

Neutral Solvent/Crown Ether Interactions 3.[★] Reorientation of the Hydrogen Bonds in the Low Temperature (–150°C) Structure of 18-Crown-6 · 2(CH₃NO₂)

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Abstract. The title complex was crystallized from a saturated solution of 18-crown-6 in nitromethane at 5°C and cooled to –150°C prior to X-ray diffraction data collection. At –150°C 18-crown-6 · 2(CH₃NO₂) is monoclinic, $P2_1/n$ with $a = 9.290(2)$, $b = 7.864(6)$, $c = 13.627(8)$ Å, $\beta = 100.84(4)^\circ$ and $D_{\text{calc}} = 1.31 \text{ g cm}^{-3}$ for $Z = 2$. Least-squares refinement using 1521 independent observed reflections [$F_o \geq 5\sigma(F_o)$] led to a final conventional R value of 0.041. The complex at –150°C is isostructural with its room temperature structure with the exception of the orientation of the methyl hydrogen atoms and their crown ether oxygen interactions. The methyl group hydrogen atoms were fully refined isotropically. The crown ether resides around a center of inversion and has D_{3d} symmetry. There is one methyl hydrogen ⋯ crown interaction at 2.35(3) Å, one apparently bifurcated hydrogen bond utilizing a second methyl hydrogen atom (2.55(3), 2.65(3) Å) and the third hydrogen atom is actually directed away from the crown ring (closest H ⋯ O contact = 2.67(3) Å).

Key words: 18-crown-6, nitromethane, solvent complex, low temperature crystal structure, C–H acidic hydrogen bonding.

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1. Introduction

18-crown-6 is flexible towards conformational change and various conformations have been found to be stabilized by fairly weak hydrogen bonds from neutral molecules [1, 2]. These interactions include NH ⋯ O(crown) hydrogen bonds [3–14], OH ⋯ O hydrogen bonds [15, 17], and even weak C–H acidic and CH ⋯ O interactions [18–24]. Many of these solvent complexes exhibit the symmetric D_{3d} crown ether conformation found in many 18-crown-6 complexes with rare earth, alkali, and alkaline earth salts. The common occurrence of this conformation in complexes of 18-crown-6 is probably due to a compensation for otherwise unfavorable electrostatic interactions between the oxygen atoms in this conformation [25].

Crystallographic studies of 18-crown-6 with polar C–H solvent guests have revealed that the number of actual C–H ⋯ O(crown) interactions and thus the superstructure, if any,

[★] For part 2, see reference [24].

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cannot always be determined in the absence of hydrogen atom positions (i.e., by C...O contact geometries alone). 18-crown-6 · C₂(COOMe)₂ [19] and 18-crown-6 · (CH₃)₂SO₄ [21] consist of infinite layers of host and guest molecules with one methyl hydrogen actually directed away from the crown ether. All three methyl hydrogen atoms participate in weak interactions with the crown ether in 18-crown-6 · 2(CH₃)₂SO₂ [20]. This latter type of interaction has also been assumed for [*trans*-Ir(CO)(CH₃CN)(PPh₃)₂ · 18-crown-6][PF₆]₂ · 2 CH₂Cl₂ [26] and [(COCPh₃)₂-18-crown-6] · 2 CH₃CN [27] although the hydrogen atoms were not located. Recently we redetermined the structure of 18-crown-6 · 2(CH₃NO₂) and found discrete 2 : 1 moieties with each methyl hydrogen interacting with one of the crown oxygen atoms (CH...O = 2.30, 2.35, 2.45 Å). Crystals used in that study decomposed slowly when removed from the solvent, although they appeared to be indefinitely stable when sealed in glass capillaries under argon. The crystals we used for the present study decompose very quickly (within 5 minutes) when removed from the solvent in air. This prompted the current investigation in order to find out if changes in the crown conformation or CH...O interactions were responsible for the different behavior.

