Formation and Structure of a Crystalline Adduct of Hexachloroacetone with Water and Dimethyl Sulphoxide[†]

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The 1 : 1 : 1 adduct of hexachloroacetone (HCA) with water and dimethyl sulphoxide (DMSO) can be obtained as a crystalline solid, which has been subjected to *X*-ray crystallographic examination. The structure contains chains of alternating units of HCA hydrate and DMSO containing bifurcated hydrogen bonding at the DMSO oxygen atom, with one bond to an oxygen atom of HCA in the same chain and another to one in an adjacent chain. Thus two chains form a pair along the crystallographic *a* axis.

A recent kinetic study of the decomposition of hexachloroacetone (HCA) in dimethyl sulphoxide (DMSO) solution has pointed to the importance of the hydration of the carbonyl group of HCA.[1] During this investigation it was noticed that drops of solutions of HCA in DMSO, when left exposed to the atmosphere, deposited white crystals around the edge of the surface. On closer examination, this solid material was found not to be a secondary product of the decomposition of HCA in DMSO but to be identical with the crystals that are precipitated when HCA, water, and DMSO are mixed in equimolar proportions. It is the composition and structure of this material which is the concern of the present paper.

A preparation of the same material from equimolar proportions of the three components had previously been reported.[2] Our product had the same m.p. as that prepared by the earlier workers, and in both cases the elemental analyses were consistent with the formulation of the substance as a 1 : 1 : 1 adduct. Schulman *et al.*[2] suggested that it was a hydrogen-bonded adduct between the hydrate of HCA and DMSO, having a chelate structure in which one DMSO molecule was linked to the two hydroxy groups of the hydrate. Alternatively, they considered a hydrogen-bonded chain structure. However, they did not resolve this question because they were unable to grow crystals that were suitable for *X*-ray crystallography. We have succeeded in overcoming this difficulty and now report the structure of the adduct. Although HCA decomposes in DMSO when water is present, the rate of crystallisation evidently competes successfully with the decomposition.

Table 1. Positional parameters with their estimated standard deviations

Atom	*x*	*y*	*z*
Cl(11)	0.272 7(7)	0.041 8(7)	0.059 7(3)
Cl(12)	0.034 0(7)	−0.024 2(7)	0.097 1(3)
Cl(13)	0.041 4(7)	0.192 0(8)	0.031 4(3)
Cl(14)	0.104 8(7)	0.069 2(8)	0.211 4(3)
Cl(15)	0.358 9(7)	0.033 0(8)	0.181 5(3)
Cl(16)	0.294(1)	0.277 3(9)	0.220 9(3)
Cl(21)	0.781 1(9)	0.792(1)	0.088 6(6)
Cl(22)	0.507 7(7)	0.800 5(6)	0.087 2(3)
Cl(23)	0.611(1)	0.622(1)	0.025 4(3)
Cl(24)	0.603 0(8)	0.742 3(8)	0.204 7(3)
Cl(25)	0.864 1(9)	0.677(1)	0.196 7(4)
Cl(26)	0.684(2)	0.484(1)	0.219 0(4)
S(1)	0.602 0(6)	0.154 1(6)	0.106 1(3)
S(2)	0.092 0(6)	0.620 2(6)	0.090 2(3)
O(1)	0.513(1)	0.272(1)	0.111 9(6)
O(2)	−0.003(1)	0.507(1)	0.095 2(7)
O(11)	0.055(1)	0.267(1)	0.133 7(6)
O(12)	0.259(1)	0.293(1)	0.114 0(5)
O(21)	0.539(1)	0.524(1)	0.121 3(6)
O(22)	0.750(1)	0.492(1)	0.113 1(5)
C(11)	0.134(2)	0.105(2)	0.084 3(9)
C(12)	0.171(2)	0.208(2)	0.127 8(8)
C(13)	0.229(2)	0.147(2)	0.182 2(9)
C(21)	0.641(2)	0.694(2)	0.084 6(9)
C(22)	0.663(2)	0.583(2)	0.124 6(8)
C(23)	0.706(3)	0.624(3)	0.182 4(8)
C(M11)	0.686(2)	0.195(3)	0.055 9(9)
C(M12)	0.744(3)	0.167(3)	0.158(1)
C(M21)	0.189(2)	0.566(3)	0.044(1)
C(M22)	0.217(2)	0.620(3)	0.147 7(8)

