Complex Formation between Guanidinium Nitrate and 1,4,7,10,13,16-Hexaoxacyclo-octadecane (18-Crown-6). Crystal Structure of the Hydrogen-bonded 2 : 1 Complex

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Reaction between guanidinium nitrate and 18-crown-6 in ethanol yielded a crystalline complex of 2 : 1 stoicheiometry. Three-dimensional *X*-ray crystal structure analysis has shown the monoclinic unit cell, $a = 8.969(1)$, $b = 10.278(2)$, $c = 14.253(1)$ Å, $\beta = 102.682(8)°$, space group $P2_1/c$, to contain two centrosymmetrical entities, nitrate–guanidinium–18-crown-6–guanidinium–nitrate, the linkages being *via* a guanidinium hydrogen atom, H . . . O 1.91(13) Å, to one oxygen atom of the ether, and from a second guanidinium hydrogen atom to one oxygen atom of the nitrate ion, H . . . O 2.08(18) Å. Full-matrix least-squares refinement gave an *R* value of 0.083 for 711 reflections measured on a CAD-4 diffractometer. While the crystalline product isolated from an ethanol solution of guanidinium chloride and 18-crown-6 also has 2 : 1 stoicheiometry, calorimetric measurements establish that in methanol solution the interaction ratio is 1 : 1 even when the concentration of guanidinium chloride exceeds that of 18-crown-6 by a ratio of 4 : 1.

PEDERSEN [1] originally demonstrated an interaction in methanolic solution between dibenzo-18-crown-6 and guanidinium salts by changes in the u.v. spectrum of the aromatic ring. Guanidinium chloride and guanidinium carbonate were two of several amino-compounds investigated and Pedersen concluded that interaction was obtained if the NH_2^+ moiety could intrude into the macrocyclic ring.

Cram and his co-workers [2] suggested from experiments with CPK models that with dibenzo-18-crown-6 the guanidinium ion could form three hydrogen bonds. They did not explicitly state that this is possible only if one N–H bond is not coplanar with the C + 3N skeleton. Our attempts to isolate a guanidinium complex of dibenzo-18-crown-6 have not been successful.

A calorimetric investigation [3] of the formation of complexes between 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6) and organic ammonium salts in methanol showed no detectable effect with change of anion. For guanidinium iodide the results indicated a 1 : 1 complex in solution held by two hydrogen bonds. Further investigation with guanidinium chloride is reported here.

From solutions of 18-crown-6 with guanidinium chloride or guanidinium nitrate we isolated crystals having a stoicheiometry guanidinium : 18-crown-6 of 2 : 1. To discover the nature of the hydrogen bonding we have determined the crystal structure of the (guanidinium nitrate)$_2$–18-crown-6 complex as described below.

EXPERIMENTAL

Guanidinium nitrate (0.122 g) and 18-crown-6 (0.246 g) were heated in ethanol (10 ml) until dissolved. The solution was filtered and allowed to crystallise slowly at room temperature. This process resulted in a mass at the bottom of the beaker and plate-like *crystals*, m.p. 162—164°, on the sides [Found: C, 33.35; H, 7.25; N, 22.15. $(CH_6N_3^+\text{-}NO_3^-)_2\cdot C_{12}H_{24}O_6$ requires C, 33.05; H, 7.15; N, 22.05%]. Few differences were found between the i.r. spectra of the crystals and of a 2 : 1 mixture of their components. This suggested that the complex is weakly bonded with little change in the ligand conformation on complexing. However, the spectrum of the complex appeared to be sharper than that of the physical mixture with small changes observed in the regions 800—1 100 and 3 100—3 500 cm^{-1}.

A preparation from guanidinium chloride and 18-crown-6 in ethanol yielded *crystals*, m.p. 175—178°, of 2 : 1 complex [Found: C, 37.05; H, 8.05; N, 18.4. $(CH_6N_3^+Cl^-)_2\cdot C_{12}H_{24}O_6$ requires C, 36.95; H, 7.95; N, 18.45%].

