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Hydration, Ion Pairing, and Sandwich Motifs in Ammonium Nitrate Complexes of Crown Ethers

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Abstract—Ammonium nitrate coordinates to 18-crown-6 through a near-ideal 'tripod' arrangement of hydrogen bonds to alternate crown ether oxygen atoms. Ion pairing interactions are apparent, with the strength of this ion pairing interaction appearing to be reduced by hydration, representing a potentially significant role of water in cation–molecule complexes. The bis(benzo-15-crown-5) complex of ammonium nitrate is of sandwich type structure, with the ammonium ion complexed between two roughly parallel crown ether rings through an unusual but efficient set of linear, bifurcated, and off-axis hydrogen bonding interactions. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Short on the heels of Pedersen's initial discovery[1] that macrocyclic poly(ethers) ('crown ethers') interact strongly with alkali metal cations came the realization that more complex cations, including ammonium and alkylammonium ions, could also form complexes with crown ethers.[2] In contrast to the charge–dipole interactions responsible for complexation of simple metal cations, ammonium complexation was presumed to be effected by hydrogen bonding. Following a number of studies elucidating the stoichiometry of ammonium ion complexation by various crown ether derivatives in solution,[3] several X-ray crystallographic studies unambiguously demonstrated the near-ideal coordination geometry afforded for ammonium ions by 18-crown-6.[4–6] The ammonium ion forms a 'perching' complex, resting above the mean plane defined by the oxygen atoms of the crown ether and forming three well-directed hydrogen bonds to alternate crown ether oxygen atoms.

Smaller crown ethers such as 15-crown-5 provide a less optimal geometry for ammonium ion complexation.[7] A variety of solution studies have pointed to the formation of complexes of 2:1 stoichiometry between such crown ethers and ammonium salts.[2,3,8,9] Early predictions that the ammonium ion would be 'sandwiched' between two crown ethers have been confirmed by several single crystal X-ray structural analyses,[10,11] and a number of related sandwich structures of 15-crown-5 derivatives with other cations have also been reported.[12–19]

Alkylammonium ion complexation has played a central role in numerous molecular recognition studies.[20] Given this, as well as our on-going interest in the recrystallization of ammonium salts through the intermediacy of soluble complexes,[21] we have focused our attention on the development of a deeper structural understanding of the complexation of simple ammonium salts by crown ethers. In the course of these studies, reported herein, we have also advanced our understanding of two other issues of long-standing interest—the role of water in crown ether complexation and the prevalence of ion-pairing interactions in crown ether complexes, as discussed below.

Results and Discussion

18-Crown-6 complexes. Ammonium salts are complexed quite efficiently by 18-crown-6,[28] with, e.g. a reported association constant on the order of 10^4 in methanol.[29] Solution studies point clearly to the formation of complexes of 1:1 stoichiometry, consistent with the near-ideal 'tripod' of hydrogen bond acceptor sites afforded by this crown ether in its generally preferred D_{3d} conformation. Although numerous crystallographic structural analyses of various alkylammonium ion complexes of 18-crown-6 and related macrocyclic chelating agents have been reported,[30–32] solid-state structural studies of simple ammonium (NH_4^+) complexes are comparatively rare.[4–6] In the course of our studies of the crown ether mediated solubilization of simple ammonium salts in unusual solvents,[21] we have characterized a series of ammonium nitrate complexes which highlight several fundamental structural motifs for the interaction of this simple ion with crown ethers, with the counteranion, and with water.

Keywords: ammonium nitrate complexes; crown ethers; ion pairing.

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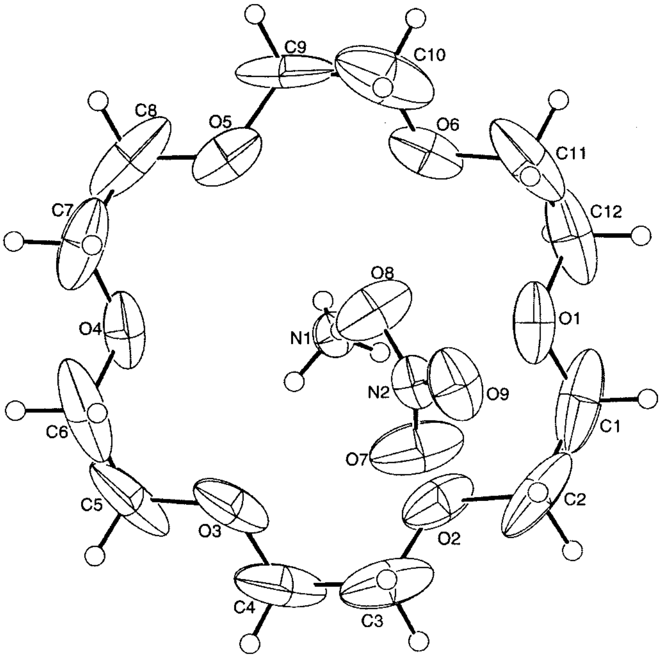

Figure 1. Molecular structure of NH_4NO_3·18-crown-6 (**1**).

Addition of 1 equiv. of 18-crown-6 to a suspension of ammonium nitrate in chloroform allows the preparation of up to a ca. 0.83 M solution of the crown ether complex. Crystallization via vapor diffusion or simple solvent–solvent interdiffusion of a precipitating solvent such as benzene results in the growth of well-formed prismatic crystals of a complex of 1:1 stoichiometry, as indicated by reaction stoichiometry, ^1H NMR spectral analysis, and elemental analysis. Single crystal X-ray structural analysis was hindered by the relatively low intensity of the reflections, but provided a sufficiently detailed picture of the structure of the complex (Fig. 1, Tables 3 and 4) to allow some conclusions to be drawn. The ammonium ion perches above the mean plane defined by the atoms of the crown ether, with the nitrogen atom ca. 0.86 Å above this plane. Three anchoring hydrogen bonds between the ammonium ion and alternate oxygen atoms in the crown ether are indicated by the short N–H···O distances to these three oxygen atoms. These distances, 2.830(5) (N1–H28···O3), 2.858(5) (N1–H26···O1), and 2.896(5) Å (N1–H27···O5), are in accord with hydrogen bonds in related ammonium complexes of crown ethers, as are the N–H···O angles,

