

A high resolution powder X-ray diffraction study of the products of reaction of dimethyl sulfide with bromine; crystal and molecular structures of $(\text{CH}_3)_2\text{SBr}_n$ ($n = 2, 2.5$ or 4)

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Received 29th July 1998, Accepted 6th November 1998

The crystal and molecular structures of three reaction products formed between dimethyl sulfide and bromine have been characterised by high resolution powder synchrotron X-ray diffraction. Depending on the method of preparation, three compounds have been identified as $(\text{CH}_3)_2\text{SBr}_2$, $(\text{CH}_3)_2\text{SBr}_{2.5}$ and $(\text{CH}_3)_2\text{SBr}_4$. The first, synthesised by the addition of bromine to dimethyl sulfide, was isolated as a single phase and is a charge-transfer adduct. The other two, both containing $(\text{CH}_3)_2\text{SBr}^+$ -like species, were found coprecipitated when dimethyl sulfide was added to bromine at -30°C .

Introduction

Compounds which are on the energy borderlines between different structural forms are currently receiving renewed attention, especially organophosphorus(v) halogen systems.¹⁻³ Interesting structural variety is also found among organosulfur adducts of halogens⁴⁻⁶ and, in particular, both ionic [e.g. $(\text{CH}_3)_2\text{SBr}^+\text{Br}^-$] and charge-transfer [$(\text{CH}_3)_2\text{S}\rightarrow\text{Br}_2$] forms have been proposed^{5,7} for the dimethyl sulfide–bromine system which is extensively used as a brominating agent in organic synthesis. Because of the difficulty of obtaining suitable single crystals for X-ray analysis, only limited structural characterisations, usually based on vibrational spectroscopy,^{6,7} have been reported.

The products of reaction of dimethyl sulfide with bromine are dependent on the reaction conditions. At room temperature, addition of bromine to dimethyl sulfide in dichloromethane yielded a yellow solid inferred by Raman spectroscopy to have a charge transfer form, $(\text{CH}_3)_2\text{S}\rightarrow\text{Br}_2$. Addition in the reverse order at -30°C gave an orange solid, apparently with an identical bromine analysis but presenting a rather different Raman spectrum interpreted as involving the $(\text{CH}_3)_2\text{SBr}^+$ bromodimethylsulfonium cation.⁶ The latter form is metastable toward the former, to which it transforms over a period of weeks on storage at room temperature, a behaviour which is reminiscent of the metastability among phosphorus halide systems.¹⁻³

As any discussion of the nature of bonding must rely at least partially on detailed structural information, we undertook a crystallographic study of the dimethyl sulfide–bromine reaction products. Owing to the aforementioned difficulty of growing suitable single crystals of the materials, high resolution powder X-ray diffraction exploiting synchrotron radiation has been employed.

Experimental

All manipulations were carried out in an inert atmosphere. The stable yellow, charge-transfer form of $(\text{CH}_3)_2\text{SBr}_2$ was prepared

by addition of bromine to dimethyl sulfide. The orange, metastable material was prepared by addition of dimethyl sulfide to bromine dissolved in dichloromethane, cooled to -30°C . The detailed syntheses are described elsewhere.⁶ The products were sealed in 0.5 mm diameter thin-walled glass capillary tubes. High resolution powder diffraction patterns were measured at the ESRF, Grenoble, using the powder diffractometer on the Swiss–Norwegian beamline BM1. The two patterns were collected in steps of 0.005° up to 65° in 2θ at wavelengths of 0.94734 \AA and 0.94718 \AA , counting for 3 s and 5 s per point for the stable and metastable forms, respectively.

For the stable form⁸ the pattern was indexed as monoclinic using the program FZON.⁹ The space group is $P2_1/a$. 964 integrated intensities were extracted by the LeBail¹⁰ method, and were input to the direct methods program SHELXS.¹¹ The structure was solved, then refined by the Rietveld method¹² using the program PROFIL.¹³ Scattering factors for neutral atoms were taken from ref. 14, with anomalous scattering terms calculated by the method of Cromer and Liebermann.¹⁵ Anisotropic thermal parameters refined to reasonable values for the bromine and sulfur atoms, and led to a significant improvement in the goodness of fit. Hydrogen atoms were restrained at 1.08 \AA from the carbon, and H–C–H angles were held at 109.5° . Final atomic parameters, R factors, etc. are given in Table 1. The observed and calculated diffraction patterns are shown in Fig. 1a.

