

## Synthesis and Characterisation of an [18]Crown-5-Ligand and its NaNCS Complex

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Crown Ether (Diphenylmethano-), X-Ray

The new [18]crown-5 ligand – [18]⟨O<sub>5</sub>-(2,2′)-diphenylmethano·2<sub>4</sub>-coronand-5⟩ [1] –, containing a benzylic CH<sub>2</sub> group, was prepared by condensation of 2,2′-dihydroxydiphenylmethane with tetraethylene glycol dichloride. The ligand exhibits an endo-conformation and short O⋯H<sub>2</sub>C contacts. The macrocycle ligates Na<sup>+</sup> by contracting its cavity so that its five O atoms form an approximately regular pentagon.

Crown ethers derived from diphenylmethane are suitable compounds for the study of the reactivity and activation of C–H bonds by neighbouring cations. A knowledge of the geometry of the diphenylmethane entity and of its conformational changes upon complex formation could facilitate the understanding of its reactions. A CH<sub>2</sub> group in place of a donor atom will probably reduce coordination abilities, as was reported for the unsubstituted [18] crown-6 system [2]. The steric requirements of the bulky C<sub>6</sub>H<sub>4</sub>–CH<sub>2</sub>–C<sub>6</sub>H<sub>4</sub> might even preclude any wrapping of cations but might on the other hand enhance the selectivity for 'fitting' guests.

The title ligand **1** was prepared, in analogy to Pedersen's method [3], by condensation of 2,2′-dihydroxydiphenylmethane with tetraethylene glycol dichloride. A relative height of 100% of the M<sup>+</sup>-peak (*m/e* = 358) in the mass spectrum may indicate the stability of the macrocycle formed. Its <sup>1</sup>H NMR spectrum shows the typical features of an annular oligoether [4]; one sharp singlet ( $\delta$  = 4.05 ppm) for both the benzylic protons proves the conformation of the diphenylmethane system in solution to be fixed neither at room temperature nor at –50 °C.

The central CH<sub>2</sub> group may serve as a functional group to introduce substituents or carbanion-centres

into the crown ring: it is not brominated by *N*-bromo-succinimide in dichloromethane but can be deprotonated by butyllithium to give the orange carbanion; this forms the corresponding carboxylic acid with CO<sub>2</sub>. Only by use of strong oxidising agents like K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in hot glacial acetic acid [5] could traces of the benzophenone analogous crown ether be obtained; trials with activated MnO<sub>2</sub> [6] or with KMnO<sub>4</sub> were unsuccessful.

Though a phase transfer [7, 8] was observed with sodium salts or potassium permanganate, preparation [9] of crystalline complexes could (until now) only be accomplished with the former. Na<sup>+</sup> (*r* = 97 pm [10]) fits approximately the [15]crown-5 system (*d*<sub>inner</sub> = 170–220 pm [11]); hence, with oligoethers consisting of –CH<sub>2</sub>–CH<sub>2</sub>–O units, it prefers five-fold equatorial coordination (*e.g.* [12, 13]). X-ray analyses reveal the ability of the present macrocycle to bring its donor atoms into the (distorted) pentagonal arrangement required (see Fig.), with strain-free torsion angles (O–C–C–O = ± sc, C–O–C–C = ap) along the coordinating chain, and with Na<sup>+</sup>⋯O contacts ranging from 237.5(2) to 254.6(2), mean 246.1 pm. The coordination pyramid of Na<sup>+</sup> is completed by the anion [Na<sup>+</sup>⋯<sup>–</sup>NCS = 233.8(3) pm].

The contraction of the inner cavity of the ligand **1** on complex formation is reflected particularly in the shortened O(1)⋯O(13) distance of 328.8(2) pm in the complex, as compared to 475.6(4) pm in **1**, where the O atoms and the central CH<sub>2</sub> group form an approximate hexagon. The resulting increase of the dihedral angle between the phenylene planes from 66.2(7)° in **1** to 82.0(5)° in **2** had already been indicated in the <sup>1</sup>H NMR spectrum of **2**: the signal of the benzylic protons is shifted by –0.1 ppm relative to **1**.

In both structures there are short contacts [227.4(6) pm in **1**, 237.6(3) pm in **2**], between *one* benzylic H atom (in a calculated ideal position) and a neighbouring O atom (see Fig.); in solution, however, <sup>1</sup>H NMR spectra (see above) provide evidence for an equivalent participation of *both* the H atoms. However, the less shielded CH<sub>2</sub> group in **2** might facilitate reactions at this group from a steric point of view; further investigations directed towards the elucidation of differences in reactivity/selectivity between the free ligand **1** and its complexes, *e.g.* in the formation of the carbanion, the diazo- and carbene derivative, are in progress.

### Experimental

**1**, [18]⟨O<sub>5</sub>-(2,2′)Diphenylmethano·2<sub>4</sub>-coronand-5⟩: Solutions of 20.0 g (100.0 mmole) 2,2′-dihydroxydiphenylmethane and 8.0 g (200.0 mmole) of NaOH in 200 ml of *n*-butanol and 23.2 g (100.0 mmole) 1,11-dichloro-3,6,9-trioxaundecane in 200 ml of *n*-butanol were added dropwise simultaneously to 200 ml of boiling *n*-butanol. After refluxing for 12 h, the solvent was distilled off in vacuo and the

