Crystal Structure Analysis of the Carbon Tetrabromide Clathrate of Hexakis(phenylseleno)benzene

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Abstract. The 1 : 2 inclusion compound of hexakis(phenylseleno)benzene (**1**) with CBr_4 is trigonal, space group $R\bar{3}$, with $a = 14.474(3)$, $c = 21.487(4)$ Å, and three host and six guest molecules in a unit cell referred to hexagonal axes. A true clathrate structure is found and in each closed cage there are two carbon tetrabromide guest molecules, orientated such that a C–Br bond of each is colinear with the c-axis of the crystal.

Key words: clathrate, X-ray crystal structure analysis, hexakis(phenylseleno)benzene host, carbon tetrabromide guest species.

1. Introduction

Recently, in connection with a systematic study of the factors responsible for inclusion-compound formation, we have described [1] the synthesis of hexakis(phenylseleno)benzene (**1**). This molecule, apart from its host properties [1], is also interesting in the sense that it represents, to our knowledge, the first example of a system possessing six selenium atoms bonded directly to a single benzene ring. Accordingly, an X-ray study of (**1**), as its CBr_4 adduct, was undertaken. The main objectives of this work were to define the molecular geometry of host (**1**), to determine the nature of the voids, and to elucidate the host-guest interactions present in this representative adduct of (**1**).

(**1**)
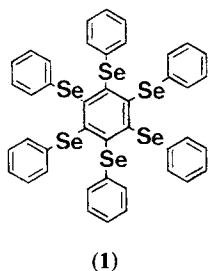
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2. Crystal Data

The CBr_4 adduct of (1) was obtained [1] as beautiful orange rhombs on recrystallisation of (1) from pentachloroethane containing excess carbon tetrabromide and an exact 1 : 2 host-guest ratio was determined by microanalysis for halogen. The compound $C_{42}H_{30}Se_6 \cdot 2CBr_4$ had a formula weight of 1671.7. Crystals were trigonal, with $a = 11.009(2)$ Å, $\alpha = 82.28(1)°$, $U = 1301.0$ Å^3, $Z = 1$, $D_c = 2.13$ g cm^{-3}, $\mu(MoK_\alpha) = 110.8$ cm^{-1}, crystallising in space group $R\bar{3}$ (No. 148). A total of 1527 independent X-ray intensities were measured at room temperature (20°) by a θ–ω scan on a Nonius CAD4 diffractometer, using graphite-mono-chromated MoK_α radiation. These comprised all possible reflections with $\sin\theta/\lambda < 0.59$ Å^{-1}. There were 1031 reflections having $F^2 > 3\sigma(F^2)$ considered as being observed, where $\sigma(F^2) = [C + 4(B_1 + B_2) + 0.0009I^2]^{1/2}/(t_cLp)$, where C is the total integrated count in time t_c, B_1 and B_2 are background counts, $I = C-2(B_1 + B_2)$, Lp is the correction factor for the Lorentz and polarisation effects, and $F^2 = I/(t_cLp)$. The intensities were corrected for absorption by an empirical method [2]. Counting coincidence errors were avoided by the use of an attenuator on high intensities. Unit cell parameters were determined by a least-squares refinement of the diffractometer setting angles for 25 reflections. Computations were carried out on a Gould SEL 32/27 computer in the laboratory (the principal computer programs used are listed in reference [3]) and the atomic scattering factors were taken from reference [4].

3. Structure Determination

The formula corresponds to six asymmetric units, so that the host molecules and pairs of CBr_4 guest molecules lie in positions which have a crystallographic $\bar{3}$ symmetry. The structure was solved by direct methods using the MITHRIL program [3] and although the hydrogen atoms were located in difference-Fourier maps during the anisotropic least-squares refinement, their positions could not be refined entirely successfully. They were therefore placed in theoretical positions with a C – H bond length of 1.084 Å and allowed to ride on their attached carbon atoms and given the fixed isotropic temperature factors $U = 0.1$ Å^2. The side-chain phenyl group atoms also failed to refine independently with an acceptable geometry and were constrained to lie in a planar hexagonal group with sides of length 1.395 Å. Minor peaks on difference maps indicated a low-occupancy secondary guest orientation, of which neither the carbon atom nor a three-fold axial Br atom could be unequivocally located. The other minor Br atom was included in the refinement with the isotropic temperature factor and occupancy both being allowed to vary and the occupancy was constrained to 1.0 minus the occupancy of the major guest orientation. The final value of the latter occupancy was 0.82(1). A value of R 0.049 for the observed reflections was obtained, with R' 0.063 $[R' = (\Sigma w\Delta^2/\Sigma w|F_O|^2)^{1/2}]$. The function minimised was $\Sigma w\Delta^2$, where $w = 1/\sigma^2(F_O)$, $\Delta = (|F_O| - |F_C|)$.