Attempts to index the pattern of the metastable sample by standard indexing programs with a single lattice were unsuccessful, implying that the sample was multi-phase. Indexing of multi-phase powder patterns in which the phases present are unknown structures is a non-trivial problem, although a few structures have previously been indexed and solved from multi-phase powder patterns, for example in $\text{Rb}(\text{C}_5\text{H}_5)$, where there are two polymorphic phases present in the same sample.¹⁶ In that case, the peaks could be divided into two groups, one group being significantly broader than the other, thus allowing the peaks from the two phases to be distinguished, and then indexed. However, nothing in the shapes or widths of the

Table 1 Stable phase, $(\text{CH}_3)_2\text{SBr}_2$, space group $P2_1/a$, no. 14, $a = 11.4090(3)$, $b = 7.3820(1)$, $c = 7.4511(2)$ Å, $\beta = 92.821(2)^\circ$, calculated density: 2.35 g cm^{-3} , $R_{\text{wp}} = 12.9\%$, $R_1 = 8.2\%$, $R_{\text{exp}} = 5.5\%$

Atom	Site	Symmetry	X	Y	Z	B_{iso}
Br(1)	4g	1	0.8456(2)	-0.0167(3)	0.2065(4)	—
Br(2)	4g	1	0.6770(2)	0.2267(3)	0.2782(3)	—
S	4g	1	1.0151(4)	0.2398(7)	-0.1586(7)	—
C(1)	4g	1	1.105(1)	0.430(2)	-0.203(2)	2.8(4)
H(11)	4g	1	1.139(7)	0.417(8)	-0.333(6)	2.8(4)
H(21)	4g	1	1.054(3)	0.551(2)	-0.20(1)	2.8(4)
H(31)	4g	1	1.175(5)	0.437(9)	-0.102(8)	2.8(4)
C(2)	4g	1	0.933(1)	0.210(2)	-0.379(2)	2.8(4)
H(12)	4g	1	0.874(6)	0.098(9)	-0.373(5)	2.8(4)
H(22)	4g	1	0.884(7)	0.330(6)	-0.413(7)	2.8(4)
H(32)	4g	1	0.994(2)	0.18(1)	-0.480(3)	2.8(4)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Br(1)	3.4(1)	3.5(2)	5.4(2)	0.4(2)	-0.9(1)	-0.4(1)
Br(2)	3.5(2)	2.8(2)	7.3(2)	-0.2(2)	0.4(2)	0.1(2)
S	3.2(3)	3.4(3)	3.6(4)	0.7(3)	0.9(3)	-0.4(3)

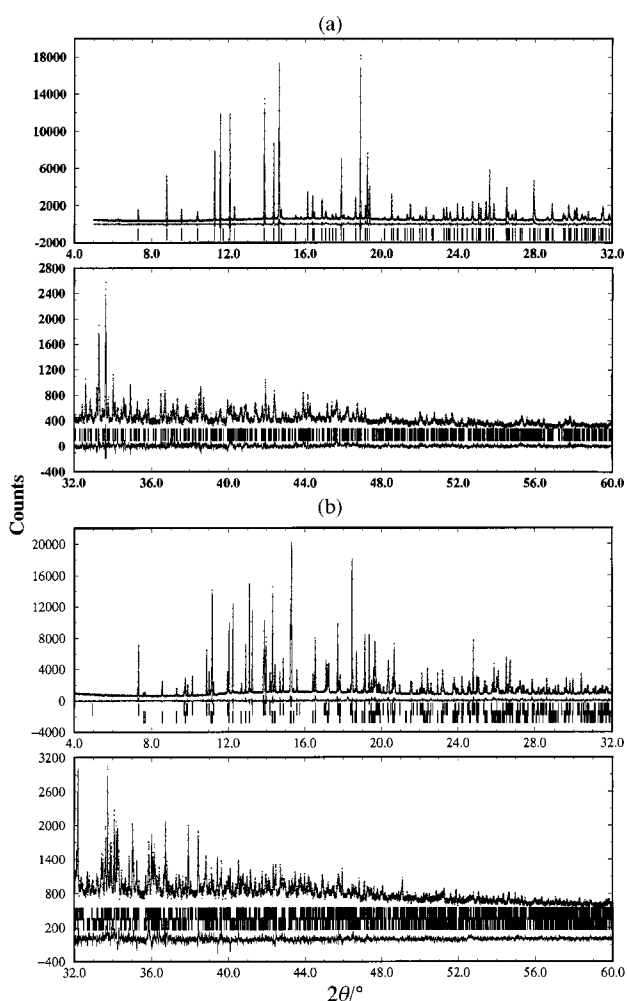


Fig. 1 Observed (points), calculated (line) and difference patterns for (a) the stable phase, and (b) the metastable phases.

diffraction peaks of the metastable product gives any clue as to the number of phases present.

