

A Reinvestigation of the Crystal and Molecular Structure of (18-Crown-6)·2CH₃NO₂: *D*_{3d} Stabilization Via Methyl Hydrogen-Crown Oxygen ‘Hydrogen Bonds’

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Abstract. The title compound was crystallized from hot nitromethane. (18-crown-6)·2CH₃NO₂ crystallizes in the monoclinic space group *P*2₁/*n* with *a* = 9.066(3), *b* = 8.284(3), *c* = 14.015(7) Å, β = 101.83(5)° and *D*_{calc} = 1.25 g cm⁻³ for *Z* = 2. Least-squares refinement using 890 independent observed reflections led to a final conventional *R* value of 0.084. The hydrogen atoms were located but not refined. The crown ether resides about a crystallographic center of inversion. There are two nitromethane molecules (one centered above and one below the crown ether) weakly interacting with the crown oxygen atoms via the methyl hydrogens stabilizing a *D*_{3d} crown conformation.

Key words: 18-Crown-6, nitromethane, crystal structure, CH···O hydrogen bonding.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82029 (5 pages).

1. Introduction

Crystallographic studies have shown 18-crown-6 to be flexible towards conformational change. The elliptical crown cavity found in uncomplexed 18-crown-6 [1] is not normally found in its complexes with metal ions [2]. The most commonly observed conformation in these complexes has *D*_{3d} symmetry and a symmetric crown cavity [3]. Besides the well-known complexation of crown ethers with alkali, alkaline earth and lanthanide ions, crown ethers form crystalline host-guest complexes with hydrogen-bond donors. Thus higher energy crown ether conformations have been stabilized with NH···O(crown) interactions as observed in structural studies of 18-crown-6 with hydrazinium perchlorate [4], hydroxylammonium perchlorate [4], methylammonium perchlorate [4], 2,4-dinitrophenylhydrazine [5], *S*-*tert*-butylthiuronium perchlorate [6], benzenesulphonamide [7], *m*-nitroaniline [8], *p*-nitroaniline [9], 2,4-dinitroaniline [10], 4-nitro-1,2-benzenediamine [11], *N,N'*-dimethylthiourea [12], urea [13], and thiourea [14] and with OH···O hydrogen bonds found in UO₂(NO₃)₂(H₂O)₂·2H₂O·(18-crown-6) [15] and UO₂(NO₃)₂(H₂O)₂(18-crown-6) [16]. Weaker CH···O interactions have also been found to be sufficient to stabilize the *D*_{3d} conformation as observed in the structures of 18-crown-6 with malononitrile [17], dimethylacetylenedicarboxylate [18], bisdimethylsulphone [19], and dimethylsulphate [20].

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Our research group has begun to look into the area of *f*-element complexation by crown ethers. We are interested in the unusual oxidation states and high coordination numbers obtainable by using crown ethers. In the course of our investigations of LaCl_3 and 18-crown-6 interactions, the title compound was isolated. Two previous reports giving X-ray diffraction data for this compound have appeared. Unit cell dimensions were reported in [21] and a more complete report on the structure was given in [22]. The latter structural study suffered from crystal decomposition during data collection, reported to be a result of the loss of nitromethane. Due to the inaccuracy which resulted, the hydrogen atom positions could not be located and the final *R* value was 13.0%. In our work we noticed no crystal decomposition (upon sealing the crystals in glass capillaries) over a period of several months. Since we had overcome the decomposition problem and thus felt we could locate the hydrogen atoms, and in order to more fully define and understand the weak interactions between the guest nitromethane and host 18-crown-6 molecules, a single crystal X-ray diffraction study was carried out.

