

The Crystal Structure of Silver Sulphimide Trihydrate, $\text{Ag}_3(\text{NSO}_2)_3 \cdot 3\text{H}_2\text{O}$

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The structure of $\text{Ag}_3(\text{NSO}_2)_3 \cdot 3\text{H}_2\text{O}$ has been determined by X-ray diffraction. Least-squares refinement with 1187 reflexions gave a final R of 0.049 for 64 parameters. The intensities were collected on a semi-automatic diffractometer with monochromated $\text{Mo K}\alpha$ radiation. The sulphimide ion is in the chair form and has symmetry $3m$ (C_{3v}) within experimental error; the mean S-N distance is 1.636 (4) Å, S-O_{ax} is 1.451 (6) Å, and S-O_{eq} is 1.427 (6) Å. Chains of silver atoms with Ag-Ag 3.032 (1) Å run parallel to c .

Introduction

The crystal structure of silver trisulphimide trihydrate, $\text{Ag}_3(\text{NSO}_2)_3 \cdot 3\text{H}_2\text{O}$, has been studied by X-ray diffraction to determine the conformation of the (NS)₃ ring in the trisulphimide anion. Fischer & Andress (1955), henceforth referred to as FA, have suggested from an incomplete X-ray analysis that the (NS)₃ ring is planar. In all other compounds of this type that have been studied, e.g. (NSOCl)₃ (Hazell, Wieggers & Vos, 1966), the rings are distinctly non-planar, in most cases they are chair formed; a complete list of references is given elsewhere (Hazell, 1974).

We have determined the structure first from the published data of FA and then with more extensive data, and find the trisulphimide anion to be chair formed. The S-N bond distances are equal within experimental error.

Crystal data

$\text{Ag}_3(\text{NSO}_2)_3 \cdot 3\text{H}_2\text{O}$, M.W. 574.1. Trigonal, $a = 10.563$ (5), $c = 5.368$ (5) Å, $U = 518.7$ Å³, $D_M(\text{FA}) = 3.82$, $Z = 2$, $D_c = 3.68$, $F(000) = 552$. Laue symmetry $\bar{3}m$ (D_3^d), systematic absences ($h, h, 2h, l$) with l odd, possible space groups $P31c$ (No. 159) or $P\bar{3}1c$ (No. 163). $P31c$ was chosen from consideration of the Patterson function. The crystals, which are colourless, crystallize from water as long needles bounded by $\{10\bar{1}0\}$ and elongated in the $[0001]$ direction. $\mu = 60.5$ cm⁻¹ for $\text{Mo K}\alpha$ radiation.

Atomic coordinates and thermal parameters, bond lengths and angles and observed and calculated structure factors are listed in Tables 1, 2, 3, and 4.

Table 2. Bond lengths and short interatomic distances and their estimated standard deviations

Symmetry-related atoms are defined as follows:

i	$1-x+y, 1-x, z$	v	$1-x, x-y, z-\frac{1}{2}$
ii	$x-y, -y, \frac{1}{2}+z$	vi	$x, y, 1+z$
iii	$y, x, z-\frac{1}{2}$	vii	$1-x, -x+y, \frac{1}{2}+z$
iv	$y, x, \frac{1}{2}+z$	viii	$1-y, x-y, z$

	l	l_{corr}
S—O(1) _{axial}	1.451 (6)	1.456*
S—O(2) _{equatorial}	1.427 (6)	1.436*
S—N	1.631 (5)	1.633†
S—N ⁱ	1.636 (6)	1.638†
Ag ^{iv} —N ⁱ	2.324 (5)	
Ag—N ⁱ	2.427 (5)	
Ag—Ag ^{iv}	3.032 (1)	
O(3)—O(3 ^{iv})	2.890 (6)	
Ag—O(1 ⁱⁱ)	2.483 (6)	
Ag—O(1 ^v)	2.660 (6)	
Ag—O(3 ⁱⁱⁱ)	2.516 (8)	

* Riding-motion correction for thermal vibration.

