A 1:1 Host-Guest Complex between 1,4,7,10,13,16-Hexaoxacyclooctadecane ('18-crown-6') and *m*-Nitroaniline: Mere Stoicheiometry or a Genuine 1:1 Adduct?

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The stoicheiometrically 1:1 adduct of 1,4,7,10,13,16-hexaoxa-cyclooctadecane with *m*-nitroaniline, $C_{18}H_{30}N_2O_8$, $M_r = 402.45$, crystallises from toluene in red-orange prisms, (probable) space group $P\bar{1}$, $a = 861.8(3)$, $b = 920.4(3)$, $c = 1403.3(4)$ pm, $\alpha = 80.40(4)$, $\beta = 79.79(4)$, $\gamma = 85.95(3)^\circ$, $V = 1.07916$ nm^3, $Z = 2$, $d_{calc.} = 1.238$ Mg m^{-3}. Structure refinement converged at $R = 0.066$ ($R_w = 0.062$) for 2915 diffractometer data.

The aniline molecules are disordered, resulting in alternating 1:2 adducts and free ligands in the cell. The H bond pattern linking host and guest molecules is comparable to that in the related 18-crown-6/*p*-nitroaniline 1:2 adduct.

A number of crystalline complexes of 18-crown-6 with neutral H bond donors $R–NH_2$ or $R–CH_2^{\delta+}–R'$ have been prepared during the last decade [1–4]. Their structural analyses proved them to be 1:2 adducts [*e.g.* 3, 5–7], *i.e.* one guest molecule (or one donor group of a bifunctional guest molecule [5]) is attached to each side of the macrocycle. This also holds for the recently reported series of adducts with hydrazines [8, 9] and anilines [10–13]. It was therefore surprising that elemental analysis [10] and cell volume of the title compound (V *ca.* 1.08 nm^3) indicated a 1:1 stoicheiometry.

This might be expected with bifunctional guest molecules such as dimethylacetylenedicarboxylate allowing ..crown..guest..crown..guest.. linkages [5]. It is normally found with highly symmetrical cationic e$^-$ acceptor groups such as $R–NH_3^+$ [14] or NH_4^+ [15], possibly due to additional interactions of the positive N atom with the lone pairs of those crown O atoms not coordinating to H atoms [16]; with the (neutral) CH_3 groups of dimethylsulphone [17], however, and with one $R\overset{..}{-}NH_2^+$ group of guanidinium nitrate [18] 1:2 adducts were obtained.

The present guest molecule *m*-nitroaniline is neither bifunctional nor is its donor group NH_2 cationic and pseudo-spherical; hence an investigation of the H bond pattern formed seemed interesting.

Experimental

Crystal data: $C_{18}H_{30}N_2O_8$, $M_r = 402.45$, probable space group $P\bar{1}$, $a = 861.8(3)$, $b = 920.4(3)$, $c = 1403.3(4)$ pm, $\alpha = 80.40(4)$, $\beta = 79.79(4)$, $\gamma = 85.95(3)^\circ$, $Z = 2$, $d_{calc.} = 1.238$ Mgm^{-3}, $\mu(MoK\alpha) = 0.091$ mm^{-1}.

A crystal of dimensions *ca.* $0.7 \times 0.5 \times 0.4$ mm was grown from toluene [10] and used for crystallographic measurements on an automated X-ray four-circle diffractometer with monochromated MoKα radiation ($\lambda = 71.069$ pm). Cell dimensions were obtained by least squares from the settings of 26 strong reflections in the range $20^\circ < 2\theta < 25^\circ$. 3776 unique data were collected up to $2\theta = 50^\circ$ in a profile fitting mode [19]; 2915 reflections with $F > 4\sigma(F)$ were considered observed.

