

Crystal Structure of Bis[1,4-bis(tetramethylenesulfonio)butane] Iodide Tris(triiodide)

Bertil Norén,^a Åke Oskarsson^b and Christer Svensson^a

^aInorganic Chemistry, Chemical Center, University of Lund, Box 124, S-221 00 Lund and ^bDepartment of Chemistry, University College of Sundsvall/Härnösand, Box 860, S-851 24 Sundsvall, Sweden

Norén, B., Oskarsson, Å. and Svensson, C., 1986. Crystal Structure of Bis[1,4-bis(tetramethylenesulfonio)butane] Iodide Tris(triiodide). – Acta Chem. Scand. A 40: 546–549.

Solid iodide solvates of the noble metals can be synthesized by treating a metal foil with a solution of iodine in a solvent coordinating via S or

N.^{1,2} Single crystals grow on the surface of the metal even at room temperature. These crystals are of a better quality than those prepared by

Table 1. Atomic coordinates and isotropic thermal parameters with estimated standard deviations. U_{iso} is calculated from the anisotropic temperature factors as $(1/6 \pi^2) \text{trace}(\beta \cdot q)$.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{iso}/\text{Å}^2$
I	1/2	–0.05670(10)	0.39879(10)	0.0504(7)
I11	1/2	0.10768(10)	0.16735(9)	0.0504(7)
I12	1/2	0.22362(10)	0.26183(9)	0.0470(6)
I13	1/2	0.34066(11)	0.36204(10)	0.0593(7)
I21	0	0.21772(11)	0.35642(10)	0.0615(7)
I22	0	0.17015(9)	0.21973(10)	0.0554(7)
I23	0	0.11999(12)	0.08932(11)	0.0694(8)
I31	1/2	0.39454(9)	0.10539(9)	0.0436(6)
I32	1/2	1/2	0	0.0370(8)
I41	0.25935(15)	0	0	0.0457(6)
I42	1/2	0	0	0.0399(8)
S1	0.3441(3)	0.2099(2)	0.4980(2)	0.034(1)
C11	0.2925(13)	0.2079(8)	0.5799(7)	0.036(6)
C12	0.2119(13)	0.2745(9)	0.5851(8)	0.044(6)
C13	0.1577(14)	0.2840(9)	0.5203(8)	0.046(7)
C14	0.2505(13)	0.2844(9)	0.4719(8)	0.040(6)
S2	0.1769(3)	–0.0167(2)	0.2537(2)	0.035(1)
C21	0.2460(14)	–0.1021(9)	0.2768(9)	0.050(7)
C22	0.3268(26)	–0.1170(18)	0.2251(12)	0.156(16)
C23	0.3225(16)	–0.0765(9)	0.1725(8)	0.049(7)
C24	0.2354(13)	–0.0155(10)	0.1748(8)	0.044(6)
C1	0.2793(13)	0.1273(9)	0.4655(7)	0.037(6)
C2	0.3007(13)	0.1214(8)	0.3945(8)	0.041(6)
C3	0.2340(13)	0.0586(8)	0.3632(8)	0.037(6)
C4	0.2597(13)	0.0532(8)	0.2932(7)	0.037(6)

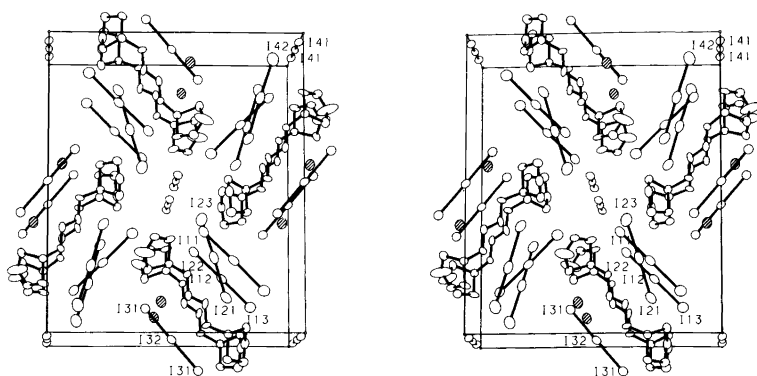


Fig. 1. Stereoscopic packing diagram of the unit cell contents. The monoiodide ions are shadowed. The origin is at the lower left hand corner with the *a* axis pointing out of the page and the *b* axis horizontal.

conventional methods, i.e. dissolving the metal halide in the hot solvent and cooling the solution, or slowly evaporating a concentrated solution. An attempt to prepare a tetrahydrothiophene (THT) solvate of platinum iodide by oxidizing Pt(0) with I₂ dissolved in THT resulted in the title compound.

