Crystallization and Structural Characterization of Dibenzo-18-crown-6·2(MeCN) and Dibenzo-18-crown-6·2($MeNO_2$); Assignment of Specific C–H · · · O Interactions†

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Stoicheiometric 2 : 1 complexes of acetonitrile and nitromethane with dibenzo-18-crown-6 have been crystallized from the corresponding solvent and their structures established by single crystal *X*-ray diffraction techniques at −150 °C.

In contrast to the large number of crystal structures reported for 18-crown-6 with neutral solvent molecules containing polar O–H, N–H, and C–H groups,[1] little is known about the exact nature of their dibenzo-18-crown-6 analogues in the solid state. *trans*-$PtCl_2(PMe_3)NH_3$·dibenzo-18-crown-6[2] is reported to contain three bifurcated N–H · · · O(crown) interactions (N · · · O 3.41, 3.32 Å) but the calculated hydrogen atom positions were not refined. In $CuI(MeCN)_4$·dibenzo-18-crown-6[3] the six crown ether oxygen atoms have methyl group contacts ranging from 3.22 to 3.41 Å to three different Me moieties, but the hydrogen atom positions were not located.

Crystallographic studies of 18-crown-6 with polar C–H solvent guests have revealed that the number of actual C–H · · · O(crown) interactions and thus the superstructure, if any, cannot always be determined in the absence of hydrogen atom positions by C · · · O contact geometries alone. 18-Crown-6·$C_2(CO_2Me)_2$[4] and 18-crown-6·Me_2SO_4[5] consist of infinite layers of host and guest molecules with one methyl hydrogen actually directed away from the crown ether. All three methyl hydrogen atoms participate in weak interactions with the crown ether in 18-crown-6·2(Me_2SO_2)[6] and 18-crown-6·2($MeNO_2$)[7] (at 22 °C). This latter type of interaction has also been assumed for {*trans*-$[Ir(CO)(MeCN)(PPh_3)_2]_2$·18-crown-6}$[PF_6]_2$·$2CH_2Cl_2$[8] and $[(COCPh_3)_2$-18-crown-6]·2(MeCN)[9] although the hydrogen atoms were not located. At −150 °C a reorientation of the hydrogen bonds in 18-crown-6·2($MeNO_2$) is observed and only two hydrogen atoms per methyl group interact with the crown ether.[10] In most of the above, the contact distances between the hydrogen donor atom and all the crown ether oxygen atoms are nearly equivalent. This and the presence of two different types of ethereal oxygen atoms in dibenzo-18-crown-6 make the study of specific H · · · O interactions in neutral molecule complexes of this crown an exciting area.

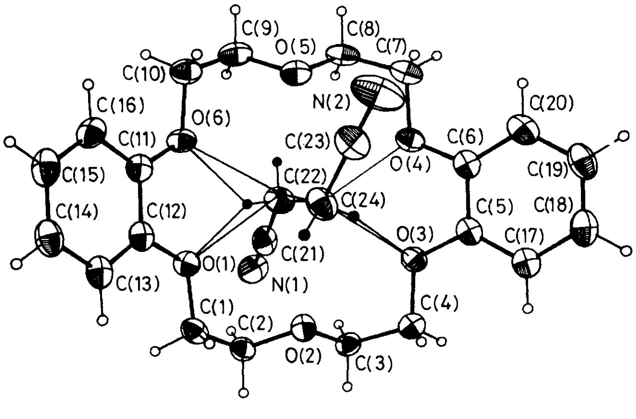

Figure 1. Crystal and molecular structure of dibenzo-18-crown-6·2(MeCN). The close methyl hydrogen · · · oxygen contacts are indicated with line bonds. Important average distances and angles for the crown ether include O–C(alkyl) 1.42(1); O–C(aryl) 1.36(2); C–C(alkyl) 1.49(2) Å; O–C–C–O(alkyl) all '$g^{\pm}$;' C–C–O–C all '*a*.' The torsion angle defined by C(23)–C(24) · · · C(22)–C(21) is 167°.

