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Crystal Structure of the 2 : 1 Acetonitrile Complex of 18-Crown-6

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Abstract. Single crystal X-ray analysis of the 2 : 1 acetonitrile complex of 18-crown-6 is reported. Crystals of the complex are monoclinic, $P2_1/n$, with $a = 9.123(3)$, $b = 8.524(3)$, $c = 13.676(4)$ Å, $\beta = 104.68(3)°$, and $D_c = 1.118$ g cm^{-3} for $Z = 2$. The complex lies on a center of symmetry, with the crown in the D_{3d} conformation. Methyl groups of the acetonitrile molecules have weak interactions with the crown oxygen atoms, and are tilted 31.7° from the host's threefold axis. Methyl hydrogen atoms are rotationally disordered about the acetonitrile axis.

Key words: Crown ether, acetonitrile, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82057 (12 pages).

1. Introduction

Fascination with the acetonitrile complex of 18-crown-6 began over a decade ago with Gokel *et al.*'s [1, 2] report of the purification of 18-crown-6, a process that was even patented [3]. Improvements in the purification of 18-crown-6 by complexation with other neutral molecules have since been reported [4], but the historical importance of the acetonitrile complex gives it a special significance in the crown ether field.

The crystal structures of several neutral complexes in which the guest is complexed via methyl or methylene groups have been reported [5–13] during the last 12 years. Surprisingly, the crystal structure of an acetonitrile complex has not appeared. However, the crystal structure of an 18-crown-6 acetonitrile complex where the acetonitrile is coordinated to iridium has been solved [5]. More recently the crystal structure of an acetonitrile complex with an 18-crown-6 derivative has been described [12].

Herein, we present the long-awaited crystal structure of the 2 : 1 complex of acetonitrile : 8-crown-6 and compare it with the structures of other neutral complexes with 18-crown-6. In addition, we compare the X-ray result to structural predictions made from previous spectroscopic studies [14–16].

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2. Experimental

2.1. CRYSTAL PREPARATION

In an atmosphere of dry N_2, 0.1 g 18-crown-6 (Aldrich, purified by the method of Gokel *et al.* [1]) was combined with 0.5 ml acetonitrile (Aldrich Gold Label) and sealed in a glass vial with a Teflon-lined cap. The vial was placed in a 70 °C water bath for 1 h, and was cooled to room temperature (*ca.* 22 °C) over a period of 1 week. The resulting crystals were large (about 5 mm per side), clear, and colorless.

2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION

Intensity data were collected from a crystal fragment of dimensions 0.28 × 0.35 × 0.38 mm, sealed in a glass capillary containing mother liquor, using an Enraf-Nonius CAD4 diffractometer equipped with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Crystal data are: $C_{12}H_{24}O_6 \cdot 2\,CH_3CN$, FW = 346.4 monoclinic, $P2_1/n$; $a = 9.123(3)$, $b = 8.524(3)$, $c = 13.676(4)$ Å; $\beta = 104.68(3)°$, $Z = 2$, $D_c = 1.118$ g cm^{-3}; $\mu = 0.79$ cm^{-1}, $T = 295$ K. One quadrant of data having $1° \leqslant \theta \leqslant 25°$ was collected by ω-2θ scans of rates varying 0.59–4.0° min^{-1} in order to measure all significant data with $I = 50\sigma(I)$. Data reduction included corrections for background, Lorentz, and polarization effects. No decay of standard reflections was noted. Redundant data were merged, with $R_{\text{int}} = 0.026$. Of 1796 unique data, 1021 were considered observed having $I > 1\sigma(I)$, and were used in the refinement.

The structure was solved using direct methods (*MULTAN* 78) [17], and refined by full-matrix least squares based upon F, with weights $w = \sigma^{-2}(F_o)$, using the *Enraf-Nonius SDP* programs [18]. Nonhydrogen atoms were treated anisotropically; H atoms were located by difference maps (0.14–0.22 e Å^{-3}) and included as fixed contributions. Crown H atoms were placed in calculated positions with $B = 12.0$ Å^2, while half-populated acetonitrile H atoms were placed from maps with $B = 8.0$ Å^2. At the conclusion of the refinement, $R = 0.066$ (0.131 for all data), $R_w = 0.069$, $S = 2.58$, for 109 variables, and the maximum residual density was 0.12 e Å^{-3}. Coordinates are tabulated in Table I.