The structure was solved by multisolution direct methods [20] in $P\bar{1}$. The best E-map gave sites of all non-hydrogen atoms except those of the nitro group (high thermal motion) which could be located from a subsequent Fourier synthesis. However, one more atom appeared in this map, occupying the second *m*-position and forming angles of *ca.* 95 and 145° at the phenyl ring. Further refinement [20] revealed the alternative orientation of the aniline, generated approximately by a 180° rotation about the $O_2N–C$ axis.

Because of this disorder, aromatic nuclei were idealised (C–C = 139.5 pm, C–H = 96 pm, all angles 120°) and refined as rigid groups; corresponding C–N and N–O distances were constrained to be equal to within ±0.5 pm. Aromatic C atoms with contacts < 40 pm to each other were given one common isotropic U value.

Amine and methylene H atoms were included in calculated positions (C–H, N–H = 96 pm). All H atoms were assigned fixed thermal parameters

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1.2 times the U values of attached atoms. Refinement of an empirical extinction correction coefficient $x = 7.6(3) \cdot 10^{-3}$ $[F' = F/(1.0 + 2x\,F^2 \cdot 10^{-3}/\sin 2\theta)^{1/4}]$ led to final R = 0.066 and $R_\omega = 0.062$ $(w^{-1} = \sigma^2(F_0))$, with occupancy factors f = 0.617(2) and f′ = 1—f for the disordered anilines (see Table I)*.

Table I. Atomic coordinates (× 10^4) and isotropic thermal parameters ($pm^2 \times 10^{-1}$). Occupancy actors: f = 0.617(2) for C(19) to H(28b), f′ = 1-f for C(19)′ to H(28b)′.

	x	*y*	*z*	U
O(1)	2522(2)	3567(2)	3746(1)	73(1)*
C(2)	2378(3)	2019(3)	3902(2)	82(1)*
C(3)	743(3)	1686(3)	3828(2)	78(1)*
O(4)	−300(2)	2086(2)	4645(1)	73(1)*
C(5)	−1902(4)	1953(3)	4568(2)	84(1)*
C(6)	−2940(3)	2362(3)	5454(2)	87(1)*
O(7)	−3036(2)	3907(2)	5390(1)	78(1)*
C(8)	−4024(3)	4403(3)	6205(2)	90(1)*
C(9)	−3984(3)	6023(3)	6104(2)	89(1)*
O(10)	2850(2)	5731(2)	406(1)	78(1)*
C(11)	3409(3)	4865(3)	1211(2)	82(1)*
C(12)	3398(3)	3281(3)	1112(2)	79(1)*
O(13)	1819(2)	2846(2)	1266(1)	74(1)*
C(14)	1679(3)	1389(3)	1123(2)	82(1)*
C(15)	−9(3)	1084(3)	1178(2)	87(1)*
O(16)	−561(2)	1967(2)	353(1)	86(1)*
C(17)	−2140(3)	1841(3)	360(2)	97(1)*
C(18)	−2643(3)	2754(3)	−516(2)	88(1)*
C(19)	2847	1979	7589	58(1)
C(20)	2555	3024	8221	59(1)
C(21)	1454	4186	8065	55(1)
C(22)	645(3)	4305(2)	7276(2)	74(1)
C(23)	937	3260	6644	81(1)
C(24)	2038	2097	6800	67(1)
N(25)	4027(4)	804(4)	7671(3)	95(2)*
O(26)	4780(4)	761(4)	8333(3)	141(2)*
O(27)	4101(6)	−187(4)	7187(4)	135(2)*
N(28)	1234(4)	5188(4)	8658(2)	84(2)*
H(28a)	1826	5106	9185	92
H(28b)	481	5996	8562	92
C(19)′	2847	1879	7443	58(1)
C(20)′	1797	2386	6798	67(1)
C(21)′	856	3663	6914	56(2)
C(22)′	965(4)	4431(3)	7675(3)	64(2)
C(23)′	2015	3923	8320	80(2)
C(24)′	2956	2647	8203	70(2)
N(25)′	3850(7)	568(6)	7446(4)	88(3)*
O(26)′	3771(6)	−107(5)	6780(4)	119(3)*
O(27)′	4930(6)	328(7)	7914(4)	115(3)*
N(28)′	−159(5)	4041(5)	6309(3)	78(2)*
H(28a)′	−226	3448	5818	90
H(28b)′	−834	4911	6359	90