In order to determine how solvent interactions, including hydrogen bonding, dipole interactions and packing effects, affect crown ether conformation and how they change crown

Table I. Crystal data and summary of intensity data collection and structure refinement

Compound	18-crown-6 · 2(CH ₃ NO ₂)	
Color/shape	Clear/parallelepiped	
Mol wt.	386.4	
Space group	<i>P</i> 2 ₁ / <i>n</i> <i>P</i> 2 ₁ / <i>n</i> [23]	
Temp., °C	- 150°C 22°C	
Cell constants (Å)		
<i>a</i>	9.290(2)	9.066(3)
<i>b</i>	7.864(6)	8.284(2)
<i>c</i>	13.627(8)	14.015(7)
<i>β</i> , deg	100.84(4)	101.83(5)
Cell vol., Å ³	977.9	1030.2
Molecules/unit cell	2	
<i>ρ</i> (calc), g cm ⁻³	1.31	
<i>μ</i> (calc), cm ⁻¹	1.19	
Radiation, graphite monochromator	MoK α (λ = 0.71073)	
Max. crystal dimensions, mm	0.35 × 0.48 × 0.63	
Scan width	0.80 + 0.35 tan θ	
Standard reflections	800, 060, (0, 0, 12)	
Decay of standards	- 6.4%	
Reflections measured	1967	
2 θ range, deg	2 < 2 θ < 50	
Range of <i>h</i> , <i>k</i> , <i>l</i>	+ 11, + 9, \pm 16	
Reflections observed [<i>F</i> _o ≥ 5 σ (<i>F</i> _o)]	1521	
No. of parameters varied	130	
Weights	Unit	
GOF	0.68	
<i>R</i>	0.041	
<i>R</i> _w	0.042	

ether reactivity and selectivity (if at all), it will be necessary to determine the exact nature of these complexes in the solid state, including: $X \cdots O$ contacts, superstructure (resulting from hydrogen bonding networks) if any, and specific $X-H \cdots O$ interactions, if any. We have thus undertaken a systematic study of several crown/solvent systems and recently communicated our preliminary studies of the crystallization and structural characterization (at -150°C) of dibenzo-18-crown-6 $\cdot 2(\text{CH}_3\text{CN})$ and dibenzo-18-crown-6 $\cdot 2(\text{CH}_3\text{NO}_2)$: two systems with quite different $H \cdots O(\text{crown})$ interactions [24]. This report details our continuing investigation into the $\text{CH}_3\text{NO}_2/18\text{-crown-6}$ interaction with the low temperature structure of 18-crown-6 $\cdot 2(\text{CH}_3\text{NO}_2)$.

2. Experimental

2.1. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR 18-CROWN-6 $\cdot 2(\text{CH}_3\text{NO}_2)$

The title complex was crystallized from a saturated solution of 18-crown-6 in 30 ml of CH_3NO_2 . The solution was heated gently for 2 h prior to crystallization which took place at 5°C . Clear single crystals of the title compound were mounted on a pin and quickly transferred

Table II. Final fractional coordinates for 18-crown-6 $\cdot 2(\text{CH}_3\text{NO}_2)$

