Formation of 2:1 Complexes between Alkylammonium Cations and Diaza Crown Ethers

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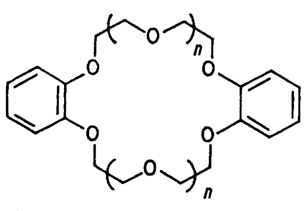
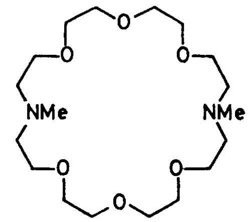
Summary The diaza-24-crown-8 derivative (**2**) forms a 2:1 complex with benzylammonium thiocyanate in deuteriomethylene chloride solution; under similar conditions the diaza-24-crown-6 derivative (**3**) forms 1:1 complexes with primary alkylammonium thiocyanates but a crystalline complex of (**3**) with benzylammonium thiocyanate is shown by *X*-ray analysis to be a 2:1 complex.

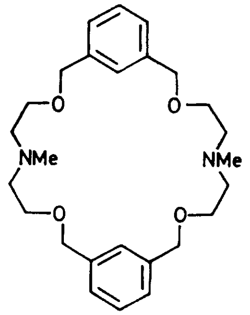
THE multiple binding sites presented by the macrocycles of dibenzo-24-crown-8 (**1a**) and dibenzo-30-crown-10 (**1b**) permit the formation of 2:1 (cation:host ratio) complexes with both sodium and potassium salts.[1] The larger crown systems have also been investigated as host molecules for organic cations, including primary alkylammonium,[2] guanidinium,[3] and imidazolium cations;[4] there have, however, been no reports of the formation of 2:1 complexes of organic guest cations with monocyclic crown ether hosts.



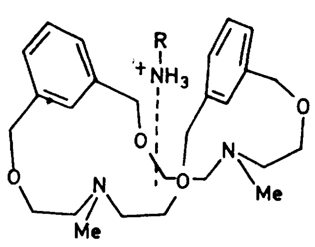
(1) a; n = 2 ; b; n = 3



(2)



(3)



(4)

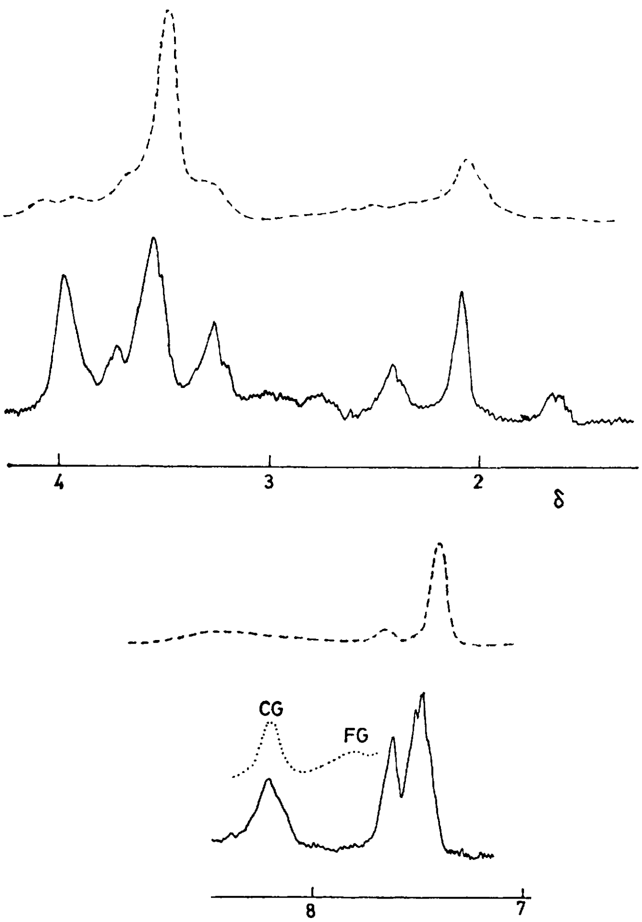


FIGURE 1. N.m.r. spectrum (220 MHz) of 2:1 complex of hosts (**2**) with benzylammonium thiocyanate in CD_2Cl_2 at −90 °C. The broken line shows the corresponding spectrum for a solution containing a 1:1 guest:host ratio and the dotted line shows the spectrum of a solution containing a 4:1 guest:host ratio. The descriptions CG and FG refer to the $\overset{+}{N}H_3$ signals of the complexed and free guest salt.

