

**Structure and Binding in Molecular Complexes of Cyclic Polyethers.
I. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6)-Dimethyl
Acetylenedicarboxylate at -160°C**

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The crystal structure of a 1:1 molecular complex of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with dimethyl acetylenedicarboxylate (DAC) was determined from three-dimensional X-ray diffraction data collected at -160°C . The crystals are triclinic with one unit of the complex in a unit cell of dimensions $a=8.173$ (3), $b=7.840$ (2), $c=9.814$ (3) Å, $\alpha=103.17$ (2), $\beta=97.28$ (3) and $\gamma=118.21$ (2) $^{\circ}$. The structure was solved by direct methods and was refined by least-squares calculations to a conventional $R=0.036$ for 2274 observations. The polyether and DAC molecules are arranged alternately along the [011] direction in the crystal, forming a column-like structure. The fact that all oxygen atoms of the 18-crown-6 molecule appear to participate in dipole-dipole interactions with the smaller 'guest' species illustrates the role that weak intermolecular binding forces can play in the structures of host-guest molecular compounds. Results of least-squares calculations based on different weighting schemes are reported, and some remarks on the usually observed shortening of C-C single bonds in 18-crown-6 and its derivatives are also included.

Introduction

Macrocyclic polyethers have several unique properties and possible interesting applications (Christensen, Hill & Izatt, 1971; Pedersen & Frensdorff, 1972; Christensen, Eatough & Izatt, 1974). Their most outstanding feature (Pedersen, 1967) is that they form complexes with many different inorganic cations, including ammonium and substituted ammonium ions. Recently, similar complexation has been observed to occur with a variety of organic compounds (Cram & Cram, 1974). In addition, selected substituted multiheteromacrocycles, acting as host molecules, show varying degrees of specificity for complexation of metal and alkylammonium ions. In fact, certain of these compounds appear to mimic biological systems. Several metal-organic ligand complexes have been considered as models for ion-carrier molecules in the investigation of active ion transport phenomena across bulk membranes (Simon, Morf & Meier, 1973; Simon & Morf, 1973). It has also been suggested that molecular complexes formed by synthetic macrocyclic polyethers with neutral and ionic guest moieties exhibit some of the properties characteristic of enzymatic catalysis and biological regulatory processes (Cram & Cram, 1974; Cram *et al.*, 1974).

The remarkable ability of these multiheteromacrocyclic compounds to bind various species in host-guest type complex is enhanced by the hydrophilic character of the central cavity, which contains several potentially binding atoms, as well as by the essentially hydrophobic molecular exteriors. In cyclic polyethers, ion-dipole and dipole-dipole interactions between guest mol-

ecules and ions and the electronegative oxygen atoms (each possessing two unshared electron pairs), which are symmetrically arranged in the macro-ring, provide the best known means of internal binding in the complexed unit. Stability of the complex is, however, also affected by complementary steric features of the participating species (Cram *et al.*, 1974). Unfortunately, most research efforts in recent years have been devoted to studies of cyclic polyether complexes with univalent and bivalent inorganic cations only (Christensen *et al.*, 1974). These compounds have been found to be stabilized mainly by ion-dipole forces (Frensdorff, 1971).

The present paper is part of a study of molecular complexes formed by cyclic polyethers with neutral and ionic organic guest molecules. Our investigation is motivated by the desire to contribute to the understanding of the structural details of these compounds, in particular, the geometry of binding sites in a complex, in order to clarify the nature of the various intermolecular interactions exhibited by the host-guest complexes. When feasible, intensity data will be collected at low temperatures so that more precise positional and thermal parameters can be obtained.

In spite of the extensive interest in polyether macrocycles and their complexes, only a relatively small number of room-temperature crystalline structures of alkali and alkaline earth complexes with synthetic polyether ligands have been described (Truter, 1973; Dunitz, Dobler, Seiler & Phizackerley, 1974). The most complete investigation was carried out by Dunitz *et al.* on compounds containing 18-membered hexa-ether rings. It was shown that in each case the conformation adopted by the ligand may depend on the size of the bound cation and its coordination properties, and also on the substituents present on the hexa-ether skeleton.

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In general, however, in complexes with large cations the shape of the symmetric cavity remains essentially constant. D_{3d} symmetry most frequently characterizes the conformation of the unsubstituted polyether, while the departure of metal ions from the mean oxygen plane is directly correlated with their ionic radii. Significant deviations from the high-symmetry conformation in the solid state were reported only for some complexes containing the small sodium cation and for the unsubstituted hexa-ether. Similar comparative analysis for molecular complexes with organic species is clearly desirable in order to achieve a more complete description of the available variety of interactions binding hosts to guests.

This paper deals with the detailed description of the complex between 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) and dimethyl acetylenedicarboxylate (DAC). Further results on other complexes of polyether moieties with alkylammonium ions will be reported elsewhere (Goldberg, 1975).

Experimental

Crystals of the title compound were kindly supplied by Professor D. J. Cram and Dr M. E. Newcomb. Further recrystallization was necessary in order to obtain good specimens for crystallographic investigation. Slow evaporation of a solution of the complex in a mixture of benzene and cyclohexane gave well-shaped colorless prisms. Preliminary photographic studies revealed that the crystals were triclinic. A computer-controlled Syntex $P\bar{1}$ diffractometer equipped with a low-temperature device (Strouse, 1974) served for intensity-data collection in our experiment. A crystal measuring $0.15 \times 0.25 \times 0.30$ mm was mounted with epoxy resin on a glass fiber and was covered by a Lindemann glass capillary with 0.3 mm diameter and 0.01 mm wall

thickness. This capillary was necessary to minimize any possible influence of the cold nitrogen stream on the equilibrium position of the mounted crystal.

The unit-cell constants at approximately -160°C , listed below, were obtained during the alignment process after the crystal had been optically centered on the four-cycle diffractometer. 15 intense reflections were used in the centering, auto-indexing and least-squares procedures, which were controlled by the manufacturer-supplied software.