Atom	x/a	y/b	z/c
O(1)	0.7361(1)	-0.1003(2)	0.1560(1)
O(2)	0.4770(1)	0.0625(2)	0.1964(1)
O(3)	0.2153(2)	0.0776(2)	0.0436(1)
C(1)	0.7267(2)	-0.0186(3)	0.2471(2)
C(2)	0.5735(2)	-0.0383(3)	0.2663(1)
C(3)	0.3310(2)	0.0547(3)	0.2140(2)
C(4)	0.2341(2)	0.1615(3)	0.1371(2)
C(5)	0.1244(2)	0.1716(3)	-0.0333(2)
C(6)	0.1228(2)	0.0839(3)	-0.1307(2)
O(4)	0.0835(2)	0.0883(2)	0.3757(1)
O(5)	0.2716(2)	0.1317(2)	0.4913(1)
N	0.1435(2)	0.1569(2)	0.4529(1)
C(7)	0.0576(3)	0.2762(3)	0.5030(2)
H(1)[C(1)]	0.746	0.102	0.243
H(2)[C(1)]	0.800	-0.073	0.305
H(1)[C(2)]	0.544	-0.150	0.261
H(2)[C(2)]	0.572	0.005	0.337
H(1)[C(3)]	0.294	-0.061	0.205
H(2)[C(3)]	0.322	0.098	0.284
H(1)[C(4)]	0.132	0.178	0.163
H(2)[C(4)]	0.278	0.275	0.134
H(1)[C(5)]	0.021	0.183	-0.018
H(2)[C(5)]	0.159	0.285	-0.038
H(1)[C(6)]	0.101	-0.035	-0.124
H(2)[C(6)]	0.044	0.138	-0.185
H(1)[C(7)]	-0.029(3)	0.303(3)	0.457(2)
H(2)[C(7)]	0.034(3)	0.216(4)	0.561(2)
H(3)[C(7)]	0.114(3)	0.372(4)	0.523(2)

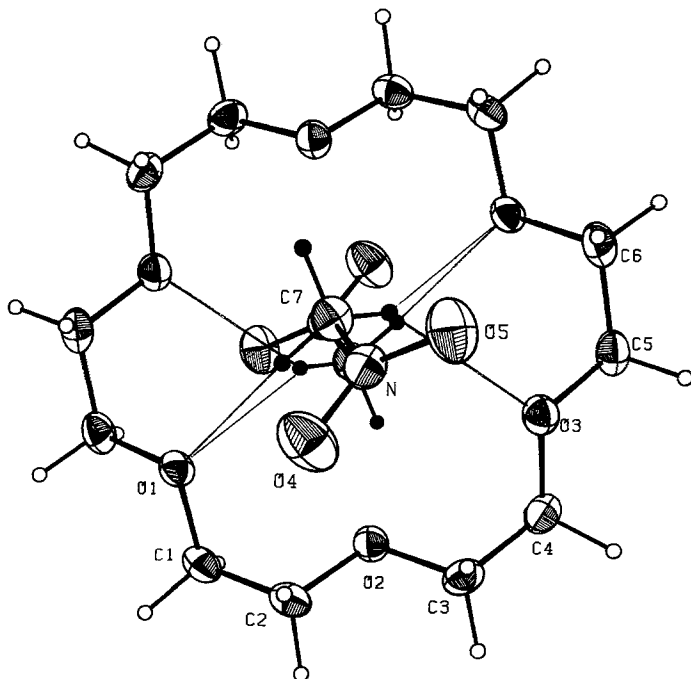


Fig. 1. Top view and atom labelling scheme for 18-crown-6 · 2(CH₃NO₂). The nitromethane molecule labelled is related to the coordinates in Table II by $1/2 - x$, $1/2 + y$, $1/2 - z$. The crown ether resides around a center of inversion. 50% probability thermal ellipsoids are depicted.