Crystal Data.—$C_{14}H_{36}N_8O_{12}$, $M = 508.48$. Monoclinic, $a = 8.969(1)$, $b = 10.278(2)$, $c = 14.253(1)$ Å, $\beta = 102.682(8)°$, $U = 1\,281.9$ Å^3, $D_m = 1.30$ g cm^{-3}, $Z = 2$, $[(CH_6N_3^+)_2(NO_3^-)_2C_{12}H_{24}O_6]$ $D_c = 1.318$ g cm^{-3}; space group $P2_1/c$ uniquely determined. Molecular symmetry required $\bar{1}$ in $C_{12}H_{24}O_6$. $F(000) = 544$, graphite monochromator, $\lambda(\text{Mo-}K_{\alpha 1}) = 0.709\,26$ Å, $\mu(\text{Mo-}K_{\alpha 1}) = 1.07$ cm^{-1}.

A crystal 0.19 × 0.18 × 0.05 mm was mounted about the *a* axis and approximate unit-cell dimensions were measured by precession photography. Because the diffraction pattern was weak the space group $P2_1/c$ was checked by axial scans on the CAD-4 diffractomer. Unit-cell dimensions were obtained from the positions of 25 high θ reflections and checked by Guinier powder photography. This technique confirmed that the whole sample was one phase. For intensity measurements the ω–2θ scan mode was used over the oscillation $(0.5 + 0.35 \tan \theta)°$. Observations were collected in range $1.3 \leqslant \theta \leqslant 20°$. Pre-scan runs at 2° min^{-1} were used to flag reflections having $\sigma(I)/I > 2$ as weak, final scans were made at slower speeds, the maximum time allowed being 90 s. Intensity control reflections, $11\bar{3}$ and 121, were measured after every 7 200 s exposure time and showed no significant change. Observations were processed,[4] an L_p correction being applied to yield a set of relative structure amplitudes (F) and standard deviations (σF).

Structure Determination.—There are four guanidinium and four nitrate ions in the unit cell and only two 18-crown-6 molecules which must themselves be centrosymmetrical.

The structure was solved by direct methods in SHELX; [5] isotropic refinement for the C, O, and N atoms led to R 0.13 for the 711 reflections having $F > 2\sigma(F)$.

Hydrogen atoms on the cyclic ether were included in calculated positions 0.98 Å from the carbon atoms and with isotropic vibration parameters 0.005 Å^2 greater than those of the attached carbon atoms. Refinement continued with anisotropic vibration parameters for atoms of the nitrate ion and the oxygen atoms in the cyclic ether and R was reduced to 0.101. A difference synthesis revealed five of the hydrogen atoms in the guanidinium ion; these were included in refinement and the sixth was located in a subsequent difference synthesis. These hydrogen atoms were allowed individual isotropic vibration parameters. A weighting analysis showed that unit weights were most satisfactory. Full-matrix refinement converged at R 0.083 (R_m 0.076), the most significant parameter shift being 0.1 times the corresponding standard deviation. Scattering factors were calculated from the analytical approximation coefficients given in Table 2.2B of ref. 6.

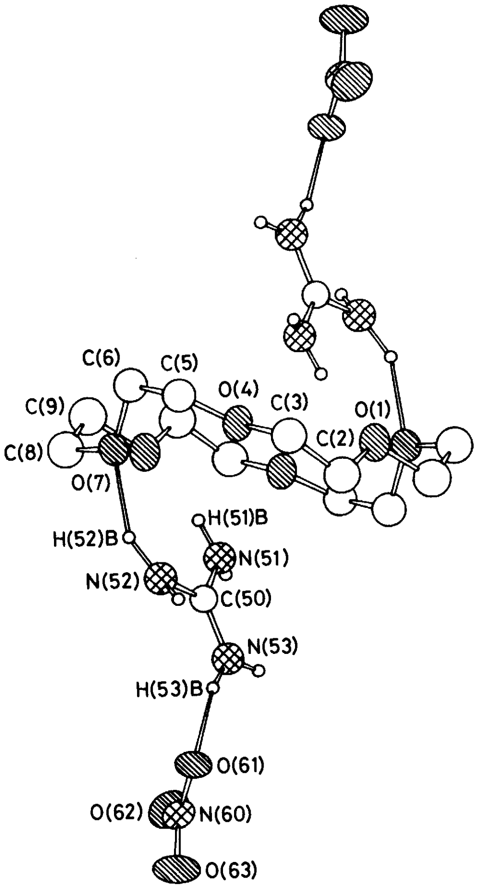

FIGURE 1 Designations of atoms including hydrogen atoms on the guanidinium ion. Roman numeral superscript I denotes atoms related by a centre of symmetry. Hydrogen atoms in the 18-crown-6 ring on atom C(n) are designated H(n)A and H(n)B

