Specific Entrapment of Methanol and Dimethyl Sulphoxide (DMSO) by a Simple Host Compound (Triphenylmethanol). Crystal Structures of the Ph_3COH·MeOH (1 : 1) and Ph_3COH·DMSO (2 : 1) Clathrate Inclusion Complexes

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Triphenylmethanol (**1**) is shown to be a specific clathrate host for methanol and dimethyl sulphoxide; host–guest interaction schemes in the two crystalline inclusion complexes are discussed.

Many organic hosts which form crystalline inclusion complexes with dipolar protic and aprotic compounds are known.[1,2] Although they follow a specific design,[3] or are rather complex in constitution,[4] high selectivity to one particular entity of both substance classes is rare. All the more surprising, then, is our discovery that triphenylmethanol (**1**), which is an extremely simple molecule, shows such specific clathration behaviour.†

Recrystallization of (**1**) from methanol, or from solvent mixtures containing MeOH and other compounds,‡ results in the rapid formation of large crystals of the pure 1 : 1 inclusion

† A previous report[5] hints at the possible inclusion behaviour of triphenylmethanol by suggesting 'solvates' with acetone (2 : 1) and CCl_4 (5 : 4). However, the host properties of this compound have not been exploited, unlike those of triphenylmethane.[6]

‡ Solvents discriminated from MeOH and DMSO (100% discrimination, equimolar solvent mixture): EtOH, Pr^nOH, Pr^iOH, Bu^nOH, Bu^iOH, Bu^sOH, Bu^tOH, 2-methylbutan-1-ol, 3-methylbutan-2-ol, n-hexanol, hexan-3-ol, cyclohexanol, heptan-4-ol, n-octanol, H_2O, 2-$BuNH_2$, Bu^tNH_2, $Pr^n{}_2NH$, $Pr^i{}_2NH$, $Pr^i{}_3N$, piperidine, 2-methylpiperidine, *N*-methylpiperazine, morpholine, propionaldehyde, butyraldehyde, acetone, acetylacetone, *N*-methylformamide, dimethylformamide, MeCN, PrCN, $MeNO_2$, $EtNO_2$, tetrahydrofuran, dioxane, cyclohexane, heptane, CS_2, CCl_4.

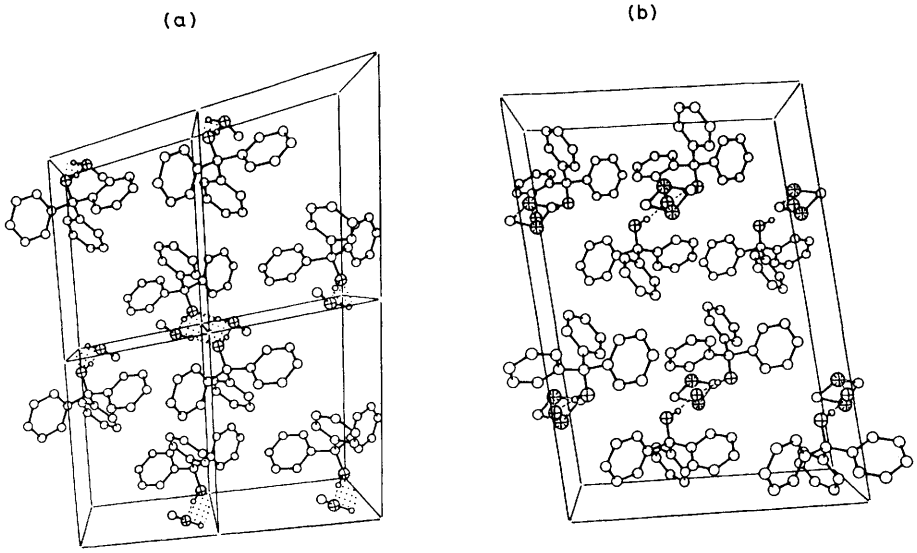

Figure 1. (a) Crystal structure of (**1**)·MeOH (1:1) viewed approximately down the *a*-axis (*b* is horizontal). The circular H-bonding pattern (dotted region) is noteworthy. Dimensions of the two hydrogen bonds are O · · · O 2.707 and 2.721 Å, O–H · · · O 171°. (b) Crystal structure of (**1**)·DMSO (2:1) viewed approximately down the *b*-axis (*a* is horizontal). Intermolecular H-bonding dimensions are O · · · O 2.842 Å, O–H · · · O 170°. The alternative orientations of the DMSO guest are shown at each binding site. Heteroatoms are marked with filled circles; for clarity, only H atoms involved in hydrogen bonds are shown.