Experimental

Preparation of the Adduct.—Water (0.46 cm^3, 26 mmol) was added dropwise to a mixture of HCA (7.0 g, 26 mmol) and DMSO (2.06 g, 26 mmol) in a large (50 cm^3) Erlenmeyer flask. The mixture was continuously swirled, both during and after the water addition. Within less than a minute the mixture became very viscous and hot and then gradually solidified to a crystalline mass which appeared to be completely free from any adhering liquids. Crystallisations from ethyl acetate, followed by drying for 1 h *in vacuo* at 30 °C, yielded a sharp-melting specimen (m.p. 55 °C). I.r. spectra taken before and after the crystallisations showed the absence of any secondary reactions during this procedure; in particular the spectrum contained no absorption in the carbonyl region, 1 500—1 800 cm^{-1} (Found: C, 16.6; H, 2.0; S, 8.7; Cl, 62.3. Calc. for $C_5H_8Cl_6O_3S$: C, 16.6; H, 2.2; S, 8.9; Cl, 59.9%, microanalyses performed at University College London).

Apart from methyl group resonance at *ca.* 2.55 (indistinguishable from that of residual protons in deuteriated DMSO used as solvent), the proton n.m.r. spectrum at 60 MHz consisted of a single sharp resonance at δ 8.26.

X-*Ray Crystallography.*—The colourless column-like crystals obtained by recrystallisation from ethyl acetate were labile in air, splitting into thin needles and eventually subliming. For the *X*-ray study they were sealed in a capillary tube with saturated light petroleum (b.p. 80—100 °C). Inclusion of saturated ethyl acetate in the capillary tube proved unsatisfactory owing to the high and temperature-dependent solubility of the compound in

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this solvent. Recrystallisation from light petroleum did not produce large crystals suitable for *X*-ray analysis.

The crystal employed for the data collection had dimensions 0.65 × 0.18 × 0.055 mm. The unit-cell parameters were determined from Weissenberg photographs and subsequently refined with an Enraf-Nonius CAD 4 diffractometer. Intensity data were collected with the diffractometer operated in the ω—2θ scan mode up to $\theta = 45°$. Three reflections were monitored after every 200 intensity measurements to check the crystal orientation. No movement of the crystal was observed. Three standard reflections were monitored for intensity stability at intervals of 1 800 s. Although sealed in a capillary tube, the crystal decomposed during the data collection. The effect was corrected[3] anisotropically, the maximum and minimum correction coefficients being 2.10 and 0.99, respectively.

Crystal data. $C_5H_8Cl_6O_3S$, $M = 360.90$, monoclinic, $a = 10.167(4)$, $b = 10.254(1)$, $c = 26.706(3)$ Å, $\beta = 99.66(1)°$, $U = 2\,745(2)$ Å^3, $D_c = 1.747$, $D_m = 1.73$ g cm^{-3}, $Z = 8$, $F(000) = 1\,440$, Cu-K_α radiation, μ ($\lambda = 1.5408$ Å) = 130.60 cm^{-1}, space group $P2_1/n$.

Structure determination. The structure was solved by the direct method using MULTAN82[4] and refined on *F* by full-matrix least-squares procedures. A series of different Fourier syntheses and least-squares refinements gradually revealed all the non-hydrogen atoms. Empirical absorption correction was applied initially using the PSI scan method[3] and later using the program of Walker and Stuart.[5] Hydrogen atoms were not located. The final *R* factor was 0.084 for 1 183 reflections with $I \geqslant 3\sigma(I)$. The highest residual electron density in the final difference Fourier map was 0.79 e Å^{-3} and the maximum shift/error was 0.63. Atomic scattering factors were taken from ref. 6. All the computations were carried out with a PDP 11/34A computer using the SDP program system.[3]

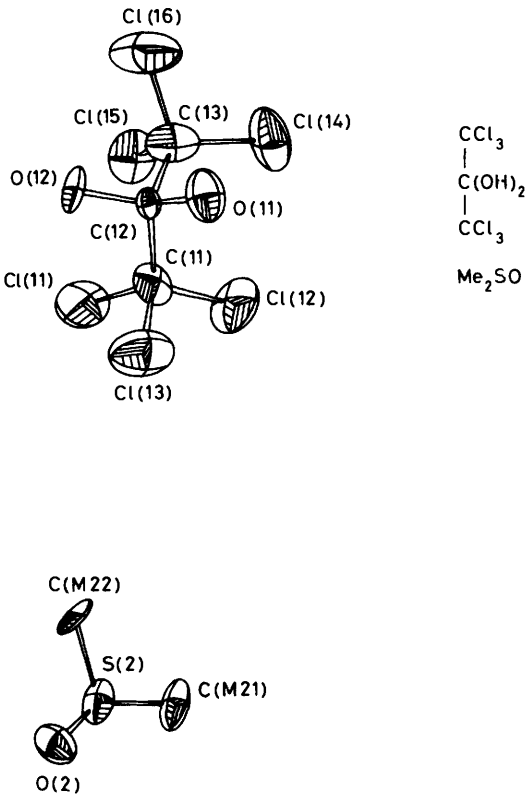

Figure 1. Molecular structures of HCA hydrate and DMSO (only one of the two independent molecules is shown)