† Approximate correction for thermal motion by adding 0.002 Å.

Table 3. Angles and their estimated standard deviations

Symmetry-related atoms are defined as in Table 2.

O(1)—S—O(2)	117.4 (4)	Ag ^{vii} —N—S	122.5 (3)
O(1)—S—N	109.6 (3)	Ag ^{vii} —N—S ⁱ	113.6 (3)
O(1)—S—N ^{viii}	110.7 (3)	Ag—N—S	105.7 (3)
O(2)—S—N	106.5 (3)	Ag—N—S ⁱ	114.8 (3)
O(2)—S—N ^{viii}	105.9 (3)	Ag—Ag ^{iv} —Ag ^{vii}	124.6 (2)
N—S—N ^{viii}	106.1 (4)	O(3)—O(3 ^{iv})—O(3 ^{vii})	136.5 (4)
S—N—S ⁱ	115.0 (3)		

Table 1. Fractional coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^{-4}$)

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ag	5453 (1)	6225 (1)	0	479 (4)	412 (3)	215 (11)	289 (3)	30 (2)	12 (2)
S	7072 (2)	2072 (2)	-142 (3)	229 (5)	221 (5)	177 (12)	118 (4)	-2 (4)	-2 (4)
O(1)	7075 (6)	1989 (6)	2554 (10)	290 (22)	276 (22)	231 (24)	122 (18)	-25 (17)	52 (16)
O(2)	7394 (7)	1108 (6)	-1504 (13)	314 (24)	291 (22)	338 (28)	197 (21)	12 (19)	-36 (19)
O(3)	8496 (9)	7910 (9)	4519 (18)	487 (37)	367 (30)	408 (38)	236 (28)	17 (29)	8 (26)
N	5473 (6)	1752 (6)	-1099 (10)	231 (19)	205 (18)	163 (19)	90 (16)	-34 (13)	-14 (13)

Experimental

Intensities hkl (l=0 to 10) were recorded with a computer-steered Supper-Pace diffractometer. Monochromatic Mo Kα radiation was used with a scintillation counter in conjunction with a pulse-height

analyser. Data were collected out to sin θ/λ=1.0 which gave, after averaging, 1187 reflexions for which the intensity, I, was greater than 2σc(I) where σc(I) is the total number of counts in the intensity measurement. The background-peak-background method was used. A needle-shaped crystal of mean radius 0.045 mm

Table 4. Observed and calculated structure factors (× 10)

Table with 4 columns: Observed hkl, Observed I, Calculated I, and Difference. The table lists data for hkl values from 100 to 210 and includes calculated structure factors and their differences from observed values.

was mounted with *c* as rotation axis. The data were corrected for absorption assuming the crystal to be cylindrical and a correction was made for the change in the volume of crystal irradiated for the different layers.

Structure determination and refinement

In the original structure analysis (FA), the space group was assumed to be $P62c$ (No. 190). This required the $(\text{NSO}_2)_3^-$ ion to be on a $\bar{6}$ ($3/m$) axis and so planar. Re-determination of the structure from the published structure amplitudes showed the anion to be chair formed, but that there was disorder. This model refined to an R of 0.12.

New data were collected and it became apparent that the Laue group was $\bar{3}m$ and not $6/mmm$, and the 'disorder' the result of a wrong choice of space group. Starting completely afresh the position of the silver atom was determined from a Patterson function. The positions of all but the hydrogen atoms were located by the heavy-atom technique. Atomic coordinates and thermal parameters, scale factors for the different layers (l), and an isotropic extinction factor, g , were refined by the full-matrix least-squares method. A final difference map did not reveal the positions of the hydrogen atoms.

The final R was 0.049 for 1187 reflexions and 64 variables; the final weighted R was 0.067. Both the real and imaginary parts of the anomalous dispersion correction for Ag and S were included in the calculation. The ratio of the R -values for the two polarities was 0.96.