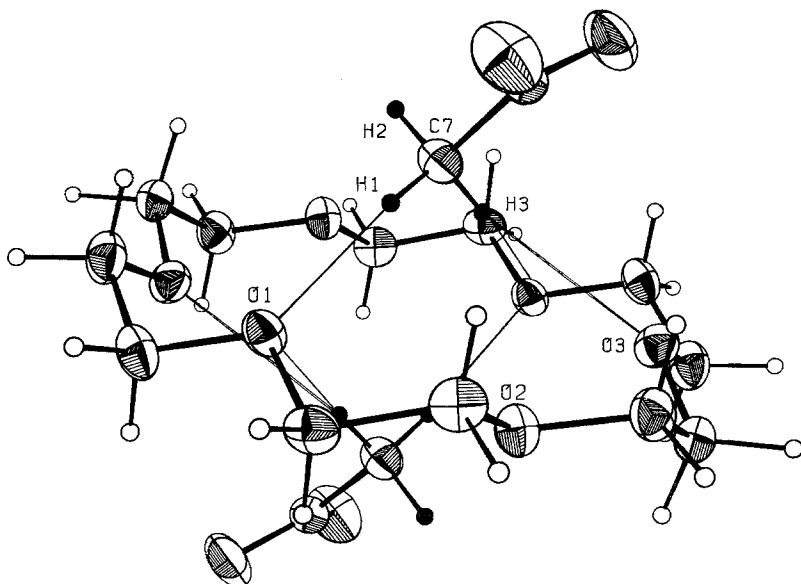


Fig. 2. Side view. Notice the orientation of H(2).

to the goniometer where they were bathed with a cold (-150°C) stream of nitrogen gas. Low temperature was necessary to prevent the rapid decomposition of crystals of the title compound observed immediately upon their removal from the solvent. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections ($\theta > 16^{\circ}$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/n$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ - 2θ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs [28]. Neutral atom scattering factors for O, N, C, and H were taken from reference [29] and the scattering was corrected for the real and imaginary components of anomalous dispersion [29].

Fractional coordinates of the nonhydrogen atoms in the room temperature structure [23] were used as a starting point in the current refinement. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma \|F_o\| - |F_c| / \Sigma |F_o| = 0.116$. The hydrogen atoms were located from a difference Fourier map and the crown hydrogen atoms fixed with $B = 5.5 \text{ \AA}^2$. The methyl hydrogen atoms were fully refined isotropically. Refinement of the nonhydrogen atoms with anisotropic temperature factors and of the methyl hydrogen atoms with isotropic thermal parameters led to final values of $R = 0.041$ and $R_w = 0.042$. A final difference Fourier showed no feature greater than $0.3 \text{ e}^- / \text{\AA}^3$. The weighting scheme was based on unit weights, no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

3. Results and Discussion

C-H acidic hydrogen bonding has been reviewed before [30] and a comparison of the room temperature structure of the title complex with the various types of $\text{CH}\cdots\text{O}$ interactions found for 18-crown-6 solvent complexes can be found in references [23, 31]. For the most part we will discuss here the differences in the 22°C and -150°C structures of 18-crown-6 $\cdot 2(\text{CH}_3\text{NO}_2)$. Top and side views of the 2:1 guest/host complex (which resides around a crystallographic center of inversion) are presented in Figures 1 and 2. Bond distances and angles for the crown ether and nitromethane molecules are given in Table III and the hydrogen bonding contacts and geometries can be found in Table IV.

At 22°C [23] and -150°C 18-crown-6 $\cdot 2(\text{CH}_3\text{NO}_2)$ has essentially the same structure with the rather obvious exception of the weak $\text{CH}\cdots\text{O}$ interactions. At 22°C , each methyl hydrogen participates in a $\text{CH}\cdots\text{O}(\text{crown})$ hydrogen bond. The $\text{H}\cdots\text{O}$ contacts range from 2.30 to 2.45 \AA , well under the van der Waals contact of 2.60 \AA . Rather sharp $\text{CH}\cdots\text{O}$ angles of 132.1 – 155.6° are also observed. The $\text{C}(\text{methyl})\cdots\text{O}$ contacts range from 3.25(2) to 3.33(2) \AA and the methyl \cdots methyl separation through the center of inversion is 3.80(1) \AA . The title complex at -150°C has a cell volume of 52.3 \AA^3 less than found at 22°C and the methyl \cdots methyl, through the ring separation decreases to 3.676(5) \AA . The $\text{C}(7)\cdots\text{O}(2)$ separation is still the closest of the three methyl \cdots O contacts (3.140(3) \AA versus 3.24 \AA at 22°C) and the remaining two unique separations are 3.313(3) (O(3)) and 3.296(2) \AA (O(1)). Without hydrogen atom positions there is not much to make one suspect that the orientation of the hydrogen atoms would be different. Review of Table IV, however, reveals an interesting pattern of $\text{CH}\cdots\text{O}$ interactions. First a reasonably strong $\text{C}(7)\text{H}(1)\cdots\text{O}(1)$ hydrogen bond is observed ($\text{H}(1)\cdots\text{O}(1) = 2.35(3) \text{ \AA}$, $\text{C}(7)\text{—H}(1)\cdots\text{O}(1) = 174(2)^{\circ}$). Next, there appears to be a bifurcated hydrogen bond between $\text{C}(7)\text{H}(3)$ and $\text{O}(3)$ ($\text{H}(3)\cdots\text{O}(3) = 2.55(3) \text{ \AA}$,

