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Neutral Solvent/Crown Ether Interactions, 4.[*] Crystallization and Low Temperature (–150 °C) Structural Characterization of 18-Crown-6 · 2(CH_3CN)

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Abstract. The crystal structure of 18-crown-6 · 2(CH_3CN) has been determined via data collection at –150 °C. The structure consists of two crown molecules each hydrogen bonded to two acetonitrile moieties in the asymmetric unit, each residing around a center of inversion. The crown ethers display their full D_{3d} symmetry; methyl···O contacts range from 3.189(8) to 3.598(8) Å. There are no close contacts indicative of any interaction between the crown/2(CH_3CN) units.

Key words: 18-Crown-6, C—H acidic hydrogen bonds, acetonitrile, low temperature crystal structure, solvent complex.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82056 (14 pages).

1. Introduction

Of the several C—H acidic solvent/crown ether interactions discussed in the literature [2, 3], the acetonitrile complex of 18-crown-6 is interesting both because of its utility and its crystalline instability. One finds reports of at least three patents which have been approved or applied for [4] concerning the purification of 18-crown-6 via the formation of crystals of the title complex. Despite this, and the resulting interest in this complex, no structural studies have been forthcoming, although structural results on other complexes containing the 18-crown-6 unit and acetonitrile have been reported, including

{[*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]$_2$ · 18-crown-6} [PF_6]$_2$ · 2(CH_2Cl_2) [5],

[$UO_2(OH_2)_5$] [ClO_4]$_2$ · 2(18-crown-6) · 2(CH_3CN) · H_2O [6],

and

[(CH_2OCPh_3)$_2$-18-crown-6] · 2(CH_3CN) [7].

We feel this may be due to the ready loss of solvent crystals of the title complex experience, making X-ray quality crystals and reasonably good data difficult to obtain as discussed below.

In the course of our recent investigations into *f*-element/crown ether complexation [8], we have observed the formation and crystallization of a number of solvent/crown

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ether complexes, often in lieu of metal complexation [1, 3, 9]. We recently redetermined the structure of 18-crown-6 · 2(CH_3NO_2) (at 22 °C) [3] in order to find the hydrogen atoms. At this temperature the six methyl hydrogen atoms are weakly interacting with the six crown oxygen atoms (H···O(crown) 2.30 to 2.35 Å). These interactions are sufficient to stabilize a D_{3d} conformation of the crown. More recently we determined this structure at −150 °C [1]. Interestingly, the hydrogen atom interactions are different. One contact remains at 2.35 Å, another increases to 2.55 Å, and the third hydrogen is directed away from the crown ether as observed for some previous structures of this type (e.g., 18-crown-6 · $(CH_3)_2SO_4$ [10]).

In some of our studies of 4*f*-metal chlorides with dibenzo-18-crown-6, large transparent single crystals formed from every reaction (3 : 1 CH_3CN/CH_3OH). The crystals lose solvent within a minute after removal from solution and contain no metal. A low temperature (necessary to prevent decomposition) X-ray study revealed a 2 : 1 acetonitrile/dibenzo-18-crown-6 complex [9]. It is still surprising to us that the weak bifurcated CH_3···O(aryl-crown) interactions (2.57 to 2.93 Å) are favored over either metal complexation or M—OH_2···crown hydrogen bonding. We have also characterized dibenzo-18-crown-6 · 2(CH_3NO_2) [9], which exhibits a hydrogen bonding pattern different from either dibenzo-18-crown-6 · 2(CH_3CN) or 18-crown-6 · 2(CH_3NO_2). The hydrogen atom···oxygen interactions associate the crown units into polymeric chains. Again, the majority of the hydrogen atom close contacts are to the aryl oxygen atoms of the crown ether.