Crystal data

($\text{C}_{12}\text{H}_{24}\text{O}_6$) ($\text{C}_6\text{H}_6\text{O}_4$), M.W. 406.4, m.p. 101°C . Triclinic, $a=8.173$ (3), $b=7.840$ (2), $c=9.814$ (3) Å; $\alpha=103.17$ (2), $\beta=97.28$ (3), $\gamma=118.21$ (2)°. $V=519.1$ Å³, $Z=1$, $D_c(-160^\circ\text{C})=1.300$ g cm⁻³. Space group $P\bar{1}$ or $P\bar{1}$, $\mu(\text{Mo } K\alpha)=1.1$ cm⁻¹.

Three-dimensional diffraction data out to $2\theta_{\text{max}}=60^\circ$ ($\sin \theta/\lambda=0.704$) were recorded with graphite-monochromated Mo $K\alpha$ ($\lambda=0.71069$ Å) radiation and a $\theta/2\theta$ scan mode. The scan rate was 2° min⁻¹ over the peak width, with a 2θ range below $K\alpha_1$ and above $K\alpha_2$ of 1.1° . The background to scan ratio was 0.8. Three standard reflexions were monitored after each group of 97 measurements. The maximum deviation of the intensities of these reflexions amounted to about 3% of their averaged values. 3318 observations, including 102 recordings of the standards, were measured but the evaluated unique set of data consisted of only 3060 reflexions.

The data were processed by program $P\bar{1}BAR$ routinely in our laboratory. The net integrated intensity (I) was calculated according to the expression

$$I = CT - (t_c/t_b)(B_1 + B_2)/2,$$

where CT is the total integrated count, B_1 and B_2 are background counts for time t_b on each side of the peak, and t_c is the time elapsed during the scan. The standard deviation of I was calculated as

$$\sigma(I) = (\sigma_s^2 + p^2 I^2)^{1/2},$$

where σ_s is the standard deviation due to counting statistics, and p is a constant (0.03 in this case). Lorentz and polarization corrections (including the monochromator polarization) were then applied to the intensity data set. Absorption corrections were not included because of the low linear absorption coefficient for Mo $K\alpha$ radiation. Of the 3060 independent F_o values available for study, 786 with $F_o^2 < 3\sigma(F_o^2)$ were given zero weight in the subsequent calculations.

The initial assumption of the space group $P\bar{1}$, based on examination of molecular models, was strongly supported by the results of the $N(z)$ and intensity moments (Foster & Hargreaves, 1963) tests. The theoretical moments of z based on Wilson (1949) statistics (for space group $P\bar{1}$, $\langle z^2 \rangle = 3$ and $\langle z^3 \rangle = 15$) compare well with the averaged experimental moments $\langle z^2 \rangle = 3.1$, $\langle z^3 \rangle = 16.1$ computed from the available data.

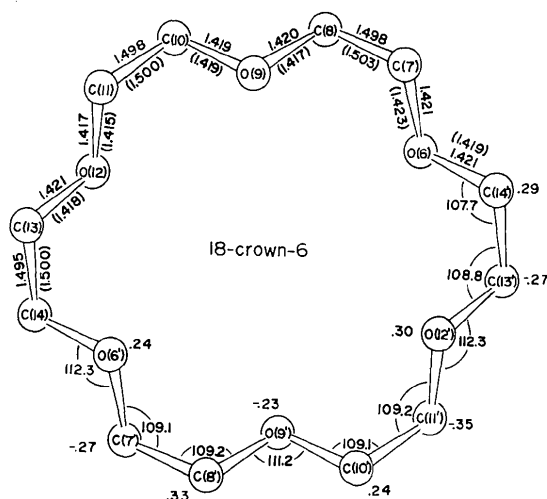


Fig. 1. Molecular geometry of 18-crown-6. Values in parentheses correspond to modified refinement with weights $1/\sigma^2(F) \cdot \exp(14 \cdot \sin^2 \theta/\lambda^2)$. Average standard deviation in bond angles is 0.15° . Bond distances are not corrected for libration.

Determination and refinement of the structure

Normalized structure amplitudes (E values) were derived from the available data. Examination of the E statistics confirmed that the structure is centrosymmetric, and in all subsequent computations space group $P\bar{1}$ was used. The structure was solved by weighted tangent-formula refinement (Germain, Main & Woolfson, 1971) applied to 231 reflections with $|E| > 1.75$. The multisolution routine, operating with the automatically selected starting set of seven reflections, yielded 16 sets of phases for the input data. The most consistent solution (apart from the trivial one for which all signs are positive) was used to calculate an E map. It revealed 14 high peaks above a somewhat noisy background, which were readily seen to correspond to the positions of the nonhydrogen atoms of the 18-crown-6-DAC complex, in the chosen asymmetric unit. An ambiguity, however, still existed with respect to the distinction between oxygen and carbon atoms in the unsubstituted 18-membered ring. Atomic form factors for carbon were, therefore, used for all ring atoms in two initial cycles of a least-squares refinement. Interatomic distances calculated with the resulting positional parameters clearly indicated the identity of all oxygens in the ring system. Two additional cycles of individual isotropic refinement of the trial structure so derived led to $R=0.105$ for 907 low-angle reflexions ($\sin \theta/\lambda \leq 0.49$). Further anisotropic refinement of the partial (heavy-atom) structure lowered R to 0.086 for 1240 equally weighted observations with $\sin \theta/\lambda \leq 0.55$.