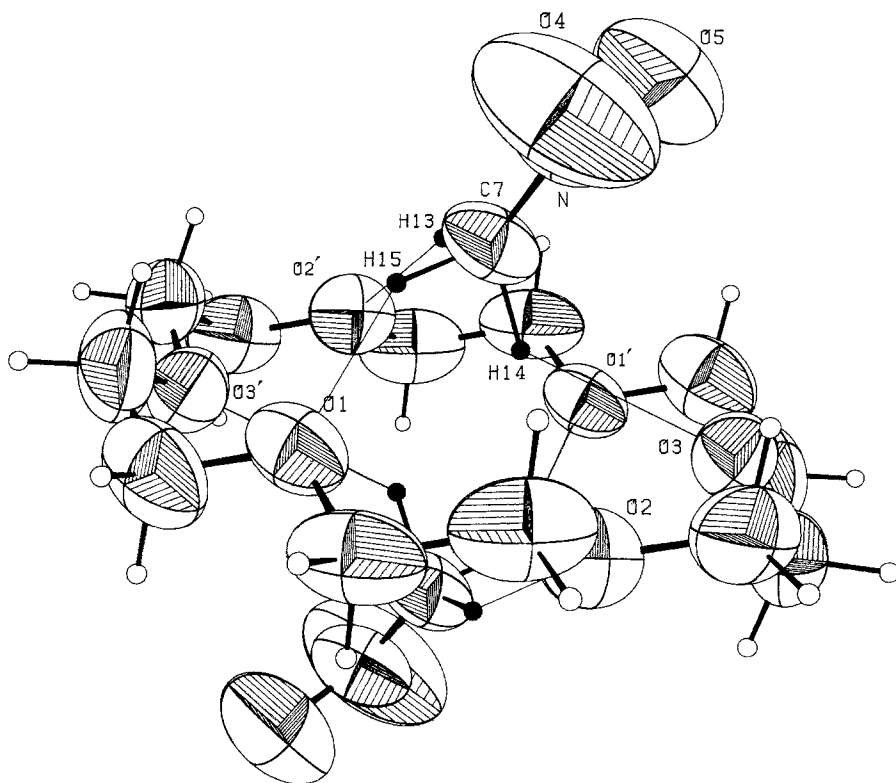


Fig. 1. Molecular structure of $(18\text{-crown-6}) \cdot 2\text{CH}_3\text{NO}_2$. The nonhydrogen atoms are represented by their 50% probability ellipsoids for thermal motion. Important contact distances ($< 2.5 \text{ \AA}$) and angles include: $\text{H}(13) \cdots \text{O}(2)' = 2.30 \text{ \AA}$, $\text{H}(14) \cdots \text{O}(3) = 2.45 \text{ \AA}$, $\text{H}(15) \cdots \text{O}(1) = 2.35 \text{ \AA}$, $\text{O}(2)' \cdots \text{H}(13) - \text{C}(7) = 155.6^\circ$, $\text{O}(3) \cdots \text{H}(14) - \text{C}(7) = 132.1^\circ$, $\text{O}(1) \cdots \text{H}(15) - \text{C}(7) = 141.9^\circ$. Primed atoms are related to those in Table IV by $1 - x, -y, -z$. The nitromethane molecule labelled is related to the coordinates in Table IV by $1/2 - x, -1/2 + y, 1/2 - z$.

2. Results and Discussion

(18-crown-6)·2CH₃NO₂ crystallizes as a 2 : 1 guest/host complex. As depicted in Figure 1, the nitromethane molecules are centered above and below the crown ether cavity and participate in weak CH···O hydrogen bonds, with each methyl hydrogen atom and each crown oxygen utilized in this fashion. (The use of the term 'hydrogen bond' for these CH···O interactions has been described in [23].) The planes defined by the nitromethane molecules make angles of 120.3° with the mean plane of the six oxygen atoms, which are displaced alternately 0.24 Å above and below this mean plane. Each set of three oxygen atoms displaced in the same direction interact with the methyl hydrogen atoms of the nitromethane molecule residing in the direction of the oxygen atom displacements. Although the hydrogen atoms in the title compound were not refined, they were located on a difference Fourier map with little difficulty. The C(7)H···O distances and C(7)H···O angles are 2.30, 2.45 and 2.35 Å (well under the van der Waals contact distance of 2.60 Å) and 155.6°, 132.1° and 141.9°, respectively. The thermal motion for C(7) is quite low compared to the NO₂ portion of the guest molecule perhaps as a result of the CH···O interactions. The three pertinent C(7)···oxygen distances are 3.24(O(2)), 3.32(O(3)) and 3.27 Å(O(1)) with C(7) 1.90 Å out of the mean plane of the six crown oxygen atoms. Values of 3.25(2), 3.33(2), and 3.26(2) Å were observed in the previous study of this compound [22].