Table III. Bond distances (Å) and angles (deg) for 18-crown-6 · 2(CH₃NO₂)

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.414(3)	O(1)—C(6)' ^a	1.423(3)
O(2)—C(2)	1.420(2)	O(2)—C(3)	1.422(2)
O(3)—C(4)	1.416(2)	O(3)—C(5)	1.423(2)
C(1)—C(2)	1.502(3)	C(3)—C(4)	1.504(3)
C(5)—C(6)	1.493(3)	O(4)—N	1.220(2)
O(5)—N	1.223(2)	N—C(7)	1.478(3)
Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(6)'	112.6(1)	C(2)—O(2)—C(3)	111.4(2)
C(4)—O(3)—C(5)	112.1(2)	O(1)—C(1)—C(2)	108.8(2)
O(2)—C(2)—C(1)	109.0(2)	O(2)—C(3)—C(4)	108.9(2)
O(3)—C(4)—C(3)	108.9(2)	O(3)—C(5)—C(6)	108.7(2)
O(1)′—C(6)—C(5)	108.6(2)	O(4)—N—O(5)	123.2(2)
O(4)—N—C(7)	118.6(2)	O(5)—N—C(7)	118.2(2)

^a Primed atoms are related to those in Table II by the crystallographic center of inversion.

Table IV. Distances (Å) and angles (deg) for hydrogen bonds in 18-crown-6 · 2(CH₃NO₂)

Atoms	Distance	Atoms	Distance
H(1)C7—C(7)	0.95(3)	H(2)C7—C(7)	0.98(3)
H(3)C7—C(7)	0.92(3)		
H(1)C7—O(1)	2.35(3)	H(2)C7—O(2)' ^a	2.67(3)
H(3)C7—O(3)	2.55(3)	H(3)C7—O(1)'	2.65(3)
C(7)—O(1)	3.296(2)	C(7)—O(2)'	3.140(3)
C(7)—O(3)	3.313(3)	C(7)—O(1)'	3.506(3)
C(7)—O(2)	3.496(3)	C(7)—O(3)'	3.523(3)
C(7)—C(7)'	3.676(5)		
Atoms	Angle	Atoms	Angle
N—C(7)—H(1)C7	108(2)	N—C(7)—H(2)C7	106(2)
N—C(7)—H(3)C7	109(2)	H(1)C7—C(7)—H(2)C7	111(2)
H(1)C7—C(7)—H(3)C7	112(2)	H(2)C7—C(7)—H(3)C7	111(2)
C(7)—H(1)C7—O(1)	174(2)	C(7)—H(2)C7—O(2)'	110(2)
C(7)—H(3)C7—O(3)	140(3)	C(7)—H(3)C7—O(1)'	154(3)

^a Atoms related by the center of inversion.

