Tetrahedron Vol 33, pp 563 to 571 Pergamon Press 1977 Printed in Great Britain

CHEMISTRY OF CROWN ETHERS

COMPLEXATION WITH ALKALI METAL TRICHLORO(ETHYLENE)PLATINUM(II) SALTS

D. N. REINHOUDT,* R. T. GRAY, F. DE JONG and C. J. SMIT
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research BV), The Netherlands

(*Received in UK 21 September 1976; Accepted for publication 7 October 1976*)

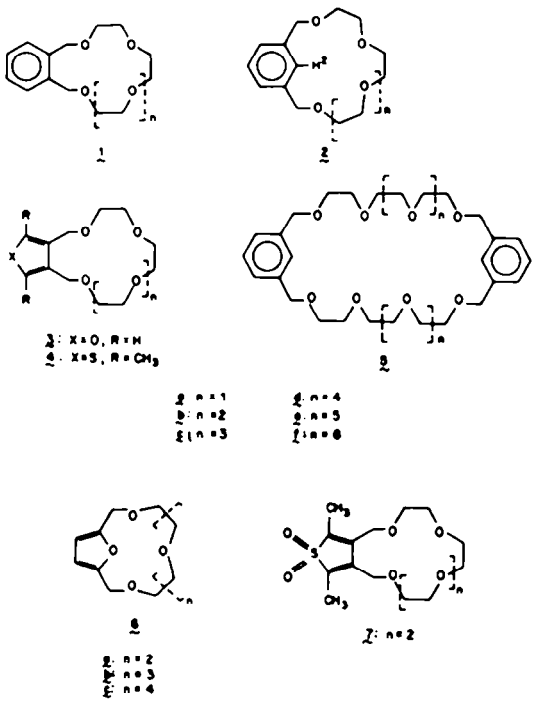
Abstract—A novel method has been developed for the determination of the complexation constants of crown ethers with alkali salts. It comprises the equilibration of crown ether (1-7) solutions in deuterochloroform with solid trichloro(ethylene)platinum(II) salts (Na^+, K^+, Rb^+, Cs^+) and the PMR spectroscopic determination of the equilibrium ratio of complex to free crown ether from the relative intensities of the ethylene and crown ether protons. The solubility of uncomplexed salt was determined independently by atomic absorption spectrometry.

The major advantages of this method over others are: (i) complexation constants in *apolar* solvents are obtained from a direct solid-liquid transition, (ii) the cation in the salt can be varied, and (iii) a simple detection technique can be used for monitoring the complexation.

The PMR spectra indicate that there are three types of complex, depending on the ratio of the diameter of the crown ether cavity to that of the cation. If this ratio is small (< 1), the aromatic ring is almost perpendicular to the flat polyether ring. With increasing ratio (~ 1.0) the flat polyether ring and the aromatic ring become almost coplanar in the complex. If the ratio is large (> 1.0) the polyether ring is *twisted* around the cation.

1. INTRODUCTION

Our previous work on the chemistry of crown ethers dealt with the synthesis of some novel classes of crown ethers (1-7), the role of cations in their synthesis and the elucidation of the structure of the macrocyclic polyethers.[1-3]



We will here discuss various aspects of a specific property of crown ethers viz. their ability to form complexes with salts.

In the complexation of crown ethers there are several important parameters to be considered:

(i) the stability of the complexes;

(ii) the relationship between the size of the crown ether cavity and that of the cation;

(iii) Changes in the conformation of the crown ether upon complexation;

(iv) rates of complexation and decomplexation.

The stability of a complex is usually expressed in terms of an association constant (K_a):

$$CE + M^+X^- \rightleftharpoons (CE\cdot M)^+\cdot X^-$$

$$K_a = \frac{[(CE\cdot M)^+\cdot X^-]}{[CE][M^+X^-]}. \qquad (1)$$

In the literature a large number of association constants of crown ether complexes have been reported.[4] They were obtained under two essentially different sets of conditions, i.e. either (i) in polar solvents (water, alcohols, dimethylformamide), by potentiometric methods using cation-selective electrodes, by calorimetry and conductometry,[5-8] or (ii) in apolar solvents, by partition between two immiscible liquid phases,[9-11] the concentrations being determined by spectroscopic techniques. Both methods for the determination of the association constants suffer from serious disadvantages. The first method affords values valid only for polar solvents while most reported practical applications of crown ethers are in apolar solvents.[12-15] The second method gives values which are obscured by unknown partition coefficients of the complexes, crown ethers and salts. Moreover, depending on the ring size of the crown ether, the structures of the complexes formed in such partition experiments are affected by the inclusion of polar solvent molecules (e.g. water).[16]