Table I. Final fractional coordinates for 18-crown-6 · 2(CH_3CN)

Atom	*x/a*	*y/b*	*z/c*
O(1)	0.0780(5)	−0.3023(5)	0.0073(4)
O(2)	0.0556(5)	−0.0544(5)	0.1939(3)
O(3)	−0.1049(5)	0.2180(5)	0.1800(3)
C(1)	0.1482(8)	−0.2999(8)	0.1046(6)
C(2)	0.0443(9)	−0.2132(8)	0.1867(6)
C(3)	−0.0374(9)	0.0339(8)	0.2699(5)
C(4)	−0.0286(8)	0.1996(8)	0.2715(5)
C(5)	−0.0987(8)	0.3725(8)	0.1740(6)
C(6)	−0.1718(9)	0.3789(8)	0.0740(6)
N(1)	0.4356(8)	0.167(1)	−0.0840(6)
C(13)	0.3366(9)	0.1232(8)	−0.0431(5)
C(14)	0.2097(7)	0.0666(9)	0.0097(5)
O(4)	−0.4262(5)	0.7818(5)	0.4407(3)
O(5)	−0.4634(5)	0.4824(5)	0.2933(3)
O(6)	−0.6163(5)	0.2316(5)	0.3520(3)
C(7)	−0.3650(8)	0.7421(8)	0.3410(5)
C(8)	−0.4768(9)	0.6254(8)	0.2717(5)
C(9)	−0.5601(9)	0.3636(9)	0.2269(5)
C(10)	−0.5454(9)	0.2160(8)	0.2575(5)
C(11)	−0.6128(8)	0.0913(8)	0.3838(6)
C(12)	−0.6798(9)	0.1203(8)	0.4865(6)
N(2)	−0.0549(9)	0.334(1)	0.5837(6)
C(15)	−0.1575(9)	0.3799(9)	0.5460(5)
C(16)	−0.2909(8)	0.4396(9)	0.4977(6)

2. Experimental

Crystals of the title complex also have been obtained from a variety of reaction systems as mentioned above for the nitromethane adduct [11]. They are however, much more susceptible to solvent loss than the nitromethane analog. We have attempted to study this system at low temperature (–150 °C), trying to get the crystalline sample to the diffractometer before major decomposition can take place. Unlike the nitromethane complex, crystals of the title complex redissolve when allowed to warm to room temperature under the solvent increasing the experimental difficulties and preventing data collection on crystals in capillaries containing some solvent. It appears to us that the rapid cooling necessary to prevent further crystal decomposition, occurring as it does while the solvent molecules have high thermal motion, often leads to crystal cracking and poor packing of the molecules. As a result we have had to collect several data sets with only the latest one, reported here, leading to a reasonable refinement of the structure [12]. Atomic coordinates are given in Table I.

3. Discussion

In the asymmetric unit of 18-crown-6·2(CH_3CN) there are two different crown ether/acetonitrile units each residing around a center of inversion. The two different

Table II. Bond distances (Å) and angles (deg) for 18-crown-6·2(CH_3CN)

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.423(8)	O(1)—C(6A)	1.407(8)
O(2)—C(2)	1.404(8)	O(2)—C(3)	1.392(8)
O(3)—C(4)	1.428(8)	O(3)—C(5)	1.412(8)
C(1)—C(2)	1.49(1)	C(3)—C(4)	1.482(9)
C(5)—C(6)	1.487(9)	N(1)—C(13)	1.130(8)
C(13)—C(14)	1.453(9)		
O(4)—C(7)	1.420(8)	O(4)—C(12B)	1.407(8)
O(5)—C(8)	1.398(8)	O(5)—C(9)	1.416(8)
O(6)—C(10)	1.403(8)	O(6)—C(11)	1.438(7)
C(7)—C(8)	1.493(9)	C(9)—C(10)	1.50(1)
C(11)—C(12)	1.48(1)	N(2)—C(15)	1.123(9)
C(15)—C(16)	1.458(9)		
Atoms	**Angle**	**Atoms**	**Angle**
C(1)—O(1)—C(6A)	112.6(5)	C(2)—O(2)—C(3)	113.1(5)
C(4)—O(3)—C(5)	112.8(5)	O(1)—C(1)—C(2)	109.4(6)
O(2)—C(2)—C(1)	110.0(5)	O(2)—C(3)—C(4)	111.4(5)
O(3)—C(4)—C(3)	109.0(6)	O(3)—C(5)—C(6)	109.0(6)
O(1A)—C(6)—C(5)	111.0(6)	N(1)—C(13)—C(14)	179.8(3)
C(7)—O(4)—C(12B)	112.6(5)	C(8)—O(5)—C(9)	113.2(5)
C(10)—O(6)—C(11)	112.3(5)	O(4)—C(7)—C(8)	108.8(5)
O(5)—C(8)—C(7)	110.0(6)	O(5)—C(9)—C(10)	110.2(5)
O(6)—C(10)—C(9)	109.4(6)	O(6)—C(11)—C(12)	108.9(6)
O(4B)—C(12)—C(11)	110.0(6)	N(2)—C(15)—C(16)	179.7(6)