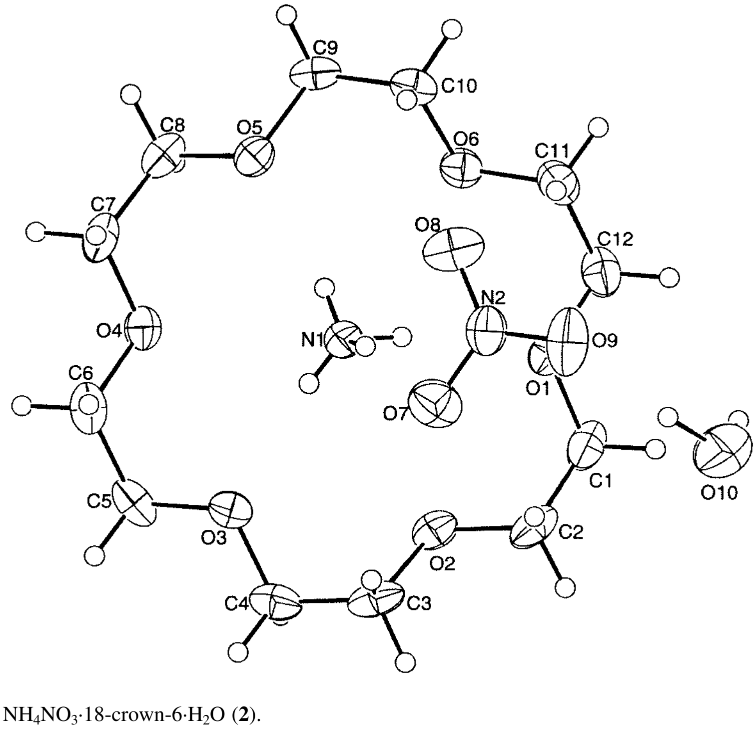

Figure 2. Molecular structure of NH_4NO_3·18-crown-6·H_2O (**2**).

Table 1. Key hydrogen bonding interactions in ammonium complexes of 18-crown-6

Complex	N–H···O (Å)	N–H···O (°)	N–H···anion (Å)	N–H···anion (°)	N···mean plane (Å)	Source
NH_4NO_3 (**1**)	2.830, 2.858, 2.896	164.6, 147.9, 148.6	2.809	172.9	0.86	This work
$NH_4NO_3{\cdot}H_2O$ (**2**)	2.855, 2.883, 2.895	158.1, 171.9, 163.4	2.908	148.5	0.939	This work
NH_4Cl (a)[a]	2.88, 2.91, 2.91	151, 155, 151	3.11	158	0.96	Ref. 5
NH_4Cl (b)[a]	2.87, 2.90, 2.92	146, 148, 152	3.19	162	1.01	Ref. 5
$NH_4Cl{\cdot}2H_2O$	2.90, 2.91, 2.91	169, 169, 169	3.25	168	1.07	Ref. 5
$NH_4Br{\cdot}2H_2O$	2.857, 2.884, 2.884	178.5, 177.5, 177.5[b]	3.438	153[b]	1.00	Ref. 4

[a] Two distinct $NH_4^+{\cdot}$18-crown-6 units present in asymmetric unit, here labeled a and b.

[b] Calculated from data provided in Ref. 4.

164.6, 147.9, and 148.6°, respectively.[20,33] The other crown ether oxygen atoms display poor distances and/or angles for hydrogen bonding, as expected given the conformation of the crown ether, which turns these oxygen atoms away from the ammonium ion. The crown ether adopts a symmetrical D_{3d}-like conformation,[34] with dihedral angles matching well with those seen in numerous other cation-18-crown-6 complexes.[35]

Each of these structural features is consistent with those reported for the 18-crown-6 complexes of ammonium chloride,[5] ammonium bromide,[4] and ammonium dithiocyanatocuprate.[6] Interestingly, each of these structures also reveals an additional bonding interaction between the crown ether-bound ammonium ion and the counteranion. Such ion pairing interactions are comparatively scarcely reported, perhaps due to the common use of salts of weakly coordinating counteranions such as picrate and perchlorate in the crystallization of complexes for structural analysis. However, these ion pairing interactions can be of great significance in determining the solution properties and stoichiometries of cation–crown ether complexes,[36,37] and it is thus of considerable interest when examples displaying discrete ion pairing interactions in the solid-state arise. The N–H···O distance to the nearest nitrate oxygen atom in the ammonium nitrate complex of 18-crown-6, at 2.809(5) Å, is shorter than any of the crown ether interactions, and this hydrogen bond is more linear as well (N1–H25···O8 angle 172.9°). A single hydrogen bond to the nitrate anion rather than a bifurcated bonding arrangement is present, with the next closest N–H···O distance well over 3 Å and a much less desirable angle of 128.8°. Analogous significant ion pairing interactions are seen in the ammonium chloride, bromide, and dithiocyanatocuprate complexes as well (vide infra).

Crystallization of the ammonium nitrate complex of 18-crown-6, not surprisingly, is influenced by the nature of the crystallization solvent. Although the same complex is obtained from a number of solvent mixtures, crystallization from chloroform/diethyl ether affords a new complex. While this complex maintains a 1:1 stoichiometry, elemental analysis and X-ray crystallographic analysis reveal it to be a monohydrate (Fig. 2). The overall structural features of this complex are in close agreement with those presented by the anhydrous complex—the crown ether adopts a highly symmetrical pseudo-D_{3d} conformation, the ammonium ion perches ca. 0.939 Å above the mean plane, the N–H···O distances are 2.855(3) (N1–H4···O3), 2.883(3) (N1–H1···O1), and 2.895(3) Å (N1–H3···O5), and the N–H···O angles are 158.2, 171.9, and 163.4°, respectively (Tables 3 and 4). Discrete ion pairing to the nitrate counteranion is again indicated, with a closest N–H···O contact of 2.908 Å (angle 148.5°), and the nitrate is additionally hydrogen bonded to the hydrate molecule, with an O–H···O contact of 2.931 Å (angle 157.1°).