The objective of the present study was to find a simple, direct method for the detection of complex formation and for the determination of the abilities of crown ethers to

complex *solid* alkali salts. We have succeeded in developing such a method by using trichloro(ethylene)platinum(II) compounds ($MPtCl_3 \cdot C_2H_4 \cdot nH_2O$) as the salts, and PMR spectroscopy as the detection techniques.†

2. RESULTS AND DISCUSSION

(a) *Starting materials*

The synthesis of the crown ethers (**1–6**) used for our studies has been described previously.[1,2] Zeise's salt was prepared from potassium hexachloroplatinate(IV) and ethylene at 10 atmospheres.‡ The other alkali trichloro(ethylene)platinum(II) salts were obtained by cation exchange of aqueous solutions of Zeise's salt with sodium, rubidium or cesium polystyrene-sulphonates. The stability of these (hydrated) salts varied greatly with the size (electrophilicity) of the cation. Both cesium and rubidium trichloro(ethylene)platinum(II)·hydrate were stable at room temperature but the sodium salt could not be obtained in an analytically pure form because it gradually decomposed. Complexation experiments with $NaPtCl_3 \cdot C_2H_4 \cdot H_2O$ were therefore carried out with a slight excess of freshly prepared material.

The solubilities of the trichloro(ethylene)platinum(II) salts in deuterochloroform were determined by atomic absorption spectrometry. Values of 4.0×10^{-4} M (K^+), 7.6×10^{-4} M (Rb^+) and 4.5×10^{-4} M (Cs^+) were obtained.

For further details the reader is referred to the Experimental Section.

(b) *Complexation experiments*

A study of complexation using PMR spectroscopy as the detection technique requires the presence of protons either in the cation or in the anion of the salt. The former requirement was fulfilled in a study, made by Cram *et al.*,[11] of the complexation of t-butylammonium isothiocyanate. We have investigated the complexation of salts in which the *anion* contains one or more protons. The advantage of our approach is that instead of being limited to one type of cation (RNH_3^+), we can study the complexation of a variety of salts containing the same anion but various cations with different ionic radii. It is known that the nature of the cation is often one of the most important factors determining the stability of a crown ether complex.

Zeise's salt ($KPtCl_3 \cdot C_2H_4 \cdot H_2O$) has several properties that make it an attractive salt for such complexation studies:

(i) it behaves as an inorganic salt, being very soluble in water but virtually insoluble in apolar solvents such as chloroform (*vide supra*), methylene chloride and benzene;

(ii) it has a yellow colour, which makes complexation visually detectable;

(iii) the four ethylene protons appear as an easily discernible group of three signals in the PMR spectrum: a singlet, and a doublet due to coupling with ^{195}Pt (34%) natural abundance); thus, the complexation can be measured quantitatively;

(iv) the potassium cation can in principle be replaced by other cations via simple ion exchange.

†Preliminary results have already been published.[17]

‡In the PMR spectrum of Zeise's salt (in 1N HCl/CD_3OD) we found a chemical shift of 4.721 ppm for the ethylene protons and a value of 65.1 Hz for the Pt-H coupling,[18] as opposed to the recently reported value of 34 Hz.[19,20]

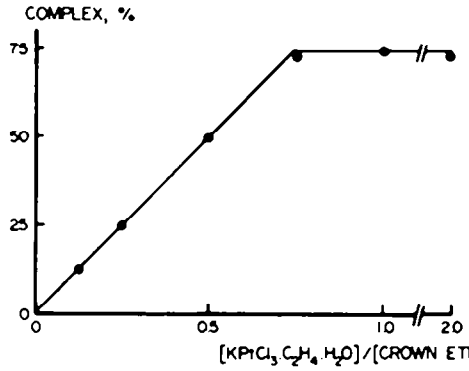


Fig. 1. Percentage complex formation versus Zeise's salt/crown ether (1, n = 2) ratio.

1. *Direct method.* Experimentally our technique is very simple. Mixtures of crown ether dissolved in deuterochloroform and various amounts of solid Zeise's salt—up to a two-fold excess— were equilibrated at room temperature; the time needed for equilibration was less than 1 min. The ratio of crown ether to complexed salt was calculated from the ratio of the PMR signal intensities of the ethylene protons to those of the crown ether benzylic protons, which served as the internal standard. The maximum percentage of complexation was calculated directly from the ratio found in the presence of an excess of Zeise's salt (Fig. 1). In Table 1 these maximum percentages are summarised for crown ethers **1–7**. Other trichloro-ethylene-platinum salts (Na^+, Rb^+, Cs^+) gave similar results but the dependence of the degree of complexation on the crown ether structure differed from that for the potassium salt.

From the results given in Table 1 the following conclusions can be drawn:

(i) the degree of complexation depends on the relationship between the cationic radius and the size of the crown ether cavity;

(ii) the ratio of salt to crown ether in solution does not exceed the value of 1.00 (± 0.10) even if an excess of solid salt is present;

(iii) crown ethers with a cavity diameter larger than the cationic diameter are more than 90% complexed in the presence of an excess of salt.