Weak CH···O (crown) interactions have been observed previously for 18-crown-6 complexes. In (18-crown-6)·2CH₂(CN)₂ [17], with a host/guest arrangement similar to the title compound, one CH···O distance of 2.24 Å was observed with the other CH···O separation >2.6 Å. Several structures have been reported which exhibit methyl hydrogen···oxygen

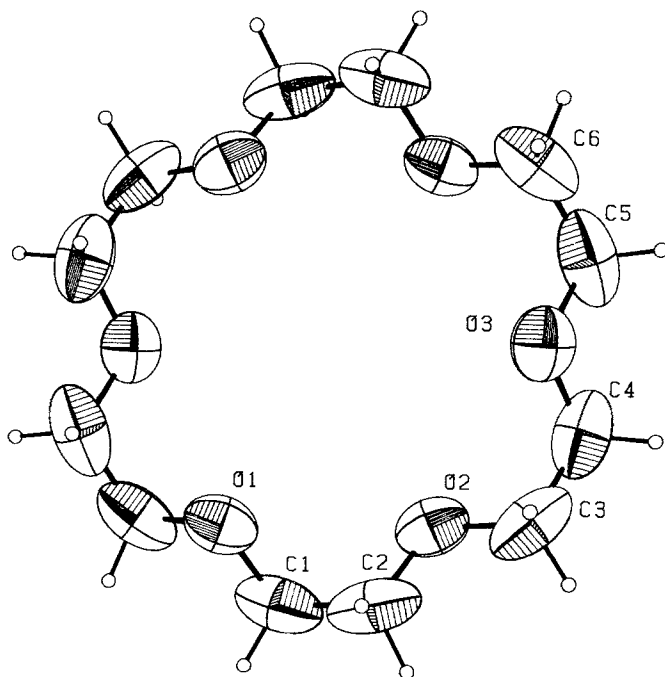


Fig. 2. Conformation of the 18-crown-6 molecule.

interactions. $\text{CH}\cdots\text{O}$ contacts under 2.6 \AA were observed in $(18\text{-crown-6})\cdot\text{C}_2(\text{COOMe})_2$ (2.45 and 2.32 \AA) [18] and $(18\text{-crown-6})\cdot(\text{CH}_3)_2\text{SO}_4$ (2.33 , 2.33 and 2.56 \AA) [20]. These two structures consist of infinite layers of host and guest molecules with one methyl hydrogen actually pointing away from the crown ether. The methyl hydrogen–crown oxygen interaction observed for $(18\text{-crown-6})\cdot 2(\text{CH}_3)_2\text{SO}_2$ [19] is similar to that found for the title compound, however only two of the $\text{CH}\cdots\text{O}$ contacts are $<2.6 \text{ \AA}$ (2.45 and 2.32 \AA). The third dimethylsulfone hydrogen atom (2.62 \AA) is very near the van der Waals contact distance, and must be interacting very weakly if at all. $\text{CH}\cdots\text{O}$ interactions are assumed for all three methyl hydrogens in $\{[\textit{trans}\text{-Ir}(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_2]_2\cdot 18\text{-crown-6}\}[\text{PF}_6]_2\cdot 2\text{CH}_2\text{Cl}_2$ [24] and $\{(\text{COCPh}_3)_2\cdot 18\text{-crown-6}\}\cdot 2\text{MeCN}$ [25].

Table I. Bond distances (\AA) and angles ($^\circ$) for $(18\text{-crown-6})\cdot 2\text{CH}_3\text{NO}_2$

| Atoms | Distance | Atoms | Distance |
|-----------------|----------|-------------------------|----------|
| O(1)–C(1) | 1.402(9) | O(1)–C(6)' ^a | 1.40(1) |
| O(2)–C(2) | 1.401(9) | O(2)–C(3) | 1.411(9) |
| O(3)–C(4) | 1.394(9) | O(3)–C(5) | 1.409(9) |
| C(1)–C(2) | 1.46(1) | C(3)–C(4) | 1.49(1) |
| C(5)–C(6) | 1.46(1) | O(4)–N | 1.157(8) |
| O(5)–N | 1.197(8) | N–C(7) | 1.388(9) |
| Atoms | Distance | Atoms | Distance |
| C(1)–O(1)–C(6)' | 114.3(6) | C(2)–O(2)–C(3) | 112.8(6) |
| C(4)–O(3)–C(5) | 113.7(7) | O(1)–C(1)–C(2) | 110.3(6) |
| O(2)–C(2)–C(1) | 110.6(7) | O(2)–C(3)–C(4) | 108.8(6) |
| O(3)–C(4)–C(3) | 110.5(7) | O(3)–C(5)–C(6) | 109.3(7) |
| O(1)'–C(6)–C(5) | 110.0(7) | O(4)–N–O(5) | 116.4(9) |
| O(4)–N–C(7) | 123.2(8) | O(5)–N–C(7) | 119.9(8) |

^a Primed atoms are related to those in Table IV by $1-x$, $-y$, $-z$.