These two structural analyses, together with the closely related ammonium chloride and ammonium bromide structures reported by others, provide a unique opportunity to examine more closely the structural details of ion pairing interactions in crown ether complexes. Key structural features for each of these complexes are summarized in Table 1. In the ammonium nitrate complexes, the N–H···O distance is lengthened by a full 0.1 Å in the hydrated complex, suggesting a weakening of the ion pairing interaction. An analogous effect is demonstrated in the available structures of two ammonium chloride complexes, with the anhydrous complex displaying N–H···Cl distances of 3.11 and 3.19 Å (for the two distinct such interactions present in the asymmetric unit) and the hydrated complex a distance of 3.25 Å. Finally, although the structure of an anhydrous ammonium bromide complex has not been reported, that of a hydrated complex has appeared. In marked contrast to the chloride and nitrate complexes, all of which display cation–anion contacts well within the sum of the ionic radii of the interacting ions, it is noteworthy that the N–H···Br contact is longer (3.438 Å) than the sum of the ionic radii [1.43 (NH_4^+), 1.96 (Br^-)]. Perhaps not unreasonably, one may conclude that hydrated anions ion pair less efficiently with the crown ether-bound ammonium ion than do anhydrous anions. Taken in a broader sense, this suggests that ion pairing interactions in crown ether complexes may be expected to be relatively insignificant in aqueous solutions, but may be anticipated to play significant roles in anhydrous media. This represents a potentially significant role for water in dictating the structural details of cation–crown ether complexes which has apparently not previously been noted.[38,39]

15-Crown-5 complexes. In contrast to the 1:1 stoichiometry observed to lead to complete solubilization of ammonium nitrate with 18-crown-6, 2 equiv. of 15-crown-5 are required to bring ammonium nitrate into solution in solvents in which it is otherwise at best sparingly soluble, including acetonitrile and acetone. This stoichiometry is consistent with that reported for the complexation of ammonium salts by 15-crown-5 derivatives by earlier workers,[2,3] and in fact was noted by Pedersen in his first reports of the synthesis and cation-binding properties of the crown ethers.[1] A 'sandwich' type structure has been inferred for the ammonium complexes of crown ethers such as

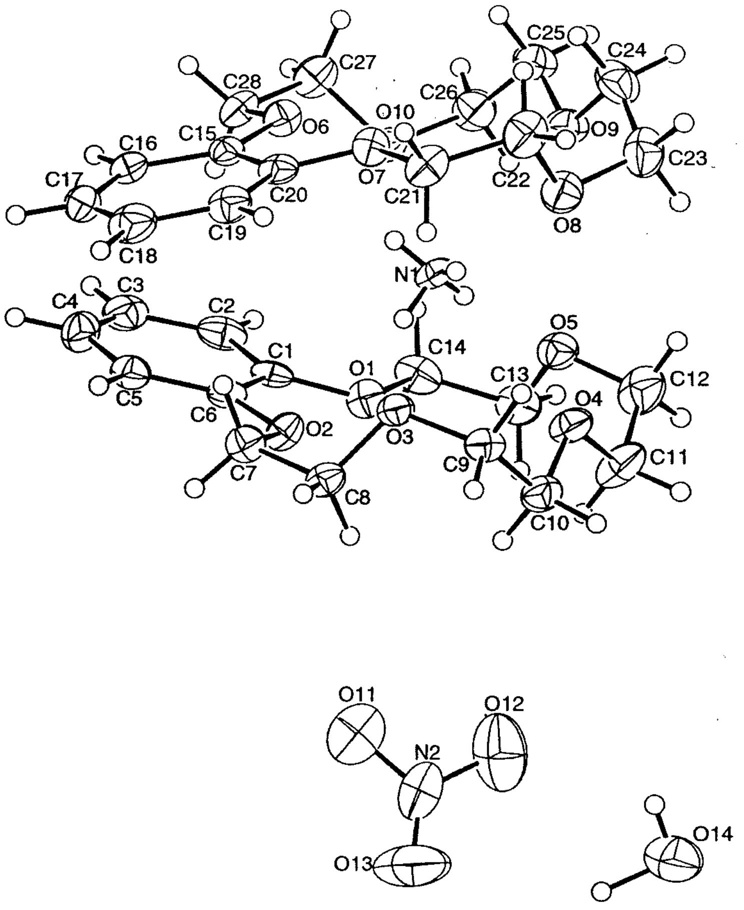

Figure 3. Molecular structure of $NH_4NO_3{\cdot}2$(benzo-15-crown-5)$\cdot H_2O$ (**3**).

15-crown-5 based on its smaller 'cavity size' (diameter ca. 1.7–2.2 Å)[40–42] relative to that in 18-crown-6 (2.6–3.2 Å). Two ammonium complexes of 15-crown-5 derivatives have been characterized structurally by single crystal X-ray diffraction analysis, one of a cyclohexano-15-crown-5 derivative,[10] the other of benzo-15-crown-5.[11] Unfortunately, our repeated efforts to grow single crystals of the apparent 2:1 complex of the 'parent' 15-crown-5 with ammonium nitrate were uniformly unsuccessful. Although crystals were obtained from a variety of solvent combinations, these crystals were frequently hollow and always extensively twinned. Unit cell parameters were determined from the limited diffraction data sets obtainable, demonstrating a single complex was formed regardless of crystallization solvent, but only fragments of the overall molecular structure were revealed during attempted structure solution.