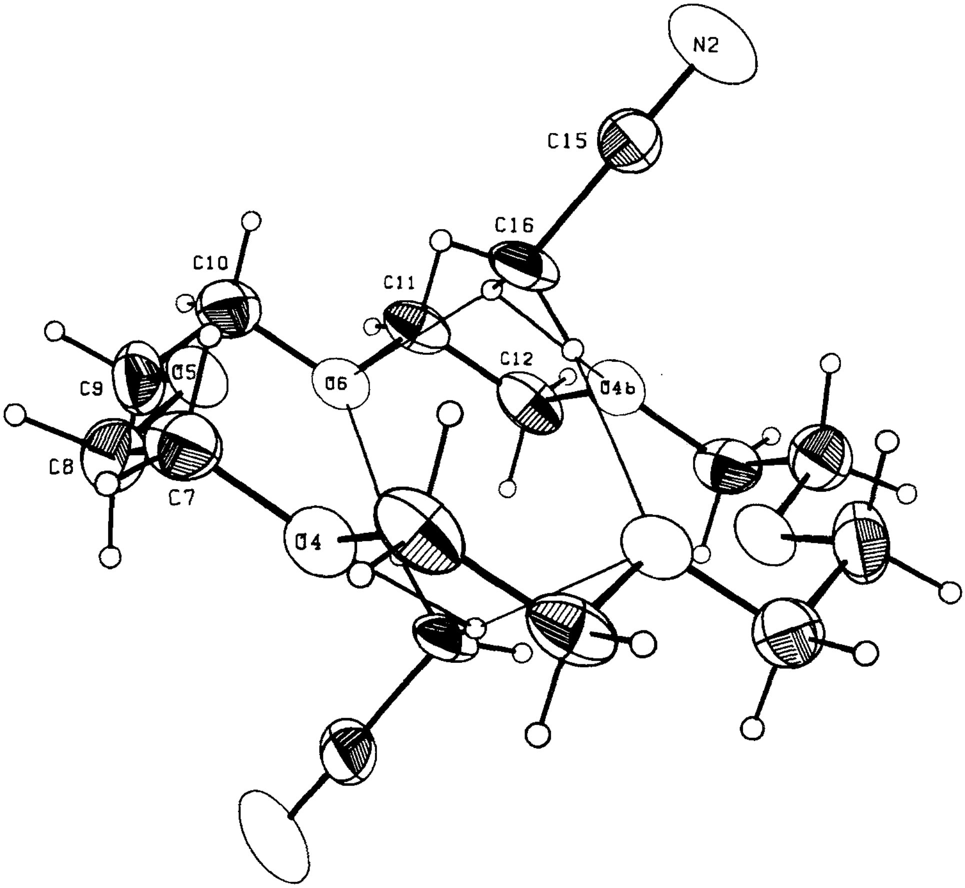

Fig. 1. Side view of one of the unique 18-crown-6 · 2(CH_3CN) units.

complexed crowns are essentially identical (Table II). A side view of one is shown in Figure 1 and a top view of the second one, displaying the full D_{3d} symmetry observed for each, is presented in Figure 2. The overall structure is very similar to that observed for 18-crown-6 · 2(CH_3NO_2). In fact, the unit cell and fractional coordinates for the title complex closely approximate the cell and symmetry ($P2_1/n$) found for the nitromethane adduct. We have never been able to obtain crystals of the title complex which are indeed $P2_1/n$ at −150 °C, however, it is interesting to note that as the temperature was raised in one study (as a result of lack of N_2(l)) the cell and systematic absences observed, did seem to indicate $P2_1/n$. These observations may again be related to the quick cooling of crystals of the title complex and deserve further study.