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

A difference map in the corresponding acentric space group showed the same disorder of the amines, possibly due to the mainly centrosymmetric character of the structure. No better R than 0.13 could be achieved by acentric refinement, but anisotropic temperature factors were included only for hetero atoms thus keeping the ratio (number of parameters refined) : (number of observed reflections) comparable to that in $P\bar{1}$. The space group ambiguity could not definitely be decided but the centrosymmetric space group seemed more probable.

Results and Discussion

The adducts of 18-crown-6 with nitroanilines were all prepared from equimolar amounts of the

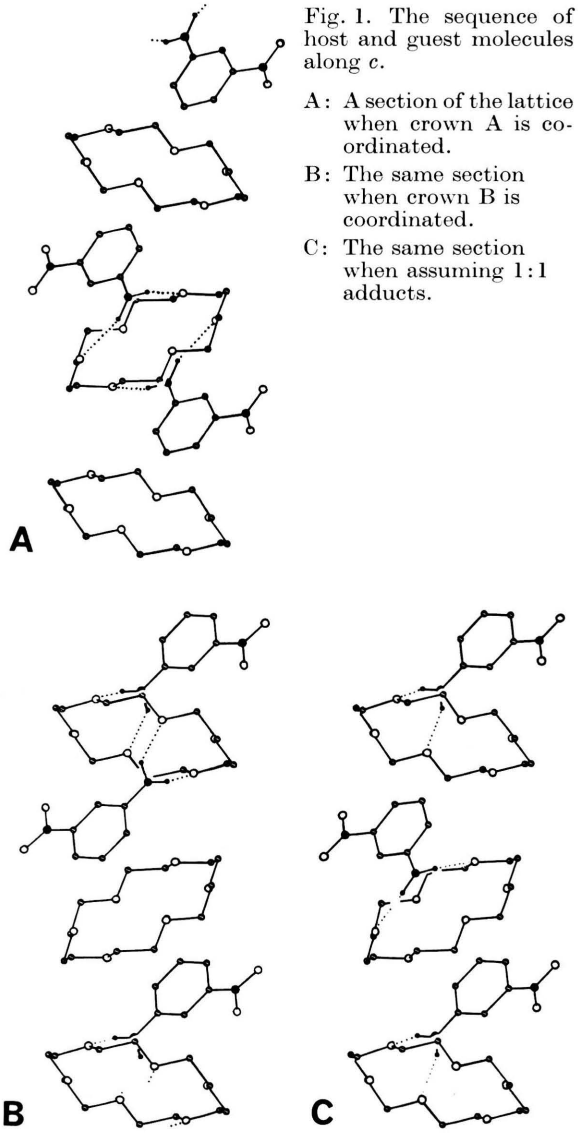

Fig. 1. The sequence of host and guest molecules along *c*.

A: A section of the lattice when crown A is coordinated.

B: The same section when crown B is coordinated.

C: The same section when assuming 1:1 adducts.

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* Structure factor Tables, H atom parameters and lists of anisotropic thermal parameters are available from GW on request.

polyether and the respective amine [10]. However, their stoicheiometry was found to be 1:2, except with *m*-nitroaniline. This indicates the strong preference of the macrocycle for a highly symmetric arrangement of the guest molecules in its host-guest complexes. Because of the *m*-position of the nitro group in the present aniline, a 180° rotation about the C–NO_2 axis would produce a crystallographically different orientation in the lattice whilst still permitting H bond formation and leaving the NO_2 environment unchanged (see Fig. 1). This fact may favour disorder, especially if there is only one donor group in the molecule (in contrast to 4-nitro-1,2-benzenediamine [13]).