The complexation data can be divided into two groups. The first group comprises the values (Table 1a) between 0.05 and 0.95, i.e. where the ratio of uncomplexed crown ether (CE) to complex is between 0.05 and 20. For these values absolute association constants can be obtained by substituting into eqn (1) the ratio of [complex]/[CE], together with the concentration of the particular salt, which is assumed to be equal to its solubility (see Section 2A) in the absence of crown ether. This procedure is not possible for the second group where the [CE]/[complex] ratio is ≥ 20 or ≤ 0.05, (corresponding to values of ≤ 0.05 and ≥ 0.95 in Table 1a). The values of K_a are given in Tables 1b and 2.

We further found that complexation affects the chemical shifts of the benzylic, aromatic (e.g. H(2) in **2**) or heteroaromatic (H(2,5) in **3**) crown ether protons. In all cases the chemical shift differences were proportional to the percentage complexation (Fig. 2). Even at −40°C only "sharp" averaged signals for the crown ether protons were observed in mixtures of complex and free crown

Table 1(a). Complexation of crown ethers 1–4 with $MPtCl_3 \cdot C_2H_4 \cdot H_2O$ in $CDCl_3$ (0.1 M solutions of crown ether; 300 K)

Crown ether n	Ratio of salt/crown ether[a] 1			2			3			4		
	K^+	Rb^+	Cs^+	K^+	Rb^+	Cs^+	K^+	Rb^+	Cs^+	K^+	Rb^+	Cs^+
1	0.27	0.05	<0.01	0.07	0.05	<0.01	0.07	0.04	0.02	0.02	0.02	0.01
2	0.74	0.60	0.26	0.91	0.61	0.52	1.00	0.78	0.60	1.00	0.64	0.65
3	0.98	0.85	0.87	0.96	0.62	0.57	1.05	1.00	0.92	1.00	0.91	0.81
4	1.00	0.98	1.00	0.92	0.60	0.60	0.98	1.10	1.06	1.05	1.12	1.06
5	1.00	1.00	0.90	1.04	0.74	0.84	1.07	0.93	1.00	1.00	1.00	1.00
6	0.95	0.94	1.00	1.00	0.89	0.81	0.94	1.00	0.83	0.95	1.00	1.04

a. Mol of salt complexed per mol of crown ether; accuracy ± 10 %. Complexation with $NaPtCl_3 \cdot C_2H_4 \cdot H_2O$ could not be measured with the same accuracy owing to broadening of the signal of the ethylene protons (the salt/crown ether ratio was approximately one in all cases).

Table 1(b). Complexation of crown ethers 5–7 with $KPtCl_3 \cdot C_2H_4 \cdot H_2O$ in $CDCl_3$ (0.1 M solutions of crown ether; 300 K)

Crown ether (CE)	[salt]/[CE]	K_a, M^{-1}
5 (n = 1)	0.30	1.1×10^3
6a (n=2)	0.50	2.5×10^3
6b (n=3)	1.00	$\geq 5 \times 10^3$
6c (n=4)	1.00	$\geq 5 \times 10^3$
7	0.57	3.3×10^3

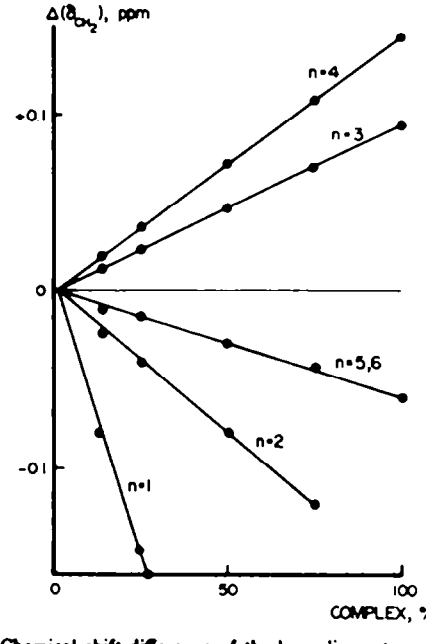


Fig. 2. Chemical shift difference of the benzylic protons versus percentage complex formation of 1 (n = 1–2) with Zeise's salt $\delta = \delta_{complex} - \delta_{CE}$.

ether. This means that all exchange processes are fast on the PMR time scale.†

2. *Indirect methods.* In those cases where the [CE]/[complex] ratio is ≤0.05 we did two types of competition experiments in order to determine the relative complexing abilities of pairs of crown ethers.