A difference synthesis computed after this step revealed all 15 unique hydrogen atoms, with peak heights ranging from 0.55 to 0.80 e \AA^{-3} . Several cycles of full-matrix least-squares calculations in which 187 parameters were adjusted (three coordinates for each of the atoms, anisotropic temperature factors for the heavy atoms, isotropic temperature coefficients for the hydrogens, and a scale factor) completed the refine-

ment procedure. All 2274 reflexions were included in the computations.*

The final discrepancy index is $R=0.037$ for all the data, and $R=0.036$ when the five strongest reflexions ($1\bar{2}1$; $0\bar{2}1$; $1\bar{2}1$; $2\bar{2}0$; $1\bar{2}0$), which appear to suffer from secondary extinction, are omitted. The final value of $[\sum w(\Delta F)^2/(n-m)]^{1/2}$ is 2.2 for $w=1.0$, $n=2274$ and $m=187$. Several peaks with heights below 0.20 e \AA^{-3} were observed on a final difference map along interatomic bonds and close to the oxygen nuclei.

* The structure factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30742 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Distribution of $\langle w(\Delta F)^2 \rangle$ as a function of $\sin \theta/\lambda$

Second and third columns refer to calculations with $w=1.0$. Fourth column refers to refinement based on a modified weighting scheme; $w=1/\sigma^2(F) \cdot \exp(14 \cdot \sin^2 \theta/\lambda^2)$.

$\langle \sin \theta/\lambda \rangle^*$	$\langle F_o \rangle$	$\langle w(\Delta F)^2 \rangle_1$	$\langle w(\Delta F)^2 \rangle_2$
0.188	96.2	9.63	52.1
0.278	72.8	7.60	47.6
0.329	63.6	5.07	63.6
0.369	48.5	2.67	50.8
0.401	45.6	2.59	45.3
0.430	53.4	3.85	44.0
0.456	44.5	2.93	64.7
0.479	39.0	3.68	84.0
0.502	36.6	3.35	92.4
0.522	36.7	2.72	94.6
0.542	35.2	2.55	124.9
0.562	28.1	2.15	119.0
0.581	27.6	2.06	159.6
0.598	26.5	2.27	205.8
0.616	26.2	2.57	288.4
0.631	26.8	2.19	284.2
0.648	25.1	2.89	360.4
0.665	25.7	2.54	379.7
0.679	24.4	2.28	435.4
0.695	24.7	2.78	646.0

* Each group contains 113 reflexions ordered on increasing $\sin \theta/\lambda$.

Table 2. Atomic fractional coordinates and thermal parameters U^{ij} (\AA^2) for the heavy atoms

The e.s.d.'s are given in parentheses in units of the last decimal place. The anisotropic temperature factor is in the form

$\exp[-2\pi^2(h_i a^i)(h_j a^j)U^{ij} \times 10^{-4}]$ where h_i and a^i are reflection indices and reciprocal unit-cell edges respectively.

	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
C(1)	-0.0307 (2)	-0.4843 (2)	0.0498 (2)	187 (6)	185 (6)	178 (6)	101 (5)	53 (5)	33 (3)
C(2)	-0.1145 (2)	-0.4546 (2)	0.1705 (1)	200 (6)	169 (6)	160 (6)	110 (5)	58 (5)	58 (5)
O(3)	-0.2845 (1)	-0.5488 (2)	0.1589 (1)	186 (5)	265 (6)	229 (5)	70 (4)	27 (4)	63 (4)
O(4)	0.0239 (1)	-0.3153 (2)	0.2898 (1)	174 (5)	230 (5)	164 (5)	104 (4)	34 (4)	52 (4)
C(5)	-0.0429 (2)	-0.2662 (2)	0.4161 (2)	223 (7)	234 (7)	158 (6)	111 (6)	22 (6)	59 (5)
O(6)	0.3886 (1)	0.1289 (2)	0.6386 (1)	181 (5)	196 (5)	199 (5)	83 (4)	34 (4)	20 (4)
C(7)	0.5167 (2)	0.2806 (2)	0.5859 (2)	138 (6)	200 (7)	389 (9)	62 (6)	101 (6)	20 (6)
C(8)	0.4509 (2)	0.2054 (2)	0.4231 (2)	202 (7)	271 (8)	378 (9)	150 (6)	173 (7)	168 (6)
O(9)	0.2806 (1)	0.2086 (2)	0.3778 (1)	205 (5)	230 (5)	192 (5)	129 (4)	63 (4)	84 (4)
C(10)	0.2203 (2)	0.1519 (2)	0.2241 (2)	304 (8)	197 (7)	183 (6)	109 (6)	63 (5)	130 (6)
C(11)	0.0390 (2)	0.1545 (2)	0.1821 (2)	368 (9)	208 (7)	155 (6)	147 (6)	72 (6)	63 (6)
O(12)	-0.1182 (2)	-0.0212 (2)	0.1947 (1)	257 (5)	246 (5)	242 (5)	156 (5)	94 (4)	49 (4)
C(13)	-0.2941 (3)	-0.0234 (3)	0.1639 (2)	356 (9)	407 (9)	173 (7)	285 (8)	91 (7)	42 (6)
C(14)	-0.4424 (2)	-0.1896 (3)	0.2071 (2)	225 (7)	311 (8)	210 (7)	171 (7)	-13 (6)	-33 (6)

Use of a weighting scheme in which equal weights are assigned to all observations in the refinement process was suggested by a reasonably constant distribution (except for a relatively small number of very low-order reflections) of $\langle w(\Delta F)^2 \rangle$ with increasing $\sin \theta/\lambda$ (Table 1). ΔF is defined as $F_o - KF_c$ with K as a scale factor. Refinement based on the experimental weights $[1/\sigma^2(F)]$ gave a relatively high value for the weighted R (Table 8). Application of different weighting schemes to the data set is discussed below.