In the present structure (Fig. 1), an additional rotation of 19(1)° about the normal of the aromatic plane and a shift of only 25(3) pm of the centre of the aromatic nucleus is sufficient to bring the NH_2 group into a coordinating position to the second crown molecule (dihedral angle between the planes of the disordered anilines = 2(1)°). The two orientations of the nitro amines in $P\bar{1}$ are mutually exclusive; therefore (a) 1:2 adducts of crown A [O(1) to C(9)] with the 38.3% occupied aniline A [C(19)′ to N(28)′] and uncomplexed crowns B, and (b) 1:2 adducts of crown B[O(10) to C(18)] with the 61.7% occupied aniline B [C(19) to N(28)] and uncomplexed crowns A are present in the lattice (Fig. 1). In the crystalline state, the conformation of uncomplexed 18-crown-6 differs substantially [21] from the approximate D_{3d} symmetry found in the current structure for both the crown molecules (Table IV) and also in most complexes of 18-crown-6 with 'fitting' cationic e^- acceptors such as alkaline metal ions [22] or NH_4^+ [15] and R–NH_3^+ [14]. A conformational disorder of the crown molecules (as a consequence of the existence of non-coordinating macrocycles in the lattice) or at least extremely anisotropic movement of its atoms might therefore have been expected but was not obvious, probably due to packing forces.

Table II. Bond lengths (pm).

A		B	
O(1) –C(2)	141.6(3)	O(10)–C(11)	140.9(3)
C(2) –C(3)	148.8(4)	C(11)–C(12)	148.9(4)
C(3) –O(4)	140.9(3)	C(12)–O(13)	141.5(3)
O(4) –C(5)	141.9(4)	O(13)–C(14)	140.5(3)
C(5) –C(6)	148.3(4)	C(14)–C(15)	148.7(4)
C(6) –O(7)	140.7(3)	C(15)–O(16)	143.3(3)
O(7) –C(8)	142.0(3)	O(16)–C(17)	137.2(3)
C(8) –C(9)	147.7(4)	C(17)–C(18)	148.2(3)
C(9) –O(1)[1]	140.1(3)	C(18)–O(10)[2]	142.4(3)
C(19)′–N(25)′	143.4(6)	C(19)–N(25)	143.5(4)
N(25)′–O(26)′	122.0(9)	N(25)–O(26)	121.8(6)
N(25)′–O(27)′	121.8(9)	N(25)–O(27)	121.7(6)
C(21)′–N(28)′	131.5(6)	C(21)–N(28)	132.5(4)

[1] Refers to the symmetry operation $-x$, $1-y$, $1-z$; [2] to $-x$, $1-y$, $-z$.

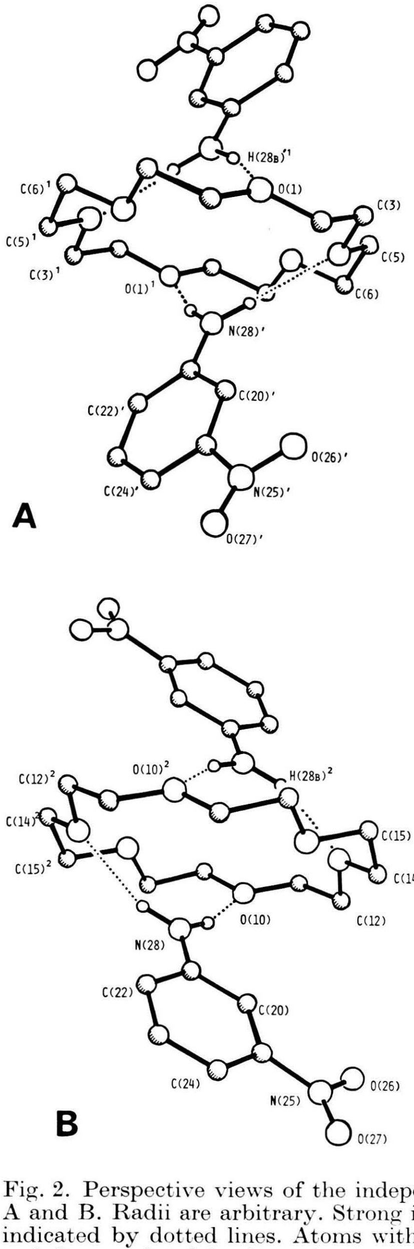

Fig. 2. Perspective views of the independent adducts A and B. Radii are arbitrary. Strong interactions are indicated by dotted lines. Atoms with superscripts 1 and 2 are related by inversion at 0, 1/2, 1/2 and at 0, 1/2, 0, respectively.