The highest peak on the final difference map was 0.43 e Å^{-3} situated on the C(2)–C(3) bond. Final parameters are in Table 1 and the numbering of the atoms is shown in Figure 1. The observed and calculated structure factors are in Supplementary Publication No. SUP 23072 (7 pp.).*

Computing.—Programs CAD4,[4] SHELX, [5] and ORTEP [7] were run on the ICL System 4 in the Computer Department, Rothamsted Experimental Station. For calculation of molecular geometry, the suite X-RAY ARC [8] was used on the IBM 1130 computer.

TABLE 1

Atomic co-ordinates (fractional × 10^4) and isotropic vibrational parameters U_{iso} (Å^2 × 10^3)

Atom	x	y	z	U_{iso}
O(1)	7 759(8)	3 492(7)	617(6)	*
C(2)	7 134(14)	4 582(13)	963(8)	89(4)
C(3)	8 142(13)	5 166(12)	1 766(8)	84(4)
O(4)	9 497(8)	5 641(7)	1 501(5)	*
C(5)	10 422(13)	6 416(12)	2 195(8)	76(4)
C(6)	11 770(13)	6 830(12)	1 826(8)	78(4)
O(7)	11 233(8)	7 620(7)	1 001(5)	*
C(8)	12 376(15)	8 146(13)	568(9)	91(4)
C(9)	13 217(15)	7 164(13)	133(9)	97(4)
C(50)	7 712(12)	7 687(10)	−652(7)	52(3)
N(51)	8 675(15)	6 791(11)	−840(10)	69(3)
N(52)	8 116(15)	8 375(11)	152(8)	72(3)
N(53)	6 437(13)	7 904(12)	−1 261(8)	70(3)
N(60)	3 878(11)	10 580(10)	−1 846(7)	*
O(61)	4 132(9)	10 005(7)	−1 060(6)	*
O(62)	4 699(9)	10 407(9)	−2 414(5)	*
O(63)	2 734(10)	11 295(9)	−2 050(5)	*
H(51)A	855(15)	659(13)	−132(9)	138(64)
H(51)B	963(14)	672(11)	−51(7)	105(45)
H(52)A	727(10)	851(8)	28(6)	50(28)
H(52)B	928(15)	842(12)	55(9)	147(52)
H(53)A	612(10)	738(10)	−175(7)	70(34)
H(53)B	578(20)	863(18)	−120(12)	223(84)

*Anisotropic vibration parameters have been deposited.

RESULTS AND DISCUSSION

Bond lengths and angles are in Table 2 and torsion angles in the 18-crown-6 ring are displayed in Figure 2. The centre of the cyclic ether is on a crystallographic centre of symmetry (the co-ordinates in Table 1 cor-

TABLE 2

Bond lengths (Å) and angles (°)

(i) The 18-crown-6 ligand

O(1)–C(2)	1.391(13)	C(9$^{\text{I}}$)–O(1)–C(2)	115.2(9)
C(2)–C(3)	1.426(14)	O(1)–C(2)–C(3)	112.9(11)
C(3)–O(4)	1.435(12)	C(2)–C(3)–O(4)	110.8(10)
O(4)–C(5)	1.394(12)	C(3)–O(4)–C(5)	114.5(8)
C(5)–C(6)	1.483(14)	O(4)–C(5)–C(6)	108.5(9)
C(6)–O(7)	1.423(12)	C(5)–C(6)–O(7)	107.6(9)
O(7)–C(8)	1.415(13)	C(6)–O(7)–C(8)	115.6(9)
C(8)–C(9)	1.476(15)	O(7)–C(8)--C(9)	114.1(11)
C(9)–O(1$^{\text{I}}$)	1.397(13)	C(8)–C(9)–O(1$^{\text{I}}$)	111.0(10)