In the first type of experiments we used the titration method previously reported[22] for the determination of the relative association constants of t-butylammonium hexafluorophosphate-crown ether complexes. In a typical example of this procedure a solution of the equilibrium mixture of crown ether **2b**/$KPtCl_3 \cdot C_2H_4 \cdot H_2O$ in $CDCl_3$ was titrated with crown ether **2d** and vice versa. The ratios of free to complexed crown ether (**2b** and **2d**) were determined from the known linear relationship of the chemical shifts of crown ether protons (in this case the H(2)-aromatic protons) and the percentage complexation. The ratio of the two association constants of the complexes of Zeise's salt with **2d** and **2b**, was thus found to be approximately 0.6.

In the second type of experiments equimolar amounts of two crown ethers dissolved in chloroform were equilibrated with various amounts of Zeise's salt. In the same manner as described above, PMR spectroscopy was used for the determination of the ratios of free to complexed crown ethers. With this method we found that $K_{1b} \approx K_{2a}$ ($KPtCl_3 \cdot C_2H_4 \cdot H_2O$).

3. *Complexation in other solvents.* Several experiments were performed in solvents other than chloroform, viz. benzene, toluene and methylene chloride. The results obtained in methylene chloride were only slightly

†In complexation experiments of these crown ethers with tert-butylammonium salts we found that the exchange is sufficiently slow to allow a kinetic study in a number of cases.[21]

Table 2. Association constants of crown ether/$MPtCl_3 \cdot C_2H_4 \cdot H_2O$ complexes in $CDCl_3$ (0.1 M solutions of crown ether, 300 K)[a]

Crown ether	K_a, mol^{-1} l		
	K^+	Rb^+	Cs^+
1a	9.3×10^4	6.9×10^3	$<2 \times 10^3$
1b	7.1×10^5	2.0×10^5	7.8×10^5
1c	$>5 \times 10^6$	7.5×10^5	1.5×10^6
2a	1.9×10^4	6.9×10^3	$<2 \times 10^3$
2b	1.7×10^6	2.1×10^5	2.5×10^5
2c	$>5 \times 10^6$	2.2×10^5	3.0×10^5
3a	3.9×10^5	5.5×10^3	4.5×10^3
3b	$>5 \times 10^6$	4.7×10^5	3.3×10^5
3c	$>5 \times 10^6$	$>2.5 \times 10^6$	2.6×10^6
4a	1.0×10^6	1.1×10^4	1.7×10^4
4b	$>5 \times 10^6$	2.3×10^5	4.3×10^5
4c	$>5 \times 10^6$	1.3×10^6	9.5×10^5

a. For all crown ether complexes 1–4 with n=4,5 and 6 $K_a > 10^6$.

different from those in chloroform. Although the crown ethers dissolve quite readily in benzene and toluene several complexes separated out rapidly from these solvents. Consequently, the equilibrium ratios of crown ether to complex could not be determined with sufficient accuracy in these media.

(c) *Structures of the complexes*

Information regarding the structures of the complexes was obtained from the PMR and ^{13}C NMR spectra of the complexes or the equilibrium mixtures of free crown ether and complex, in chloroform.

1. *The ethylene ligand.* In the PMR spectra of the complexes the ethylene protons appear as three sharp signals (ratio 1:4:1) with the central line at 4.45 ± 0.04 ppm.† The coupling constant $J(^{195}Pt\text{–}H)$ is almost the same as in Zeise's salt (65 ± 1 Hz). The carbon atoms absorb at 68.0 ± 0.5 ppm ($J(^{195}Pt\text{-}C) = 194 \pm 1$ Hz) in the ^{13}C NMR spectrum, which values are in good agreement with those reported earlier.[19]

2. *The "benzylic" groups.* The signals of the "benzylic" protons in the complexes are shifted either upfield or downfield relative to those of the free crown ether, depending on the ring size, the structure of the crown ether and the type of cation that is complexed in the cavity (Table 3). An upfield shift is observed with small and very large crown ethers (relative to the cation) and a downfield shift when the diameters of the cavity and cation are about the same. We associate these chemical shift differences with differences in the sum of cationic (deshielding) and anionic (shielding) influences in order to obtain a qualitative picture of the structure of the complex. When the cation just fits in the cavity the polyether is almost flat and consequently the "benzylic" protons are close to the cation which causes the deshielding effect. CPK models show that when the cavity is too small to accommodate the cation the benzylic protons in the complex are situated on the side of the rigid polyether ring opposite to that where the O atoms are coordinated to the cation. In the complexes with the very large rings a twisting of the polyether chain occurs (*vide infra*) and in such a twisted conformation the cation is shielded from the benzylic protons by part of the chain. Consequently the benzylic protons will be in the immediate vicinity of the anion, causing a shielding effect.