Table II. Torsion Angles ($^\circ$) for $(18\text{-crown-6})\cdot 2\text{CH}_3\text{NO}_2$

| Atoms | Angle |
|------------------------------------|------------|
| C(6)' ^a –O(1)–C(1)–C(2) | 175.9 (a) |
| O(1)–C(1)–C(2)–O(2) | –69.8 (g–) |
| C(1)–C(2)–O(2)–C(3) | –179.5 (a) |
| C(2)–O(2)–C(3)–C(4) | –176.8 (a) |
| O(2)–C(3)–C(4)–O(3) | 70.3 (g+) |
| C(3)–C(4)–O(3)–C(5) | –179.9 (a) |
| C(4)–O(3)–C(5)–C(6) | 176.2 (a) |
| O(3)–C(5)–C(6)–O(1)' | –70.7 (g–) |
| C(5)–C(6)–O(1)'–C(1)' | –179.7 (a) |

^a Primed atoms are related to those in Table IV by $1-x$, $-y$, $-z$.

The conformation of the crown ether and atom numbering scheme are presented in Figure 2. The crown ether resides around a crystallographic center of inversion. As seen in Table I the average C—O (1.403(6) Å) and C—C (1.47(2) Å) distances and O—C—C (109.9(7)°) and C—O—C (113.6(8)°) angles are similar to values observed in other 18-crown-6 structures. The weak hydrogen bonds are sufficient to stabilize the D_{3d} crown ether conformation ($ag^+ aag^- aag^+ aag^- aag^+ aag^- a$: Table II). (This conformation is the most commonly observed for 18-crown-6 [3] and was found for all of the structures containing CH \cdots O bonds [17–20]). The resulting oxygen cavity is fairly symmetric with center of inversion-to-oxygen distances of 2.84, 2.81, and 2.85 Å. In the free crown ether [1] a ($g^+ g^- aag^+ aaaag^- g^+ aag^- aaaa$) conformation results in an elliptical cavity with center-to-oxygen values of 3.48, 3.42, and 2.11 Å. A stereoview of the unit cell packing is presented in Figure 3.

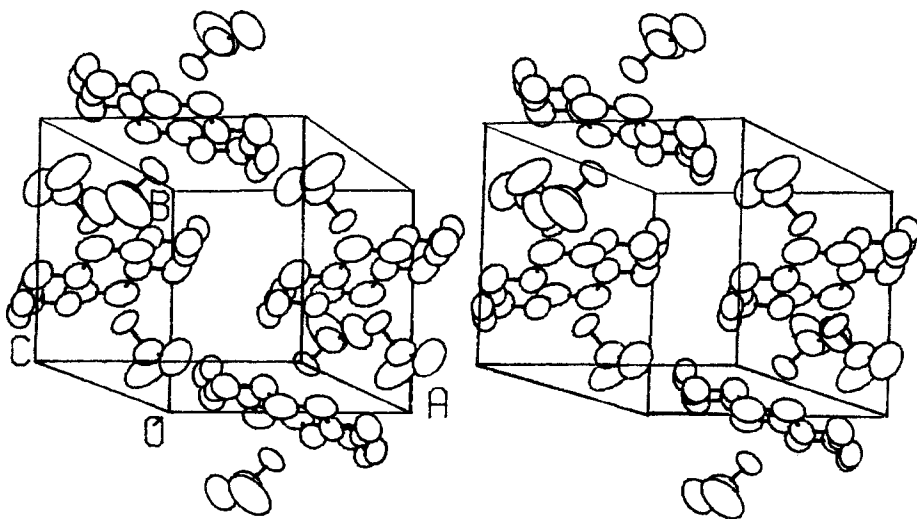


Fig. 3. Stereoview of the unit cell packing for (18-crown-6)·2CH₃NO₂.

3. Experimental

3.1. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR (18-CROWN-6)·2CH₃NO₂

Single crystals of (18-crown-6)·2CH₃NO₂ were obtained from a hot nitromethane solution also containing LaCl₃. Literature preparations for this compound from a variety of solvent systems can be found in [26]. The air-stable crystals were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 17^\circ$) accurately centered on the diffractometer are given in Table III. The space group was uniquely determined as $P2_1/n$. No loss of intensity during data collection was observed.