Table 3. Atomic parameters for the hydrogen atoms

The numbering of each hydrogen atom corresponds to that of the carbon atom to which the hydrogen is bonded.

$$\langle \sigma(p) \rangle = 0.023 \text{ \AA}, p = x, y, z$$

$$\langle \sigma(U) \rangle = 0.005 \text{ \AA}^2$$

	x	y	z	$U(\text{\AA}^2)$
H(5a)	-0.1204	-0.2050	0.3929	0.020
H(5b)	-0.1052	-0.3836	0.4467	0.026
H(5c)	0.0696	-0.1579	0.4878	0.025
H(7a)	0.6432	0.3084	0.6152	0.033
H(7b)	0.5206	0.4149	0.6290	0.023
H(8a)	0.4211	0.0588	0.3804	0.024
H(8b)	0.5525	0.2921	0.3861	0.033
H(10a)	0.1952	0.0047	0.1770	0.021
H(10b)	0.3202	0.2506	0.1896	0.026
H(11a)	0.0162	0.1638	0.0817	0.029
H(11b)	0.0529	0.2880	0.2466	0.025
H(13a)	-0.3388	-0.0462	0.0594	0.032
H(13b)	-0.2764	0.1187	0.2192	0.028
H(14a)	-0.4487	-0.3240	0.1651	0.022
H(14b)	-0.5685	-0.2055	0.1709	0.028

The final heavy-atom parameters and their standard deviations are given in Table 2; those of the hydrogen atoms are in Table 3. The standard deviations of the parameters were estimated from the corresponding diagonal elements of the inverse matrix of the normal equations.

The *BDSL* computer program used in the refinement calculations, which minimizes $\sum w(\Delta F)^2$, is described elsewhere (Goldberg & Shmueli, 1971). Atomic scattering factors used in this study were taken from Hanson, Herman, Lea & Skillman (1964) for carbon and oxygen, and from Stewart, Davidson & Simpson (1965) for hydrogen.

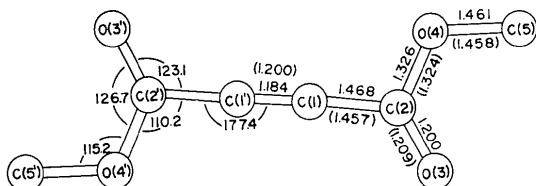


Fig. 2. Molecular geometry of dimethyl acetylenedicarboxylate. Values in parentheses correspond to modified refinement with weights $1/\sigma^2(F) \cdot \exp(14 \cdot \sin^2 \theta/\lambda^2)$. Average standard deviation in bond angles is 0.13° . Bond distances are not corrected for libration.

Molecular geometry and the weighting scheme

The molecular geometry of the two constituents of the compound is shown in Figs. 1 and 2 and in Tables 4, 5 and 6. For clarity, the hydrogen atoms of 18-crown-6 have been omitted from the figures.

Table 4. Bond distances (\AA)

Columns (a) and (b) refer to unmodified (unit weights) and modified ($r = 14 \text{ \AA}^2$, $w = 1/\sigma^2(F)$; see text) refinements respectively. Bond distances in DAC are corrected for thermal motion.

	(a)	(b)		
C(1)—C(1')	1.184 (2)	1.201 (2)	C(5)—H(5a)	0.99 (3)
C(1)—C(2)	1.469 (2)	1.458 (2)	C(5)—H(5b)	0.96 (2)
C(2)—O(3)	1.206 (2)	1.213 (2)	C(5)—H(5c)	0.94 (2)
C(2)—O(4)	1.332 (1)	1.329 (1)	C(7)—H(7a)	0.94 (3)
O(4)—C(5)	1.461 (2)	1.458 (2)	C(7)—H(7b)	1.02 (2)
O(6)—C(7)	1.421 (2)	1.423 (2)	C(8)—H(8a)	1.02 (2)
C(7)—C(8)	1.498 (3)	1.503 (2)	C(8)—H(8b)	0.97 (2)
C(8)—O(9)	1.420 (3)	1.417 (2)	C(10)—H(10a)	1.05 (2)
O(9)—C(10)	1.419 (2)	1.419 (2)	C(10)—H(10b)	0.99 (2)
C(10)—C(11)	1.498 (3)	1.500 (3)	C(11)—H(11a)	1.01 (2)
C(11)—O(12)	1.417 (2)	1.415 (2)	C(11)—H(11b)	1.04 (2)
O(12)—C(13)	1.421 (3)	1.418 (3)	C(13)—H(13a)	0.99 (2)
C(13)—C(14)	1.495 (3)	1.500 (2)	C(13)—H(13b)	1.05 (2)
C(14)—O(6')	1.421 (2)	1.419 (2)	C(14)—H(14a)	1.01 (2)
			C(14)—H(14b)	0.98 (3)

Table 5. Dihedral angles ($^\circ$) in 18-crown-6

Atoms	Dihedral angle	Distance
1 2 3 4	1-2-3-4	1-4
C(14')—O(6)—C(7)—C(8)	-179.9°	
O(6)—C(7)—C(8)—O(9)	72.1	2.898 \AA
C(7)—C(8)—O(9)—C(10)	176.0	
C(8)—O(9)—C(10)—C(11)	179.1	
O(9)—C(10)—C(11)—O(12)	-75.6	2.931
C(10)—C(11)—O(12)—C(13)	176.8	
C(11)—O(12)—C(13)—C(14)	-169.2	
O(12)—C(13)—C(14)—O(6')	69.6	2.838

The DAC molecule (not including the methyl groups) is essentially planar, the maximum deviation from its best plane being 0.01 \AA for C(1). The methyl carbons lie 0.05 \AA above and below the plane of the conjugated system (Table 6). The molecular dimensions of DAC are close to those reported for other molecules with similar functional groups (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1960). The bond lengths C(1)—C(1') and C(2)—O(3) appear, however, to be somewhat shorter than the corresponding documented values for carbonyl and triple carbon-carbon bonds (see below).