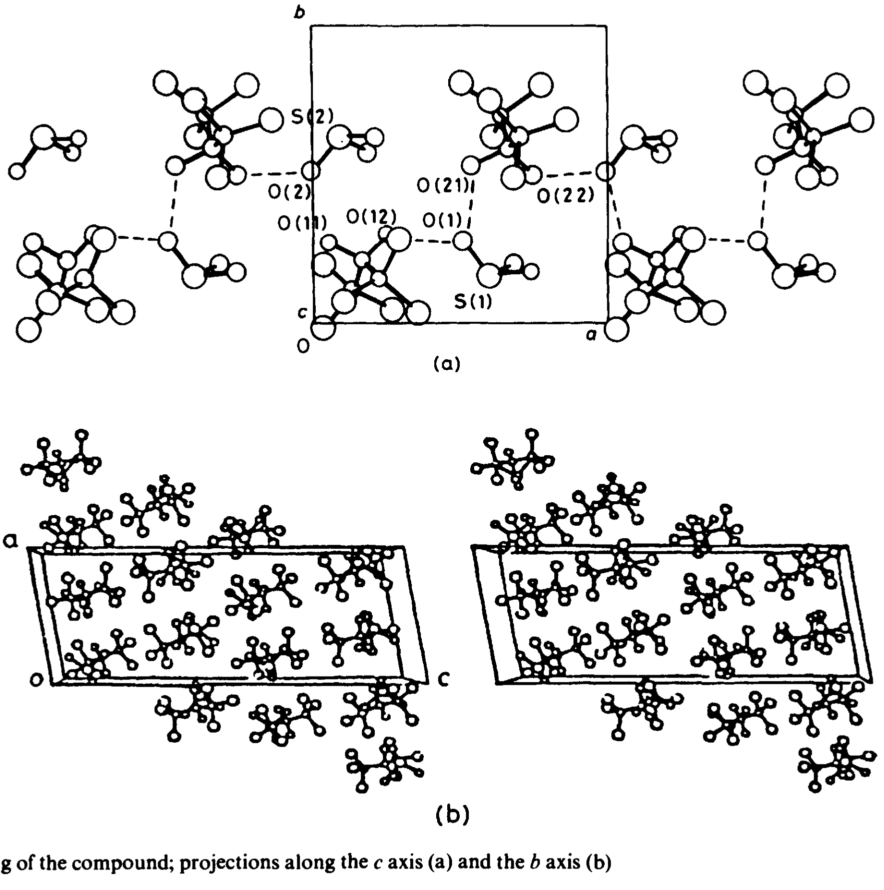

Figure 2. Crystal packing of the compound; projections along the *c* axis (a) and the *b* axis (b)

Table 2. Bond distances (Å) and angles (°)