The crystallization of solvent complexes of dibenzo-18-crown-6 is apparently competitive with either direct co-ordination to metal ions or crystallization as a hydrogen bonded moiety to solvent or water co-ordinated to the metal. Dibenzo-18-crown-6·2(MeCN) crystallized from several reaction mixtures of MCl_3·nH_2O (M = lanthanide) and the crown in a 1 : 3 solvent mixture of MeOH and MeCN. Solutions were heated for 2.5 h at 60 °C, slowly cooled, and stored at 5 °C. Crystallization took from 1 day to 2 weeks. The *X*-ray analysis of this complex was carried out on a crystal grown from a dibenzo-18-crown-6 (10 mmol)–acetonitrile (50 ml) solution (treated as above).‡ The cell parameters of crystalline samples from several different reaction mixtures were identical. Crystals of this complex are stable indefinitely at room temperature in the presence of the solvent; however, they turn opaque and lose their crystallinity within 5 min of removal from the solvent. *X*-Ray data were collected at −150 °C and no decomposition was observed at this temperature.

The solid state structure of dibenzo-18-crown-6·2(MeCN) is presented in Figure 1. The methyl hydrogen atoms were easily locatable and their positional parameters were refined. The structure consists of discrete 2 : 1 complexes with no interaction between symmetry related molecules. Hydrogen atom orientation suggests that two hydrogen atoms from C(22) participate in very weak bifurcated hydrogen bonds exclusively with aryl ether oxygen atoms of the crown and not the more basic alkyl ether oxygen atoms. The H · · · O contacts range from 2.57(6) to 2.61(5) Å. Two of the H[C(24)] atoms also have their closest contacts with aryl ether oxygen atoms, each with one contact near those found for H[C(22)] · · · O

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† For Part 1 of the series Neutral Molecule/Crown Ether Interactions see ref. 7.

‡ *Crystal data:* dibenzo-18-crown-6·2(MeCN), $C_{20}H_{24}O_6$·$2C_2H_3N$, triclinic, space group $P\bar{1}$ (at −150 °C): $a = 9.458(6)$, $b = 9.570(5)$, $c = 14.404(5)$ Å, $\alpha = 73.18(4)$, $\beta = 79.85(5)$, $\gamma = 66.82(6)°$, $U = 1144$ Å^3, $Z = 2$, $D_c = 1.28$ g cm^{-3}. 2951 Independent observed reflections $[F \geqslant 5\sigma(F)]$ measured on a CAD4 diffractometer using Mo-K_α radiation were used in the refinement. The structure was solved using the direct methods program MULTAN.[12] Methyl hydrogen atoms were located on a difference Fourier map and refined with *B* fixed at 3.2 Å^2. Anisotropic refinement of non-hydrogen atoms led to $R = 0.105$.

Dibenzo-18-crown-6·2($MeNO_2$), $C_{20}H_{24}O_6$·$2(CH_3NO_2)$, monoclinic, space group $P2_1/c$, (at −150 °C): $a = 9.573(2)$, $b = 14.636(2)$, $c = 33.471(7)$ Å, $\beta = 93.77(2)°$, $U = 4679$ Å^3, $Z = 8$, $D_c = 1.03$ g cm^{-3}. Data were measured and collected (4316 observed reflections) as for the previous compound. Anisotropic refinement of non-hydrogen atoms and full isotropic refinement of the methyl hydrogen atoms led to $R = 0.054$. 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.

