An Unusual Case of Molecular Recognition: X-Ray and Structural Analysis of an Alcohol–Dimethyl Sulphoxide Coordinatoclathrate

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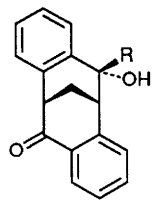
Structural and X-ray crystallographic analyses are reported accounting for the formation and precipitation of a 1 : 1 coordinatoclathrate when dimethyl sulphoxide is added to solutions of alcohol **1a**.

Specific recognition of one chemical entity by another,[1] and progress towards the understanding and prediction of such behaviour,[2] are contemporary topics of major importance. We report here on the remarkable affinity between the two substances 11,12-dihydro-*endo*-12-hydroxy-12-methyl-5,11-methanodibenzo[*a*,*e*]cycloocten-6(5*H*)-one **1a**[3] and dimethyl sulphoxide (DMSO).

Addition of DMSO to solutions of **1a** in many solvents (including diethyl ether, acetonitrile, benzene, acetone, and even water) results in rapid precipitation of a highly crystalline white solid. Spectral and X-ray analysis† reveals that this material is the 1:1 adduct (**1a**·DMSO) shown in Fig. 1.



1 a; R = Me
b; R = H

† *Crystal data*: $C_{18}H_{16}O_2 \cdot C_2H_6OS$, M = 342.5, monoclinic, $P2_1/c$, a = 7.3324(5), b = 29.947(1), c = 8.4414(5) Å, β = 111.606(3)°, U = 1723.3(2) Å^3, Z = 4, D_m = 1.31, D_c = 1.33 g cm^{-3}, λ(Cu-Kα) = 1.5418 Å, μ = 17.4 cm^{-1}. Anisotropic thermal parameters were refined for all non-H atoms, final R = 0.039 for 2767 independent observed reflections and 218 variables [$I/\sigma(I) > 3$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Hydrogen bonding between a sulphoxide oxygen non-bonding pair and the hydrogen of the *endo*-hydroxy group allows the DMSO sulphur atom to position itself almost centrally in the V-shaped concavity of the guest molecule, with the sulphur

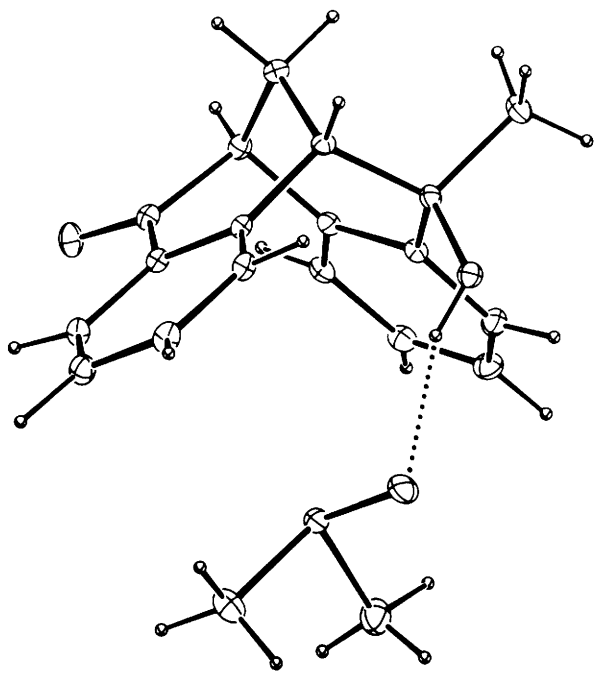


Fig. 1 Crystal structure of the **1a**·DMSO adduct showing the hydrogen bonded interaction between host and guest

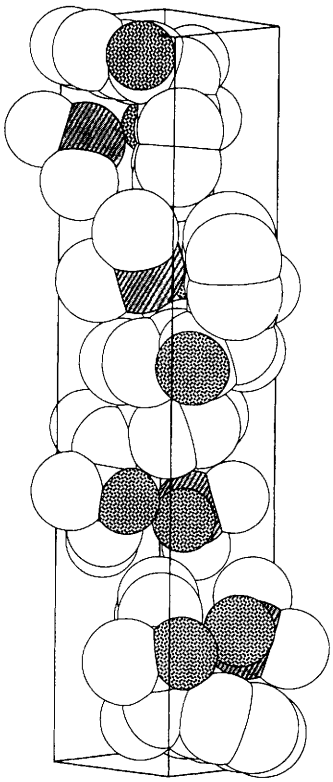


Fig. 2 Unit cell packing of **1a**·DMSO units in the crystalline precipitate

non-bonding pair occupying the other portion of available space.

The resulting umbrella-shaped adduct is a typical example of coordinatoclathrate behaviour.[4,5] It is well known that solute–solvent interaction between alcohols and DMSO reduces the HO exchange rate such that vicinal ^{1}H NMR couplings may be observed,[6] but crystalline complexes are not expected. In this case the overall stability of the adduct is a combination[7] of coordination involving the hydroxy sensor group, van der Waals interaction of the concave surface of **1a** with the guest, and the crucial role of the *exo*-methyl as a spoiler group preventing more conventional crystal packing. The latter function is readily apparent from comparison of **1a** with its lower homologue **1b** which does not exhibit similar inclusion behaviour: **1a**, m.p. 92–94 °C, ν_{max} (OH; paraffin mull) 3470 cm^{-1}; (**1a**·DMSO) *ca.* 160 °C, 3240 cm^{-1}; **1b** 178 °C, 3200 cm^{-1}. High m.p. and low wavenumber values for the latter two materials indicate strong intermolecular HO–HO hydrogen bonding, not present in pure **1a** which must seek alternative packing arrangements.

Although **1a** can form inclusion compounds with other guests (*e.g.* acetone) it fails to produce crystalline precipitates when its solutions are treated with a range of other sulphoxides, sulphones and small polar molecules. Its unexpected behaviour with DMSO therefore appears to be unique. This property is most unusual since interaction between separate **1a**·DMSO adducts involves only weak forces. However, the crystal packing represented in space-filling form (Fig. 2) reveals an exquisite complementarity not just between host and guest,[8] but also between the 1 : 1 adducts themselves.

Not only does alcohol **1a** have considerable potential as a sequestration agent for dimethyl sulphoxide, but deliberate design of new host–guest pairs with suitably in-built complementarity should allow development of a range of combined precipitants.

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