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The Synthesis and Complexation of Two 24-Crown-8 Cyclic Polyethers

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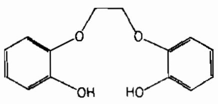
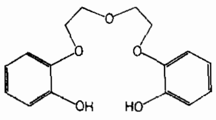
Studies of larger macrocyclic crown ether rings such as dibenzo-24-crown-8 (III) and dibenzo-30-crown-10 have shown that these molecules may adopt a variety of conformations both as free ligands [1] and when complexing alkali and alkaline earth metals [1b, 2, 3]. In addition, complexes of different stoicheiometries of metal:ligand may be isolated in the crystalline state [2, 4], and also observed in solution [3, 4]. Finally, it has been shown possible that dibenzo-24-crown-8 may complex a 'hydrated cation', where both metal and water interact with the ether oxygens of the ligand [5]. In order to extend the range of these versatile molecules, we have synthesised IV and V, named trivially* asymmetric dibenzo-24-crown-8 and very asymmetric dibenzo-24-crown-8. These have been characterised by microanalysis, mass spectra and X-ray molecular weight, and ^{13}C NMR (Table II), and also by isolating several sodium and calcium complexes (Table I). In the process of isolating V, a crystalline solid VI was obtained, which analysed well for the dimer of V, had very similar ^{1}H and ^{13}C NMR spectra to V, and gave the expected X-ray and solution molecular weight for the dimer of V. Isolation of V itself was made possible by separating the ligand as its calcium or sodium complex from the crude reaction mixture, then



I



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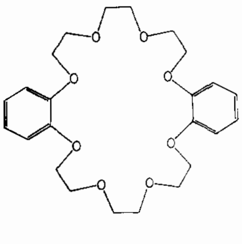

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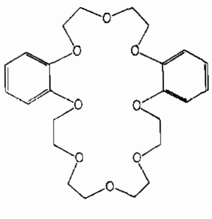
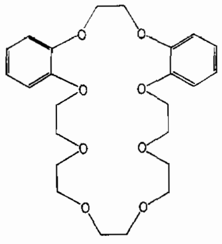


IV



V

TABLE I. Preparations and Analytical Data of Complexes.

Compound	Solvent	M.p. (°C)	Analysis					
			Found %			Calcd. %		
			C	H	N	C	H	N
$NaClO_4 \cdot IV$	acetone	167–8	50.63	5.68		50.48	5.65	
$NaBPh_4 \cdot IV$	methylene chloride/ethanol	176–7	72.90	6.58		72.91	6.63	
$Ca(NCS)_2 \cdot IV \cdot H_2O$	ethylacetate/acetone	215–7[a]	49.89	5.50	4.44	50.16	5.51	4.50
$NaClO_4 \cdot V$	acetone	165	50.69	5.73		50.48	5.65	
$Ca(NCS)_2 \cdot X \cdot H_2O$	ethylacetate/methanol	172.5	50.27	5.34	4.56	50.16	5.51	4.50

[a] Loses solvent at 130 °C.

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*IV = Dibenzo[b,k]6,7,9,10,12,13,15,16,23,24,26,27-dodecahydro-1,4,7,10,13,16,19,22-octaoxacyclotetracosin; V = dibenzo[b,h]6,7,9,10,12,13,15,16,18,19,26,27-dodecahydro-1,4,7,10,13,16,19,20-octaoxacyclotetracosin.

TABLE II. ^{13}C NMR Resonances of Dibenzo-24-crown-8 Rings (measured in ppm from TMS in $CDCl_3$).

III	IV	V	VI
–149.1	–149.37	–149.44	–149.1 [a]
	–149.01	–149.01	
–121.4	–121.83	–122.07	–121.89[a]
	–121.43	–121.59	
–114.4	–115.64	–116.19	–115.34[a]
	–114.30	–115.28	
–71.1	–71.11	–70.92	–70.62[a]
	–70.74	–70.74	
–69.9	–70.32	–69.71	–69.77
–69.4	–69.77	–69.35	–69.17
	–69.17	–68.62	–68.32

[a] Two peaks just resolved.

TABLE III. 1:1 $\log_{10}$ Formation Constants Measured by e.m.f. Titrations in Methanol.

Ligand	Metal		
	Na	K	Rb
III	2.25	3.6	3.85[a]
IV	2.15	3.45	3.8
V	2.55	3.85	4.2

[a] Solid addition.

purifying the complex by crystallisation, before subsequently regenerating the free ligand.

The crystalline complexes of IV and V isolated with sodium perchlorate and sodium tetraphenylborate were found to be 1:1 anhydrous, and the infrared spectra of the perchlorate complexes do not show splitting of the ClO_4^- asymmetric bending frequency at about 630 cm^{-1} (unlike $NaClO_4$·benzo-15-crown-5 which has three peaks in the 630 cm^{-1} region [6], and has been shown by X-ray analysis to involve direct bonding between perchlorate and sodium ion [7]). This suggests that, as for dibenzo-24-crown-8 [6], the anion is not bonded to the metal cation in these complexes, and that both ligands are able to wrap around the sodium ion to exclude solvent. IV and V will both solubilise potassium perchlorate (in 1:1 ligand/metal ratio) in hot methanol, but on cooling, potassium perchlorate crystallises out, presumably because of its low solubility in methanol.