The effect of complexation is also noticeable in the ^{13}C NMR spectra but it does not provide any significant information about the relative positions of anion and cation.‡ The absorptions of the polyether and "benzylic" carbon atoms appear in the 68.5–72.5 ppm region for both the complex and the free crown ether (Table 4). Consequently, it is impossible to arrive at unambiguous assignments. Moreover, in this region chemical shift differences between complexed and free crown ethers are small.

3. *Aromatic rings.* The effect of complexation on the chemical shift of the "internal" aromatic (H(2)) proton in crown ethers 2 is greatly dependent on the ring size (Table 5). In the smaller rings (**2a** and **2b**) complexation requires that the aromatic and the (planar) polyether rings be almost perpendicular. Consequently the internal H(2) proton extends into the shielding sphere of the anion ($\Delta\delta < 0$).§ These steric requirements become less important with increasing ring size. Thus with a decreasing angle between polyether and aromatic rings the "internal" aromatic proton becomes increasingly deshielded by the cation ($\Delta\delta > 0$).¶ Complexation of crown ethers 3 affects the chemical shifts of furan protons (H(2,5)) in the opposite way; in nearly all cases a downfield shift is observed. This finding complies with a complex in which the anion is situated on the sterically less hindered side of the polyether ring, viz. opposite to the aromatic ring. With increasing ring size this steric constraint becomes less

†In the complexes with $NaPtCl_3 \cdot C_2H_4 \cdot H_2O$ the absorption of the ethylene protons is broad due to slow exchange with free ethylene formed by decomposition of the salt.

‡^{13}C NMR spectra of crown ether complexes have been reported; in most cases chemical shift differences were less than 1.0 ppm.[23]

§A similar shift was observed for the H(2) protons in complex of **2b** with tert-butylammonium salts.[21,22]

¶The effect of complexation on the other aromatic protons in crown ethers 2 (or the four aromatic protons in 1) has not been analysed. The respective AA'B and AA'BB' systems are very complicated.

Table 3. Differences between chemical shifts (Δδ)[a] of the "benzylic" protons of free and complexed crown ethers (1–4)[b]

Crown ether / n	1: δ_{CH_2}	1: $\Delta\delta_{CH_2}$ K^+	1: $\Delta\delta_{CH_2}$ Rb^+	1: $\Delta\delta_{CH_2}$ Ca^+	2: δ_{CH_2}	2: $\Delta\delta_{CH_2}$ K^+	2: $\Delta\delta_{CH_2}$ Rb^+	2: $\Delta\delta_{CH_2}$ Ca^+	3: δ_{CH_2}	3: $\Delta\delta_{CH_2}$ K^+	3: $\Delta\delta_{CH_2}$ Rb^+	3: $\Delta\delta_{CH_2}$ Ca^+	4: δ_{CH_2}	4: $\Delta\delta_{CH_2}$ K^+	4: $\Delta\delta_{CH_2}$ Rb^+	4: $\Delta\delta_{CH_2}$ Ca^+
1	4.786	[illegible]	[illegible]		4.620	[illegible]	-0.150	–	[illegible]	[illegible]	–	–	4.567	-0.182	-0.669	-0.271
2	4.726	-0.151	-0.155	-0.208	4.620	-0.128	[illegible]	+0.06	4.518	[illegible]	[illegible]	-0.065	[illegible]	-0.117	-0.167	[illegible]
3	4.685	+0.066	+0.007	-0.064	[illegible]	-0.026	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	+0.081	+0.006	-0.075
4	4.676	+0.138	[illegible]	+0.082	4.587	+0.017	+0.010	-0.077	[illegible]	[illegible]	[illegible]	+0.015	4.448	+0.144	+0.139	+0.107
5	4.672	-0.059	+0.016	+0.039	4.587	+0.066	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	-0.023	+0.007	+0.039
6	4.662	-0.062	-0.049	-0.033	4.577	+0.045	[illegible]	[illegible]	4.489	[illegible]	[illegible]	-0.005	4.476	-0.048	[illegible]	-0.075

a. $\Delta\delta = \delta_{complex} - \delta_{crown\ ether}$.

b. At 300 K in $CDCl_3$ (0.1 M).

Table 4. ^{13}C NMR data of crown ethers (1)/Zeise's salt complexes[a,b]

Crown ether	% Complex[c]	δ (ppm) Aromatic carbon atoms			δ (ppm) Polyether carbon atoms				
1a	27[d]	136.28	130.82	128.55	71.16	69.21	68.30		
1b	74[d]	135.63	131.61	129.20	71.62	70.19	69.80	68.95	
1c	98[d]	136.02	130.63	128.36	72.80	69.80	69.67	68.95	
1d	100	136.48	130.70	128.36	72.40	70.06	69.80	69.47	68.50
1e	100	136.22	130.96	128.94	71.68	68.96	68.76	68.11	
1f	95[d]	136.35	131.09	128.62	71.94	69.34	69.22	68.69	68.05
					68.30	67.98			

a. In $CDCl_3$ (0.1 M) at 300 K; chemical shifts, in ppm, relative to TMS.

b. The ^{13}C chemical shifts of the free crown ethers have been reported previously[1].

c. As determined by NMR spectroscopy.

d. Values observed for the equilibrium mixture.