Nevertheless a two-phase indexing was attempted using TREOR90.¹⁷ Possible indexations for any half of the first 50 peaks were exhaustively sought by systematically varying the maximum permitted unit-cell volume and axis length, the maximum Miller indices of the base lines, and the maximum number of unindexed peaks. Once a solution was found, the remaining

unindexed peaks were then reprocessed independently. A complete solution was eventually found, corresponding to two monoclinic cells with M_{20} values¹⁸ of 122 and 198; the latter cell could be transformed to *C*-centred orthorhombic. The high resolution of the data proved to be crucial for the success of such an indexing scheme. In particular, refitting several very slightly broadened peaks as doublets was necessary to identify one of the cells which has a monoclinic angle very near to 90° . The first peaks of both phases were either systematically absent or of unobservably low intensity, adding to the difficulty of indexing the pattern.

Systematic absences implied space groups *Cmce* and $P2_1/n$, respectively, in which integrated intensities were extracted by the LeBail method using FULLPROF.¹⁹ Both phases were then solved by direct methods using SIRPOW92.²⁰ The monoclinic phase was solved directly from the initial intensity extraction, the orthorhombic phase with intensities extracted while using a refined structural model to describe the intensities of the peaks belonging to the monoclinic phase. Additional peaks in the E-map revealed excess bromine in both phases. The final stoichiometries were found to be $(\text{CH}_3)_2\text{SBr}_{2.5}$ and $(\text{CH}_3)_2\text{SBr}_4$, for the orthorhombic and monoclinic phases, respectively, with weight fractions 39.4(2)% and 60.6(2)%, so the crystalline component of the sample is 80.7% Br by weight.

The two structures were refined using PROFIL.¹³ Hydrogen atoms and thermal parameters were treated as for the stable phase. Final parameters are given in Tables 2 and 3. The observed and calculated diffraction patterns are shown in Fig. 1b.

CCDC reference number 186/1241.

Discussion

Crystal structures

In all three phases, the sulfur atoms were found to be three-coordinate, with two methyl groups and one bromine atom, Br(1). The two C–S bonds in the dimethyl sulfide units are of different lengths, and the S–Br(1)–Br(2) arrangements are nearly linear. The atoms which participate in the $(\text{CH}_3)_2\text{SBr}_2$ units are labeled in Fig. 2; interatomic distances and angles for the three structures are given in Table 4.

Unequal C–S bond lengths are also seen in $(\text{CD}_3)_2\text{S}$, whose crystal structure has recently been determined by powder neutron diffraction,²¹ although the difference between the lengths of the two bonds is in this case smaller [$\approx 0.04(1)$ Å]. In the monoclinic phase, one C–S bond is much longer than expected, 1.99(2) Å, although C–S bonds of up to 2.1 Å are known. We

Table 2 Metastable orthorhombic phase, $(\text{CH}_3)_2\text{SBr}_{2.5}$, space group $Cmce$, no. 64, $a = 21.9676(2)$, $b = 11.1972(1)$, $c = 11.05307(8)$ Å, calculated density: 2.56 g cm^{-3} , weight fraction 39.4%, $R_{\text{wp}} = 9.8\%$, $R_1 = 9.0\%$, $R_{\text{exp}} = 5.2\%$