A piece of platinum foil was treated with a solution of 0.5 g I₂ in 5 mL THT. No reaction was observed at room temperature. Heating to 110°C for several hours followed by cooling to room temperature resulted in dark red needle-shaped crystals. The yield increased with exposure time at 110°C. Comparative experiments with no plat-

inum foil present gave the same product as verified with powder photograms. Furthermore, the platinum seemed to have no influence on the reaction rate. The crystals were washed with cool ethyl acetate and analysed for carbon and hydrogen using an automatic Carlo Erba elemental analyzer. Sulfur and iodine were determined by the Schöniger flask combustion method. The following results were obtained (calculated values for the empirical formula, C₁₂H₂₄I₃S₂, are given in parentheses): C, 17.4% (16.6); H, 2.77% (2.79); S, 7.8% (7.4); I, 73.3% (73.2). A single crystal with the dimensions 0.29×0.09×0.06 mm was used for data collection on a CAD-4 diffract-

Table 2. Selected interatomic distances (Å) and angles (°) with estimated standard deviations.

A. Geometry of the tetrahydrothiophenium rings.

S1-C11	1.83(2)	S1-C11-C12	105.6(1)	S2-C21	1.81(2)	S2-C21-C22	105.2(2)
C11-C12	1.55(2)	C11-C12-C13	107.3(1)	C21-C22	1.49(3)	C21-C22-C23	119.0(3)
C12-C13	1.52(2)	C12-C13-C14	106.1(1)	C22-C23	1.32(3)	C22-C23-C24	113.3(7)
C13-C14	1.52(2)	C13-C14-S1	104.9(1)	C23-C24	1.52(2)	C23-C24-S2	107.1(9)
C14-S1	1.84(2)	C14-S1-C11	94.7(1)	C24-S2	1.81(2)	C24-S2-C21	94.1(5)

B. Parameters along the sulfur - butane - sulfur chain.

S1-C1	1.81(2)	C11-S1-C1	101.0(1)	C2-C3-C4	110.8(1)	S1-C1-C2-C3	-172(1)
C1-C2	1.52(2)	C14-S1-C1	102.1(1)	C3-C4-S2	112.1(1)	C1-C2-C3-C4	-179(1)
C2-C3	1.54(2)	S1-C1-C2	110.7(1)	C4-S2-C21	101.7(1)	C2-C3-C4-S2	-177(1)
C3-C4	1.51(2)	C1-C2-C3	112.4(1)	C4-S2-C24	101.2(5)		
C4-S2	1.81(2)						

C. Geometry of the triiodide ions.

I11-I12	2.873(3)	I11-I12-I13	178.6(1)	I21-I22	2.997(3)	I21-I22-I23	178.4(1)
I12-I13	2.971(3)			I22-I23	2.885(3)		
I31-I32	2.911(2)			I41-I42	2.928(3)		

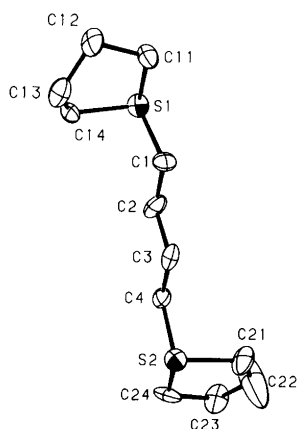


Fig. 2. Perspective view of the 1,4-bis(tetramethylenesulfonio)butane ion showing atom labelling as identified in Table 1. Hydrogen atoms are not shown.

ometer employing graphite-monochromatized MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). Laue class and systematic extinctions are consistent with the space groups $P2_1n$ and $Pmnn$. Unit cell dimensions were determined by least-squares calculations from θ angles for 25 reflections measured on the diffractometer in the bisecting mode: $a = 12.165(9)$; $b = 17.90(2)$; $c = 21.021(8) \text{ \AA}$; $Z = 4$. The intensities of 3134 reflections in one octant of the reflection sphere ($3.0 < \theta < 22.0$) were measured with ω - 2θ scan ($\Delta\omega = 0.9^\circ + 0.5^\circ \tan \theta$). The ratio $\sigma_c(I)/I$ requested in a scan was 0.03 and the maximum recording time 120 s. The total variations in 2 standard reflections were less than 10%; no correction was applied. I and $\sigma_c(I)$ were corrected for Lorentz, polarisation and absorption effects (transmission factors 0.390–0.696). Only the 1574 reflections with $I > 3\sigma_c(I)$ were used in the difference Fourier and least-squares calculations.