(ii) The guanidinium ion

C(50)–N(51)	1.329(13)	N(51)–C(50)–N(52)	118.5(12)
N(51)–H(51)A	0.71(13)	N(51)–C(50)–N(53)	120.1(13)
N(51)–H(51)B	0.88(11)	N(52)–C(50)–N(53)	121.4(12)
C(50)–N(52)	1.327(13)	H(51)A–N(51)–H(51)B	115(13)
N(52)–H(52)A	0.83(9)	C(50)–N(51)–H(51)A	116(12)
N(52)–H(52)B	1.07(13)	C(50)–N(51)–H(51)B	123(8)
C(50)–N(53)	1.295(12)	H(52)A–N(52)–H(52)B	136(8)
N(53)–H(53)A	0.88(10)	C(50)–N(52)–H(52)A	101(6)
N(53)–H(53)B	0.97(19)	C(50)–N(52)–H(52)B	121(7)
		H(53)A–N(53)–H(53)B	117(11)
		C(50)–N(53)–H(53)A	121(7)
		C(50)–N(53)–H(53)B	122(10)

(iii) The nitrate ion

N(60)–O(61)	1.243(10)	1.258[a]	O(61)–N(60)–O(62)	120.7(10)
N(60)–O(62)	1.220(10)	1.253	O(61)–N(60)–O(63)	118.0(10)
N(60)–O(63)	1.243(10)	1.277	O(62)–N(60)–O(63)	121.2(10)

(iv) Hydrogen bonding

N(52)–O(7)	2.898(15)	N(52)–H(52)B · · · O(7)	151(11)
N(52)–H(52)B	1.07(13)	C(6)–O(7) · · · H(52)B	130(4)
H(52)B · · · O(7)	1.91(13)	C(8)–O(7) · · · H(52)B	113(4)
		C(6)–O(7)–C(8)	115.6(9)
O(61) · · · H(53)B	2.08(18)	N(53)–H(53)B · · · O(61)	172(15)
N(53)–H(53)B	0.97(19)	N(60)–O(61) · · · H(53)B	103(5)
O(61)–N(53)	3.046(14)		

[a] Corrected for libration.

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* See Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

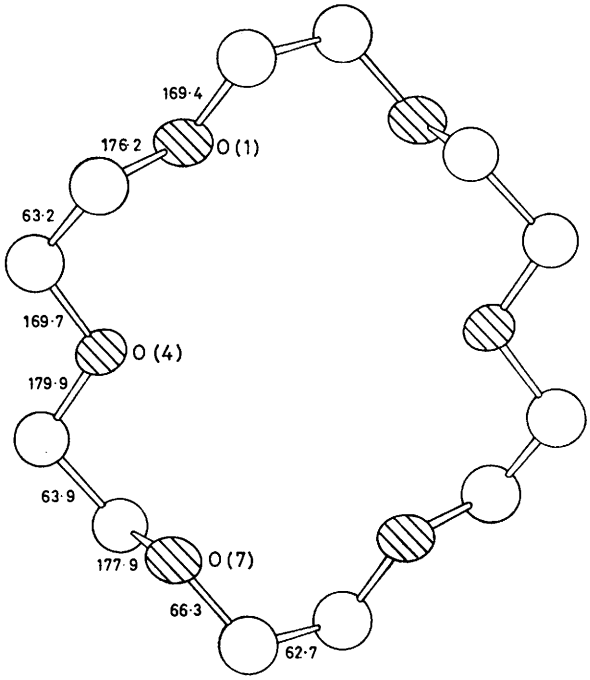


FIGURE 2 Torsion angles in the 18-crown-6 molecule

respond to the centre at 1, ½, 0). The carbon–carbon bond lengths exhibit the apparent shortening normally observed in macrocyclic polyethers; much of this is probably spurious, resulting from torsional libration, but even at 100 K the average C–C in 18-crown-6 is 1.510 Å.[9] For the nitrate ion a rigid-body analysis was carried out [10] and the corrected bond lengths are also shown in Table 2; the largest oscillation is about the O(61)–N(60) bond as can be seen in Figure 3.