Attempts to analyse the thermal vibration of the anion assuming the $(\text{NS})_3$ ring to be a rigid body were unsuccessful. The S–O distances were corrected assuming the oxygen atoms to ride on the sulphur atoms. An arbitrary correction was made to the S–N bonds by adding 0.002 Å (the mean correction which had been obtained for the S–N bonds in $(\text{CH}_3\text{NSO}_2)_3$ (Hazell, 1974).

Computational details

Least-squares refinement was carried out with the full-matrix program *LINUS* (Coppens & Hamilton, 1970); the quantity minimized was $r = \sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2$ where $w = 1/\sigma^2$ and $\sigma = \sqrt{[\sigma_c(F_o^2) + 1.03F_o^2] - |F_o|}$.

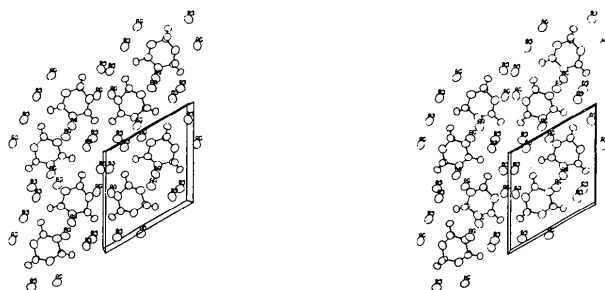


Fig. 1. Stereoscopic view of four unit cells viewed down the *c* axis.

The scattering factors were those of Cromer & Waber (1964) for silver, Doyle & Turner (1968) for sulphur, and Cromer & Mann (1968) for oxygen and nitrogen. Anomalous dispersion corrections (Cromer & Liberman, 1970) were included for silver and sulphur.

Bond distances and angles were calculated with *ORFFE* (Busing, Martin & Levy, 1964); the drawing was made with *ORTEP* (Johnson, 1965).

Discussion

The sulphimide ion is chair formed and has approximate symmetry $3m$ (C_{3v}). The sulphur–nitrogen distances are equal within experimental error; the mean value is 1.636 (4) Å. The sulphur–oxygen bonds are not equal, the axial bond, 1.456 (6) Å, being longer than the equatorial bond, 1.436 (6) Å; the difference may result from weak interactions between O(1) and the silver atoms. The silver atoms form zigzag chains which run parallel to *c*. The silver–silver distance is 3.032 (1) Å which is only slightly longer than that, 2.899 Å, in the metal (Pearson, 1967). The water molecules also form zigzag chains parallel to *c*, the distance between oxygen atoms being 2.890 (6) Å indicating that the water molecules are linked together by hydrogen bonding. Each of the nitrogen atoms of the sulphimide ion is weakly bound to two silver atoms, the sulphimide ions linking together triplets of chains of silver atoms (Fig. 1). The silver–nitrogen distances are intermediate between that for a single bond, e.g. that in $\text{Hg}(\text{CN})_2\text{AgNO}_3 \cdot 2\text{H}_2\text{O}$, 2.11 (6) Å (Mahon & Britton, 1971), and that in AgN_3 , 2.561 Å (Hughes, 1971) which is regarded as having bond order $\frac{1}{2}$. The bonds presumably have considerable ionic character. Silver–nitrogen distances similar to those in silver sulphimide are found in complexes between AgI and morpholine, 2.39 Å (Ansell & Finnegan, 1969*a*), piperazine, 2.32 Å (Ansell & Finnegan, 1969*b*), and piperidine, 2.329 Å (Ansell, 1971). The silver–oxygen distances are also longer than single bonds and may be compared to those in AgNO_3 (Lindley & Woodward, 1966) in which the distances range from 2.48 to 2.99 Å, the interactions being regarded as largely ionic. The sulphur–nitrogen bonds are longer than those in $\alpha(\text{NSOCl})_3$, 1.571 (4) Å. The geometry and the bonding of the sulphimide ion and a comparison with other $(\text{NS})_3$ systems will be given in the following article on $(\text{CH}_3\text{NSO}_2)_3$. The mean bond distances and angles are