The structure was solved using the MULTAN 80 program with magic integers³ assuming the noncentrosymmetric space group $P2_1n$. The first run revealed all iodine atoms located at positions corresponding to the mirror plane, m , and the intersection of the mirror plane and the two-fold axis, $2/m$, in the space group $Pmnn$. A difference Fourier in the centrosymmetric space group $Pmnn$ revealed the S and C atoms. The positions of the H atoms in the CH₂ groups were calculated assuming tetrahedral C atoms with C–H =

1.00 \AA . The positions of the H atoms were not refined and they were assigned fixed isotropic thermal parameters, $U_{\text{iso}} = 0.1 \text{ \AA}^2$. All other atoms were refined anisotropically. In the final cycles of full matrix least-squares refinement, the weights were calculated from $w^{-1} = \sigma_c^2(|F_o|) + (0.03|F_o|)^2$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized. The final R values were $R = 0.035$ and $R_w = 0.044$. A δR plot resulted in a straight line with slope 1.01 and intercept -0.05 . Scattering factors with corrections for anomalous dispersion were taken from International Tables for X-ray crystallography.⁴ Tables of $|F_o|$, $\sigma(|F_o|)$ and $|F_c|$ are available on request from the authors. Final atomic parameters are given in Table 1, and selected distances and angles in Table 2. The computer programs used are those compiled and amended by Lundgren.⁵

The structure is composed of disulfonium, moniodide and triiodide ions. The packing is shown in Fig. 1. The labelling of the atoms in the disulfonium ion is given in Fig. 2. The geometry around the sulfur atoms is pyramidal, suggesting a state of sp^3 hybridization with a lone pair of electrons.^{6–8} The C–S bond lengths within the ring systems are not significantly different from those observed in metal-coordinated THT^{9,10} or those observed for the THT molecule in the gaseous phase¹¹ (Table 2A). The five-ring at S1 is approximately a C12, C13 half-chair. The other ring at S2 seems to have a more planar conformation, which could be the average of a disorder between two C22 envelope forms. The conformation of the carbon chain joining the two THT molecules is all *trans* and is almost planar (Table 2B). Such a conformation gives a maximum charge separation assuming that the positive charge is located primarily on the S atoms. The geometry of the triiodide ions is given in Table 2C. They are all close to linear. The bond distances within two of them are equal by symmetry. The two I–I distances within the other two triiodide ions are significantly different. The dimensions of an I₃[−] ion are thus dependent on the environment, which is further supported by other studies.^{12,13} The shortest interionic I...I contacts are 4.011(2) \AA between I11 and I42, and 4.254(3) \AA between I23 and I41.

It is known that THT reacts with tungsten halides to form 1,4-dihalobutanes, e.g. $\text{WCl}_6 + \overline{\text{CH}_2(\text{CH}_2)_3\text{S}} \rightarrow \text{WCl}_4\text{S} + \text{Cl}(\text{CH}_2)_4\text{Cl}$.¹⁴ The 1,4-

dihalobutane may react with excess THT to form the 1,4-bis(tetramethylenesulfonio)butane ion.¹⁴ In the present investigation, it was found that metal complexes are not needed for the formation of the sulfonium ion; it is formed directly by heating THT and I₂.

References

1. Ahrland, S., Norén, B. and Oskarsson, Å. *Inorg. Chem.* 24 (1985) 1330.
2. Nilsson, K. and Oskarsson, Å. *Acta Chem. Scand. A* 39 (1985) 663.
3. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, J. P., Declercq, J.-P. and Woolfson, M. M. *MULTAN: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, University of York, England and Louvain, Belgium 1980.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
5. Lundgren, J. O. *Crystallographic Computer Programs*, Report No. UUIC-B13-4-05, University of Uppsala, Uppsala 1982.
6. Lopez-Castro, A. and Truter, M. R. *Acta Crystallogr.* 17 (1964) 465.
7. Barnes, W. and Sundaralingam, M. *Acta Crystallogr. B* 29, (1973) 1868.
8. Grue-Sørensen, G., Kjær, A., Norrestam, R. and Wiczorkowska, E. *Acta Chem. Scand. B* 31 (1977) 859.
9. Norén, B. and Oskarsson, Å. *Acta Chem. Scand. A* 38 (1984) 479.
10. Norén, B. and Oskarsson, Å. *Acta Chem. Scand. A* 39 (1985) 701.
11. Náhlovská, Z., Náhlovský, B. and Seip, H. M. *Acta Chem. Scand.* 23 (1969) 3534.
12. Tebbe, K.-F. *Z. Anorg. Allg. Chem.* 489 (1982) 93.
13. Tebbe, K.-F., Freckmann, B., Hörner, M., Hiller, W. and Strähle, J. *Acta Crystallogr. C* 41 (1985) 660.
14. Boorman, P. M., Chivers, T. and Mahadev, K. N. *Can. J. Chem.* 55 (1977) 869.

Received May 22, 1986.