Table I. Coordinates for 18-crown-6 · 2 Acetonitrile

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	0.7125(2)	0.0796(2)	0.0339(2)	C(4)	1.2343(5)	–0.0301(4)	0.2549(3)
O(2)	0.9802(2)	0.0514(2)	0.1989(1)	C(5)	1.3834(4)	–0.0947(4)	0.1424(3)
O(3)	1.2403(3)	–0.1058(2)	0.1631(2)	C(6)	1.3758(4)	–0.1705(4)	0.0452(3)
C(1)	0.7337(4)	0.1486(4)	0.1305(3)	N(1A)	1.1778(5)	0.4273(4)	–0.0781(3)
C(2)	0.8286(5)	0.0449(4)	0.2071(3)	C(1A)	1.1292(4)	0.3337(4)	–0.0414(2)
C(3)	1.0790(5)	–0.0452(4)	0.2693(2)	C(2A)	1.0646(3)	0.2143(3)	0.0032(2)

3. Results and Discussion

The 2 : 1 complex of acetonitrile with 18-crown-6, Figure 1, is essentially isomorphous with the analogous complex with nitromethane [6, 7], exhibiting similar unit cell dimensions and coordinates for the atoms of the crown ether. The complex lies

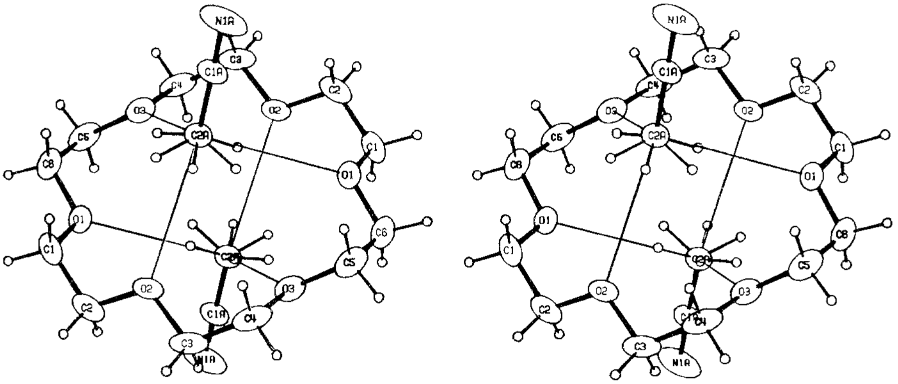

Fig. 1. Stereoscopic representation of the 2 : 1 complex, illustrating the numbering scheme and disorder of acetonitrile methyl groups.

on the inversion center (at 1, 0, 0), and the ring has the approximate D_{3d} symmetry observed in 18-crown-6 complexes with potassium salts [19] and neutral molecules [5–13] (Table II). Average distances (C—O, 1.412(6) Å; C—C, 1.474(9) Å) and angles (C—O—C 113.3(4)°; O—C—C 109.3(4)°) are also similar to those found in other 18-crown-6 complexes [5–13]. The two acetonitrile methyl groups, C(2A) and its inversion equivalent, lie approximately on the local threefold axis of the crown. Each has three nearly equal distances to three oxygens: C(2A)···O(1) 3.346(3), C(2A)···O(2) 3.276(3), C(2A)···O(3) 3.249(3) Å, as illustrated in Figure 2. The vector defined by the acetonitrile molecule, however, does not coincide with the local threefold axis, but is tilted 31.7° away from it. The tilt is such that the six nonhydrogen atoms (C(2A), C(1A), N(1A), C(2A′), C(1A′), N(1A′)) of the two acetonitrile molecules