Table 5. Comparison of mean distances and angles in $(\text{NXO}_2)_3^-$ where X = S or Se

	X=S	X=Se
X–O	1.446 (4)	1.622 (8)
X–N	1.636 (4)	1.768 (11)
O–X–O	117.4 (4)	111.7 (3)
N–X–O _{axial}	110.2 (2)	111.4 (3)
N–X–O _{equatorial}	106.2 (2)	105.9 (3)
N–X–N	106.1 (4)	112.1 (4)
X–N–X	115.0 (3)	113.1 (4)

compared with those of the triselenylimide ion in $K_3(NSeO_2)_3$ (Kocman & Rucklidge, 1974) in Table 5.

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The Crystal Structure of Methyl Sulphimide, $(CH_3NSO_2)_3$

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The structure of $(CH_3NSO_2)_3$ has been determined by X-ray diffraction. Least-squares refinement with 1177 reflexions gave a final R of 0.037 for 96 parameters. The intensities were collected on a semi-automatic diffractometer with monochromatized $Mo\ K\alpha$ radiation. The sulphimide molecule is in the chair form and has symmetry $3m$ (C_{3h}) within experimental error, the mean S–N distance is 1.669 (1) Å, S–O_{ax} 1.407 (1) Å, S–O_{eq} 1.409 (1) Å, C–N 1.492 (2) Å. The geometry of the molecule is compared with that of sulphanuric chloride, $(NSOCl)_3$, and with the trisulphimide ion, $(NSO_2)_3^{3-}$.

Introduction

The sulphur–nitrogen bonds in α -sulphanuric chloride, $(NSOCl)_3$, are short and equal in length (Hazell, Wiegiers & Vos, 1966). The shortness of the bonds is explained, e.g. Salem (1966), by two kinds of π -bonding: between d -orbitals on the sulphur atom and the p_z orbital on the nitrogen atom, and to exocyclic π' -bonding in the plane of the nitrogen atom and its adjacent sulphur atoms from the overlap of the lone pair on the sp^2 hybridized nitrogen atom with d -orbitals from the sulphur atoms.

The structures of the trisulphimide ion, $(NSO_2^-)_3$, in the silver salt (Dalgaard, Hazell & Hazell, 1974) and of methyl sulphimide, $(CH_3NSO_2)_3$, have been studied. In the methyl compound the lone pairs on the nitrogen atoms are replaced by methyl groups which would if the nitrogen atom retained its sp^2 hybridization remove the possibility of π' -bonding. Alternatively, the nitrogen atom could become sp^3 hybridized with the lone pair in the axial or the equatorial position.

The S–N bonds are found to be significantly longer than those in sulphanuric chloride or in the sulphimide ion (Table 1) but the geometry about the nitrogen atom is intermediate between planar trigonal and tetrahedral.

Crystal data

Methyl sulphimide, $(CH_3NSO_2)_3$; $M = 279.3$. Orthorhombic, $a = 8.021$ (10), $b = 10.648$ (10), $c = 11.537$ (10) Å, $U = 985.4$ Å³; $D_c = 1.88$, $Z = 4$. The systematic absences are: $0kl$ for $k+l$ odd, and $hk0$ for $h+k$ odd; the space group is $Pnma$ (No. 62) or $Pn2_1a$ (No. 33). The structure determination confirms $Pnma$. The compound crystallizes from toluene as colourless needles elongated in the [010] direction. μ for $Mo\ K\alpha$ radiation is 7.48 cm^{-1} .

Experimental

The crystals were provided by Dr A. J. Banister.

Intensities were collected on a linear diffractometer of the Arndt & Phillips (1961) design. $Mo\ K\alpha$ radiation