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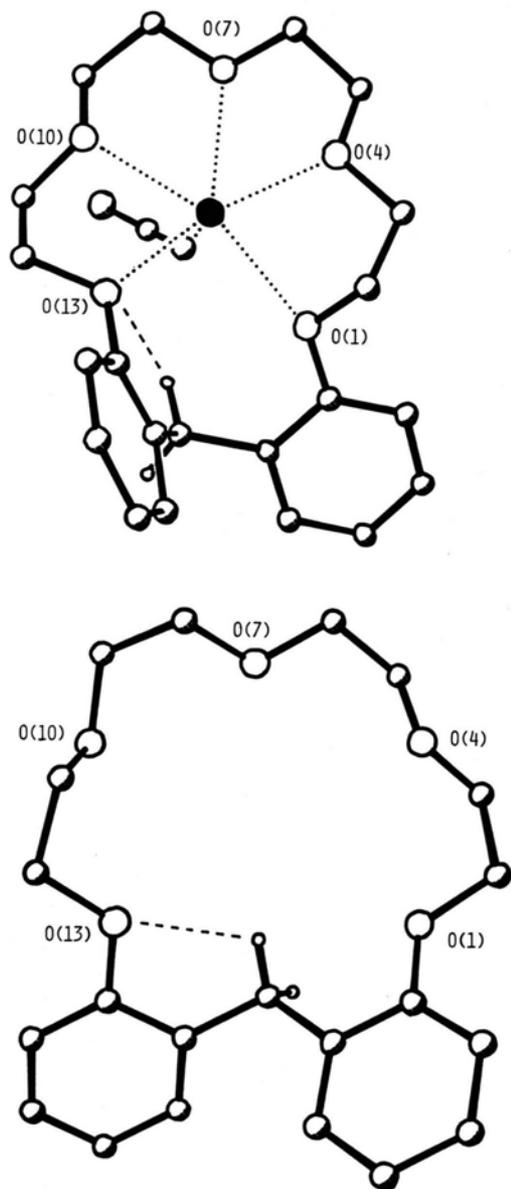


Figure. Perspective views of the NaNCS complex (top) and of the free ligand **1** (bottom); radii are arbitrary. Broken lines indicate short  $\text{CH}_2 \cdots \text{O}$  contacts; in **1** there is a further contact of 257.8(6) pm between the same H atom and O(1).

remaining oil dissolved in dichloromethane. The filtered solution was washed with 2% aqueous potassium hydroxide and water, dried over  $\text{MgSO}_4$  and concentrated. The macrocycle crystallised on addition of 50 ml ether and standing at  $-25^\circ\text{C}$ ; it was purified by recrystallisation from ether. Yield 8.23 g (23%); m.p.  $96\text{--}97^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{TMS}_{\text{int.}}$ ):  $\delta = 3.65$  (s, Alkyl-H), 3.7–4.2 (m, Alkyl-H), 4.05 (s, Benzyl-H), 6.9 (s, Aryl-H), 6.7–7.4 (m, Aryl-H).

$\text{C}_{21}\text{H}_{26}\text{O}_5$  (358.4)

Calcd	C 70.38	H 7.30,
Found	C 70.32	H 7.30.

**2**, NaNCS·**1**: 0.179 g (0.5 mmole) **1** in 15 ml ethyl acetate were added to 0.04 g (0.5 mmole) of NaNCS dissolved in the minimum amount of hot methanol. The solution was concentrated and the complex precipitated with petroleum ether. Recrystallisation from ethyl acetate/methanol yielded 0.164 g (75%) colourless crystals, m.p.  $168\text{--}170^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3/\text{TMS}_{\text{int.}}$ ):  $\delta = 3.65$  (s, Alkyl-H), 3.7–4.2 (m, Alkyl-H), 3.95 (m, Benzyl-H), 6.6–7.3 (m, Aryl-H).

$\text{C}_{22}\text{H}_{26}\text{NNaO}_5\text{S}$  (439.5)

Calcd	C 59.72	H 5.96	N 3.18,
Found	C 59.72	H 6.05	N 3.16.

X-ray analyses of **1** and **2**: **1**. monoclinic,  $\text{P}2_1/c$ ,  $a = 1156.9(2)$ ,  $b = 1174.9(2)$ ,  $c = 1440.5(3)$  pm,  $\beta = 100.62(4)^\circ$ ,  $Z = 4$ ,  $d_{\text{calc}} = 1.237 \text{ Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.082 \text{ mm}^{-1}$ . **2**. triclinic,  $\text{P}\bar{1}$ ,  $a = 883.6(4)$ ,  $b = 1095.0(5)$ ,  $c = 1301.5(6)$  pm,  $\alpha = 101.54(8)$ ,  $\beta = 95.60(7)$ ,  $\gamma = 112.09(9)^\circ$ ,  $Z = 2$ ,  $d_{\text{calc}} = 1.300 \text{ Mg m}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.186 \text{ mm}^{-1}$ .

3367 data up to  $2\theta = 50^\circ$  for **1** and 3105 data up to  $2\theta = 46^\circ$  for **2** were collected on an automated four-circle diffractometer with a profile fitting procedure [14] and corrected for  $L_p$  and crystal decay. Both structures were solved by direct methods [15] and refined anisotropically using 1959 observed [ $F > 4\sigma(F)$ ] reflections for **1** and 2864 for **2**. With H atoms included in calculated positions ( $\text{C-H} = 96 \text{ pm}$ ,  $U = 1.2$  times the  $U$  value of attached atoms), and after an empirical extinction correction, the final  $R$  was 0.060 ( $R_w = 0.058$ ) for **1** and 0.037 (0.046) for **2**. Further information may be received at: "Fachinformationszentrum Energie, Physik, Mathematik, GmbH, D-7514 Eggenstein-Leopoldshafen 2". The Registry-Nr., CSD 50305, the name of the author, and the reference should be given.

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