Table 5. Differences between chemical shifts ($\Delta\delta$)[a] of the aromatic protons of free and complexed crown ethers 2 (H(2)) and 3 (H(2,5))[b]

Crown ether / n	2				3			
	$\Delta\delta_{H(2)}$				$\Delta\delta_{H(2,5)}$			
	$\delta_{H(2)}$	K^+	Pb^{2+}	Cs^+	$\delta_{H(2,5)}$	K^+	Pb^{2+}	Cs^+
1	7.93	-0.355	-0.220	-[c]	7.375	+0.146	-[c]	-[c]
2	7.[illegible]	-0.[illegible]	-0.[illegible]	-0.[illegible]	7.355	+0.166	+0.132	+0.120
3	7.[illegible]	+0.065	+0.172	+0.246	7.375	+0.016	+0.058	+0.117
4	7.[illegible]	+0.[illegible]	+0.[illegible]	+0.267	7.371	-0.009	-0.019	-0.019
5	7.[illegible]	+0.038	+0.205	+0.139	7.371	+0.124	+0.039	+0.013
6	7.39	+0.[illegible]	+0.[illegible]	+0.[illegible]	7.38	+0.078	+0.095	+0.083

a. $\Delta\delta = \delta_{complex} - \delta_{crown\ ether}$

b. At 300 K in $CDCl_3$ [illegible] M.

c. Owing to the low percentage of complexation ($\leq$ 5 %) the value of the chemical shift in the complex cannot be obtained with sufficient accuracy.

important if the polyether ring is assumed to have a more or less flat conformation.

A twisted polyether ring (*vide infra*) has the same steric requirements as a smaller planar one. This can be seen from a discontinuity in the data when, on the basis of other arguments, twisting is assumed to occur. From the chemical shift differences between the (hetero)aromatic carbon atoms in the ^{13}C NMR spectra no conclusions can be drawn about the structures of the complexes as we are unable to assign the absorptions unambiguously.

4. *Polyether rings.* Generally the effect of complexation on the chemical shift of the polyether chain protons is small. Apart from small differences in the chemical shifts ($\leq$ 0.050 ppm), the absorptions retain the same multiplicity (one or two broad singlets[1,2]). Exceptions are found in those complexes in which the size of the crown ether cavity is more than suffcient to accomodate the cation. In those cases the absorption of the polyether protons consists of four well-separated, sharp peaks which are shifted partly up-field and partly down-field (see Fig. 3, Table 6). The relative intensities of the peaks differ from case to case with a ratio of roughly 4:8:n:8 (in order of increasing chemical shift), where n correlates with the number of $-CH_2CH_2O-$ moieties in the ring. Space-filling CPK models indicate that this non-equivalence of groups of polyether protons must be related to the polyether chain being wrapped around the cation (Fig. 4),† which results in an almost perfect spacing of the O atoms for optimal complexation of the cation. Such a twisting is only possible above a particular ring size. The different shielding and deshielding effects of the anion and cation in such complexes on the protons of the polyether rings are reflected in the differences in their chemical shift. As a result of this twisting, the groups of protons close to the aromatic residue will be separated from the cation in the cavity and be close to the anion; these are the most shielded protons (intensities 4 and 8). Another group of protons, inside the cavity, is shifted downfield due to the close proximity of the cation; the effects of cation and

†In mixtures of complexed and free crown ether the chemical shift differences are proportional to the degree of complexation (Fig. 5).