Table II. Distances, angles, and torsion angles

Atoms	Distances (Å)	Atoms	Distances (Å)
O(1)—C(1)	1.413(3)	C(4)—O(3)	1.424(4)
O(1)—C(6)	1.406(4)	O(3)—C(5)	1.408(4)
C(1)—C(2)	1.473(4)	C(5)—C(6)	1.464(4)
C(2)—O(2)	1.416(3)	N(1A)—C(1A)	1.095(3)
O(2)—C(3)	1.407(3)	C(1A)—C(2A)	1.391(3)
C(3)—C(4)	1.485(5)		
Atoms	**Angle (°)**	**Atoms**	**Angle (°)**
C(1)—O(1)—C(6′)	113.9(3)	O(2)—C(3)—C(4)	109.0(2)
C(2)—O(2)—C(3)	113.1(3)	O(3)—C(4)—C(3)	109.2(2)
C(4)—O(3)—C(5)	113.0(3)	O(3)—C(5)—C(6)	108.7(3)
O(1)—C(1)—C(2)	109.4(2)	O(1)—C(6)—C(5)	110.0(3)
O(2)—C(2)—C(1)	109.3(2)	N(1A)—C(1A)—C(2A)	178.6(4)
O(1)—C(1)—C(2)—O(2)	72.9(3)	C(4)—O(3)—C(5)—C(6′)	-177.8(3)
C(1)—C(2)—O(2)—C(3)	-179.7(3)	O(3)—C(5)—C(6′)—O(1′)	70.5(4)
C(2)—O(2)—C(3)—C(4)	-179.9(3)	C(5)—C(6′)—O(1′)—C(1′)	-176.4(3)
O(2)—C(3)—C(4)—O(3)	-71.5(3)	C(6)—O(1)—C(1)—C(2)	-179.4(3)
C(3)—C(4)—O(3)—C(5)	178.9(3)		

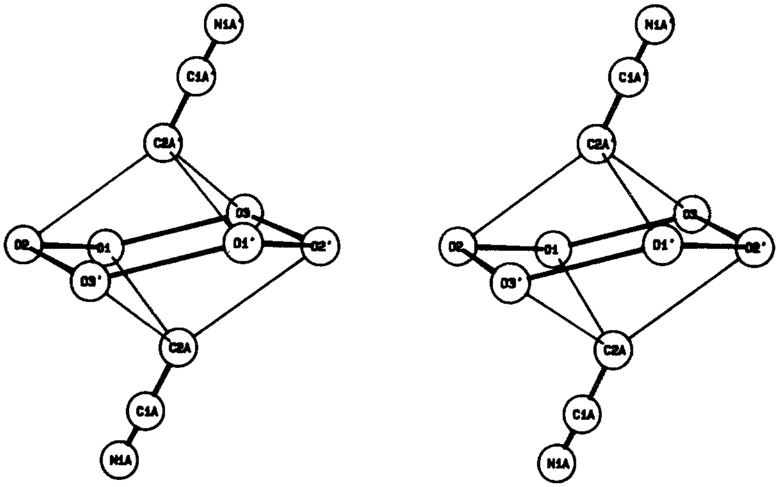

Fig. 2. Stereoscopic skeletal drawing of the 2 : 1 complex illustrating connectivity of oxygen atoms of 18-crown-6 and the tilting of the acetonitriles.

and two atoms (O(2), O(2′)) of the crown molecule lie within 0.09 Å of a common plane. The methyl hydrogen atoms do not form three linear C—H···O contacts, as might be anticipated, but are disordered. The model chosen for this disorder, with six half-populated sites distributed at *ca.* 60° torsion-angle intervals about the acetonitrile principal axis, is a reflection of the appearance of difference maps.

The tilt of the C—C≡N axis *vis-à-vis* the six oxygen mean plane can be compared with that observed in other complexes in which the guest presents a methyl group to 18-crown-6. These tilt angles are tabulated, along with C···O contact distances and distances of methyl carbon atoms to oxygen mean planes, in Table III. The tilt angles vary widely but in no case does the methyl group parallel the host's molecular threefold axis. The magnitude of the tilt angle is not correlated with either the distance to the oxygen mean plane nor to the C···O contact distances. Most probably, the observed tilt angle results from optimization of packing and guest-guest dipolar interactions between neighboring complexes in the crystal. The values in Table III demonstrate that the 2 : 1 acetonitrile complex typifies this class of inclusion compounds.

