

## Nesting Inclusion Compounds. The X-Ray Structure of the 15-Crown-5 Sodium Diphenylethyl Diphenylmethyl Cyanoacetate Complex

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**Abstract.** The action of sodium cyanide on *gem*-diphenyl-chloropropanone under phase transfer conditions in the presence of 15-crown-5 yields the title compound as a minor product. The crystal structure of this complex reveals that, in the solid state, the [15-crown-5-Na<sup>+</sup>] guest species is found within a loose cage of diphenylethyl diphenyl cyanoacetate molecules with one open side of the cage blocked by an adjacent 15-crown-5 molecule. Colourless crystals of the compound belong to the monoclinic space group *P*21/*n* with *a* = 12,255(2) Å, *b* = 13,005(1) Å, *c* = 23,433(2) Å,  $\beta$  = 95,92(1)° and *D*<sub>c</sub> = 1.23 g cm<sup>-3</sup> for *Z* = 4.

**Key words.** Crystal structure, crown ether, clathrate.

**Supplementary data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82109 (31 pages).

### 1. Introduction

In the rapidly expanding field of supramolecular science the main axes of research have generally concerned the study of discrete molecular complexes [1]. Recently attention has turned to higher order supramolecular systems in which inclusion complexes are themselves included in other host systems or form organised assemblies. The first class of complex has recently been observed for 12-crown-4 with  $\gamma$ -cyclodextrin [2], crown ethers with clays [3] and cyclodextrins with intercalating minerals [4]; the second class of complex is exemplified by the 'organic clays' formed by calix[4]arene sulfonates [5], the inclusion compounds formed by modified cyclodextrin Langmuir–Blodgett films [6] and the micellar assemblies formed by modified cyclodextrins [7].

The title compound represents a third class of high-order supramolecular assembly in which one part of the host or guest species contains sufficient conformational flexibility to form a second host–guest assembly. In this case the [15-crown-5–

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Na<sup>+</sup>] guest is included within a clathrato-system formed by a number of neighbouring ligands to give a nesting inclusion complex.

## 2. Experimental

### 2.1. PREPARATION OF 15-CROWN-5 SODIUM DIPHENYL ETHYL DIPHENYL METHYL CYANOACETONATE

The complex was prepared as previously described by Galons [8]. Colorless crystals of a suitable size were obtained by recrystallisation from chloroform.

### 2.2. X-RAY DATA AND STRUCTURE SOLUTION

Single crystals of the complex were sealed in thin glass capillaries. The data were collected on an ENRAF NONIUS CAD 4 diffractometer. Final lattice parameters and a summary of data collection parameters and structural refinement are presented in Table I.

Structure solution was accomplished by means of direct methods with MULTAN-81 [9] and refined by full matrix least squares on Fs. All H atoms have been located in theoretical positions and not refined. Calculations were performed on a PDP 11 computer. The final values of the positional parameters are given in Table II.

### 2.3. MOLECULAR GRAPHICS

Molecular graphics analyses of the title compound and the related ethylacetoacetate sodium enolate compound reported by Bram [10] were carried out using SYBYL 5.10 [11]. Energy calculations were carried out on the uncomplexed crown ether fragments with no charges applied. The operations were performed using an Evans and Sutherland PS 330 Graphics station piloted by a Microvax computer.

## 3. Results and Discussion

The X-ray structural analysis shows the sodium atom to be seven-coordinate. The two enolate oxygen atoms are at 2.365(3) and 2.278(3) Å distance. The crown ether oxygen atoms are paired for O(1) and O(5) (2.521(3) and 2.518(3) Å) and O(2) and O(4) (2.458(3) and 2.462(3) Å), with O(3) being 2.429(3) Å from the sodium cation. The local environment of the sodium is given in Figure 1 (coplanarity 0.07 Å), O(1), O(2), O(4) and O(5) form a plane with O(3) lying 1.1 Å above the plane. The sodium is displaced in the opposite direction towards the enolate oxygen atoms by 0.96 Å with regard to the mean of all the crown ether oxygen atoms and a smaller distance (0.70 Å) with regard to the coplanar oxygen atoms.