In an attempt to circumvent these crystallinity problems, we explored the complexation of ammonium nitrate by benzo-15-crown-5. As for 15-crown-5 itself and consistent with a recent structural report,[11] a 2:1 stoichiometry was suggested by the need for 2 equiv. of this crown ether to solubilize ammonium nitrate in acetone or acetonitrile. Crystallization from acetonitrile solutions using a variety of precipitating solvents, including ethyl acetate, benzene, toluene, and tetrahydrofuran, afforded well-formed crystals. Twinning problems were indeed substantially eliminated, allowing successful structure solution and refinement, although diffraction peaks were still rather weak. As a result, the refinement did not progress as far as desired to allow a detailed analysis of the structure [$wR(F^2) = 10.6\%$], but nonetheless, the significant features of the structure are clearly revealed (Fig. 3, Tables 5 and 6). This complex displays a number of interesting features, as best highlighted by comparison with the published structures of other benzo-15-crown-5 sandwich complexes.[11–17,19]

As long inferred from the stoichiometry of complexation, the ammonium ion is 'sandwiched' between two crown ether moieties. The ammonium ion, as expected, perches above the mean planes defined by the crown ether atoms. It is appreciably more out-of-plane than in the 18-crown-6 complexes (1.961 and 2.015 Å, for the two rings vs. ca. 1 Å for the 18-crown-6 complexes), consistent with the smaller 'cavity' size of 15-crown-5 derivatives. Other benzo-15-crown-5 sandwich complexes display similar features, differing in only two primary respects—the location of the complexed cation relative to the crown ether rings and the relative orientations of the two rings. Thus, for example, the potassium iodide complex displays an analogous 'sandwich' structure, although the potassium ion, only slightly smaller than the ammonium ion (1.33 Å vs. 1.43 Å), is nestled appreciably more tightly into the crown ethers (1.67 Å out of plane). The two aromatic rings in the ammonium nitrate complex are rotated by ca. 45° with respect to one another, as seen in the complementary structure of a benzo-15-crown-5 ammonium complex reported by Rogers et al.,[11] while they are *anti* to one another in the potassium

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for complex **3** ($B_{\mathrm{eq}} = (8\pi^2/3)S_iS_jU_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
O(1)	0.3878(2)	0.5231(2)	0.8938(3)	3.84(9)	C(7)	0.4568(4)	0.4067(3)	0.6635(4)	3.86(13)
O(2)	0.4384(2)	0.4515(2)	0.7460(2)	3.60(9)	C(8)	0.4551(4)	0.3363(3)	0.7065(4)	3.87(14)
O(3)	0.3535(2)	0.3223(2)	0.7283(2)	3.70(9)	C(9)	0.3502(4)	0.2654(2)	0.7959(4)	3.80(14)
O(4)	0.3105(2)	0.3258(2)	0.9435(2)	4.37(9)	C(10)	0.3853(~)	0.2818(3)	0.9098(4)	4.35(15)
O(5)	0.2596(2)	0.4596(2)	1.0174(2)	4.14(9)	C(11)	0.3391(5)	0.3468(3)	1.0482(4)	5.98(17)
O(6)	0.1145(2)	0.5092(2)	0.5939(2)	3.67(9)	C(12)	0.2618(5)	0.3975(4)	1.074B(4)	6.06(19)
O(7)	0.0916(3)	0.3801(2)	0.5836(2)	3.87(9)	C(13)	0.3391(4)	0.5080(3)	1.0585(4)	4.88(16)
O(8)	0.0621(3)	0.3149(2)	0.7664(3)	4.85(10)	C(14)	0.3505(4)	0.5592(3)	0.9762(4)	4.39(14)
O(9)	0.0129(3)	0.4426(2)	0.8601(3)	4.45(9)	C(15)	0.1632(4)	0.4778(3)	0.5201(4)	3.14(13)
O(10)	0.1161(2)	0.5630(2)	0.7907(2)	3.79(9)	C(16)	0.2205(4)	0.5111(3)	0.4538(4)	3.81(14)
O(11)	0.7133(4)	0.3139(2)	0.8897(4)	8.61(16)	C(17)	0.2679(4)	0.4727(4)	0.3850(4)	4.83(16)
O(12)	0.6738(5)	0.2644(3)	1.0176(4)	10.68(19)	C(18)	0.2594(5)	0.4026(4)	0.3832(4)	5.51(18)
O(13)	0.8226(4)	0.2493(4)	0.9757(6)	16.2(3)	C(19)	0.2003(4)	0.3700(3)	0.4476(4)	4.28(14)
O(14)	0.7090(3)	0.1569(2)	1.1741(3)	8.07(13)	C(20)	0.1521(4)	0.4056(3)	0.5167(4)	3.36(13)
N(1)	0.2128(3)	0.4292(2)	0.7929(3)	3.69(10)	C(21)	0.0795(4)	0.3077(3)	0.5869(4)	4.56(16)
N(2)	0.7443(6)	0.2754(3)	0.9628(5)	7.2(2)	C(22)	0.0097(4)	0.2950(3)	0.6653(5)	5.26(17)
C(1)	0.4009(3)	0.5600(3)	0.8059(4)	3.40(13)	C(23)	−0.0068(5)	0.3222(3)	0.8405(4)	5.72(18)
C(2)	0.3869(4)	0.6302(3)	0.7939(4)	4.30(15)	C(24)	−0.0613(4)	0.3893(3)	0.8326(4)	5.67(18)
C(3)	0.4034(4)	0.6606(3)	0.7016(5)	4.77(16)	C(25)	−0.0340(4)	0.5078(3)	0.8477(4)	5.22(17)
C(4)	0.4323(4)	0.6224(3)	0.6231(4)	4.69(16)	C(26)	0.0487(4)	0.5619(3)	0.8668(4)	4.98(16)
C(5)	0.4460(4)	0.5524(3)	0.6355(4)	3.82(14)	C(27)	0.0747(4)	0.6003(3)	0.6987(4)	4.80(15)
C(6)	0.4304(3)	0.5201(3)	0.7260(4)	3.17(13)	C(28)	0.1328(4)	0.5807(2)	0.6126(4)	3.99(14)

iodide complex,[12] disposed centrosymmetrically about the potassium ion. The latter orientation is also seen in a cesium complex,[19] although other examples of both cesium[16] and potassium complexes[15] in which the rings are rotated only ca. 50–60° with respect to one another have also been characterized. It appears clear that the factors affecting these conformational preferences are subtle. Interestingly, analysis of CPK molecular models led Smid et al. to propose an eclipsing arene–arene interaction in a chelating bis(benzo-15-crown-5) complex, in which the arenes are constrained to lie over one another,[43] and a loosely eclipsing arrangement is also seen in a cyclohexano-15-crown-5 derivative reported by Owen.[10]

In the metal cation complexes, the crown ether rings adopt quite symmetrical conformations, allowing coordination of all five oxygen atoms in each ring to the complexed metal ion. In marked contrast, the crown ethers adopt rather skewed conformations in the ammonium nitrate complex (**3**). This conformation appears to allow formation of one simple and one bifurcated hydrogen bond with one crown ether (the lower ring in Fig. 3) and two simple hydrogen bonds with the other (the upper ring in Fig. 3).