complex (**1**)·MeOH. This applies to equimolar two-component solvent mixtures including MeOH,‡ as well as to solvent mixtures with the secondary component in high (*e.g.* tenfold) excess and even multi-component solvent mixtures with MeOH (*e.g.* an equimolar mixture of all the alcohols listed‡ or MeOH in the presence of different amines, *etc.*). Thus, isolation of the inclusion compound is easy, and (**1**) may be used as an effective sequestering agent for MeOH in solution. Treatment of the MeOH inclusion crystals for 10 min at 15 mm Hg and 80 °C decomposes the complex and regenerates unsolvated (**1**) (under ambient conditions the complex is stable for a long time). Remarkably, MeOH in the vapour state is also absorbed highly specifically from vaporous solvent mixtures (see above) by solid (**1**) to form the MeOH complex (*i.e.* reverse process of dissociation). For instance, treatment of solid (**1**) with the MeOH-containing vapour at room temperature for a few hours yielded a host : guest stoicheiometry of nearly 1:1 which is characteristic of the MeOH complex. Thus, (**1**) is also useful for sequestering MeOH in the vapour state. Inclusion complexes accomplished directly *via* solid host–gaseous guest interaction are rare.[1,2]

Though the selectivity of (**1**) to form the 1:1 complex with methanol is extraordinarily high,‡ in the absence of MeOH inclusion complexes are also obtained with piperidine (1:1), *N*-methylpiperazine (1:1), morpholine (1:1), acetone (2:1), dimethyl sulphoxide (DMSO) (2:1), dioxane (1:1), and CCl_4 (1:1). To the best of our knowledge, DMSO is the only other solvent able to compete with MeOH in complexation to (**1**); this solvent is much preferred over all the other solvents used.‡ Hence, (**1**) is also effective for sequestering DMSO from solvent mixtures, as long as MeOH is absent; a non-specific entrapment occurs, however, when both compounds are present in the solution. Among the other compounds enclathrated by (**1**), morpholine is favoured over *N*-methylpiperazine, and both *N*-methylpiperazine and dioxane are preferred over acetone.

In view of this unique behaviour of (**1**) towards MeOH and DMSO, we studied the crystal structures of the corresponding clathrate inclusions [(**1**)·MeOH (1:1) and (**1**)·DMSO (2:1)] by *X*-ray diffraction.§ The two compounds represent two distinct structure types.

The methanol clathrate consists of tetrameric units of hydrogen-bonded molecules (two hosts and two guests) clustered around the crystallographic centres of inversion (Figure 1a). Each guest is inserted between two hosts and each host between two guests, forming a circular pattern of nearly linear H-bonds. Similar centrosymmetric arrangements involving four hydroxy groups have also been observed in other complexes with methanol as well as with higher alcohols.[3d,7] The preferential enclathration of methanol over higher alcohols in the present case may be attributed to the very efficient van der Waals packing of the hydrocarbon substituents, facilitating aryl · · · aryl and methyl · · · aryl (the methyl group lies about 3.4 Å from an aryl ring of a

§ *Crystal data* for (**1**)·MeOH (1:1): $C_{19}H_{16}O{\cdot}CH_4O$, M = 292.38, triclinic, space group $P\bar{1}$, a = 8.467(3), b = 9.250(3), c = 11.576(4) Å, α = 78.09(3), β = 82.44(4), γ = 65.89(3)°, Z = 2, D_c = 1.201 g cm^{-3}; (**1**)·DMSO (1:0.5) : $C_{19}H_{16}O{\cdot}0.5(C_2H_6OS)$, M = 299.39, monoclinic, space group $C2/c$, a = 16.335(3), b = 8.700(2), c = 22.881(5) Å, β = 96.30(1)°, Z = 8, D_c = 1.231 g cm^{-3}.