Atom	Site	Symmetry	X	Y	Z	B_{iso}
Br(1)	16g	1	-0.1706(2)	0.1074(2)	0.6248(2)	—
Br(2)	8e	.2.	3/4	-0.0680(4)	3/4	—
Br(3)	8m	<i>m.</i>	0	0.3712(4)	0.3629(4)	—
Br(4)	8m	<i>m.</i>	0	0.0299(4)	0.6057(4)	—
S	16g	1	-0.1105(3)	0.2377(6)	0.5260(6)	—
C(1)	16g	1	-0.1659(8)	0.326(1)	0.456(1)	1.8(3)
H(11)	16g	1	-0.145(2)	0.405(5)	0.42(1)	1.8(3)
H(12)	16g	1	-0.187(4)	0.276(4)	0.384(7)	1.8(3)
H(13)	16g	1	-0.200(3)	0.351(9)	0.522(3)	1.8(3)
C(2)	16g	1	-0.0803(6)	0.337(2)	0.647(1)	1.8(3)
H(21)	16g	1	-0.070(5)	0.424(3)	0.609(3)	1.8(3)
H(22)	16g	1	-0.114(2)	0.348(8)	0.717(5)	1.8(3)
H(23)	16g	1	-0.040(3)	0.299(5)	0.686(7)	1.8(3)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Br(1)	4.1(2)	4.2(2)	3.2(2)	-0.9(2)	-0.4(2)	-1.3(2)
Br(2)	3.6(3)	4.9(3)	3.3(3)	0	0.8(2)	0
Br(3)	3.6(3)	6.6(4)	2.9(3)	-0.7(3)	0	0
Br(4)	4.5(3)	4.9(3)	3.8(3)	-1.0(3)	0	0
S	3.0(4)	4.9(5)	1.7(4)	-0.6(4)	1.7(4)	-1.1(4)

Table 3 Metastable monoclinic phase, $(\text{CH}_3)_2\text{SBr}_4$, space group $P2_1/n$, no. 14, $a = 9.03811(7)$, $b = 11.65889(9)$, $c = 8.88592(7)$ Å, $\beta = 90.1338(5)^\circ$, calculated density: 2.71 g cm^{-3} , weight fraction 60.6%, $R_{\text{wp}} = 9.8\%$, $R_1 = 6.8\%$, $R_{\text{exp}} = 5.2\%$

Atom	Site	Symmetry	X	Y	Z	B_{iso}
Br(1)	4e	1	0.4445(4)	0.1441(3)	0.5915(4)	—
Br(2)	4e	1	0.6293(3)	0.3509(3)	0.0837(3)	—
Br(3)	4e	1	0.5421(4)	0.0941(3)	0.0266(4)	—
Br(4)	4e	1	0.5336(4)	0.4612(3)	0.3810(3)	—
S	4e	1	0.6959(7)	0.1291(8)	0.6040(7)	—
C(1)	4e	1	0.730(2)	0.262(1)	0.707(2)	2.7(4)
H(11)	4e	1	0.72(1)	0.246(3)	0.827(2)	2.7(4)
H(12)	4e	1	0.840(6)	0.294(6)	0.68(1)	2.7(4)
H(13)	4e	1	0.649(9)	0.326(4)	0.68(1)	2.7(4)
C(2)	4e	1	0.751(2)	0.165(2)	0.392(2)	2.7(4)
H(21)	4e	1	0.71(1)	0.250(4)	0.364(5)	2.7(4)
H(22)	4e	1	0.869(2)	0.16(1)	0.380(4)	2.7(4)
H(23)	4e	1	0.70(1)	0.103(6)	0.317(2)	2.7(4)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Br(1)	6.2(2)	5.8(3)	4.3(2)	-0.7(2)	1.7(2)	0.1(3)
Br(2)	2.1(2)	7.6(3)	8.0(3)	-0.5(3)	0.9(2)	-0.1(2)
Br(3)	5.2(2)	6.6(3)	5.6(2)	0.2(2)	0.1(2)	0.2(2)
Br(4)	8.1(3)	6.0(3)	4.9(2)	-0.1(2)	0.9(2)	-0.9(2)
S	1.1(4)	11.7(9)	5.4(6)	-0.2(6)	-1.1(4)	2.5(5)

have no explanation for this anomalous bond length, other than recognising that refining two complex structures from a single powder pattern is far from optimum. Constraining the C–S bonds to more reasonable values, for example the lengths found for the stable and orthorhombic phases, led to only a slight degradation of the fit ($\approx 0.2\%$ in R_1), but did not change significantly any of the other atomic positions. Since we cannot assign with certainty an “accepted” value for such bonds, the bond length was allowed to remain free in the final refinement.

In $(\text{CH}_3)_2\text{SBr}_2$, the S–Br(1) and Br(1)–Br(2) distances are close to those of the related complex between thiophene and bromine⁴ [2.321(4) Å and 2.724(2) Å, respectively]. The interaction between the sulfur (donor) atom and the bromine molecule (acceptor), and the consequent lengthening of the Br–Br distance from the value in molecular Br_2 [2.287(10) Å],²² are evidence for the charge-transfer nature of this complex, in agreement with the conclusions of the spectroscopic studies. A view of the crystal structure is given in Fig. 2.