This is somewhat different from the situation of the acetylacetate sodium enolate (AAE) complex previously reported by Bram [10]. In this complex the oxygen atoms are paired at 2.42 and 2.43 Å; 2.56 and 2.55 Å with the fifth oxygen at 2.49 Å. The crown ether is more planar in this case with the two most closely bound

Table I. Crystallographic data collection and structure refinement

Crystal colour	Colorless
Crystal size, mm	0.40 × 0.30 × 0.50
$\rho_{\text{measured}}$ kg m <sup>-3</sup>	1.23
$\mu(\text{CuK}\alpha)$ , cm <sup>-1</sup>	7.38 – no correction
Corrections	Background, Lorentz, Polarization
Space Group	P2 <sub>1</sub> /n
<i>a</i> , Å	12.255 (2)
<i>b</i> , Å	13.005 (1)
<i>c</i> , Å	23.433 (2)
$\beta$ , deg	95.92 (1)
<i>V</i> , Å <sup>3</sup>	3715
<i>Z</i>	4
Diffractometer	CAD4 Nonius
Monochromator	Graphite
Radiation	CuK $\alpha$ ( $\lambda = 1.54184$ Å)
Temperature, °C	RT (room temperature)
Scan type	$\omega/2\theta$
Scan range, deg	1.0 + 0.14 tan $\theta$
2 $\theta$ range, deg	4–110
Scan speed, deg mm <sup>-1</sup>	depending upon reflection
Background	half of scan time, in fixed position, before and after every scan
Standard reflections	3 $\bar{2}$ 3, 0 $\bar{5}$ 5, 4 $\bar{1}$ 3; measured every other hour
Variation of standards	< 1%
Reflections measured	2 octants, <i>hkl</i> , $\bar{h}kl$
Reflections collected	4644
Unique reflections	4344
Reflections kept for refinement	( $F > 3\sigma$ ) 3675
Computing program	SDP (B. A. Frenz, 1985) [12]
Atomic form factors	<i>International Tables</i> (vol. 4) [13]
Minimized function	$\Sigma \omega( F_0  -  F_c )^2$
Secondary extinction	~ 6.4503 E-07
Weighting scheme	unit weights for all observed reflections
Maximum shift/e.s.d.	0.03
No. of reflection/ No. of parameters varied	8.2
<i>R</i>	0.054
<i>R</i> <sub>w</sub>	0.051
<i>S</i>	1.49

oxygen atoms lying one above and one below the mean plane, the sodium cation being displaced 1.05 Å from this towards the enolate oxygen atoms.

The two structures as taken from molecular graphics are shown for comparison in Figure 2. It is obvious that for the diphenylethyl diphenylmethyl cyanoacetate (DDCA) complex the crown ether ring is more distorted, with one carbon and one oxygen above the mean plane. The remaining four oxygen atoms lie at 1.126 Å from the sodium cation, close to the value of 1.05 Å for the AAE complex. This increased distortion may not arise from electrostatic interactions which are the same in both cases and hence must be packing derived. This is confirmed in solution

Table II. Final fractional atomic coordinates and equivalent thermal parameters (esd's are in parentheses)