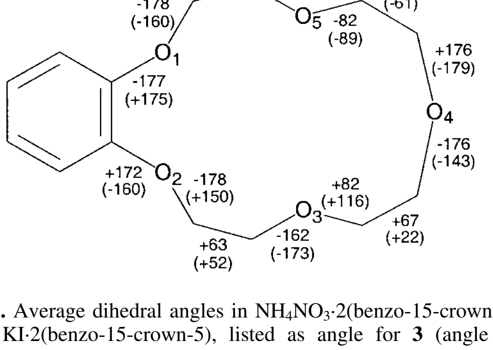

Figure 4. Average dihedral angles in $NH_4NO_3\cdot2$(benzo-15-crown-5)$\cdot H_2O$ (**3**) and KI·2(benzo-15-crown-5), listed as angle for **3** (angle for KI complex).

The simple hydrogen bond to O5 is both short (2.934 Å) and well-directed (N–H···O angle=174°), while those to the other ring are less optimal (N–H···O6 distance=3.101 Å, angle=162°; N–H···O8 distance 2.943 Å, angle=147°). The bifurcated hydrogen bond involves O2 and O3 (N–H···O distances=2.980, 3.101 Å, N–H···O angles=141°, 146°). Other potential N–H···O interactions display lengths and/or angles inconsistent with effective hydrogen bonding. This analysis, perhaps, suggests a simple reason for the crystallographic difficulty in refining the positions of the ammonium hydrogen atoms, in that a disordered ammonium ion is likely present, in which the hydrogen bonding scheme is reversed for the 'upper' and 'lower' crown ether rings.

The conformation of the 15-crown-5 ring appears similar to that in the other structurally characterized ammonium complexes of 15-crown-5 derivatives. Although each displays some similarity to the more symmetrical cationic metal complexes, significant distortions are evident, as revealed by an analysis of the dihedral angles in comparison with those in the potassium iodide complex[12] (Fig. 4). There is reasonable structural similarity in the vicinity of the fused benzene ring and out into the crown ether ring up to O5, which is involved in a typical linear hydrogen bond with the ammonium ion. However, severe distortions from the

Table 3. Bond lengths (Å) for NH_4NO_3·18-Crown-6 (**1**) and NH_4NO_3·18-Crown-6·H_2O (**2**)

Bond	1	2	Bond	1	2
O(1)–C(1)	1.35(1)	1.421(4)	O(6)–C(11)	1.44(1)	1.419(4)
O(1)–C(12)	1.42(1)	1.420(4)	O(7)–N(2)	1.172(5)	1.233(4)
O(2)–C(2)	1.43(1)	1.417(4)	O(8)–N(2)	1.202(5)	1.234(4)
O(2)–C(3)	1.41(1)	1.418(4)	O(9)–N(2)	1.229(5)	1.233(4)
O(3)–C(4)	1.382(9)	1.415(4)	C(1)–C(2)	1.53(1)	1.489(5)
O(3)–C(5)	1.46(1)	1.430(4)	C(3)–C(4)	1.53(1)	1.485(5)
O(4)–C(6)	1.33(1)	1.415(4)	C(5)–C(6)	1.51(1)	1.485(5)
O(4)–C(7)	1.451(9)	1.427(4)	C(7)–C(8)	1.46(1)	1.483(5)
O(5)–C(8)	1.38(1)	1.413(4)	C(9)–C(10)	1.43(2)	1.477(5)
O(5)–C(9)	1.48(1)	1.433(4)	C(11)–C(12)	1.38(1)	1.490(5)
O(6)–C(10)	1.35(2)	1.418(4)			

Table 4. Bond Angles (Å) for NH_4NO_3·18-Crown-6 (**1**) and NH_4NO_3·18-Crown-6·H_2O (**2**)

Bond	**1**	**2**	Bond	**1**	**2**
C(1)–O(1)–C(12)	111.7(7)	112.8(3)	O(2)–C(2)–C(1)	107.9(7)	109.5(3)
C(2)–O(2)–C(3)	114.1(7)	112.8(3)	O(3)–C(4)–C(3)	109.5(7)	108.7(3)
C(4)–O(3)–C(5)	114.0(7)	113.9(3)	O(3)–C(5)–C(6)	107.7(8)	109.1(3)
C(6)–O(4)–C(7)	111.9(8)	111.3(3)	O(4)–C(6)–C(5)	110.5(9)	110.0(3)
C(8)–O(5)–C(9)	116.2(7)	112.6(3)	O(4)–C(7)–C(8)	108.4(6)	110.2(3)
O(7)–N(2)–O(8)	116.9(5)	119.0(3)	O(5)–C(8)–C(7)	108.3(7)	109.5(3)
C(10)–O(6)–C(11)	108.7(9)	112.3(3)	O(5)–C(9)–C(10)	111.8(8)	109.5(3)
O(7)–N(2)–O(9)	122.5(6)	119.6(4)	O(6)–C(10)–C(9)	106.2(8)	109.0(3)
O(8)–N(2)–O(9)	120.6(5)	121.5(4)	O(6)–C(11)–C(12)	109(1)	109.5(3)
O(1)–C(1)–C(2)	111.1(8)	108.5(3)	O(1)–C(12)–C(11)	106.5(8)	108.4(3)
O(2)–C(3)–C(4)	111.7(6)	109.3(3)			