In orthorhombic $(\text{CH}_3)_2\text{SBr}_{2.5}$ the S–Br(1) distance is 0.08 Å shorter and the Br(1)–Br(2) distance 0.26 Å longer than the equivalent distances in $(\text{CH}_3)_2\text{SBr}_2$. Each Br(2) is coordinated by two Br(1) atoms from symmetry-related $(\text{CH}_3)_2\text{SBr}(1)$ groups. This clearly resembles an ionic arrangement where a single $\text{Br}(2)^-$ ion is coordinated by two $(\text{CH}_3)_2\text{SBr}(1)^+$ species. The structure is shown in Fig. 3. The $\text{Br}(2)^-$ and $(\text{CH}_3)_2\text{SBr}(1)^+$ species form layers perpendicular to the crystallographic a axis. The remaining bromine is found between the layers in the form of near-linear, centrosymmetric Br_4^{2-} ions, with a long–short–long arrangement of distances, corresponding to the $\text{Br}(3)\cdots\text{Br}(4)$, $\text{Br}(4)\text{–Br}(4)$ and $\text{Br}(4)\cdots\text{Br}(3)$ distances respectively (Fig. 5a). This species has been observed in several other compounds such as W_6Br_{16} ²³ and intercalated graphite.²⁴ For each $(\text{CH}_3)_2\text{SBr}(1)^+$ there is 0.25 Br_4^{2-} , leading to a formulation of this compound as $(\text{CH}_3)_2\text{SBr}^+\text{Br}^-_{0.5}(\text{Br}_4^{2-})_{0.25}$.

Monoclinic $(\text{CH}_3)_2\text{SBr}_4$ has a somewhat more complicated structure, with features that are comparable with the other two

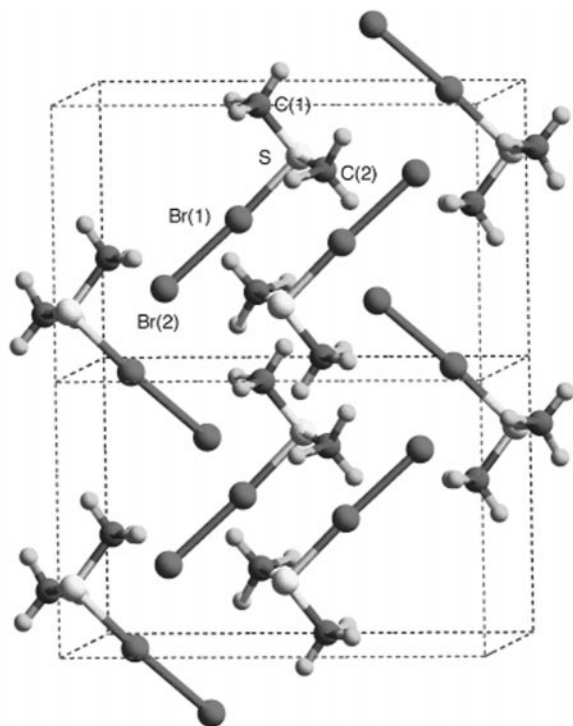


Fig. 2 A view of the structure of the stable phase $(\text{CH}_3)_2\text{SBr}_2$. Bromine atoms are dark grey, sulfurs are light grey, and carbons are medium grey. Atoms in the $(\text{CH}_3)_2\text{SBr}_2$ units, common to all three phases, are labelled.