Atom	x	y	z	$\text{\AA}^2$	Atom	x	y	z	$\text{\AA}^2$
Na	0.1414(1)	0.228(1)	0.32321(6)	3.82(3)	C(17)	-0.2884(3)	0.3948(3)	0.3948(2)	5.1(1)
O(1)	0.3102(2)	0.3224(2)	0.2982(1)	6.61(8)	C(18)	-0.2617(3)	0.1626(3)	0.4516(2)	5.3(1)
C(1)	0.3889(4)	0.2414(4)	0.3064(3)	9.70(2)	C(19)	-0.1997(4)	0.0787(3)	0.4699(2)	5.2(1)
C(2)	0.4072(4)	0.2213(5)	0.3703(4)	11.9(2)	C(20)	-0.1529(3)	0.0167(3)	0.4305(2)	3.95(8)
O(2)	0.3054(3)	0.1907(2)	0.3897(2)	7.68(9)	C(21)	-0.0843(3)	-0.1323(3)	0.3455(1)	3.47(7)
C(3)	0.2911(5)	0.2115(4)	0.4487(2)	10.4(2)	C(22)	-0.1501(3)	-0.2157(3)	0.3286(2)	5.3(1)
C(4)	0.1729(4)	0.2047(4)	0.4561(2)	9.1(2)	C(23)	-0.1221(4)	-0.3136(3)	0.3483(2)	7.3(1)
O(3)	0.1160(3)	0.2782(2)	0.4208(1)	5.87(7)	C(24)	-0.0285(4)	-0.3286(3)	0.3844(2)	7.4(1)
C(5)	-0.0003(4)	0.2829(4)	0.4251(2)	7.3(1)	C(25)	0.0390(4)	-0.2487(3)	0.4003(2)	6.1(1)
C(6)	-0.0481(4)	0.3553(4)	0.3806(2)	7.3(1)	C(26)	0.0117(3)	-0.1500(3)	0.3809(2)	4.54(9)
O(4)	-0.380(2)	0.3103(3)	0.3279(1)	7.02(8)	C(27)	0.0661(3)	0.0823(2)	0.2152(1)	2.85(7)
C(7)	-0.0734(4)	0.3751(5)	0.2797(3)	9.5(2)	C(28)	0.0705(3)	0.0597(3)	0.1523(1)	3.30(7)
C(8)	0.0155(4)	0.4411(4)	0.2664(3)	8.4(2)	C(29)	0.1324(3)	0.1407(3)	0.1209(1)	2.93(7)
O(5)	0.1030(2)	0.3779(2)	0.2561(1)	6.28(8)	C(30)	0.1628(3)	0.0971(2)	0.0646(1)	2.82(7)
C(9)	0.1941(4)	0.4307(4)	0.2407(2)	7.6(1)	C(31)	0.0991(3)	0.1119(3)	0.0134(1)	3.76(8)
C(10)	0.2861(4)	0.3547(4)	0.2404(2)	7.2(1)	C(32)	0.1297(3)	0.0711(3)	-0.0372(2)	4.61(9)
O(6)	0.0417(2)	0.0771(2)	0.33891(9)	3.81(5)	C(33)	0.2233(4)	0.0142(3)	-0.0372(2)	5.0(1)
O(7)	0.1390(2)	0.1357(2)	0.24049(9)	3.73(5)	C(34)	0.2861(4)	-0.0026(4)	0.0130(2)	6.1(1)
N(1)	-0.1643(3)	-0.0688(3)	0.1804(1)	7.7(1)	C(35)	0.2559(3)	0.0383(3)	0.0637(2)	5.0(1)
C(11)	-0.0997(3)	-0.0219(3)	0.2086(1)	4.39(9)	C(36)	0.0709(3)	0.2424(3)	0.1117(1)	3.33(8)
C(12)	-0.0196(3)	0.0351(2)	0.2435(1)	2.74(7)	C(37)	-0.0398(3)	0.2529(3)	0.1155(2)	5.0(1)
C(13)	-0.0249(3)	0.0353(2)	0.3037(1)	2.84(7)	C(38)	-0.0916(4)	0.341(4)	0.1040(2)	6.6(1)
C(14)	-0.1212(3)	0.0245(3)	0.3268(1)	3.05(7)	C(39)	-0.0345(4)	0.4302(4)	0.0883(2)	6.7(1)
C(15)	-0.1695(3)	0.0384(3)	0.3726(1)	3.05(7)	C(40)	0.0769(4)	0.4215(3)	0.0853(2)	6.5(1)
C(16)	-0.2331(3)	0.1229(3)	0.3551(2)	4.24(9)	C(41)	0.1286(3)	0.3278(3)	0.0970(2)	4.83(9)