Each complexed crown ether in the title complex is hydrogen bonded to two acetonitrile molecules, with no interaction between complexed crown ethers. The methyl groups have contacts ranging from 3.189(8) to 3.598(8) Å from the crown oxygen atoms (Table III). 18-crown-6 with D_{3d} symmetry exhibits oxygen atoms which alternate ± from a mean plane of all six oxygen atoms. The Me···O contacts average 3.25(4) Å to the three oxygen atoms which deviate towards the methyl group (O(3A), O(2), O(1A) for C(14); O(5), O(6B), O(4B) for C(16)) and 3.51(5) Å to the

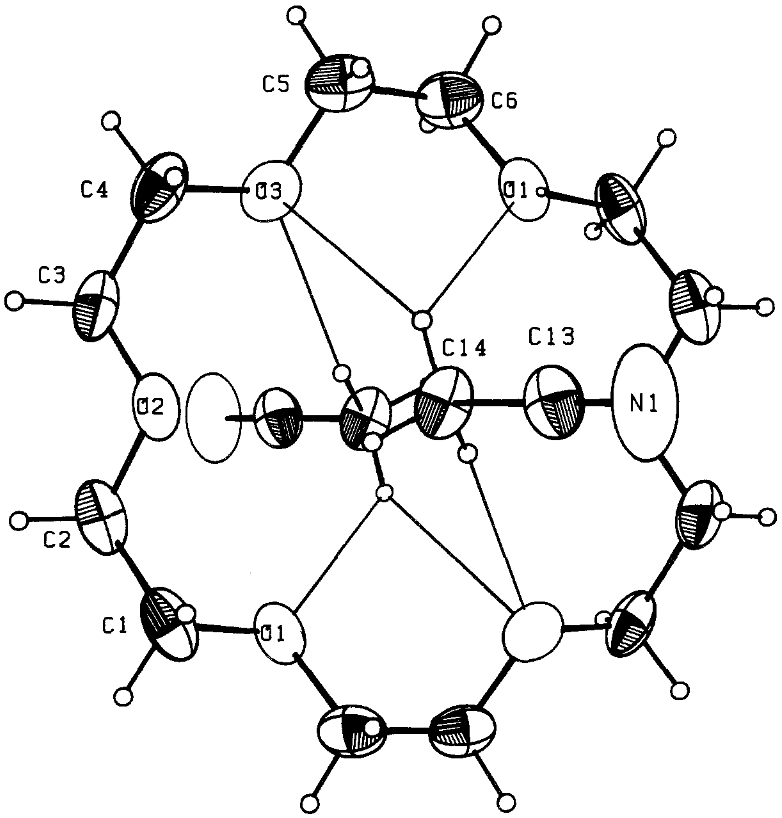

Fig. 2. Top view of the second crown ether complex.

remaining oxygen atoms. The O···Me—C contact angles suggest that it is unlikely for three single C—H···O hydrogen bonds to exist to the three closest oxygen atoms, but that two to O(3A) and O(1A) for C(14), and O(6) and O(4B) for C(16) may be present. These O···C—C angles average 100° and the O···C···O angles average 99°. A third hydrogen bond to O(2A) or O(5B) which have O···C—C angles of 89.9 and 96.9°, respectively, can be ruled out from the O···C···O angles (to the two atoms in each ether mentioned above) which average 51°.

By analogy to the nitromethane adduct [1], we cannot rule out bifurcated C—H···O hydrogen bonds. Two models for inclusion of the hydrogen atoms were attempted. Coordinates for the methyl hydrogen atoms were located from a difference Fourier map and fixed with $B = 5.5$ Å^2. (Successful refinement of these atoms was not possible.) A second model introduced rigid methyl groups allowing rotation around the C—C bonds. This latter model was used in the final refinement. Both models suggest a hydrogen bonding pattern similar to that observed in 18-crown-6·2(CH_3NO_2) (at low temperature): a single hydrogen bond to O(3A) and O(6B), a bifurcated hydrogen bond to [O(1A), O(3)] and [O(6), O(4B)], and one hydrogen atom on each methyl group with no hydrogen bonding interactions.