4. Results

The atomic coordinates and their estimated standard deviations are given in Table I and Table II shows selected bond lengths, bond angles and torsion angles. The labelling of the atoms is shown in Figure 1. Anisotropic temperature factors and observed and calculated structure factors are given in Supplementary Publication Sup. 82002.

Table I. Fractional atomic coordinates and isotropic temperature factors (Ångstrom squared), with standard deviations in the least significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors are shown.

	x/a	y/b	z/c	U
Se(2)	0.74127(8)	0.14409(8)	0.13147(9)	0.0322(6)
Br(1)	0.4202(2)	0.1750(2)	0.3159(2)	0.118(2)
Br(2)^a	0.5197(15)	0.2875(15)	0.3984(15)	0.171(7)
Br(3)	0.4206(3)	0.4206	0.4206	0.210(3)
C(1)	0.8894(7)	0.0604(8)	0.0528(8)	0.027(5)
C(3)	0.7924(10)	0.3026(7)	0.1339(7)	0.039(6)
C(4)	0.9134(9)	·0.3210(8)	0.1437(12)	0.048(7)
C(5)	0.9416(7)	0.4390(10)	0.1531(9)	0.068(9)
C(6)	0.8487(10)	0.5385(7)	0.1528(7)	0.08(1)
C(7)	0.7276(9)	0.5201(8)	0.1430(12)	0.08(1)
C(8)	0.6994(7)	0.4022(10)	0.1336(9)	0.060(9)
C(9)	0.3275(17)	0.3275	0.3275	0.082(9)
H(4)	0.9857	0.2438	0.1439	0.100
H(5)	1.0357	0.4534	0.1606	0.100
H(6)	0.8705	0.6302	0.1600	0.100
H(7)	0.6553	0.5974	0.1428	0.100
H(8)	0.6054	0.3878	0.1261	0.100

^{a} Br(2) is the symmetry-unique non-axial bromine atom corresponding to a minor guest orientation.

Table II. Roman numerals refer to the following transformations of the atomic coordinates: I $1-y$, $-z$, $1-x$; II $1-z$, $1-x$, $-y$, III y, z, x

(a) Bond lengths (Ångstroms)

Se(2) – C(1)	1.921(8)	Se(2) – C(3)	1.909(8)
Br(1) – C(9)	1.854(9)	Br(3) – C(9)	1.998(13)
C(1) – C(1)^I	1.400(12)		

(b) Valency angles (degrees)

C(1) – Se(2) – C(3)	100.5(4)	Se(2) – C(1) – C(1)^I	118.9(6)
Se(2) – C(1) – C(1)^{II}	121.2(6)	Se(2) – C(3) – C(4)	123.6(7)
Se(2) – C(3) – C(8)	116.3(8)	Br(1) – C(9) – Br(3)	106.0(8)
Br(1) – C(9) – Br(1)^{III}	112.7(9)		

(c) Torsion angles (degrees)

C(1) – Se(2) – C(3) – C(4)	– 31.3(9)	C(1) – Se(2) – C(3) – C(8)	152.8(8)
C(1)^I – C(1) – Se(2) – C(3)	126.9(8)	C(1)^{II} – C(1) – Se(2) – C(3)	– 53.1(7)
Se(2) – C(3) – C(4) – C(5)	– 175.7(14)	Se(2) – C(3) – C(8) – C(7)	176.0(13)

5. Discussion of the Structure

Figure 1 shows a general view of the hexakis(phenylseleno)benzene (**1**) host molecule in its CBr$_4$ inclusion compound which is located on a point of $\bar{3}$ symmetry and the crystallographically equivalent phenyl groups are situated, alternately, above and below the plane of the central benzene ring. The relative disposition of the central and side-chain aromatic rings may be appreciated by considering the torsion angles C(1)^{II} – C(1) – Se(2) – C(3) and
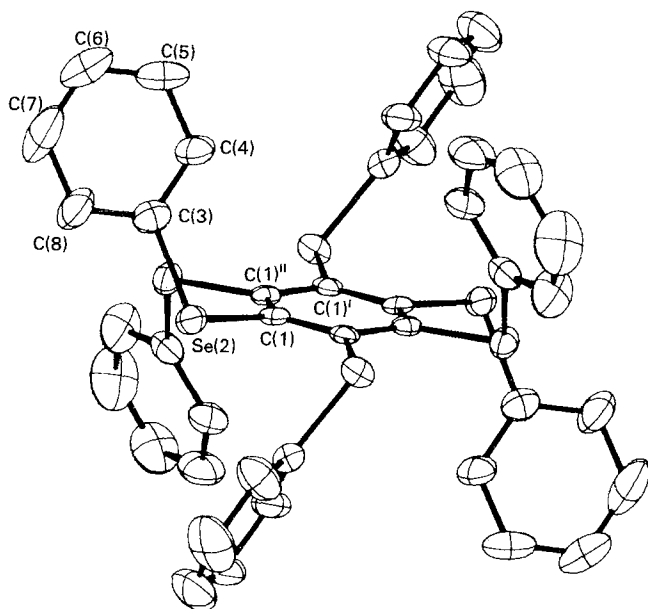
Fig. 1. A general view illustrating the molecular structure of the host hexa-kis(phenylseleno)benzene (1) in the crystal of its CBr_4 clathrate. The superscripts refer to the following transformations of the atomic coordinates: I, $1-y$, $-z$, $1-x$; II, $1-z$, $1-x$, $-y$.