The 18-crown-6 molecule, composed of three nearly equivalent $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$ units, has approximate D_{3d} symmetry. All chemically equivalent bond distances in the cyclic ether are almost equal, and the spread about their mean values is within one standard deviation. The six oxygen atoms lie alternately about 0.25 \AA below and above their mean plane. All observed C—O bond distances are in the range $1.417-1.421 \text{ \AA}$, the values for C—C bonds are $1.495-1.498 \text{ \AA}$. C—O—C angles in the molecule are 112.3 , 112.3 and 111.2° , while

O–C–C angles are almost tetrahedral, averaging to 108.9°. The torsion angles (Table 5) are close to 180° about the C–O bonds and close to 70° for the C–C bonds, corresponding to a *gauche* conformation of the ethyleneoxy units.

The observed values of the 15 C–H bond lengths range from 0.93 to 1.05 Å with an average of 1.00 ± 0.01 Å.

The molecular dimensions of 18-crown-6 in the present compound are similar to those observed in other structures (Dunitz *et al.*, 1974; Mercer & Truter, 1973), the geometry of the 18-membered ring being in all cases characterized by short C–C bond distances in the range 1.47–1.51 Å. The usually quoted reference value for a single aliphatic C–C bond is 1.537 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1960). A C–C bond distance of 1.523 Å is reported by Davis & Hassel (1963) for gas-phase 1,4-dioxane. Other geometrical features appear to be normal.

To our knowledge all of the published studies on macrocyclic polyethers and their complexes refer to experiments done at room temperature. Most observed thermal vibration parameters are rather large, principal components of the atomic vibration tensors U ranging from 0.04 to 0.11 Å². The previous studies showed that large-amplitude internal ring vibrations are common to the unsubstituted 18-crown-6 molecule in several crystal structures (Dunitz *et al.*, 1974), and no reliable corrections for the effects of thermal motion have been estimated.

In the present structure, similar conclusions may be drawn with respect to the flexibility of the 18-membered ring. Thermal motion rigid-body analysis (Cruickshank, 1956) based on the final thermal parameters

Table 7 (*cont.*)

		R.m.s. amplitudes		Principal axes		
L	6.2°	I_1	0.9981	0.0469	0.0398	
	1.0	I_2	0.0052	−0.7091	0.7051	
	0.6	I_3	0.0613	−0.7035	−0.7080	
	0.14 Å	t_1	−0.4648	−0.8329	0.3005	
T	0.13	t_2	−0.8708	0.4915	0.0153	
	0.12	t_3	−0.1605	−0.2546	−0.9536	

Eigenvalues (in parentheses, in units of atomic weight $\times \text{Å}^2$), and eigenvectors (l, m, n) of the tensor of inertia referred to the reference base vectors a, b^* and $a \times b^*$:

(101)	l	0.5266	−0.2585	−0.8099
(955)	m	0.7090	0.6593	0.2505
(1058)	n	0.4691	−0.7061	0.5304

listed in Table 2 shows a large discrepancy between the experimental and calculated parameters, $\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.0046 \text{ Å}^2$. The results of this calculation indicate however, that the major component of the average motion of 18-crown-6 appears to be libration of the molecule about the axis of highest inertia (Fig. 3), with an approximate amplitude of 2.3°. This apparently unusual type of motion is observed in many crystals of molecular complexes, in which dissimilar packing restrictions are imposed on the constituent molecules (Herbstein, 1971; Goldberg & Shmueli, 1973).

On the other hand, the DAC molecule fits the rigid-body model much better (Table 7). The respective root-mean-square discrepancy for this model is 0.0014 Å^2 , while the estimated value of $\langle \sigma^2(U_{ij}) \rangle^{1/2}$ is 0.0006 Å^2 . Such a result is consistent with the unsaturated character of DAC.

Table 6. *Best planes*

(a) Equations of best planes

x, y, z are fractional coordinates of a point in the plane and the right-hand side is the distance of the plane from unit-cell origin.

1.	$3.645x - 7.111y - 1.890z = 0.945 \text{ Å}$	18-Crown-6
2.	$3.650x - 7.165y - 1.728z = 0.864 \text{ Å}$	Six oxygens of 18-crown-6
3.	$3.834x - 7.551y + 4.580z = 3.776 \text{ Å}$	DAC
4.	$3.811x - 7.569y + 4.521z = 3.785 \text{ Å}$	DAC without C(5) and C(5')

(b) Deviations (Å) from the best planes

	O(6)	C(7)	C(8)	O(9)	C(10)	C(11)	O(12)	C(13)	C(14)
1.	0.24	−0.27	0.33	−0.23	0.24	−0.35	0.30	−0.27	0.29
2.	0.25	−0.27	0.31	−0.26	0.19	−0.41	0.25	−0.33	0.25
	C(1)	C(2)	O(3)	O(4)	C(5)				
3.	0.01	0.00	−0.01	−0.02	0.02				
4.	0.01	0.01	0.00	0.00	0.05				

Table 7. *Results of the rigid-body motion analysis for dimethyl acetylenedicarboxylate*

Libration tensor L and translation tensor T , and the corresponding unit vectors (l, t_i) along their principal axes are referred to the axial system of the tensor of inertia defined below.

$$L = \begin{pmatrix} 1188 & 55 & 47 \\ & 24 & -9 \\ & & 23 \end{pmatrix} \text{ rad}^2 \times 10^5$$

$$T = \begin{pmatrix} 1677 & 64 & -44 \\ & 1758 & -75 \\ & & 1544 \end{pmatrix} \text{ Å}^2 \times 10^5$$

$$\langle \sigma(L) \rangle = 0.0003 \text{ rad}^2$$

$$\langle \sigma(T) \rangle = 0.0007 \text{ Å}^2$$

$$\langle \sigma(L_{ii}) \rangle = 0.0013 \text{ rad}^2$$

Dunitz *et al.* (1974) have suggested recently that the apparent bond shortenings observed in cyclic polyethers are mainly spurious effects arising from inadequate treatment of molecular thermal motion in crystallographic analysis. They also proposed the use of an exponentially modified weighting scheme in least-squares refinement calculations (Dunitz & Seiler, 1973), and showed that a refinement with suitably adjusted weights sometimes leads to more acceptable positional parameters of the atomic nuclei. Since our investigation is based on low-temperature diffraction data, the averaged thermal vibration of the structure being highly reduced (Table 2), it was decided to follow the Dunitz-Seiler procedure to see to what extent application of the modified weighting scheme in refinement calculations would affect the atomic positions.

