O_5 powder of Johnson and Matthey Co. as raw material. For the X-ray measurements, which were carried out at room temperature, a spherical specimen of radius 0.171 mm was made.

The unit-cell dimensions were obtained by the least-squares method based on 2θ angles measured on a four-circle diffractometer (Rigaku) using monochromated Mo $K\alpha$ radiation ($\lambda=0.70926$ Å). The intensities were collected on the same diffractometer. In the range of $2\theta \leq 90^\circ$, 24945 reflexions were measured of which 19278 were greater than zero. The observed intensities were reduced to a set of 10140 independent non-zero reflexions by averaging the equivalent ones, and then corrected for absorption ($\mu=56.3$ cm⁻¹). The zero reflexions were not used for further calculations.

Structure refinement

The structure was refined by the full-matrix least-squares method with *ORFLS* (Busing, Martin & Levy, 1962). The temperature factors of the Nb atoms were assumed to be anisotropic and the extinction correction of Zachariasen (1968) was applied. The following simplified formula with \bar{g} as one of the parameters to be refined was used:

$$F_o = sF_c [1 + \bar{g}(\bar{T}/\sin 2\theta) (1 + \cos^4 2\theta) \times (1 + \cos^2 2\theta)^{-1} F_c^2]^{-1/4}.$$

The mean path length \bar{T} weighted with the absorption term was calculated in advance as a function of $\sin \theta$ and given in the form of a table; \bar{T} ranged from 0.139 to 0.229 mm. The partial polarization of the incident X-rays through the monochromator was neglected. As the capacity of the computer (FACOM 270-20) did not