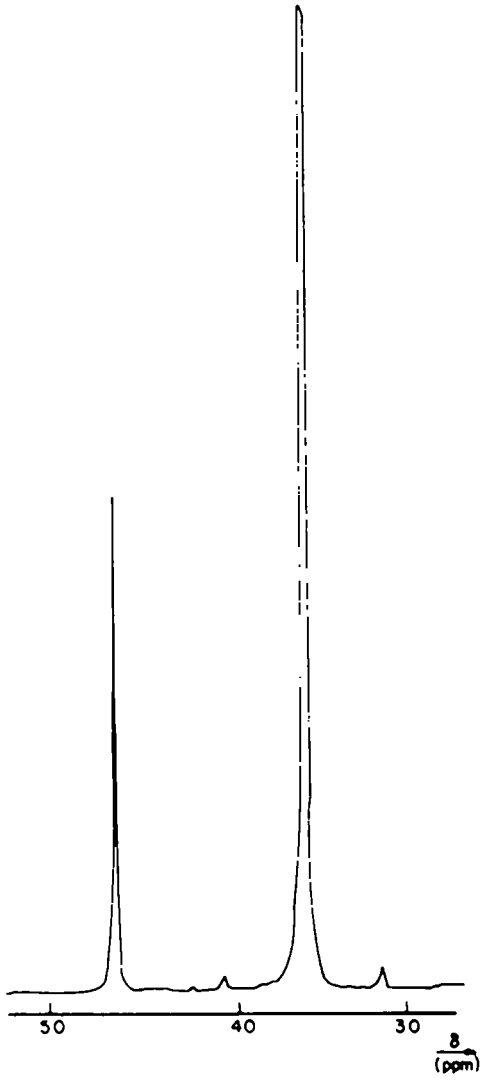


Fig. 3a. PMR spectrum of crown ether 1e.

Fig. 3b. PMR spectrum of the $KPtCl_3 \cdot C_2H_4 \cdot H_2O$–1e complex.

anion on the remaining protons compensate each other. The relationship between ring size of the crown ether, cationic diameter and degree of twisting is shown in Fig. 6 for crown ethers of type 1.

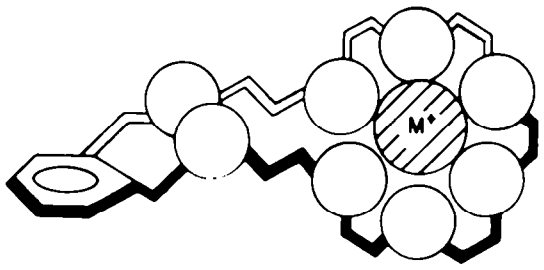


Fig. 4.

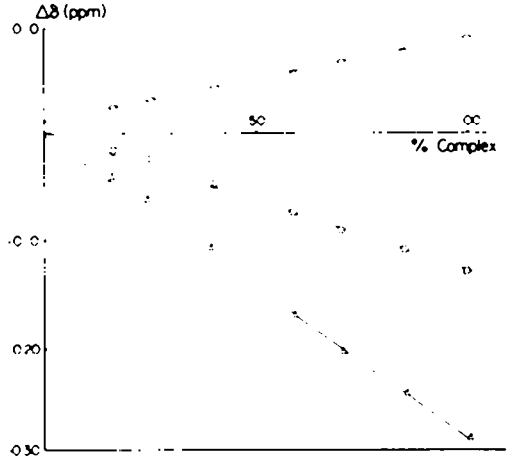


Figure 5. Relationship between % complexation and the chemical shift difference ($\Delta\delta$) of the polyether protons in $KPtCl_3 \cdot C_2H_4 \cdot H_2O$–1e complex/1e mixtures.

Similar phenomena were observed in the spectra of the complexes of the other crown ethers in which the aromatic ring is linked via the α and β positions to the polyether ring (3, 4), but in the complexes of type 2 this non-equivalence of polyether protons was absent.

In the complex of 1f with $NaPtCl_3 \cdot C_2H_4 \cdot H_2O$ the polyether ring protons are magnetically almost equivalent. This might be due to an increased flexibility of the

Table 6. Differences between chemical shifts ($\Delta\delta$)[a] of the polyether ring protons of free and complexed crown ethers (1)[b,c]

Crown ether	Ring size	Cation	$\delta_{CH_2CH_2O}$	$\Delta\delta_{CH_2CH_2O}$[d]			
				I	II	III	IV
1d	23	Na^+	3.671	−0.256	−0.120	+0.010	+0.107
1e	26	Na^+	3.661	−0.139	−0.092	+0.020	+0.078
1e	26	K^+	3.661	−0.251	−0.120	+0.020	+0.095
1f	29	K^+	3.640–3.660	−0.207	−0.061	+0.004	+0.069
1e	26	Rb^+	3.661	−0.272	−0.129	+0.013	+0.033
1f	29	Rb^+	3.640–3.660	−0.155	−0.043	+0.021	+0.049
1f	29	Cs^+	3.640–3.660	−0.119	−0.054	+0.008	+0.050

a. $\Delta\delta = \delta_{complex} - \delta_{crown\ ether}$

b. At 300 K in $CDCl_3$ (0.1 M).

c. Similar chemical shift differences were observed for the corresponding complexes of crown ethers 3 and 5.

d. Chemical shift differences of groups of polyether protons in the complex.