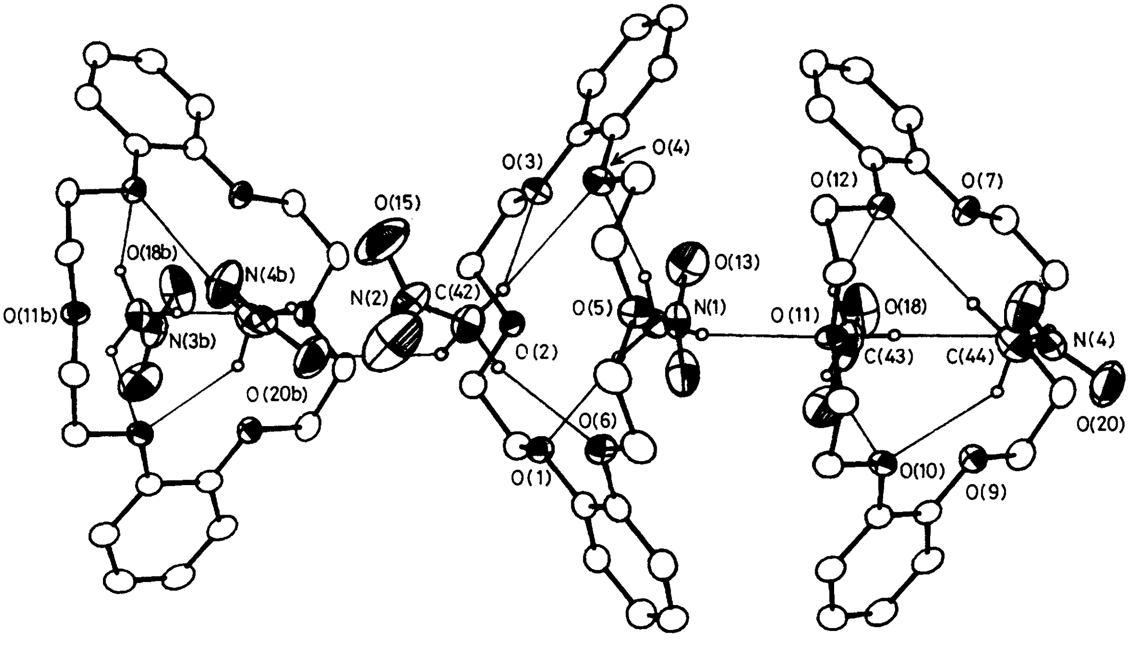

Figure 2. Crystal and molecular structure of dibenzo-18-crown-6·2($MeNO_2$). The two crown ether molecules with O(7)—O(12) indicated are related by a unit translation along *b*. Important average distances and angles include: O–C(alkyl) 1.431(6); O–C(aryl) 1.372(4); C–C(alkyl) 1.496(3) Å; O–C–C–O(alkyl) all '$g^{\pm}$;' C–C–O–C all '*a*.' The planes defined by the nitromethane molecules intersect at angles of 33° [N(1)/N(2)] and 72° [N(3)/N(4)] with each other and angles of 43 [N(1)], 65 [N(2)], 45 [N(3)], and 72°[N(4)] with the mean planes defined by the six oxygen atoms of each crown molecule.

separations [2.62(5), 2.57(6) Å] and one much longer [2.71(5), 2.93(5) Å]. All the H · · · O contacts are near to or greater than the van der Waals contact distance of 2.60 Å and all are much larger than the H(Me) · · · O contacts of 2.30, 2.45, and 2.35 Å observed for 18-crown-6·2($MeNO_2$)[12] (22 °C). (This may explain the instability of the MeCN complex out of its solvent environment.) It is interesting that one hydrogen from each methyl group is directed away from the crown even though O(2) and O(5) are available for hydrogen bonding, and that the closest C · · · O contacts for each methyl group are C(22) · · · O(5) 3.270(8) Å and C(24) · · · O(2) 3.330(8) Å. {Average of all C · · · O contacts: 3.40(7) [C(22)] and 3.43(8) Å [C(24)].}

Dibenzo-18-crown-6·2($MeNO_2$) was crystallized from a solution of 0.4 mmol of crown ether in 10 ml of $MeNO_2$. The solution was gently heated (60 °C; 1 h), slowly cooled, and stored at 5 °C. Clear plate-like crystals grew slowly over a period of 3 days from solution. Crystals of this complex behaved similarly to those for the acetonitrile complex. They are stable indefinitely in solution, but lose crystallinity (and presumably solvent) when removed from the solvent.