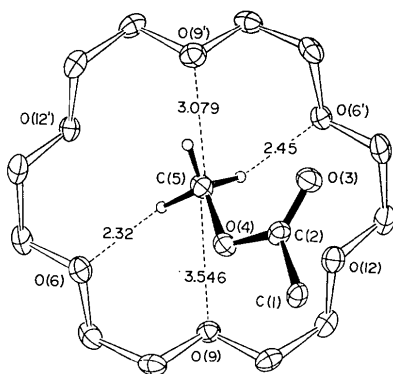


Fig. 3. Relative arrangement of 18-crown-6 and DAC molecules in the structure. View down the normal to the best plane of 18-crown-6. For clarity, only the unique half of DAC is shown, and its equivalent unit (related by inversion at the center of 18-crown-6) on the opposite side of the ether ring is also omitted. This figure, with 50% probability thermal ellipsoids, was produced with the aid of the program ORTEP (Johnson, 1965).

Tables 1 and 8 and Figs. 1 and 2 show some results of these computations. Different kinds of weighting schemes were applied (Table 8), where unit or experimental weights are also modified by a function $\exp(r \sin^2 \theta/\lambda^2)$, $r \geq 0$. Hydrogen atomic parameters were kept fixed in this process.

Evidently, no very significant changes were observed in the C-C and C-O bond distances of 18-crown-6. The largest lengthening in any particular C-C bond did not exceed 0.005 Å [$\langle \sigma(\text{C-C}) \rangle = 0.0025$ Å]. The C-O bond distances remain close to the expectation value of 1.42–1.43 Å (Tables of Interatomic Distances and Configuration in Molecules and Ions, 1960; Davis & Hassel, 1963). On the other hand, bond lengths in DAC are significantly altered for $r > 0$. An increase in the triple-bond distance by 0.014–0.022 Å and in the carbonyl bond distance by 0.007–0.010 Å, along with a shortening of 0.009–0.015 Å in the adjacent C-C bond, are observed.

Atomic thermal vibration parameters and their fit to the assumed rigid-body molecular model are not signif-

Table 9. Atomic fractional coordinates from the modified refinement with $r = 14 \text{ \AA}^2$ and $w = 1/\sigma^2(F)$

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-0.0311	-0.4838	0.0505
C(2)	-0.1140	-0.4546	0.1704
O(3)	-0.2852	-0.5491	0.1589
O(4)	0.0238	-0.3154	0.2898
C(5)	-0.0427	-0.2662	0.4159
O(6)	0.3886	0.1289	0.6387
C(7)	0.5172	0.2806	0.5858
C(8)	0.4506	0.2054	0.4225
O(9)	0.2805	0.2084	0.3775
C(10)	0.2205	0.1524	0.2240
C(11)	0.0384	0.1541	0.1819
O(12)	-0.1184	-0.0211	0.1948
C(13)	-0.2937	-0.0231	0.1638
C(14)	-0.4427	-0.1896	0.2072

$$\langle \sigma(p) \rangle = 0.0015 \text{ \AA}, p = x, y, z.$$

Table 8. Some results of least-squares calculations with a modified weighting scheme

Adjusted weights are defined as $w \cdot \exp(r \cdot \sin^2 \theta/\lambda^2)$ (Dunitz & Seiler, 1973).

<i>w</i>	<i>r</i> = 0		<i>r</i> = 14 Å ²		<i>r</i> = 18 Å ²		<i>r</i> = 36 Å ²		Reference bond lengths*
	Unit	1/σ _F ²	Unit	1/σ _F ²	Unit	1/σ _F ²	Unit	1/σ _F ²	
<i>R</i>	3.6%	3.7%	4.4%	4.4%	4.8%	5.5%	5.5%		
<i>R_w</i> †	3.9	8.2	4.5	3.9	3.8	4.2	3.5		
Bond lengths (Å)									
	(a)	(b)	(c)	(d)	(e)	(f)	(g)		
C-C (crown, ave.)	1.497	1.495	1.501	1.501	1.501	1.500	1.501		≥ 1.523 Å
C-O (crown, ave.)	1.420	1.420	1.419	1.419	1.418	1.420	1.419		≥ 1.423
C≡C (DAC)	1.184	1.183	1.198	1.200	1.201	1.206	1.203		1.204
C=O	1.200	1.198	1.207	1.209	1.209	1.210	1.209		≥ 1.207
C-C	1.468	1.467	1.459	1.457	1.457	1.453	1.455		1.460
O-CH ₃	1.461	1.461	1.457	1.458	1.457	1.457	1.456		≥ 1.43
C-O (carboxyl)	1.326	1.324	1.324	1.324	1.323	1.319	1.319		≤ 1.36

R for 1319 high-angle reflections with $\sin \theta/\lambda \geq 0.50$ in refinement (a) is 4.4%.

R for 1233 low-angle reflections with $\sin \theta/\lambda < 0.55$ in refinement (a) is 3.4%.

R for 1319 high-angle reflections with $\sin \theta/\lambda \geq 0.50$ in refinement (d) is 3.9%.

* For references see text.

† $R_w = [\sum w \cdot (\Delta F)^2 / \sum w \cdot F_o^2]^{1/2}$.

icantly affected by the modified calculation. Approximate corrections for rigid-body libration of the DAC molecule, mainly about its long axis, are 0.001 Å for C(1)–C(1'), C(1)–C(2) and O(4)–C(5) bond lengths, and 0.005 Å for the C=O and C–O bonds which form an angle of about 60° with this direction.