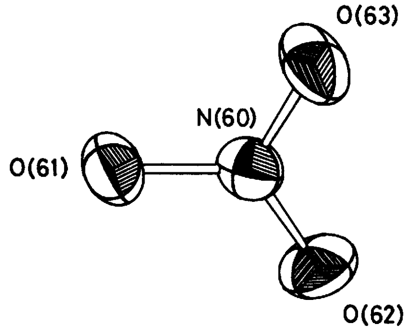
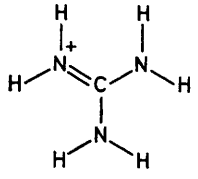


FIGURE 3 Thermal ellipsoids for the nitrate ion, drawn at the 50% probability level [7]



The guanidinium ion has three equivalent canonical forms. Equal contribution from all three would give an ion with trigonal symmetry with all 10 atoms coplanar. The N(53), H(53)A, H(53)B group is nearly coplanar with the CN_3 skeleton (plane 4 of Table 3). The deviations of the hydrogen atoms from that plane have the effect that pairs of NH bonds are not parallel as in the idealised molecule.

TABLE 3

Mean planes through groups of atoms with respect to orthogonal axes parallel to *a*, *b*, and c^*, with deviations (Å) of atoms from the planes (non-weighted planes)

Plane 1

$$0.6530x - 0.5283y + 0.5427z - 3.1415 = 0$$

Atoms in plane

O(1), O(4), O(7), $O(1^{I})$, $O(4^{I})$, $O(7^{I})$

Deviations (Å)

O(1)	−0.154(7)	N(52)	−2.85(1)
O(4)	0.183(7)	H(52)A	−3.35(9)
O(7)	−0.149(7)	H(52)B	−1.97(13)

Plane 2

$$-0.0729x + 0.8074y + 0.5855z - 6.4270 = 0$$

Atoms in plane

C(6), O(7), C(8)

Deviations (Å)

N(52)	0.12(5)
H(52)A	0.39(10)
H(52)B	0.41(13)

Plane 3

$$-0.4794x - 0.5720y + 0.6655z + 9.7526 = 0$$

Atoms in plane

C(9), $O(1^{I})$, $C(2^{I})$

Deviations (Å)

N(51)	1.13(5)
H(51)B	1.12(12)

Plane 4

$$0.5617x + 0.6799y - 0.4715z - 9.8099 = 0$$

Atoms in plane

C(50), N(51), N(52), N(53)

Deviations (Å)

C(50)	−0.012(8)	H(52)B	0.29(13)
N(51)	0.004(12)	N(53)	0.004(12)
H(51)A	0.20(14)	H(53)A	−0.12(10)
H(51)B	0.16(11)	H(53)B	0.13(18)
N(52)	0.004(12)	O(7)	0.34(2)
H(52)A	−0.44(9)	O(61)	0.14(3)

Plane 5

$$0.4861x + 0.7717y + 0.4101z - 9.2980 = 0$$

Atoms in plane

N(60), O(61), O(62), O(63)

Deviations (Å)

N(60)	0.013(8)	C(50)	−0.11(2)
O(61)	−0.004(8)	H(53)B	−0.43(18)
O(62)	−0.004(9)	N(53)	−0.75(2)
O(63)	−0.004(9)		

Angles between normals to planes

Planes	1	2	3	4
2	99.0(6)			
3	69.5(7)	92.1(7)		
4	104.4(4)	76.6(6)	166.4(29)	
5	82.4(3)	34.1(10)	113.7(7)	52.8(5)

Of six hydrogen atoms in the guanidinium ion two, H(52)B and H(53)B, take part in hydrogen bonds. These are indicated by N · · · O contacts, the angle subtended at the hydrogen, and the H · · · O contact as shown in Table 2. The shortest contacts are H(52)B to

O(7) and the centrosymmetrically related pair, O(7^{I}) and H(52^{I})B. The other hydrogen-bonded contact is to O(61) of the anion. These close contacts yield a centrosymmetrical five-entity complex as shown in Figure 1, anion · · · cation · · · crown · · · cation · · · anion.