Table 5. Bond lengths (Å) for NH_4NO_3·2(benzo-15-Crown-5 (**3**)·H_2O

Bond		Bond		Bond	
O(1)–C(1)	1.384(5)	O(8)–C(23)	1.423(6)	C(7)–C(8)	1.487(6)
O(1)–C(14)	1.431(5)	O(9)–C(24)	1.419(6)	C(9)–C(10)	1.506(6)
O(2)–C(6)	1.366(5)	O(9)–C(25)	1.409(6)	C(11)–C(12)	1.486(7)
O(2)–C(7)	1.435(5)	O(10)–C(26)	1.422(5)	C(13)–C(14)	1.489(7)
O(3)–C(8)	1.413(5)	O(10)–C(27)	1.423(5)	C(15)–C(16)	1.387(6)
O(3)–C(9)	1.422(5)	O(11)–N(2)	1.225(6)	C(15)–C(20)	1.420(6)
O(4)–C(10)	1.416(5)	O(12)–N(2)	1.262(7)	C(16)–C(17)	1.386(7)
O(4)–C(11)	1.408(6)	O(13)–N(2)	1.119(7)	C(17)–C(18)	1.375(7)
O(5)–C(12)	1.423(6)	C(1)–C(2)	1.391(6)	C(18)–C(19)	1.380(7)
O(5)–C(13)	1.431(6)	C(1)–C(6)	1.401(6)	C(19)–C(20)	1.366(6)
O(6)–C(15)	1.375(5)	C(2)–C(3)	1.386(7)	C(21)–C(22)	1.490(7)
O(6)–C(28)	1.433(5)	C(3)–C(4)	1.364(7)	C(23)–C(24)	1.484(7)
O(7)–C(20)	1.357(5)	C(4)–C(5)	1.387(6)	C(25)–C(26)	1.492(7)
O(7)–C(21)	1.426(5)	C(5)–C(6)	1.379(6)	C(27)–C(28)	1.497(6)
O(8)–C(22)	1.424(6)				

Table 6. Bond angles (Å) for NH_4NO_3·2(benzo-15-Crown-5 (**3**)·H_2O

Bond		Bond		Bond	
C(1)–O(1)–C(14)	117.6(4)	C(2)–C(3)–C(4)	120.8(5)	C(16)–C(15)–C(20)	120.6(5)
C(6)–O(2)–C(7)	118.3(4)	C(3)–C(4)–C(5)	120.0(5)	C(15)–C(16)–C(17)	119.0(5)
C(8)–O(3)–C(9)	113.7(4)	C(4)–C(5)–C(6)	121.1(5)	C(16)–C(17)–C(18)	120.6(6)
C(10)–O(4)–C(11)	113.3(4)	O(2)–C(6)–C(1)	115.3(5)	C(17)–C(18)–C(19)	120.1(6)
C(12)–O(5)–C(13)	114.9(4)	O(2)–C(6)–C(5)	126.5(5)	C(18)–C(19)–C(20)	121.4(5)
C(15)–O(6)–C(28)	118.1(4)	C(1)–C(6)–C(5)	118.2(5)	O(7)–C(20)–C(15)	114.3(5)
C(20)–O(7)–C(21)	117.6(4)	O(2)–C(7)–C(8)	105.7(4)	O(7)–C(20)–C(19)	127.3(5)
C(22)–O(8)–C(23)	113.4(4)	O(3)–C(8)–C(7)	109.2(4)	C(15)–C(20)–C(19)	118.3(5)
C(24)–O(9)–C(25)	112.3(4)	O(3)–C(9)–C(10)	113.8(4)	O(7)–C(21)–C(22)	105.5(4)
C(26)–O(10)–C(27)	113.9(4)	O(4)–C(10)–C(9)	109.1(4)	O(8)–C(22)–C(21)	109.7(4)
O(11)–N(2)–O(12)	111.7(8)	O(4)–C(11)–C(12)	110.0(4)	O(8)–C(23)–C(24)	112.6(5)
O(11)–N(2)–O(13)	124.3(8)	O(5)–C(12)–C(11)	113.7(5)	O(9)–C(24)–C(23)	110.0(4)
O(12)–N(2)–O(13)	123.8(8)	O(5)–C(13)–C(14)	109.2(4)	O(9)–C(25)–C(26)	110.0(4)
O(1)–C(1)–C(2)	125.2(5)	O(1)–C(14)–C(13)	107.0(4)	O(10)–C(26)–C(25)	113.5(4)
O(1)–C(1)–C(6)	114.0(5)	O(6)–C(15–C(16)	125.3(5)	O(10)–C(27)–C(28)	109.3(4)
C(2)–C(1)–C(6)	120.9(5)	O(6)–C(15)–C(20)	114.2(5)	O(6)–C(28)–C(27)	106.8(4)
C(1)–C(2)–C(3)	119.0(5)				

geometry seen in the potassium complex are revealed surrounding O4 and O3 in the ammonium complex. Interestingly, this portion of the crown ether was reported by Owen[10] to be disordered, perhaps suggesting the possibility of a number of conformations of very similar energies (see Tables 3–6).

Summary

The anhydrous and the monohydrated complexes of ammonium nitrate with 18-crown-6 display a number of structural features in common with both one another and with other ammonium salt complexes of 18-crown-6. A near-ideal 'tripod' arrangement of hydrogen bonds to alternate oxygen atoms within the crown ether ring, which adopts a highly symmetrical psuedo-D_{3d} conformation, is displayed in each complex. Discrete ion pairing interactions are apparent in each structure, but the strength of this ion pairing interaction appears in part to be influenced by the extent of hydration, with hydrated counteranions residing at greater distances (relative to ionic radii) from the crown