Bond lengths shown in parentheses in Figs. 1 and 2 refer to least-squares refinement with $r=14 \text{ \AA}^2$ and $w=1/\sigma^2(F)$. From among the tested weighting schemes, this one led to the most acceptable geometry of the 18-crown-6 and DAC molecules. Dependence of $\langle w(\Delta F)^2 \rangle$ on $\sin \theta/\lambda$ is also reasonable in this case (Table 1). The final atomic coordinates which resulted from the modified calculation are listed in Table 9.

In conclusion, our results also indicate, as suggested by others, that overweighting of high-order observations in least-squares refinement of X-ray data may lead to more reasonable atomic equilibrium positions, and consequently to an improved presentation of molecular geometry. However, it is demonstrated above that the sensitivity of C–C and C–O bond lengths in the hexa-ether to the weighting scheme used in refinement analysis is limited, even for extreme overweighting of high-order reflections in the available data set. This outcome is similar to the results reported by Dunitz & Seiler (1973) for room-temperature studies.

Molecular packing

The relative arrangement of unlike molecules in the crystal is illustrated in Figs. 3 and 4. Both constituents of the complex are located on crystallographic centers of symmetry, and the elongated but planar DAC molecules are clustered between two 18-crown-6 molecules displaced by $(\mathbf{b} + \mathbf{c})$ relative to each other, producing a column-like structure (Fig. 4). The normal to the mean plane of 18-crown-6 forms an angle of 54.9° with the axis of least inertia of DAC, and an angle of 24.9° with \mathbf{b} . Methyl groups of DAC fill the empty space inside the heterocyclic system, by interacting from both sides of the ring with all six ligating oxygen atoms. The methyl carbons are 1.89 Å from the mean plane of the crown ether. This distance, along with the corresponding observed deviations of Rb⁺ (1.19 Å) and Cs⁺ (1.44 Å) ions in their complexes with 18-crown-6 (Dunitz *et al.*, 1974), may be correlated with the relevant ionic or van der Waals radii: 1.47, 1.67 and 2.0 Å for Rb⁺, Cs⁺ and a methyl group, respectively.

Intermolecular close approaches found in the present structure involve mainly oxygen atoms of the hexa-ether and terminal methyls of DAC. Thus, observed short distances for the heavy atoms are C(5)···O(9') 3.08, C(5)···O(6) 3.38, C(5)···O(12) 3.39 and C(2)···O(12) 3.37 Å. When hydrogen atomic positions are modified to correspond to C–H bond lengths of 1.08 Å, H(5a)···O(6') and H(5c)···O(6) distances (2.45 and 2.32 Å respectively) are 0.2–0.3 Å shorter than the sum of the appropriate van der Waals radii (Pauling, 1960). The corresponding angles C(5)–H(5a)–

O(6') and C(5)–H(5c)–O(6) are 162 and 169°, respectively.

The fact that the thermal vibrations of the crown molecule are chiefly in its plane may be explained by these packing restrictions on potential motion in other directions. No short contacts are observed between molecules in adjacent columns of the complexed structure.

Discussion

The present structure differs in several respects from others reported for compounds containing the hexa-ether 18-membered ring. While the potential function of this moiety to serve as a host for complexing inorganic cations has been demonstrated in detail (Truter, 1973), this structure involves an organic guest. All six oxygen atoms of each crown-ether molecule participate in binding two DAC molecules, which approach opposite sides of the 'crown', by means of dipole–dipole interactions. In other structures, where stronger ion–dipole forces appear to be dominating, a 1:1 or 2:1 interrelationship between the host molecule and the guest ion is observed.

Some of the specific nonbonded interactions in the present structure are reflected in observed short contacts between the electronegative oxygen atoms in 18-crown-6 and the electropositive carbon atoms and methyl groups in DAC. Thus, the C(5)–O(9') distance of 3.08 Å is shorter by about 0.3 Å than the usually quoted van der Waals contact (3.4 Å; Pauling, 1960), indicating the presence of a definite attractive nonbonded interaction. Two hydrogen atoms attached to C(5) are also involved in contacts with other oxygen atoms, O(6) and O(6'), (Fig. 3) in a similar way to that observed in another hydrogen-bonded complex (Goldberg, 1975). The distribution of residual electron density $\Delta\rho$ and geometrical considerations show that the charge density of the nonbonded lone-pairs on O(6) is concentrated approximately on a plane defined by O(6), H(5c) and H(5a') [H(5a') is related to H(5a) by

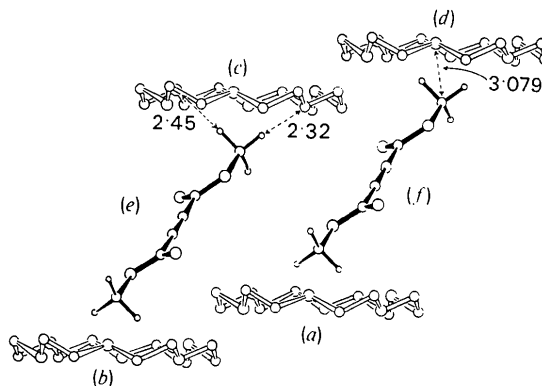


Fig. 4. Molecular packing. View of the structure along one in-plane axis of inertia of 18-crown-6. Molecules are located on centers of symmetry: (a) 0, 0, $\frac{1}{2}$; (b) 0, 0, $-\frac{1}{2}$; (c) 0, 1, $\frac{1}{2}$; (d) 0, 1, $\frac{1}{2}$; (e) 0, $\frac{1}{2}$, 0; (f) 0, $\frac{1}{2}$, 1.

inversion at $0,0,\frac{1}{2}$]. The third unique oxygen atom O(12) participates in long-distance interactions with C(2) and C(5) (Bürgi, Dunitz & Shefter, 1974). Atom O(12) departs from the mean plane of the 'crown' by 0.06 \AA more than the two other oxygens, to form a somewhat short contact (3.37 \AA) with the positively charged C(2). Consistently, the $O(12)\cdots O(12')$ distance is 5.94 \AA , while other diagonal dimensions of the cavity are 5.73 \AA for $O(6)\cdots O(6')$ and 5.45 \AA for $O(9)\cdots O(9')$; O(9) and O(9') interact strongly with the centered methyl carbons.