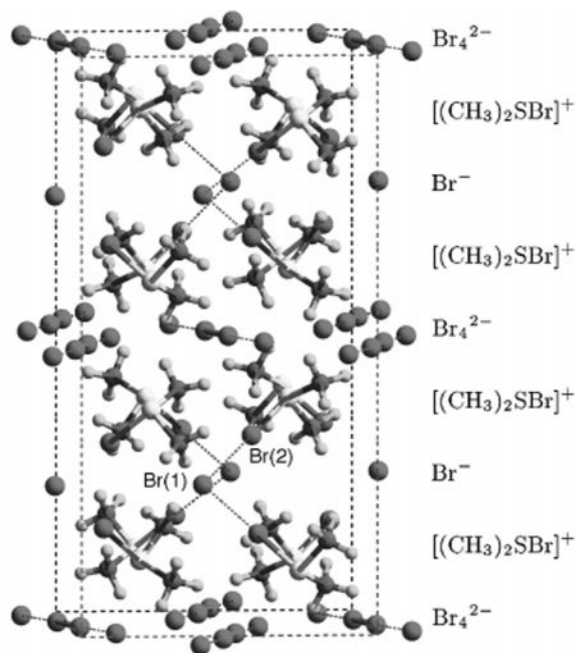


Fig. 3 A view of the structure of the orthorhombic phase $(\text{CH}_3)_2\text{SBr}_{2.5}$. The nature of the ionic layers is indicated at the right. Atoms are shaded as in Fig. 2, and Br(1) and Br(2) are indicated. See Fig. 5a for the labelling of the other bromine atoms.

phases described above. The S–Br(1) and Br(1)–Br(2) bonds are intermediate in length between those of the other two phases, with S–Br(1) 0.05 Å shorter and Br(1)–Br(2) 0.15 Å longer than the equivalent lengths in $(\text{CH}_3)_2\text{SBr}_2$. The Raman spectrum suggests only the presence of $(\text{CH}_3)_2\text{SBr}^+$ units in the metastable sample, implying that the monoclinic phase is also essentially ionic in character. However, whereas in the orthorhombic phase each $\text{Br}(2)^-$ is shared equally between two cations, the $\text{Br}(2)^-$ of the monoclinic metastable phase are coordinated by a single $(\text{CH}_3)_2\text{SBr}^+$, and, more distantly, by two Br_2 units. This

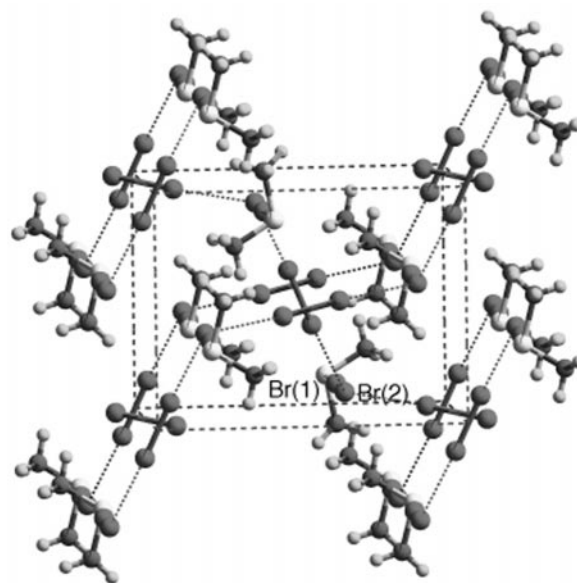


Fig. 4 A view of the structure of the metastable monoclinic phase $(\text{CH}_3)_2\text{SBr}_4$. The dashed lines indicate the Br networks. Atoms are shaded as in Fig. 2, and Br(1) and Br(2) are indicated. See Fig. 5b for the labelling of the other bromine atoms.

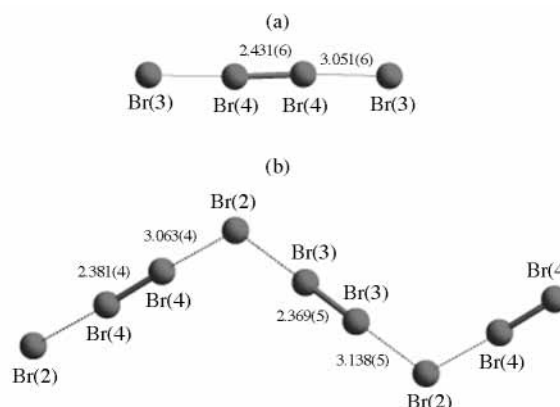


Fig. 5 (a) A Br_4^{2-} ion from the orthorhombic phase. (b) A section of the Br network from the metastable monoclinic phase.

configuration results in Br(1)–Br(2) distances intermediate between those found in the charge-transfer and orthorhombic ionic phases.

The two Br_2 units, at 3.138(5) Å and 3.063(4) Å to Br(2), are composed of two Br(3) or two Br(4) atoms, whose bond lengths are themselves increased by 0.08 Å and 0.09 Å with respect to diatomic Br_2 , respectively. Each of these Br_2 units coordinates to two Br(2), thus linking together the $(\text{CH}_3)_2\text{SBr}_2$ units into a structure consisting of interleaving $\cdots \text{Br}(3)\text{--Br}(3)\cdots \text{Br}(2)\cdots \text{Br}(4)\text{--Br}(4)\cdots$ chains.