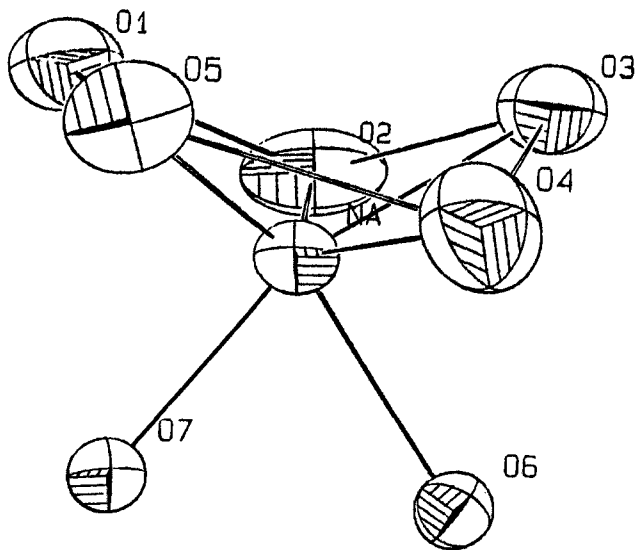


Fig. 1. Coordination around the  $\text{Na}^+$  cation, with atomic numbering.

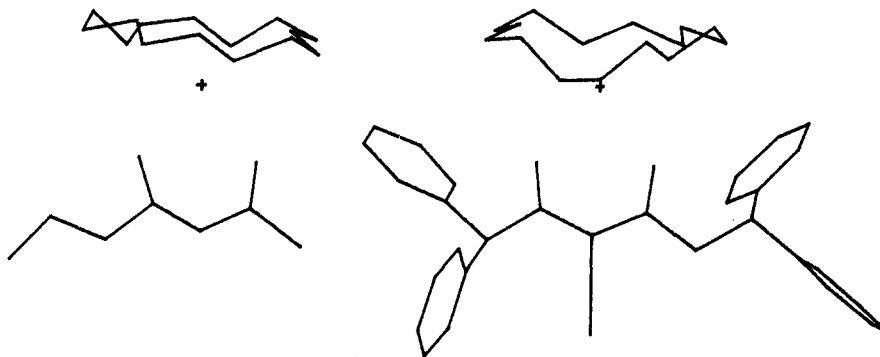


Fig. 2. Molecular graphics representation of the DDCA [15-crown-5] Na (right) and AAE [15-crown-5] Na (left) complexes.

when only one resonance is observed for the crown ether methylenic protons suggesting a symmetrical structure. Interestingly, energy calculations suggest that this distorted conformation, treated as a free molecule, is slightly ( $\sim 12 \text{ kJ mol}^{-1}$ ) energetically more favourable than that of the more symmetrical AAE complex.

The environment about the  $[\text{15-crown-5 Na}^+]$  cation is shown in Figure 3. From this it is observed that the cyano group of an adjacent molecule is directed towards the out of plane  $\text{CH}_2$  of the crown ether with a  $\text{CH-N}$  angle of  $148^\circ$  and a  $\text{C-N}$  distance of  $3.52 \text{ \AA}$ . While the distance appears to be overly long for an  $\text{N} \cdots \text{HC}$  hydrogen bond, we feel that this interaction is probably responsible for the crown ether distortion.