The structures of $[(Ph_3COCH_2)_2 \cdot 18\text{-crown-}6] \cdot 2CH_3CN$ [12] and 18-crown-6·2 malononitrile [13] also resemble that of 18-crown-6·2 acetonitrile. In all three complexes, the crown adopts the D_{3d} conformation, and the guest presents its CH_3 group to the host. In the acetonitrile complex, the methyl carbon atoms lie 1.900 and 2.036 Å from the oxygen mean plane, and make contacts ranging from 3.171–3.307 Å to oxygen atoms. The two nitrile vectors form tilt angles of 35.0° and 38.6° with the host molecular threefold axis. In the malononitrile complex, the methyl carbon atom lies 1.972 Å from the oxygen mean plane, and makes contacts ranging from 3.257(3)–3.400(3) Å to oxygen atoms. The two nitrile vectors form tilt angles of 53.3 and 57.2° with the host molecular threefold axis. Because these two vectors are attached to the same tetrahedral atom, these tilt angles must differ from that observed in the acetonitrile complex.

Taylor and Kennard [11] have reviewed C—H···O interactions and have presented criteria for using the term 'hydrogen bond' with respect to this type of interaction. The structure of the 18-crown-6 acetonitrile 2 : 1 complex suggests that designating these contacts as hydrogen bonds is not warranted. Instead, the disordered hydrogen atoms indicate that no strong orienting influence is present. By contrast, the methyl group appears ordered in the 2 : 1 nitromethane complex [7], which is nearly isomorphous to our structure. The greater acidity of the methyl hydrogens or the lower symmetry of nitromethane compared to acetonitrile may supply such an influence.

Our X-ray diffraction study confirms McLachlan's 1974 conclusion [14], based on polarized Raman spectra of a single crystal of the complex, that the macroring is in the D_{3d} conformation. The crystal structure also verifies the conclusion drawn by Gold and Rice [15] from ^{1}H NMR and Raman spectroscopic studies that the methyl group of acetonitrile is oriented toward the macroring. An increase in the C—N stretching frequency is observed [15] when comparing the spectrum of acetonitrile in the liquid state to that of the solid-state acetonitrile-crown complex. Mosier-Boss and Popov [16] observed a similar shift in solution when comparing infrared spectra of uncomplexed and complexed acetonitrile.

The origin of this shift is unknown, although Gold and Rice [15] have suggested that it arises from a change in the inductive effect of the methyl group when it is complexed to the crown. (Presumably more electron density is donated to the nitrile group.) This explanation is predicated on the existence of hydrogen bonding between acetonitrile and 18-crown-6. As discussed above, hydrogen bonding in the classic sense [11, 20] does not occur. Further evidence for the lack of true hydrogen bonding in this system comes from the observation that the C—H stretching frequency of acetonitrile *does not shift* upon complexation [21].

The tilt of the acetonitrile off the perpendicular to the mean O plane leads us to propose a different explanation for the shift in the nitrile stretching frequency. As has been pointed out by Elbasyouny *et al.* [22], six noncoplanar dipoles, 1.3 D each, are directed towards the interior of 18-crown-6 in its D_{3d} conformation. They suggest that complexation occurs by a combination of hydrogen bonding and dipole-dipole interactions between the crown and the neutral guest. They ascribe the guests' tilt to intracomplex dipole-dipole interactions between the guest molecules in 2 : 1 complexes. We propose that an intracomplex dipole-dipole interaction between crown dipoles and the nitrile dipole causes the shift in nitrile stretching frequency because the same shift occurs in the solution spectrum of the complex [16] as in the solid-state spectrum.

Table III. Structural parameters of 18-crown-6 complexes with guest methyl groups

Guest	C to Mean O Plane (Å)	Range of C···O contacts (Å)	Tilt Angle (°)	Ref.
CH_3CN	1.923	3.249(3)–3.346(3)	31.7	this work
$[CH_3CNIr(CO)(PPh_3)_2]^+$	1.975	3.24(7)–3.38(12)	36.5	[5]
CH_3NO_2	1.862	3.24(2)–3.32(2)	28.0	[7]
$(CH_3)_2SO_2$	1.996	3.314(4)–3.363(4)	26.2	[8]
$(CH_3O)_2SO_2$	1.978	3.220(7)–3.318(8)	34.9, 39.6	[9]
$CH_3OOCC{\equiv}CCOOCH_3$	1.896	3.079(3)–3.546(3)	56.1	[10]

In conclusion, the crystallographic results suggest that rather than hydrogen bonding, the structure of the complex is determined by dipole-dipole interactions between host and guest and between guests in neighbouring complexes in the crystal. This conclusion is supported by spectroscopic studies [15, 16, 21], which show changes only in the nitrile group stretching frequency, and not the methyl C—H stretching frequency.

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