A section of such a chain is shown in Fig. 5b, and is indicated by dashed lines in Fig. 4. The slightly asymmetric $\cdots \text{Br}(2)\cdots \text{Br}\text{--Br}\cdots \text{Br}(2)\cdots$ segments of the chains are nearly linear, as seen for the Br_4^{2-} ions in $(\text{CH}_3)_2\text{SBr}_{2.5}$. However, with the formation of extended chains, and the coordination of Br(2) also to Br(1), the units are not isolated Br_4^{2-} , and this is reflected in a Br–Br distance on average 0.06 Å shorter and a Br \cdots Br distance on average 0.05 Å longer than in the distinct Br_4^{2-} ions seen in the orthorhombic structure. Zigzagging bromine chains have occasionally been observed in compounds such as CsBr_3 ²⁵ and PBr_7 ,²⁶ although in these cases the building blocks were Br_3^- ions.

The end products precipitated by the two methods presumably reflect the situation in solution. When dimethyl sulfide is added to bromine, the high bromine concentration favours the

Table 4 Bond distances (Å) and angles (°) in the three phases

a In the (CH ₃) ₂ SBr ₂ units				
Phase	C(1)–S	C(2)–S	S–Br(1)	Br(1)–Br(2)
(CH ₃) ₂ S→Br ₂	1.778(14)	1.862(12)	2.329(6)	2.705(3)
(CH ₃) ₂ SBr ⁺ Br ⁻ _{0.5} (Br ₄ ²⁻) _{0.25}	1.747(17)	1.867(17)	2.251(7)	2.969(4)
(CH ₃) ₂ SBr ⁺ Br ⁻ Br ₂	1.829(19)	1.989(17)	2.281(7)	2.851(4)
b In the (CH ₃) ₂ SBr ₂ units				
Phase	C(1)–S–C(2)	C(1)–S–Br(1)	C(2)–S–Br(1)	S–Br(1)–Br(2)
(CH ₃) ₂ S→Br ₂	101.5(6)	97.2(5)	95.8(4)	176.1(2)
(CH ₃) ₂ SBr ⁺ Br ⁻ _{0.5} (Br ₄ ²⁻) _{0.25}	103.3(7)	99.9(6)	104.3(6)	178.6(2)
(CH ₃) ₂ SBr ⁺ Br ⁻ Br ₂	104.9(8)	97.2(6)	100.8(5)	176.4(3)
c In the Br ₄ ²⁻ unit in (CH ₃) ₂ SBr ⁺ Br ⁻ _{0.5} (Br ₄ ²⁻) _{0.25}				
Br(3)–Br(4)	Br(4)–Br(4)	Br(1)–Br(2)–Br(1)	Br(3)–Br(4)–Br(4)	
3.051(6)	2.431(6)	97.17(14)	174.68(21)	
d In the Br ⁻ ⋯Br ₂ ⋯Br ⁻ chains in (CH ₃) ₂ SBr ⁺ Br ⁻ Br ₂				
Br(3)–Br(2)	Br(4)–Br(2)	Br(3)–Br(3)	Br(4)–Br(4)	
3.138(5)	3.063(4)	2.369(5)	2.381(4)	
e In the Br ⁻ ⋯Br ₂ ⋯Br ⁻ chains in (CH ₃) ₂ SBr ⁺ Br ⁻ Br ₂				
Br(1)–Br(2)–Br(3)	Br(1)–Br(2)–Br(4)	Br(3)–Br(2)–Br(4)	Br(2)–Br(3)–Br(3)	Br(2)–Br(4)–Br(4)
105.87(13)	104.78(13)	117.95(12)	175.14(16)	176.88(16)

Table 5 Revised stretching mode assignments and relative intensities of Raman bands of the three forms

(CH ₃) ₂ S→Br ₂			(CH ₃) ₂ SBr ⁺ Br ⁻ _{0.5} (Br ₄ ²⁻) _{0.25} and (CH ₃) ₂ SBr ⁺ Br ⁻ Br ₂		
Wavenumber/ cm ⁻¹	Relative intensity	Assignment	Wavenumber/ cm ⁻¹	Relative intensity	Assignment ^a
720	2	S–C asym str	718	1	ν ₅ (A'') S–C asym str
672	6	S–C sym str	666	2	ν ₁ (A') S–C sym str
			346	93	ν ₂ (A') S–Br str
304	sh	} ν(SBr)	232	100	ν(Br–Br) of Br ₂ str
295	45				
285	100				
215	37	} ν(Br–Br)			
204	sh				