Table III. Bond angles (deg.). For superscripts see Table II.

A		B	
C(2) – O(1) – C(9)^1	112.9(2)	C(11) – O(10) – C(18)^2	111.8(2)
O(1) – C(2) – C(3)	109.2(2)	O(10 – C(11) – C(12)	109.0(2)
C(2) – C(3) – O(4)	109.0(2)	C(11) – C(12) – O(13)	109.3(2)
C(3) – O(4) – C(5)	112.1(2)	C(12) – O(13) – C(14)	113.7(2)
O(4) – C(5) – C(6)	109.7(2)	O(13) – C(14) – C(15)	110.1(2)
C(5) – C(6) – O(7)	109.3(2)	C(14) – C(15) – O(16)	108.0(2)
C(6) – O(7) – C(8)	113.3(2)	C(15) – O(16) – C(17)	113.0(2)
O(7) – C(8) – C(9)	109.6(2)	O(16) – C(17) – C(18)	110.8(2)
C(8) – C(9) – O(1)^1	110.5(2)	C(17) – C(18) – O(10)^2	111.4(2)
C(20)′ – C(19)′ – N(25)′	127.0(3)	C(20) – C(19) – N(25)	123.0(2)
C(24)′ – C(19)′ – N(25)′	113.0(3)	C(24) – C(19) – N(25)	116.9(2)
N(28)′ – C(21)′ – C(20)′	116.8(3)	N(28) – C(21) – C(20)	118.8(2)
N(28)′ – C(21)′ – C(22)′	123.1(3)	N(28) – C(21) – C(22)	121.2(2)
C(19)′ – N(25)′ – O(26)′	113.5(5)	C(19) – N(25) – O(26)	116.2(3)
C(19)′ – N(25)′ – O(27)′	123.0(6)	C(19) – N(25) – O(27)	120.5(4)
O(26)′ – N(25)′ – O(27)′	121.5(6)	O(26) – N(25) – O(27)	122.7(4)

Table IV. Torsion angles in the macrocycles (deg.). For superscripts see Table II.

A		B	
C(9)^1 – O(1) – C(2) – C(3)	174.2(2)	C(18)^2 – O(10) – C(11) – C(12)	172.6(2)
O(1) – C(2) – C(3) – O(4)	— 70.1(2)	O(10) – C(11) – C(12) – O(13)	— 70.2(2)
C(2) – C(3) – O(4) – C(5)	173.4(2)	C(11) – C(12) – O(13) – C(14)	176.0(3)
C(3) – O(4) – C(5) – C(6)	179.0(2)	C(12) – O(13) – C(14) – C(15)	—173.0(2)
O(4) – C(5) – C(6) – O(7)	76.6(3)	O(13) – C(14) – C(15) – O(16)	67.0(3)
C(5) – C(6) – O(7) – C(8)	179.3(2)	C(14) – C(15) – O(16) – C(17)	—176.3(2)
C(6) – O(7) – C(8) – C(9)	176.8(2)	C(15) – O(16) – C(17) – C(18)	—179.0(2)
O(7) – C(8) – C(9) – O(1)^1	— 71.2(3)	O(16) – C(17) – C(18) – O(10)^2	— 78.4(3)
C(8) – C(9) – O(1)^1 – C(2)^1	175.8(3)	C(17) – C(18) – O(10)^2 – C(11)^2	—176.8(2)

Table V. H bond geometry (pm and deg.). Coordinates of the unprimed amino group as given in Table I are to be shifted by —1 in z. For superscripts see Table II.