In the title complex the Me···O contacts compare favorably with those found in

Table III. Hydrogen bonding contact geometries for 18-crown-6 · $2(CH_3CN)$

Atoms	Distance	Atoms	Distance
C(14)—O(1)	3.459(9)	C(16)—O(4)	3.56(1)
C(14)—O(2)	3.268(9)	C(16)—O(5)	3.204(9)
C(14)—O(3)	3.598(8)	C(16)—O(6)	3.498(8)
C(14)—O(1A)	3.279(9)	C(16)—O(4B)	3.320(9)
C(14)—O(2A)	3.463(8)	C(16)—O(5B)	3.479(8)
C(14)—O(3A)	3.189(8)	C(16)—O(6B)	3.235(8)
HlC(14)—O(1A)	2.59	HlC(16)—O(4B)	2.62
HlC(14)—O(3)	2.77	HlC(16)—O(6)	2.60
H3C(14)—O(3A)	2.32	H3C(16)—O(6B)	2.33

Atoms	Angle	Atoms	Angle
C(13)—C(14)—O(1)	132.4(5)	C(15)—C(16)—O(4)	142.2(5)
C(13)—C(14)—O(2)	155.6(5)	C(15)—C(16)—O(5)	148.8(5)
C(13)—C(14)—O(3)	138.8(5)	C(15)—C(16)—O(6)	127.9(5)
C(13)—C(14)—O(1A)	101.3(5)	C(15)—C(16)—O(4B)	96.0(5)
C(13)—C(14)—O(2A)	89.9(4)	C(15)—C(16)—O(5B)	96.9(5)
C(13)—C(14)—O(3A)	94.7(4)	C(15)—C(16)—O(6B)	108.2(4)
C(14)—HlC(14)—O(1A)	130.0	C(16)—HlC(16)—O(4B)	131.0
C(14)—HlC(14)—O(3)	146.0	C(16)—HlC(16)—O(6)	158.0
C(14)—H3C(14)—O(3A)	151.0	C(16)—H3C(16)—O(6B)	160.0

18-crown-6 · $2(CH_3NO_2)$, $[(COCPh_3)_2$-18-crown-6$]$ · $2(CH_3CN)$ [7],

and

$\{[$*trans*-$Ir(CO)(CH_3CN)(PPh_3)_2]_2$ · 18-crown-6$\}$ $[PF_6]_2$ · $2(CH_2Cl_2)$ [5].

It is interesting to note, however, a much smaller Me···Me through the crown contact distance in the title complex (3.66(1) Å average) and 18-crown-6 · $2(CH_3NO_2)$ (3.676(5) Å), than observed in the latter two complexes above (3.952 and 3.93 Å, respectively). The acetonitrile axes are parallel by symmetry in the title complex and make an angle of 174° in $[(CH_2OCPh_3)_2$-18-crown-6$]$ · $2(CH_3CN)$. In the dibenzo-18-crown-6 · $2(CH_3CN)$ [9] analog, this angle is only 167°.

The crown ether parameters are normal for the D_{3d} conformation. The average parameters include: C—O = 1.41(1) Å, C—C = 1.489(7) Å, C—O—C = 112.8(3)°, and C—C—O = 109.8(8)°.

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11. Crystals for the present study were grown from 5 mL of an acetonitrile solution containing 2 mL of '15-crown-5' (containing 18-crown-6 as an impurity) at -5 °C. The crystals redissolve when removed from the freezer within three minutes and grow again overnight. The above also demonstrates the known utility of CH_3CN as a purification agent for 18-crown-6.
12. 18-crown-6 $\cdot$ 2(CH_3CN), formula weight $= 346.4$ g mol^{-1}, crystallizes in the triclinic space group $P1$ with $a = 8.343(7)$, $b = 8.982(4)$, $c = 13.576(4)$ Å, $\alpha =$ 105.50(3), $\beta = 91.80(8)$, $\gamma = 91.28(9)$°, and $D_{calc} = 1.17$ g cm^{-3} for $Z = 2$. Data were collected on an Enraf-Nonius CAD-4 diffractometer utilizing the $\theta/2\theta$ scan technique with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) out to $2\theta_{max} = 50°$. The asymmetric unit consists of two halfs of different formula units residing around crystallographic centers of inversion. The crown hydrogen atoms were placed in calculated positions riding with $B = 5.5$ Å^2 on the bonded carbon atom.The methyl hydrogens were treated as described in the text. Refinement of all nonhydrogen atoms anisotropically led to a final conventional R value of 0.103 utilizing 2372 independent observed [$F_o \geqslant 5\sigma(F_o)$] reflections.