^a (CH₃)₂SBr⁺ assignments are made on the basis of a C₂SBr skeleton of C_s symmetry.

formation of the bromine-rich monoclinic (CH₃)₂SBr₄. When the concentration of bromine falls, (CH₃)₂SBr_{2.5} is formed. If the addition of the reactants is reversed, and bromine is added to dimethyl sulfide, competition between the dimethyl sulfide molecules for the relatively few bromine molecules in solution leads to the compound with the lowest bromine content being formed. This compound, (CH₃)₂SBr₂, is the most stable of the three, and over a period of weeks is formed in the solid state by the gradual bromine loss by the other two. On the basis of the bromine content of the two metastable phases, the bromine content of the metastable sample should be 80.7% by weight, as compared to the 72.1% required for a (CH₃)₂SBr₂ stoichiometry and initially found by chemical analysis. The reason for the

discrepancy in the bromine chemical analysis probably derives from the instability of the metastable material.

A simple conversion from a metastable ionic form to the isomeric charge transfer form is now clearly ruled out. However, that the system is delicately balanced on an energy borderline between different structural forms is amply confirmed by the X-ray data with the identification of two metastable modifications, one ionic in nature, the other having a predominantly ionic character, in addition to the charge transfer form. There is presumably only a very small difference in the stability of the two metastable forms, particularly as the metastable monoclinic material displays structural features intermediate between the charge-transfer and orthorhombic ionic forms.

Raman spectra

In light of the structural information now available, some revision of the original⁶ Raman band assignments is necessary. Suggested new assignments (made mainly on the basis of the bond length data) are shown in Table 5. The original assignment of $\nu(\text{S}-\text{Br})$ at 346 cm^{-1} remains unchanged. This vibration is shifted to low frequency (by $\approx 60\text{ cm}^{-1}$) relative to the same vibration in salts such as $(\text{CH}_3)_2\text{SBr}^+\text{AlBr}_4^-$ which presumably reflects some weakening of the S–Br bond due to the significant interaction between the cationic bromine and the Br^- of the anion. It is clear that the original Raman spectrum of the ionic material does not clearly differentiate between the two metastable forms which have now been characterised, only a single band being observed at 346 cm^{-1} . However, a spectrum recorded at -100°C shows splitting of this S–Br stretching mode and also of the band now assigned to the Br–Br stretch. It is possible that these splittings may arise from the low temperature resolution of bands originating from the two closely related structures.

Conclusion

The use of powder synchrotron X-ray diffraction has allowed the structures of three adducts formed between dimethyl sulfide and bromine to be determined.

For the metastable material, two distinct phases are found to be coprecipitated. Solution of these two structures from one powder diffraction pattern relies crucially on the excellent resolution of the diffraction data, to identify and allow indexing of the peaks from the two phases. For the single-phase, stable $(\text{CH}_3)_2\text{S}\rightarrow\text{Br}_2$, a structure consistent with a charge-transfer complex has been found. Metastable orthorhombic $(\text{CH}_3)_2\text{SBr}_{2.5}$ has clearly an ionic structure, with each Br^- ion coordinated by two $(\text{CH}_3)_2\text{SBr}^+$ units in a layer-like arrangement. Between the layers are found discrete Br_4^{2-} ions. The second metastable phase, monoclinic $(\text{CH}_3)_2\text{SBr}_4$, appears to be a structure intermediate between the other two, with S–Br(1) and Br(1)–Br(2) distances midway between the ionic and charge transfer values. The Br(2) atoms are linked together by Br_2 units as part of extended zigzag chains, with $\cdots\text{Br}(2)\cdots\text{Br}-\text{Br}\cdots\text{Br}(2)\cdots$ segments resembling the Br_4^{2-} ions in the orthorhombic structure. However the Br(2) $\cdots\text{Br}$ and Br–Br distances are modified and reflect the fact that in the extended chain the Br(2) is associated more closely with a $(\text{CH}_3)_2\text{SBr}^+$ than with the Br_2 units which link them together.

Acknowledgements

We thank the Swiss–Norwegian beam line (BM1) at the ESRF for provision of synchrotron radiation beam time.

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