A		B	
N(28)′ ... O(1)^1	289.3(5)	N(28) ... O(10)	315.0(4)
N(28)′ ... O(4)	320.0(5)	N(28) ... O(13)^2	308.2(4)
N(28)′ ... O(7)	300.9(5)	N(28) ... O(16)^2	313.5(4)
H(28a)′ ... O(4)	224.1(5)	H(28a) ... O(10)	223.3(4)
H(28a)′ ... O(7)	258.6(5)	H(28a) ... O(16)^2	296.4(4)
H(28b)′ ... O(1)^1	195.5(5)	H(28b) ... O(13)^2	217.8(4)
H(28b)′ ... O(7)	280.9(5)	H(28b) ... O(16)^2	261.6(4)
N(28)′ – H(28a)′ ... O(4)	178.1(3)	N(28) – H(28a) ... O(10)	159.6(2)
N(28)′ – H(28a)′ ... O(7)	106.9(3)	N(28) – H(28a) ... O(16)^2	91.2(2)
N(28)′ – H(28b)′ ... O(1)^1	164.7(3)	N(28) – H(28b) ... O(13)^2	156.6(2)
N(28)′ – H(28b)′ ... O(7)	92.6(3)	N(28) – H(28b) ... O(16)^2	114.3(2)

The asymmetric unit consists of two independent halves of crown molecules and one (disordered) aniline thus stoicheiometrically resulting in a 1:1 adduct. The overall arrangement of the adducts (see Fig. 2) is similar to those previously found [9, 12, 13]: Two nitroaniline molecules, related by a centre of inversion, are inclined with dihedral angles 66(1)° (for A) and 53(1)° (for B) 'above' and 'below' the planes formed by the six O atoms of the macrocycles (co-planar to within ± 26 pm in both crowns). Four strong and (possibly) two more very weak H bridges (Table V) link guest and host molecules in a pattern resembling that of 18-crown-6/*p*-nitroaniline 1:2 [11] (Fig. 3). This might be taken as

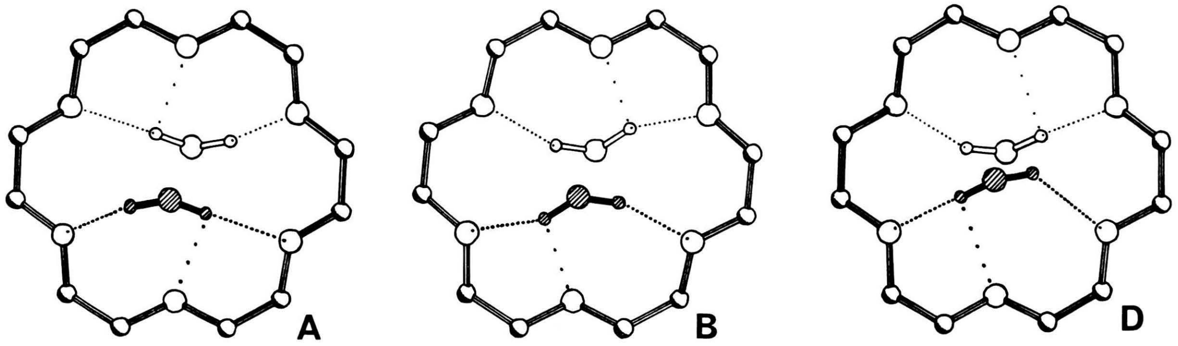

Fig. 3. Projections normal to the best planes of the six O atoms in A, B and in the 1:2 adduct with *p*-nitroaniline (D) [11] showing the conformations of the ligands (approximate D_{3d} symmetry) and the H bond pattern; narrowly/widely spaced dots indicate O···H distances of $<$ 230 pm/260–265 pm, respectively.

further evidence for the tendency to 1:2 character in the present complex.

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