The n.m.r. spectrum of (**2**) and benzylammonium thiocyanate (1 : 1) in CD_2Cl_2, although temperature dependent, does not provide evidence for slow guest–host exchange processes, contrary to the situation[5] in analogous aza-15-crown-5 and aza-18-crown-6 systems. At a 2 : 1 guest : host ratio, strikingly different results are obtained. At low temperatures the n.m.r. spectrum is reasonably well defined (Figure 1), demonstrating that face to face guest exchange is slow compared with the n.m.r. time scale. There is no evidence for the presence of more than one kind of complex and the guest signals differ, at all temperatures, from those in the spectrum of the 1 : 1 mixture. A similar situation obtains for the 4 : 1 mixture and additionally, at low temperatures, signals corresponding to the $\overset{+}{N}H_3$ group in the free and complexed guest are observed (Figure 1). We conclude from these results that the host (**2**) forms a weak 1 : 1 complex with benzylammonium thiocyanate at low guest : host ratios but at guest : host ratios of 2 : 1 or greater the solution contains a 2 : 1 complex. The n.m.r. spectrum of the 2 : 1 complex (Figure 2) is not definitive but it is consistent with a centrosymmetric complex in which the guest molecules are bound to opposite ends and faces of the host macrocycle, as found in analogous complexes of sodium and potassium salts.

The 24-crown-6 system (**3**) forms 1 : 1 complexes in CD_2Cl_2 with primary alkylammonium thiocyanates and the n.m.r. spectra of their solutions provide evidence for slow face to face guest exchange at low temperature (*cf.* ref. 5). The high field shifts of the $C\mathit{H}\overset{+}{N}$ signals of the guest (for example $Me\overset{+}{N}H_3NCS^-$, δ 1·60 in the complex at 25 °C as compared with δ 2·5 for the free guest) which are more pronounced at low temperatures, are consistent with a 1 : 1 complex having a structure along the lines indicated in (**4**). The spectrum of a solution containing a 2 : 1 guest : host ratio shows similar behaviour of the host signals but the guest signals have chemical shifts intermediate between those of free and complexed guest ($Me\overset{+}{N}H_3NCS^-$, δ 2·06 at 25 °C). At very low temperatures the guest signals broaden but separation into signals assignable to free and complexed guest does not occur in the available temperature range (down to −110 °C). We conclude that the solution contains largely the 1 : 1 complex together with free guest.

Crystallisation of the residue after evaporation of a solution of (**3**) containing benzylammonium thiocyanate in a 1 : 1 ratio gave a crystalline 2 : 1 complex. The crystal structure of this complex has been determined from *X*-ray diffraction measurements. The crystals are triclinic with $a = 9{\cdot}651(3)$, $b = 10{\cdot}813(2)$, $c = 12{\cdot}388(3)$ Å, $\alpha = 115{\cdot}16(2)$, $\beta = 64{\cdot}82(2)$, $\gamma = 100{\cdot}38(2)°$, $Z = 1$, space group $P\bar{1}$. The molecule lies on a crystallographic centre of symmetry. The structure was solved by direct methods and refined by least-squares analysis; the final R was 0·04 for 1852 reflections. The structure is shown in (**5**).† It can be seen that one of the N–H bonds of the benzylammonium cation participates in intramolecular hydrogen bonding with the nitrogen atom of the host macrocycle. The other two N–H bonds form intermolecular and intramolecular hydrogen bonds to the nitrogen atom of one thiocyanate anion and the sulphur atom of another thiocyanate anion.‡

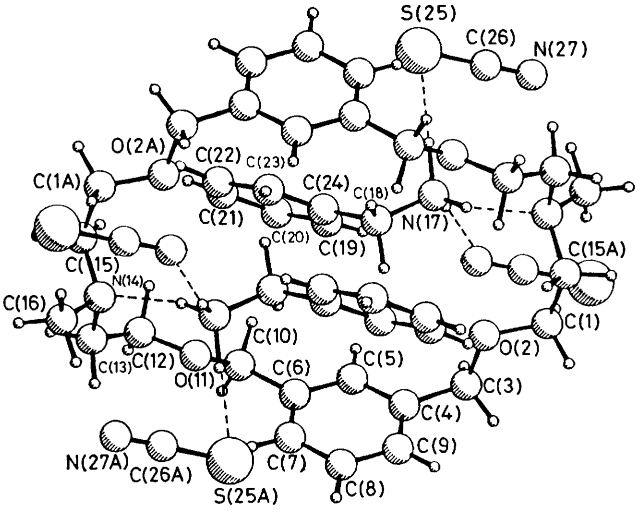


FIGURE 2. Benzylammonium thiocyanate complex of diaza-24-crown-6 (2:1) (**5**).

The preferential formation of 2 : 1 complexes in solution, analogous to the complex formed between benzylammonium thiocyanate and host macrocycle (**2**), has potential as a method for the recognition of the quantity of a guest species present in solution; previous studies of the complexes of alkylammonium cations have concentrated upon the recognition of guest structure.

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† Details of the structure will be given in the full paper. The broken bonds in (**5**) represent the hydrogen bonds.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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