The stable 'crown' conformation of the ether ring is probably also affected by its binding molecules on both sides. The displacements of oxygen atoms from the mean plane of 18-crown-6 are 0.05 \AA larger than in other complexes (Dunitz *et al.*, 1974). Consequently, all dihedral angles about C-C bonds depart significantly from 65° (Table 5). The small strain involved in the distortion of an idealized synclinal conformation is most probably compensated by the energy gain from improved host-guest binding interactions.

The above-examined correlations demonstrate the role of relatively weak dipole-dipole interactions in structuring host-guest molecular complexes. The symmetry of the cyclic ligand, resulting in an availability of multiple potential binding sites, provides the essential favorable steric conditions. Formation constants for such systems have not yet been studied.

Finally, it appears that the question of whether the shortening of C-C bonds in the 18-membered ring is genuine or is an artifact remains unresolved. Opposing views are expressed on this subject in the literature (Mercer & Truter, 1973; Dunitz & Seiler, 1973; Dunitz *et al.*, 1974). In a recent publication, Ruysink & Vos (1974) estimated the possible error due to bonding effects introduced by use of standard spherical atomic form factors in a routine least-squares analysis. This theoretical study on a simplified model structure shows that a triple-bonded carbon atom may be displaced from its correct position by as much as $0.008\text{--}0.010 \text{ \AA}$ when only diffraction data with $\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$ are included in a refinement based on unit weights. An effective shortening of $0.016\text{--}0.020 \text{ \AA}$ is predicted, therefore, for a C \equiv C bond, in excellent agreement with the present results. Correspondingly, a smaller effect should be expected for atoms with a more symmetric density distribution.

In view of the limited thermal motion in the present structure, and considering the fact that a similar and sometimes more pronounced shortening has been observed in *all* other studies of substituted or unsubstituted polyether molecules,* we tentatively conclude that the observed shortening of the C-C bond distances is real. No reasonable explanation can be offered at this point. Recent papers of Robb, Haines & Csizmadia

(1973) and of Kollman (1974) suggest, however, that careful correlations of observed molecular geometry with the size and orientation of nonbonded lone pairs and with the nature of C-C and C-O bonding orbitals may contain the clue. Neutron-diffraction experiments, low-temperature studies of high-order X-ray data, and application of acceptable constrained models of internal molecular motion in refinement procedures may provide relevant information.

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* Similar features have been found in other structures of substituted 18-crown-6 molecules with low-temperature data (Goldberg, 1975).

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Structural and E.p.r. Search for Exchange Striction in Pyrazine Copper Acetate*

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The crystal structure of pyrazine copper acetate ($\text{Cu}_2\text{Ac}_4 \cdot \text{pyrazine}$), a binuclear copper acetate system in which the Cu–Cu separation in the triplet state has been estimated to be 0.12 Å longer than that in the singlet state, has been determined and refined by least-squares methods using three-dimensional Mo $K\alpha$ data (to $57^\circ 2\theta$) at 298 and 100 K. In a complementary study of possible exchange striction in this singlet-triplet system, 35 GHz (Q -band) e.p.r. spectra were measured at 298 and 120 K. Pyrazine copper acetate crystallizes in space group $C2/m$ in a cell of dimensions $a = 7.967$ (19), $b = 14.211$ (1), $c = 7.3210$ (8) Å and $\beta = 101.23$ (2)° at 298 K and $a = 7.9156$ (9), $b = 14.025$ (3), $c = 7.3022$ (9) Å and $\beta = 100.99$ (2)° at 100 K. The 298 K Cu–Cu separation of 2.583 (1) Å is significantly shorter than those found in similar dimer compounds and is only 0.007 Å longer than at 100 K. The small changes in the e.p.r. fine structure observed at 298 and 120 K show that the exchange in the excited state changes by less than 1% and suggest a constant Cu–Cu separation in the triplet state, as occurs in an exchange-striction model. The single-crystal e.p.r. also provides an experimental separation of the fine structure into spin-orbit and dipolar contributions.

Introduction

Recently the crystal structures and phase transitions of several linear-chain magnetic systems (Bartkowski & Morosin, 1972; Peercy, Morosin & Samara, 1973; Richards, Quinn & Morosin, 1973) have been examined. These systems consist of chemically bonded transition-metal ions arranged equidistant from each other with separations within the chain much smaller than those between the chains. Pyrazine copper acetate (PzCuAc), represents a different, novel linear-chain complex in which binuclear copper acetate units, $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4$, are linked by the pyrazine ligand, $\text{C}_4\text{H}_4\text{N}_2$. This system was first prepared and studied by Valentine, Silverstein & Soos (1974), hereinafter referred to as VSS.

Binuclear copper clusters are known in quite a few other copper alkanoates and carboxylates (Martin, 1968; Kokoszka & Gordon, 1969). The magnetic properties of such binuclear clusters have been intensively studied by static susceptibility and e.p.r. measurements. Typically one finds a rather strong antiferromagnetic exchange interaction, J , within the cluster, with $|J|$ of the order of 400K. However, the exchange interaction between clusters, J' , is much smaller and more difficult to measure and interpret since very low temperatures are required and in such temperature regions, other approximations are suspect. A further complication results if J' is of the same order as the electron dipolar interactions between clusters; then even n.m.r. measurements may prove unable to distinguish between intercluster exchange and dipolar contributions. Such is the case for the familiar hydrate of copper acetate, HyCuAc (Obata, 1967).

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