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

| | |
|---|-----------------------------------|
| Cmpd. | $C_{12}H_{24}O_6 \cdot 2CH_3NO_2$ |
| Mol. wt. | 386.4 |
| Space group | $P2_1/n$ |
| Cell constants | |
| <i>a</i> , Å | 9.066(3) |
| <i>b</i> , Å | 8.284(2) |
| <i>c</i> , Å | 14.015(7) |
| β, deg | 101.83(5) |
| Cell vol, Å ³ | 1030.2 |
| Molecules/unit cell | 2 |
| ρ(calc), g cm ⁻³ | 1.25 |
| μ(calc), cm ⁻¹ | 1.14 |
| Radiation | MoKα |
| Max crystal dimensions, mm | 0.60 × 0.80 × 0.95 |
| Scan width | 0.70 + 0.20 tan θ |
| Standard reflections | (080), (040), (600) |
| Decay of standards | ± 2% |
| Reflections measured | 2130 |
| 2θ range | 2° < 2θ < 50° |
| No. of observed reflections [$I \geq 2.5\sigma(I)$] | 890 |
| No. of parameters varied | 118 |
| GOF | 1.02 |
| <i>R</i> | 0.084 |
| <i>R_w</i> | 0.075 |

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 III. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Calculations were carried out with the SHELX system of computer programs [27]. Neutral atom scattering factors for C, H, O and N were taken from [28]. The scattering was corrected for the real and imaginary components of anomalous dispersion [28].

The structure was solved via the straightforward application of the direct methods program MULTAN [29]. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.134$. The hydrogen atoms of the crown ether were placed at calculated positions 0.97 Å from the bonded carbon atom, given a fixed isotropic thermal parameter of $B = 5.5 \text{ \AA}^2$ and were not refined. The methyl hydrogen atoms were located with the aid of a difference Fourier map. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.084$ and $R_w = 0.075$. A final difference Fourier showed no feature greater than $0.3 e/\text{\AA}^3$. 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 IV.

Acknowledgement

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Table IV. Fractional coordinates for (18-crown-6) · 2CH₃NO₂

| Atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>U</i> (eqv) |
|-------------|------------|------------|------------|----------------|
| O(1) | 0.7402(5) | -0.1014(6) | 0.1520(4) | 0.079 |
| O(2) | 0.4857(6) | 0.0697(6) | 0.1940(3) | 0.087 |
| O(3) | 0.2188(5) | 0.0912(6) | 0.0442(4) | 0.089 |
| C(1) | 0.736(1) | -0.023(1) | 0.2400(6) | 0.093 |
| C(2) | 0.584(1) | -0.028(1) | 0.2597(5) | 0.105 |
| C(3) | 0.337(1) | 0.069(1) | 0.2106(6) | 0.109 |
| C(4) | 0.2405(9) | 0.169(1) | 0.1343(8) | 0.109 |
| C(5) | 0.1280(9) | 0.179(1) | -0.0320(8) | 0.114 |
| C(6) | 0.1208(9) | 0.093(1) | -0.1240(7) | 0.103 |
| O(4) | 0.101(1) | 0.105(1) | 0.3828(6) | 0.202 |
| O(5) | 0.2738(9) | 0.134(1) | 0.4955(7) | 0.186 |
| N | 0.1462(9) | 0.1651(9) | 0.4575(5) | 0.099 |
| C(7) | 0.0681(8) | 0.2832(9) | 0.4971(5) | 0.087 |
| H(1)[C(1)] | 0.810 | -0.068 | 0.293 | (iso) |
| H(2)[C(1)] | 0.763 | 0.091 | 0.236 | (iso) |
| H(3)[C(2)] | 0.589 | 0.004 | 0.329 | (iso) |
| H(4)[C(2)] | 0.553 | -0.141 | 0.258 | (iso) |
| H(5)[C(3)] | 0.294 | -0.042 | 0.202 | (iso) |
| H(6)[C(3)] | 0.331 | 0.100 | 0.275 | (iso) |
| H(7)[C(4)] | 0.296 | 0.271 | 0.135 | (iso) |
| H(8)[C(4)] | 0.149 | 0.197 | 0.156 | (iso) |
| H(9)[C(5)] | 0.028 | 0.206 | -0.023 | (iso) |
| H(10)[C(5)] | 0.174 | 0.286 | -0.043 | (iso) |
| H(11)[C(6)] | 0.079 | -0.022 | -0.124 | (iso) |
| H(12)[C(6)] | 0.055 | 0.137 | -0.184 | (iso) |
| H(13)[C(7)] | 0.051 | 0.295 | 0.565 | (iso) |
| H(14)[C(7)] | 0.079 | 0.420 | 0.491 | (iso) |
| H(15)[C(7)] | -0.053 | 0.297 | 0.475 | (iso) |

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