Intensity data were measured at room temperature on CAD4 and upgraded Picker diffractometers using Mo-K_α (λ = 0.7107 Å) radiation to $2\theta_{max}$ = 50°. The least-squares refinements converged smoothly at R = 0.061 for 1300 observations above the threshold of $3\sigma(I)$ (out of 2430 unique data above zero), and at R = 0.044 for 1931 (out of 2850) reflections, for the methanol and DMSO adducts, respectively. All the hydroxy H-atoms were located directly from difference-Fourier maps; the remaining hydrogens were introduced in calculated positions, the guest methyl being refined as a riding group. The nonplanar DMSO guest exhibits static disorder in the second structure, assuming alternating orientations at different binding sites around the twofold axis. In the crystallographic refinement, the S and methyl C-atoms were located in general positions, while the guest O-atom was constrained to lie on the symmetry axis; all the guest atoms were assigned an occupancy factor of 0.5 to account for the disorder.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

neighbouring tetramer, one of its H-atoms pointing directly at the aromatic substituent) attractions between adjacent entities.[8] Owing to the particular shape of host (**1**), the presence of larger and bulkier alkyl substituents on the guest may not allow a similarly tight arrangement in the crystal lattice (Figure 1a) without creating voids in the structure or distorting the H-bonding scheme.

A different organization characterizes the DMSO clathrate. The polar guest is trapped between and associates strongly with two proton-donating hosts in a typical manner.[9] The resulting structure consist of bilayers of the host species (with their lipophilic sides turned inward), which are interspaced by polar zones with DMSO (Figure 1b). The binding sites are characterized by a crystallographic twofold symmetry. Correspondingly, the bent molecules of DMSO are statically disordered in the crystal, assuming alternating orientations at different sites, without apparent disruption of their bonding to the neighbouring hosts. The remaining space between two adjacent sites displaced along the *b*-axis of the unit cell is occupied by the lone pair electrons of sulphur.[9] Less effective interaction schemes are expected with the other solvents used,‡ owing to their weak affinity for hydrogen bonds and different topology.¶

The particular inclusion properties of (**1**) should find applications involving the concentration, separation, and purification of MeOH and DMSO from industrial and environmental solutions and vapours. We were able to separate MeOH from a mixture with formaldehyde in a composition close to that occurring in a technical oxidation process.[12] Also, pure MeOH was successfully separated from aqueous methanolic solutions (*e.g.* 60% MeOH/40% H_2O) and from a mixture with EtOH, by crystal inclusion with (**1**). Entrapment of MeOH is of general importance in environmental analysis owing to its toxic effects in humans. Furthermore, DMSO and MeOH are very hygroscopic and difficult to store in anhydrous form; this becomes possible *via* clathration and subsequent declathration with (**1**) (see above).‖ This work may stimulate not only the design of sophisticated hosts, but also more attention to simple compounds which may also reveal extraordinary inclusion behaviour.

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¶ Crystallographic analysis of the corresponding (2:1) clathrate between Ph_3COH and acetone [monoclinic, space group *C2/c*, a = 8.652(1), b = 16.164(2), c = 23.076(2) Å, β = 97.41(1)°, Z = 8] reveals a different organization and weaker binding due to the 'thin' planar shape (as compared with that of DMSO) of the acetone molecule. The carbonyl group of the latter is roughly perpendicular to the twofold symmetry axis, and is within H-bonding distance from only one host. At the other end, clathrates with larger solvents are not stable and deteriorate rather quickly, reflecting also on noncomplementary host–guest interactions. Relatively stable crystals of (**1**) with rhombohedral space symmetry can be obtained from lipophilic hydrocarbon solvents (*e.g.*, *p*-xylene).[10] In the absence of a suitable guest, triphenylmethanol self-associates by forming H-bonded tetramers which pack rather loosely in the crystalline state.[11] Refinement of the structural model has been unsatisfactory, however, owing to the consistently poor quality of the crystals, possibly resulting from twinning or inclusion of small nonstoicheiometric amounts of the solvent.

‖ Higher analogues and bridged derivatives of triphenylmethanol also form selective inclusion complexes with organic molecules (refs. 7b and 11).