The vibration parameters for the two hydrogen atoms taking part in hydrogen bonds are greater than those for the other four hydrogen atoms. These other hydrogens have apparently shorter N–H bonds; even if new positions were calculated by extending the N–H bond to 1.04 Å the H · · · O contacts would be 2.2 Å. A small change of orientation of the guanidinium ion could bring H(51)B near enough to O(1^{I}) to provide a second hydrogen-bonding contact. The second hydrogen on N(52) has O(61) in anion II as nearest neighbour (see Figure 4) while one hydrogen atom on each of N(51) and N(53) has, as nearest neighbour, O(63) and O(62) respectively in the anion III and, similarly, cation I to anion IV (Figure 4). These cation–anion contacts lie round the screw axes at $0, y, \pm 1/4$. There is an anion–anion contact from O(61) to the centrosymmetrically related atom in anion II at 3.08 Å (reduced to 3.055 Å with the libration correction).

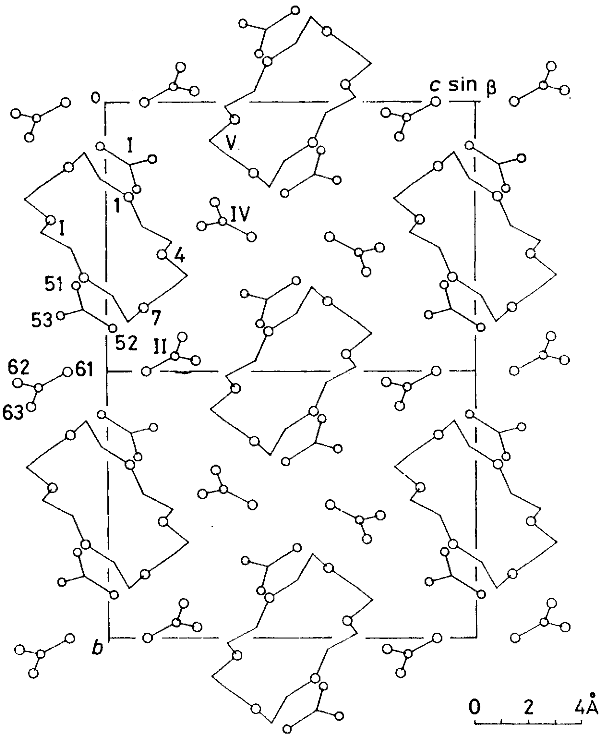


FIGURE 4 Projection of the structure along the *a* axis. Some atoms of the crystal chemical unit in Table 1 are labelled. Roman numerals correspond to the following equivalent positions with reference to *x*, *y*, *z* in Table 1:

I $2 - x, 1 - y, -z$
II $1 - x, 2 - y, -z$
III $1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
IV $1 + x, 1\frac{1}{2} - y, \frac{1}{2} + z$
V $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

H · · · O contacts less than 2.5 Å are H(52)A · · · O(61^{II}) 2.40, H(53^{I})A · · · O(62^{IV}) 2.38, H(51^{I})A · · · O(63^{IV}) 2.37, and H(51)B · · · O(1^{I}) 2.39 Å. The only contacts less than 3.0 Å between 18-crown-6 molecules are H(3)B to H(5^{V})A and H(6^{V})B, 2.84 and 2.50 Å, respectively

This can be considered as a distance of van der Waals contact, or possibly slight mutual repulsion. The effect of the electrostatic interaction which holds the crystal in three dimensions is to isolate the crown molecule from others of its kind and there are only two hydrogen–hydrogen contacts <3.0 Å between these molecules.

It is not only guanidinium salts which deposit crystals having stoicheiometry different from that of interaction with the cyclic ether in solution. While crystalline complexes of potassium thiocyanate with dibenzo-24-crown-8 [11] and sodium thiocyanate with dibenzo-30-crown-10 have 2 : 1 stoicheiometry,[12] careful e.m.f. measurements show no evidence of stoicheiometries other than 1 : 1 in methanol solution.[13,14] Possibly the 1 : 1 complex allows sufficient flexibility in the rest of the crown molecule to make crystallisation difficult, whereas 2 : 1 entities, although in low concentration at equilibrium, provide a more rigid system.