The  $[\text{15-crown-5 Na}^+]$  fragment is held within a cage composed of neighbouring DDCA molecules with the phenyl groups positioned over open areas between the

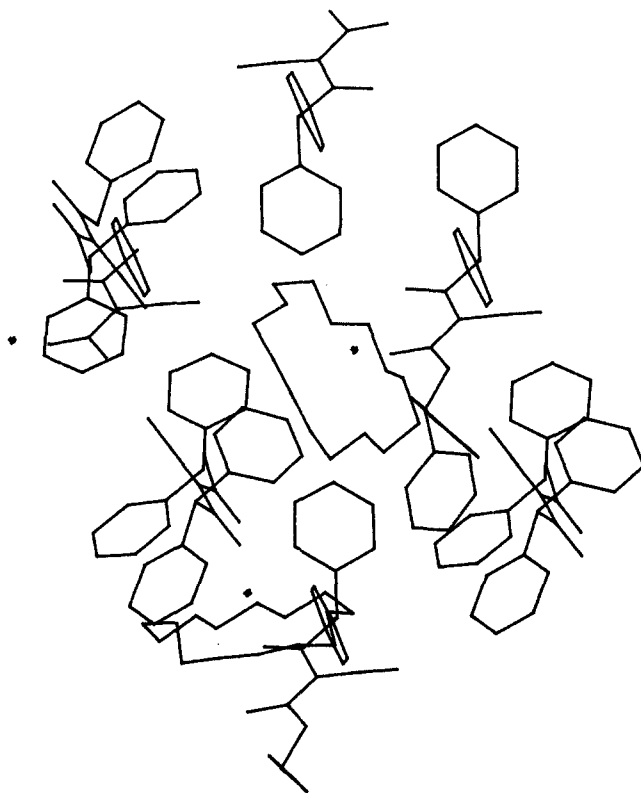


Fig. 3. Molecular graphics representation of the environment of the [15-crown-5-Na]<sup>+</sup> cation.

Table III. Bond distances and angles around the sodium atom

Atom 1—Atom 2	Distance Å	Atom 1—Atom 2—Atom 3	Angle °
Na—O(1)	2.521(3)	O(1)—Na—O(2)	67.1(1)
Na—O(2)	2.458(3)	O(1)—Na—O(3)	106.1(1)
Na—O(3)	2.429(3)	O(1)—Na—O(4)	123.9(1)
Na—O(4)	2.462(3)	O(1)—Na—O(5)	65.5(1)
Na—O(5)	2.518(3)	O(1)—Na—O(6)	152.6(1)
Na—O(6)	2.365(3)	O(1)—Na—O(7)	90.0(1)
Na—O(7)	2.278(3)	O(2)—Na—O(3)	68.5(1)
		O(2)—Na—O(4)	137.1(1)
		O(2)—Na—O(5)	129.7(1)
		O(2)—Na—O(6)	98.0(1)
		O(2)—Na—O(7)	112.0(1)
		O(3)—Na—O(4)	68.8(1)
		O(3)—Na—O(5)	110.3(1)
		O(3)—Na—O(6)	87.5(1)
		O(3)—Na—O(7)	161.8(1)
		O(4)—Na—O(5)	65.1(1)
		O(4)—Na—O(6)	82.7(1)
		O(4)—Na—O(7)	109.4(1)
		O(5)—Na—O(6)	132.2(1)
		O(5)—Na—O(7)	83.8(1)
		O(6)—Na—O(7)	74.41(9)

linear enolate fragments. There is a close intramolecular contact between enolate oxygen and a phenyl hydrogen (3 Å). The cage is completed by a CH<sub>2</sub>—CH<sub>2</sub>—O fragment of a neighbouring crown ether.

The nearest crown ether carbon–phenyl carbon distances are in the range 4.0–4.5 Å, with crown ether–phenyl hydrogen distances at 2.4 to 3.2 Å, being slightly greater than the sum of the van der Waals radii (~2.2 Å). These values are close to those of 2.5 and 2.9 Å found in models for the β-cyclodextrin-menthol interactions which forms a highly stable inclusion complex [14]. The compound may be considered to be a clathrate system formed mostly by the rigid phenyl and enolate groups within which is included the [15-crown-5-Na<sup>+</sup>] ion, for which the crown ether may be considered as a host molecule for the sodium cation.

This would thus seem to be a nesting compound in which one inclusion system is contained within another.

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