$C(1) - Se(2) - C(3) - C(4)$, which are -53 and $-31°$ respectively. These may be compared with the corresponding torsion angles of -56 and $-28°$ for hexakis(phenylthio)benzene, $C_6(SPh)_6$, in its carbon tetrachloride clathrate [5]. The selenium atom is displaced by 0.12 Å both from the phenyl and central benzene ring planes. The carbon-selenium bond lengths in (1), 1.91(1) and 1.92(1) Å, may be compared with those for the selenium(II)-aryl bonds available in the literature, for example 1.93(3) Å for di-p-tolyl selenide [6], 1.92(5) Å for 1,4-$(SeCN)_2C_6H_4$ [7], and 1.93(5) Å for diphenyl diselenide [8].

The host-guest packing in the crystal is shown in the stereoview in Figure 2. There are two carbon tetrabromide guest molecules present in each closed cage, orientated such that a C–Br bond of each lies along the rhomb diagonal. Notwithstanding the noticeably large temperature factor for the axial Br atom, the intermolecular Br...Br contact of 3.41(1) Å
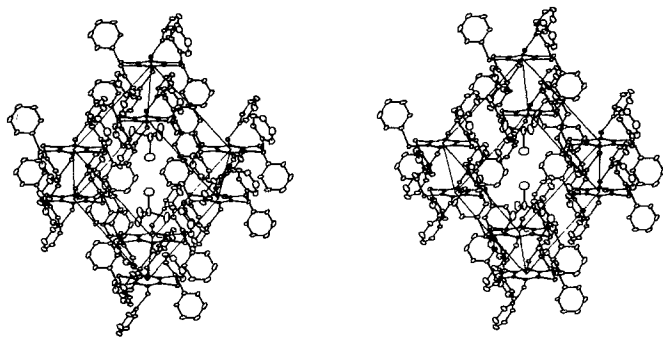

Fig. 2. A stereoview showing the host-guest packing in the crystal of the CBr_4 clathrate of (1).

appears to be shorter than the shortest intermolecular distance between bromine atoms, 3.78(2) Å found in the molecular crystal of CBr$_4$ (phase II) [9]. Interestingly, the corresponding Cl$\cdots$Cl distance of 3.41(1) Å in the CCl$_4$ clathrate of C$_6$(SPh)$_6$ [5] is also significantly shorter than the average of the four shortest Cl...Cl distances, 3.58(1) Å, found in phase II of crystalline carbon tetrachloride [10]. The guest molecule, one C–Br bond length of which appears to be artificially shortened by thermal motion [11], is not greatly distorted from tetrahedral geometry. Although one cannot discount completely the possibility of some degree of charge-transfer stabilisation between host and guest, the interaction (3.83(1) Å) between the host Se and a non-axial Br atom shows only a modest shortening relative to the van der Waals sum of 3.95 Å. However, the accuracy of the host-guest distances may be adversely affected by thermal motion effects.

References

1. D. D. MacNicol, P. R. Mallinson, A. Murphy, and G. J. Sym: *Tetrahedron Lett.* **23**, 4131 (1982).
2. N. Walker and D. Stuart: *Acta Crystallogr.* **A39**, 158 (1983).
3. GX Crystallographic Package, C. J. Gilmore, P. R. Mallinson, K. W. Muir, and D. N. J. White: *Acta Crystallogr.* **A37**, C-340 (1981); MITHRIL Direct Methods Package, C. J. Gilmore: *Computational Crystallography* (Ed. D. Sayre), p. 138, Clarendon Press (1982).
4. International Tables for X-ray Crystallography, v. IV, Kynoch Press, Birmingham, 1974, pp. 100 and 149.
5. A. D. U. Hardy, D. D. MacNicol, and D. R. Wilson: *J. Chem. Soc., Perkin Trans.* 2, 1011 (1979).
6. W. R. Blackmore and S. G. Abrahams: *Acta Crystallogr.* **8**, 323 (1955).
7. W. S. McDonald and I. D. Pettit: *J. Chem. Soc. (A)*, 2044 (1970).
8. R. Marsh: *Acta Crystallogr.* **5**, 458 (1952).
9. M. More, F. Baert, and J. Lefebvre: *Acta Crystallogr.* **B33**, 3681 (1977).
10. S. Cohen, R. Powers, and R. Rudman: *Acta Crystallogr.* **B35**, 1670 (1979).
11. A. Domenicano, A. Vaciago, and C. A. Coulson: *Acta Crystallogr.* **B31**, 221 (1975); and references therein.