The effect of the pair of centrosymmetrically related hydrogen bonds on the crown molecule is to change one pair of torsion angles from those found in the crystal of the free molecule, and the smallness of this change is consistent with the similarity between the i.r. spectra of the free molecule and its complex. A similar conformation was found for the 2 : 1 complex of benzenesulphonamide,[15] in which the centrosymmetrical 18-crown-6 is the recipient of a pair of N–H · · · O(4) bonds, 1.994 Å, with the other amine hydrogen 2.337 Å from O(4′); the designations of the atoms are the same as those in the present work so that the recipient oxygen atom is not the ' expected ' O(7).

The change in a pair of torsion angles from the free molecule is from *trans* to *gauche* about C(5)–C(6) and C(5^{I})–C(6^{I}). A further change from *gauche* to *trans* about the pair O(7)–C(8) and O(7^{I})–C(8^{I}) is required to give the most symmetrical conformation for 18-crown-6, which gives a characteristically simple i.r. spectrum. That conformation has all C–C torsion angles *gauche* with alternating signs and all O–C torsion angles *trans* so it approximates to D_{3d} symmetry. It is found for complexes with potassium and larger metallic cations,[16] in the complexes with ammonium bromide,[17] and benzylammonium thiocyanate.[18] It may also be induced in crystals having 18-crown-6 as a solvate, receiving hydrogen bonds from co-ordinated water molecules; the first example was uranyl nitrate [19] and, more recently, hexaaquamanganese perchlorate, 18-crown-6 (as calculated with the co-ordinates in ref. 20). Even when the crystal contains only neutral molecules with CH_2 or CH_3 as donor entities, this conformation has been induced, as in the 2 : 1 complex malononitrile–18-crown-6 [21] or in dimethyl acetylenedicarboxylate–18-crown-6 (1 : 1),[22] respectively.

Molecular mechanics calculations [18] have shown the approximate D_{3d} conformation to be 7.84 kcal mol^{-1} above the minimum energy conformation which is that found in the uncomplexed molecule. The conformation found here is 5.01 kcal mol^{-1} above the minimum. Intuitively, it seems reasonable that fewer interactions than those found in complexes which lead to the D_{3d} conformation will result in a smaller deviation from the minimum energy conformation. While the free energy of complex formation in solution is affected by many factors other than the conformation of the ligand, the order of magnitude of the free energies is of interest. From ref. 3 we calculate a value of 5.8 kcal mol^{-1} at 25° for the ammonium complex and 1.4 kcal mol^{-1} for the guanidinium 1 : 1 complex.

Other conformations which have been found for hydrogen-bonded complexes include the hexa-aquacobalt complex in $[Co(H_2O)_6][CoCl_4]C_{12}H_{24}O_6{\cdot}C_3H_6O$ [23] where there are two pairs of three contiguous *gauche* bonds C–O–C–C, O–C–C–O, and C–C–O–C; this was not considered in the molecular mechanics treatment.[18]

A survey of published compounds containing the guanidinium ion [24] reveals a variety of hydrogen-bonding patterns. The involvement of only two, as found here, is the minimum; others up to six as in the carbonate [25] have been found. In the carbonate all are to oxygen atoms of the anion and there is no correlation between the length of the hydrogen bond and the distance of the atoms from the plane.

In light of the *X*-ray crystallographic results, it was of interest to determine whether the 2 : 1 (guanidinium–18-crown-6) complex species could be detected in methanol solution. The reaction of guanidinium ion with 18-crown-6 was previously studied in methanol by calorimetric titration and the log *K*, ΔH, and $T\Delta S$ values [3] reported from this work were valid for a reaction stoicheiometry of 1 : 1. Solutions used in these experiments were fairly dilute, the highest total guanidinium ion concentration being 0.008M and the mole ratio of guanidinium ion to 18-crown-6 always less than one. These data provided no hint of the presence of product species other than the 1 : 1 complex in the reaction mixture. This did not rule out the possibility that measurable amounts of 2 : 1 complex species might be detected under more favourable conditions. Consequently, further calorimetric titration experiments have been performed at much higher guanidinium ion concentrations which ought to be more favourable to the formation of the bisguanidinium complex found in the solid phase.