Cl(11)–C(11)	1.77(3)	Cl(21)–C(21)	1.73(2)
Cl(12)–C(11)	1.74(2)	Cl(22)–C(21)	1.75(2)
Cl(13)–C(11)	1.80(2)	Cl(23)–C(21)	1.73(3)
Cl(14)–C(13)	1.78(3)	Cl(24)–C(23)	1.77(3)
Cl(15)–C(13)	1.77(3)	Cl(25)–C(23)	1.68(3)
Cl(16)–C(13)	1.75(3)	Cl(26)–C(23)	1.77(3)
O(11)–C(12)	1.36(3)	O(21)–C(22)	1.39(3)
O(12)–C(12)	1.34(3)	O(22)–C(22)	1.35(3)
C(11)–C(12)	1.56(3)	C(21)–C(22)	1.55(3)
C(12)–C(13)	1.60(3)	C(22)–C(23)	1.59(3)
S(1)–O(1)	1.53(2)	S(2)–O(2)	1.53(2)
S(1)–C(M11)	1.76(3)	S(2)–C(M21)	1.80(3)
S(1)–C(M12)	1.82(2)	S(2)–C(M22)	1.82(2)
Cl(11)–C(11)–Cl(12)	109.(1)	Cl(21)–C(21)–Cl(22)	105.(1)
Cl(11)–C(11)–Cl(13)	104.(1)	Cl(21)–C(21)–Cl(23)	109.(2)
Cl(11)–C(11)–C(12)	115.(1)	Cl(21)–C(21)–C(22)	111.(2)
Cl(12)–C(11)–Cl(13)	106.(1)	Cl(22)–C(21)–Cl(23)	106.(1)
Cl(12)–C(11)–C(12)	116.(2)	Cl(22)–C(21)–C(22)	117.(2)
Cl(13)–C(11)–C(12)	106.(2)	Cl(23)–C(21)–C(22)	108.(2)
O(11)–C(12)–O(12)	112.(2)	O(21)–C(22)–O(22)	107.(2)
O(11)–C(12)–C(11)	106.(2)	O(21)–C(22)–C(21)	104.(2)
O(11)–C(12)–C(13)	105.(2)	O(21)–C(22)–C(23)	106.(2)
O(12)–C(12)–C(11)	109.(2)	O(22)–C(22)–C(21)	112.(2)
O(12)–C(12)–C(13)	110.(2)	O(22)–C(22)–C(23)	109.(2)
C(11)–C(12)–C(13)	115.(2)	C(21)–C(22)–C(23)	118.(2)
Cl(14)–C(13)–Cl(15)	107.(1)	Cl(24)–C(23)–Cl(25)	107.(2)
Cl(14)–C(13)–Cl(16)	108.(1)	Cl(24)–C(23)–Cl(26)	104.(1)
Cl(14)–C(13)–C(12)	113.(2)	Cl(24)–C(23)–C(22)	115.(2)
Cl(15)–C(13)–Cl(16)	107.(1)	Cl(25)–C(23)–Cl(26)	110.(2)
Cl(15)–C(13)–C(12)	114.(2)	Cl(25)–C(23)–C(22)	114.(2)
Cl(16)–C(13)–C(12)	107.(2)	Cl(26)–C(23)–C(22)	107.(2)
O(1)–S(1)–C(M11)	105.(1)	O(2)–S(2)–C(M21)	105.(1)
O(1)–S(1)–C(M12)	106.(1)	O(2)–S(2)–C(M22)	107.(1)
C(M11)–S(1)–C(M12)	98.(1)	C(M21)–S(2)–C(M22)	101.(1)

Table 3. Hydrogen bonding (distances in Å)

O(1)···O(12)	2.60(2)
O(1)···O(21)	2.61(2)
O(2)···O(11)	2.69(2)
O(2)···O(21)[a]	2.64(2)

[a] Symmetry operation $(x - 1, y, z)$

Discussion

The final atomic parameters with estimated standard deviations are listed in Table 1. Figure 1 shows the molecular structures with the atomic numbering scheme. The compound is in effect a 1:1 adduct of 1,1,1,3,3,3-hexachloro-2,2-dihydroxypropane (HCA hydrate) and DMSO. There are two crystallographically independent adducts in an asymmetric unit and they are related by a pseudo *a* glide plane at $y \simeq 0.4$. The average S–O bond distance is 153 pm and the angle C–S–C is 99.7(1)°. The molecular geometry of DMSO is very similar to that reported in the literature.[7] The C–O distance in HCA hydrate is 136 pm on average which is shorter than that of similar compounds, *e.g.* 144.2 pm in 2,3,4-trimethylpentane-2,3,4-triol.[8]

The O–O bond lengths (between the hydrogen-bonded oxygen atoms of DMSO and HCA hydrate) are in the range 265 ± 5 pm (Table 3), indicative of hydrogen bonding of medium strength.[9]

Although the crystal structure was not determined very accurately owing to the unstable nature of the crystal and hence to the poor quality of the diffraction data, an interesting hydrogen-bonding scheme was revealed. There are infinite chains of alternating DMSO and HCA hydrate along the *a* axis. Two of these chains are staggered, stacked on top of each other and linked by hydrogen bonds [see Figure 2(a)]. A DMSO oxygen atom forms bifurcated hydrogen bonds, one to an oxygen atom of HCA hydrate in the same chain, and another to an oxygen atom of HCA hydrate which is in the chain above (or below). In this way the two infinite chains along the *a* axis form a pair. There is no other hydrogen bonding in the crystal (see Table 3). On decomposition, the column-like crystals reduce to thin needles along the *a* axis. This cleavage can be easily explained by the crystal packing and hydrogen bonding of the crystal [Figure 2(a) and (b)].

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