C(7)—H(3)···O(3) = 140(3)° and O(1)′ (H(3)···O(1)′ = 2.65(3) Å, C(7)—H(3)···O(1)′ = 154(3)°), even though the H(3)···O(1)′ separation is quite long. The third hydrogen atom appears to have no real hydrogen bonding interactions. The closest C(7)H(2)···O contact is 2.67(3) Å and the C(7)—H(2)···O(2) angle is only 110(2)°. The orientation observed at -150°C is not unlike that found for one of the nitromethane molecules in dibenzo-18-crown-6 · 2(CH₃NO₂) (also at -150°C) [24].

The reorientation of the hydrogen bonds may be responsible for the observed increase in the dihedral angle between the plane of the nitromethane molecule and the mean plane of the

Table V. Torsion angles for 18-crown-6 · 2(CH₃NO₂)

Atoms	Angle
C(6)' ^a —O(1)—C(1)—C(2)	178.4
O(1)—C(1)—C(2)—O(2)	-70.1
C(1)—C(2)—O(2)—C(3)	-177.3
C(2)—O(2)—C(3)—C(4)	-179.2
O(2)—C(3)—C(4)—O(3)	72.0
C(3)—C(4)—O(3)—C(5)	-179.9
C(4)—O(3)—C(5)—C(6)	174.2
O(3)—C(5)—C(6)—O(1)'	-69.0
C(5)—C(6)—O(1)'—C(1)'	179.2

^a Atoms related by the center of inversion.

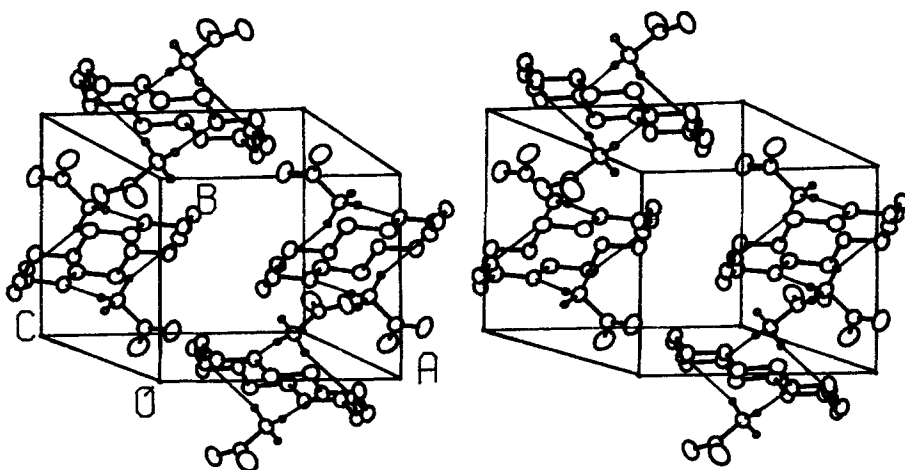


Fig. 3. Stereoview of the unit cell contents. All hydrogen atoms except for the methyl hydrogens have been omitted.

six oxygen atoms (127.3° at -150°C versus 120.3° at 22°C). In addition, the N—C and N—O bond lengths are significantly (3σ level) longer than the values found for 18-crown-6 · 2(CH₃NO₂) at 22°C : N—C(7) = 1.478(3) Å (1.388(9) Å at 22°C), N—O(4), O(5) = 1.220(2), 1.223(2) Å (1.157(8), 1.197(8) Å). This latter is presumably due to the higher thermal motion of the solvent molecule at 22°C .

Despite the different arrangement of hydrogen bonds and the apparent changes in the nitromethane molecule, the crown ether moiety is relatively unchanged. The average C—O (1.420(4) Å) and C—C (1.500(6) Å) distances and C—O—C ($112.0(6)^\circ$) and O—C—C ($108.8(1)^\circ$) angles are identical at 3σ to those found for the same structure at 22°C . The torsion angles are also relatively unchanged (Table V) and are indicative of a D_{3d} crown ether conformation ($ag^- aag^+ aag^- a$ [25]). A stereoview of the unit cell packing is presented in Figure 3.

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