Table 7. Crystallographic data for ammonium nitrate complexes

	Complex		
	1	**2**	**3**
Composition	$C_{12}H_{28}N_2O_9$	$C_{12}H_{28}N_2O_9{\cdot}H_2O$	$C_{28}H_{44}N_2O_{13}{\cdot}H_2O$
Formula weight	344.36	362.38	634.68
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a (Å)	8.5564(23)	10.7279(12)	12.888(4)
b (Å)	11.9530(17)	7.8202(7)	19.562(5)
c (Å)	18.3602(37)	22.1930(21)	12.979(3)
β (°)	90	90.103(9)	99.78(2)
V (Å^3)	1878(1)	1861.9(6)	3225(2)
z	4	4	4
d_{calc} (g cm^{-3})	1.218	1.293	1.307
T (°C)	22	22	22
λ (Å)	0.71073	0.71073	0.71073
μ (cm^{-1})	0.972	1.05	1.05
Rel trans coeff	0.93–1.00	0.983–1.000	0.96–1.00
No. obs., all rflns	1358 [$I \geq \sigma(I)$], 1891	1809 [$I \geq 1.5\sigma(I)$], –	2657 [$I \geq \sigma(I)$], 5610
$R(F)$, $wR(F)$[a]	0.073, 0.075	0.055, 0.049	0.089, 0.052
$R(F^2)$, $wR(F^2)$[b]	0.093, 0.149	–, –	0.144, 0.106

[a] $R(F) = \Sigma||F_o| - |F_c||/\sum|F_o|$.

[b] $WR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

ether-bound ammonium ion than unsolvated counteranions. This represents a potentially significant role of water in defining the structural details of cation–molecule complexes.

Both 15-crown-5 and benzo-15-crown-5 form complexes with ammonium nitrate of 2:1 (crown ether:salt) stoichiometry. The bis(benzo-15-crown-5) complex (and, by inference, the 15-crown-5 complex itself) is of the sandwich type structure, with the ammonium ion positioned between two roughly parallel crown ether rings. The two benzo-15-crown-5 units are rotated by ca. 45° with respect to one another, making possible a rather efficient set of linear and bifurcated hydrogen bonding interactions with the ammonium ion.

Experimental

$NH_4NO_3{\cdot}$18-crown-6 (1). To a suspension of 0.0399 g of ammonium nitrate (0.50 mmol) in 6 mL of chloroform was added 0.1320 g of 18-crown-6 (0.50 mmol, 1.0 equiv.). The mixture was submitted to ultrasound treatment in a standard ultrasonic cleaning bath until dissolution of the ammonium nitrate was complete. Onto a ca. 5 mL aliquot of this solution in a glass test tube was carefully layered a comparable volume of benzene. Interdiffusion resulted in the formation of clear, colorless thin prisms. Anal: Calcd for $C_{12}H_{28}N_2O_9$: C, 41.85; H, 8.20; N, 8.13. Found: C, 42.29; H, 8.15; N, 7.86.

Crystallographic analysis of $NH_4NO_3{\cdot}$18-crown-6 (1). A colorless cleaved fragment of dimensions 0.45×0.50×0.54 mm^3 was mounted on a fiber. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range $14° \leq \theta \leq 15°$. Table 7 contains a summary of crystal data and final residuals. The systematic absences together with the acentric distribution of intensities indicated the space-group $P2_12_12_1$. Absorption corrections were not required. A MITHRIL[22] E-map showed the majority of the non-hydrogen atoms, and a cycle of DIRDIF[23] gave the positions of the remainder. The hydrogen atoms of the ammonium cation were located in difference syntheses and included without refinement; those bonded to carbon atoms were included at calculated positions with $B(H) = 1.2B_{eq}(C)$ and updated after each cycle of refinement. The final difference synthesis was featureless. The TEXSAN program suite,[24] incorporating complex atomic scattering factors,[25] was used in all

Table 8. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for complex **1** ($B_{eq} = (8\pi^2/3)S_iS_jU_{ij}a_i^*a_j^*\boldsymbol{a_i}{\cdot}\boldsymbol{a_j}$)

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
O(1)	0.1601(5)	0.3128(3)	0.4352(3)	9.4(1)	C(2)	0.237(1)	0.2443(8)	0.3187(6)	14.4(4)
O(2)	0.3977(6)	0.2683(4)	0.3319(2)	9.7(1)	C(3)	0.483(1)	0.2984(8)	0.2690(4)	13.1(3)
O(3)	0.6581(5)	0.4211(5)	0.3297(2)	10.5(1)	C(4)	0.652(1)	0.3261(9)	0.2869(4)	13.5(3)
O(4)	0.7332(5)	0.5360(4)	0.4611(3)	9.6(1)	C(5)	0.815(1)	0.452(1)	0.3526(5)	14.8(4)
O(5)	0.4872(8)	0.5785(4)	0.5578(2)	9.8(1)	C(6)	0.802(1)	0.558(1)	0.3980(7)	16.1(5)
O(6)	0.2398(6)	0.4268(5)	0.5618(2)	9.2(1)	C(7)	0.720(1)	0.6352(7)	0.5063(6)	12.9(3)
O(7)	0.2312(7)	0.5405(4)	0.2801(2)	12.9(2)	C(8)	0.641(2)	0.6044(7)	0.5741(5)	14.9(4)
O(8)	0.2066(6)	0.6453(3)	0.3659(3)	10.1(1)	C(9)	0.385(2)	0.5522(7)	0.6206(4)	13.0(3)
O(9)	0.0606(4)	0.6671(4)	0.2742(2)	9.5(1)	C(10)	0.229(2)	0.525(1)	0.5980(6)	16.0(5)
N(1)	0.4020(4)	0.4761(3)	0.4204(2)	4.9(1)	C(11)	0.085(1)	0.393(1)	0.5401(6)	14.8(4)
N(2)	0.1669(5)	0.6176(4)	0.3057(3)	5.7(1)	C(12)	0,093(1)	0.2911(9)	0.5046(9)	13.4(4)
C(1)	0.159(1)	0.2208(7)	0.3923(8)	14.0(4)					

Table 9. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for complex **2** ($B_{eq} = (8\pi^2/3)S_iS_jU_{ij}a_i^*a_j^*\boldsymbol{a_i}\cdot\boldsymbol{a_j}$)