The reagents used in the calorimetric experiments were the same as those reported previously: guanidinium chloride was *ca.* 98% pure and the 18-crown-6 >99% pure.[3] A 2.0M-guanidinium chloride solution in methanol was titrated into 0.05 or 0.1M-18-crown-6 in a 25-ml Tronac isoperibol calorimeter. The total concentration of guanidinium ion in the reaction vessel at the end of the titration was *ca.* 0.2M. Thus the mole ratio of guanidinium ion to 18-crown-6 approached 4 : 1 and 2 : 1 under the two experimental conditions.

At the indicated high reactant concentrations in a solvent (methanol) of dielectric constant less than half that of water, activity coefficients were probably far from unity and ion pairing was significant. Thus, the values of log *K* and ΔH derived from these experiments, which agree very well internally but which differ slightly from those reported previously, are not treated as thermodynamically correct and are not reported herein. Rather, discussion centres on whether or not the calorimetric data support the presence of measurable amounts of the 2 : 1 complex in methanol.

A relatively large amount of heat was measured at the concentrations used in the titration experiments. Figure 5 is a computer-generated plot of the data points collected in one experiment with heat in calories plotted *versus* the mole ratio of guanidinium ion to 18-crown-6. As expected when the total measured heat was high (in this case *ca.* 5 cal), the amount of thermal ' noise ' was very small, and reproducibility between runs was excellent. The degree of curvature in the plot in Figure 5 was more than sufficient to allow an unambiguous and narrowly-defined minimum in a least-squares fitting procedure to determine log *K* and ΔH. Figure 5 shows the experimental and calculated curves superimposed on each other. Because the fit is very good, it is difficult to distinguish the experimental from calculated points. When an additional reaction involving production of the 2 : 1 complex was included in the reaction scheme to which the data were fitted, a poorer fit of the calculated curve to the experimental data was obtained and the formation constant for the 2 : 1 species was relatively small (<0.5). Indeed, under these conditions, the data point by data point species distribution tables for best-fit parameters (log *K* and ΔH) listed the concentration of 2 : 1 complex as <1% of the total 18-crown-6 concentration at the end of the titration. Since the calculations are expected to be no more precise than this, the method neither rules out nor proves the presence of a very small amount of 2 : 1 complex. It does show, however, that the amount of 1 : 1 species in the reaction mixture far exceeds the amount of 2 : 1 species, if any, under these conditions.

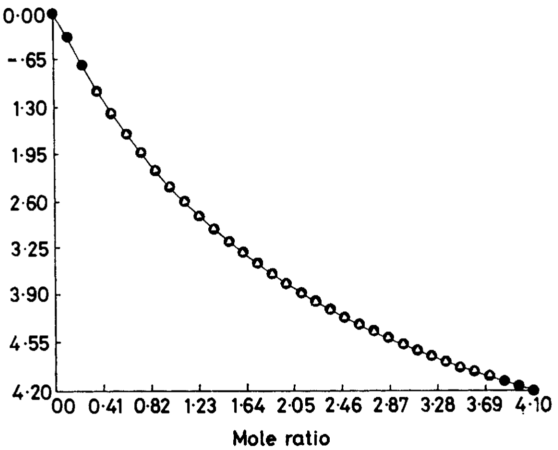


FIGURE 5 Computer-generated plot of heat (cal) *versus* the mole ratio of guanidinium ion (titrant) to 18-crown-6 (titrate) for titration of 2M-guanidinium chloride into 0.05M-18-crown-6. From points 4—32, the calculated curve (●) from least-squares fit best values of log *K* and ΔH is superimposed on the experimental curve (△) assuming production of only 1 : 1 complex species

While the calorimetric method is a good indicator of reaction stoicheiometry and thermodynamics, it reveals almost nothing concerning the structure of products. It was previously noted [3] that while the binding constant for reaction of guanidinium ion with 18-crown-6 was in the same range as that for $R_2NH_2^+$ ions, the ΔH value was not. It was postulated that the highly ordered solvation shell around the guanidinium ion was responsible for the difference in ΔH. However, it is conceivable that other factors are responsible, including an irregular mode of binding. This is an area which remains open to investigation.

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