Experiments with space filling models suggest that of III, IV and V, ligand V should be best for wrapping round a cation, and this is reflected in the measured formation constants (Table III). No 2:1 metal/ligand complexes of IV and V have been isolated as yet, and the e.m.f. titration curves refine satisfactorily for 1:1 complexation.

Experimental

Infrared spectra were recorded as nujol mulls or potassium bromide discs on a Perkin-Elmer 457 Grating Spectrophotometer. Melting points were determined on a Koffler hot stage melting point apparatus. Elemental analyses were determined at the Microanalytical Laboratory, U.C.L.. ^{13}C NMR spectra in $CDCl_3$ were obtained on a JEOL JNM-PS100 Fourier transform instrument using TMS as internal standard. Solution molecular weights were measured in benzene using a Hewlett Packard 302 Vapour Pressure Osmometer.

Preparation of IV

Diol II (16.1 g), the ditosylate of tetraethylene glycol (28.0 g) and potassium hydroxyde pellets (7.0 g) were refluxed together with stirring in absolute alcohol (100 ml) for 6 h. The mixture was then allowed to cool to room temperature, filtered, and the filtrate concentrated on a rotary evaporator. The resulting oil was dissolved in chloroform (100 ml), and washed with 10% sodium hydroxide solution (100 ml), followed by water (4 X 300 ml). The chloroform was removed from the organic layer on a rotary evaporator yielding an oil which was eluted down a neutral alumina column with toluene. The product was rechromatographed on neutral alumina using petrol ether/ethyl acetate (3:1), and concentration of the eluate, followed by addition of diethyl ether gave colourless needle crystals. Yield 5.8 g, m.p. 60–1 °C. *Anal.* Calcd. for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19%. Found: C, 64.47; H, 7.23%. M. wt. by vapour pressure osmometry in benzene 446; IX req. 448.5.

Preparation of V

Diol I (12.3 g), the ditosylate of pentaethylene glycol (27.3 g) and potassium hydroxide pellets (6.5 g) were refluxed together with stirring for 16 h. The solution was cooled to room temperature, filtered, and the filtrate concentrated on a rotary evaporator. The light brown oil was dissolved in chloroform (100 ml) and washed with 10% sodium hydroxide solution (100 ml), followed by water (3 X 100 ml). Chloroform was removed from the organic layer on a rotary evaporator and the resulting oil eluted down a basic alumina column with toluene, and then rechromatographed on basic alumina using ethyl acetate/diethyl ether (1:1). Solvent was removed from the eluate, and the colourless oil was dissolved in ethyl acetate (50 ml) and treated with excess calcium thiocyanate dissolved in ethyl acetate (50 ml). A white precipitate was formed which was collected on a sinter, well washed with diethyl ether, and dried *in vacuo*. Yield 16.5 g. This solid was suspended in chloroform (30 ml) and boiled with water (5 X 10 ml). Removal of chloroform from the organic layer gave a colourless oil which was dissolved in methanol (20 ml) and refrigerated for 48 h. A small number of colourless crystals of VI were formed, which were collected on a sinter, washed with methanol and dried. Yield 0.21 g, m.p. 80 °C. *Anal.* Calcd. for $C_{48}H_{64}O_{16}$: C, 64.26; H, 7.19%. Found: C, 64.18; H, 7.23%. M. wt. measured by X-ray analysis 890.78 and by vapour pressure osmometry 940; VI req. 897.1. The combined mother liquor and methanol washings were concentrated to give a colourless oil (9.2 g) which did not crystallise on standing. This was dissolved in methanol (20 ml) and treated with sodium perchlorate (4.5 g) in methanol (10 ml) when a crystalline precipitate formed almost immediately. Recrystallisation from methanol produced colourless crystals, m.p. 165 °C. *Anal.* Calcd. for $C_{24}H_{32}$-$NaClO_{12}$: C, 50.48; H, 5.65%. Found: C, 50.69; H, 5.73%. The purified complex was then suspended in chloroform (20 ml) and boiled with water 4 X 100 ml). Removal of chloroform *in vacuo* from the organic layer gave a colourless oil. M. wt. by vapour pressure osmometry in benzene 438; V req. 448.5. *Anal.* Calcd. for $C_{24}H_{32}O_8$: C, 64.26; H, 7.19%. Found: C, 63.87; H, 7.38%.

Preparation of Complexes

The ligand and metal salt in the required stoicheiometry were dissolved in hot solvent, filtered and allowed to crystallise. The crystalline products were collected on a sinter, washed with a small amount of solvent, and dried *in vacuo*.

Formation Constants

Formation constants of the alkali metal bromides were measured in methanol by an electrometric method using the method of Frensdorff [8] and a modified cell previously described [9]. The contents were obtained from the titration curves using the MINIQUAD program [10].

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