Atom	*x*	*y*	*z*	B_{eq}	Atom	*x*	*y*	*z*	B_{eq}
O(1)	0.7821(2)	0.1746(3)	0.4123(1)	5.0(1)	C(1)	0.7206(4)	O.O947(5)	0.4615(2)	5.5(2)
O(2)	0.5194(2)	0.1864(3)	0.43063(9)	4.6(1)	C(2)	0.6090(4)	O.1985(6)	0.4774(2)	5.6(2)
O(3)	0.3775(2)	0.3179(3)	0.3351(1)	4.3(1)	C(3)	0.4161(4)	0.2967(5)	0.4394(2)	5.5(2)
O(4)	0.4694(2)	0.2832(3)	0.2165(1)	4.2(1)	C(4)	0.3236(3)	0.2684(5)	0.3906(2)	5.2(2)
O(5)	0.7331(2)	0.3163(3)	0.2018(2)	4.1(1)	C(5)	0.2980(3)	0.2918(5)	0.2841(2)	4.9(2)
O(6)	0.8852(2)	0.1784(3)	0.2947(1)	4.4(1)	C(6)	0.3569(3)	0.3693(5)	0.2301(2)	4.7(2)
O(7)	0.6890(3)	0.6221(4)	0.4134(1)	6.3(2)	C(7)	0.5282(4)	0.3552(5)	0.1648(2)	4.9(2)
O(8)	0.8516(3)	0.6197(4)	0.35882(14)	7.0(2)	C8)	0.6507(4)	0.2724(5)	0.1545(2)	4.7(2)
O(9)	0.8664(3)	0.6613(4)	0.4544(2)	8.4(2)	C(9)	0.8565(3)	0.2513(5)	0.1925(2)	4.6(2)
O(10)	0.8678(3)	0.4106(5)	0.5526(2)	9.8(2)	C(10)	0.9323(3)	0.2810(5)	0.2472(2)	4.7(2)
N(1)	0.6406(2)	0.3603(4)	0.3232(1)	3.8(1)	C(11)	0.9S69(3)	0.1943(5)	0.3482(2)	5.1(2)
N(2)	0.8033(3)	0.6327(4)	0.4090(2)	4.9(2)	C(12)	0.8969(4)	0.0946(6)	0.3975(2)	5.6(2)

calculations. Atomic coordinates and final equivalent isotropic parameters are provided in Table 8.

NH_4NO_3·18-crown-6·H_2O (2). Diffusion of diethyl ether into a chloroform solution of ammonium nitrate and 18-crown-6 prepared as described above afforded clear, colorless prisms. Anal: Calcd for $C_{12}H_{28}N_2O_9$·H_2O: C, 39.77; H, 8.34; N, 7.73. Found: C, 40.63; H, 8.05; N, 7.90.

Crystallographic analysis of NH_4NO_3·18-crown-6·H_2O (2). A colorless block of dimensions 0.14×0.20×0.27 mm^3 was mounted on a fiber. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range $12.0° \leq \theta \leq 13.8°$. Table 7 contains a summary of crystal data and final residuals. The systematic absences and centric distribution of intensities indicated the space-group $P2_1/c$. Absorption corrections were not needed. A MITHRIL[22] E-map showed all C and O atoms of the crown ether, and a cycle of DIRDIF[23] gave the positions of the remaining non-hydrogen atoms. Hydrogen atoms of the crown ether were included at calculated positions with $B(H) = 1.2B_{eq}(C)$ and updated after each cycle of refinement; other hydrogen atoms were included without refinement at the positions indicated by difference syntheses. The final difference synthesis was featureless. The TEXSAN program suite,[24] incorporating complex atomic scattering factors,[25] was used in all calculations. Atomic coordinates and final equivalent isotropic parameters are provided in Table 9.

NH_4NO_3·2(benzo-15-crown-5)·H_2O (3). To a suspension of 0.0386 g of ammonium nitrate (0.483 mmol) in 10 mL of acetonitrile was added 0.2594 g of benzo-15-crown-5 (0.967 mmol, 2 equiv.). The mixture was submitted to ultrasound treatment in a standard ultrasonic cleaning bath until dissolution of the ammonium nitrate was complete. Onto an aliquot of this solution in a glass test tube was carefully layered a comparable volume of diethyl ether. Interdiffusion resulted in the formation of clear, colorless prisms. Comparable results were obtained using ethyl acetate, benzene, toluene, or tetrahydrofuran as the precipitating solvent.

Crystallographic analysis of NH_4NO_3·2(benzo-15-crown-5)·H_2O (3). A crystal of dimensions 0.40×0.12×0.10 mm^3 was mounted on a fiber and protected with a coating of epoxy resin. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range $13.5° \leq \theta \leq 14.3°$. Table 7 contains a summary of crystal data and the final residuals. The crystal diffracted sharply but weakly, and only 2657 out of 5610 reflections (excluding systematic absences) in the range $1.5° \leq \theta \leq 25°$ had intensities greater than $\sigma(I)$. The systematic absences indicated the space-group $P2_1/c$. A SIR92 E-map[26] showed all the non-hydrogen atoms. Refinement was on $|F|^2$, with all reflections included. Hydrogen atoms bonded to carbon were included at calculated positions [B(H)=1.2B_{eq}(C); d(C–H)=0.95 Å] and updated after each cycle of refinement; hydrogen atoms bonded to nitrogen and oxygen were included without refinement at positions derived from a difference synthesis. The TEXSAN program suite,[24] incorporating complex atomic scattering factors,[25] was used in all calculations. Atomic coordinates and final equivalent isotropic parameters are provided in Table 2.

NH_4NO_3·2(15-crown-5)·nH_2O. Diffusion of various precipitating solvents (e.g. diethyl ether, tetrahydrofuran, hexane, ethyl acetate) into acetone or acetonitrile solutions of ammonium nitrate containing 2 equiv. of 15-crown-5 generally afforded the complex in crystalline form.[27] Although solvent-dependent habit variations were noted, unit cell determination consistently demonstrated the formation of the same crystalline phase. Extensive twinning precluded determination of the structure of this complex.

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