An ORTEP view of the structure determined by *X*-ray analysis at −150 °C is shown in Figure 2.[12] The methyl hydrogen atoms were fully refined. There are two independent formula units in the asymmetric unit. The two are associated to form a hydrogen bonded chain along *b via* H(1)[C(41)] · · · O(11) [crown alkyl oxygen, 2.41(4) Å] and H(2)[C(42)] · · · O(20) [nitromethane oxygen, 2.59(6) Å] interactions. The remaining C(41) and C(42) hydrogen atoms interact with the aryl oxygen atoms exclusively. The H(2)[C(41)] · · · O(1) contact is strong [1.97(4) Å]; there are two others at 2.41(5) and 2.45(4) Å and one bifurcated hydrogen bond between H(3)[C(42)] and O(3) and O(4) [2.67(7), 2.70(6) Å, respectively]. Hydrogen atoms bonded to C(43) and C(44) interact exclusively with O(7)—O(12), the contacts ranging from 2.55(4) to 2.97(4) Å. The latter is the closest contact to H(1)[C(44)] and may be indicative of little or no interaction for that hydrogen atom.

An analysis of methyl group contact distances reveals some other interesting features. The benzene rings are folded towards C(41) and C(43) and these atoms appear to exhibit closer C · · · O contacts [3.29(8), 3.35(5) Å] than C(42) and C(44) [3.43(9), 3.5(1) Å]. This is presumably due to axial hydrogen (crown) steric interaction outside the crown 'envelope.' The through-the-ring C · · · C contact between C(41) and C(42) [3.805(6) Å] is much less than that observed for C(43) · · · C(44) [4.079(7) Å] and that in dibenzo-18-crown-6·2(MeCN) [4.071(8) Å]. C(41), which exhibits the strongest C–H · · · O interaction, is only 1.77 Å from the mean plane of the six ether oxygen atoms compared to 2.03, 1.91, and 2.16 Å for C(42), C(43), and C(44), respectively.

Despite the various weak interactions between the solvent and the crown ether, there are no significant differences in the dibenzo-18-crown-6 moieties themselves. The torsion angles and bond distances and angles are all internally consistent with complexed dibenzo-18-crown-6 structures in the literature; however, even the weak hydrogen bonds found in the title complexes are sufficient to stabilize a conformation slightly different from that of the uncomplexed ether.[11] The inability of dibenzo-18-crown-6 to adopt different conformations with various solvent guests doubtless plays a role in the instability of these complexes and their resulting, rather intricate, structure of extremely weak hydrogen bonds.

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the N.S.F. Chemical Instrumentation Program for support of this research.

Received, 23rd October 1986; Com. 1514

References

1 F. Vögtle, H. Sieger, and W. M. Muller, in 'Host Guest Complex Chemistry Macrocycles Synthesis, Structures, Applications,' eds. F. Vögtle, and E. Weber, Springer-Verlag, Berlin, 1985, p. 319, and references therein.

2 H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 847.

3 J. P. Jasinski, N. P. Rath, and E. M. Holt, *Inorg. Chim. Acta*, 1985, **97**, 91.

4 I. Goldberg, *Acta Crystallogr., Sect. B*, 1975, **31**, 754.

5 G. Weber, *J. Mol. Struct.*, 1983, **98**, 333.

6 J. A. Bandy, M. R. Truter, and F. Vögtle, *Acta Crystallogr., Sect. B*, 1981, **37**, 1568.

7 R. D. Rogers and L. M. Green, *J. Incl. Phenom.*, 1986, **4**, 77.

8 H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, *J. Am. Chem. Soc.*, 1982, **104**, 1426.

9 B. L. Allwood, S. E. Fuller, P. C. Y. K. Ning, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1984, 1356.

10 R. D. Rogers and P. D. Richards, *J. Incl. Phenom.*, 1986, in the press.

11 D. Bright and M. R. Truter, *J. Chem. Soc. B*, 1970, 1544.

12 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.