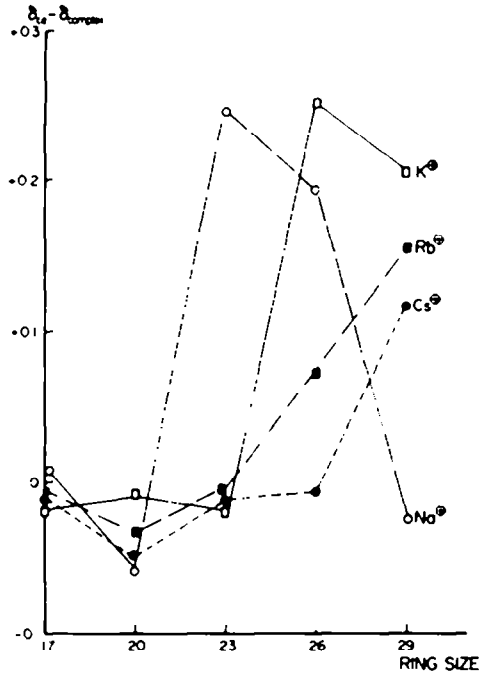


Fig. 6. Chemical shift differences of the polyether protons in crown ethers (1)/$MPtCl_3 \cdot C_2H_4 \cdot H_2O$ complexes.

complexed crown ether ring with the increased ratio of cavity size to cationic diameter.

From the above analysis of the PMR data it is clear that the structure of the complexes varies with the size of the polyether ring.

All the data, in particular those of mixtures of free and complexed crown ethers, point to the predominant formation of complexes with a stoichiometric (1:1) composition.† A transition of such a complex to one having a different stoichiometry (e.g. as a result of an increased complex/crown ether ratio) would undoubtedly have disturbed the linear relationships between chemical shifts and percentage complexation. We can distinguish three types of structure:

(i) The polyether ring and the aromatic ring are nearly perpendicular to each other when the crown ether cavity is small relative to the cation [$\Delta\delta_{H_{aromatic}}$ (1–4) and $\Delta\delta_{H(2)}$ (2) < 0].

(ii) The crown ether is almost planar when the crown ether cavity and the cation have almost the same size [$\Delta\delta_{H_{aromatic}}$ (1–4) and $\Delta\delta_{H(2)} > 0$].

(iii) The polyether chain is "twisted" when the crown ether cavity is substantially larger than the cation [$\Delta\delta_{H_{aromatic}}$ (1, 3, 4) ≤ 0 and *non-equivalent groups* of *polyether protons*].

In the literature twisted conformations have been suggested for complexes of large crown ethers in solution in order to explain the unexpectedly high stability of K^+ complexes of dibenzo-30-crown-10 in methanol.[25] Furthermore, X-ray crystallographic data point to a marked deformation of the crown-10 ring when it complexes potassium ions.[26] The PMR evidence presented by us indicates clearly that such twisted conformations in solution indeed exist. In the series of crown ether we investigated, only polyethers linked to adjacent C atoms of the (hetero)aromatic ring (1, 3, 4) are capable of adopting such a twisted conformation. In crown ethers of structure 2 with rings containing fewer than 30 atoms, such twisting is prevented by steric factors, as is demonstrated by CPK models.

†Complexes of crown ethers 3b–d with t-butylammonium thiocyanate formed in the presence of excess of solid salt[24] have a different stiochiometry (1:2).

3. CONCLUSIONS

The use of PMR spectroscopy to monitor the complexation of crown ethers with trichloro(ethylene)platinum(II) salts provides a simple technique for the determination of the minimum crown ether cavity size required for complexation of a particular cation. Absolute or relative association constants in chloroform are obtained directly without the interference of unknown partition coefficients. PMR spectroscopy has provided evidence that the polyether ring in complexes of large crown ethers has a twisted conformation.

EXPERIMENTAL

PMR and NMR spectroscopy. PMR and ^{13}C NMR spectra were recorded on a Bruker WH 90 instrument, using deuterochloroform as the solvent with TMS as internal reference.

Synthesis of Zeise's salt ($KPtCl_3 \cdot C_2H_4 \cdot H_2O$). A soln of 16.0 g (0.036 mol) of K_2PtCl_4 in 100 ml 1.3 N HCl was stirred for 6 hr under an atmosphere of ethylene (10 bar). The mixture was concentrated *in vacuo* at room temp. and subsequently cooled in ice. The crystals formed were filtered off, washed with 0.5 N HCl and cold EtOH, and then dried over P_2O_5, *in vacuo*. The yield of Zeise's salt was 11.5 g (77%). Found: C, 6.0; H, 1.0; Cl, 26.9. Calc. for $KPtCl_3 \cdot C_2H_4 \cdot H_2O$(386.62): C, 6.2; H, 1.5; Cl, 27.5%).

Synthesis of $MPtCl_3 \cdot C_2H_4 \cdot H_2O$ *from Zeise's salt.* Amberlyst 300 was treated with an excess of alkali salt or hydroxide (NaCl, CsCl or RbOH). Subsequently, aqueous solns of Zeise's salt were passed through a column filled with the Amberlyst 300 in the salt form and eluted with water. 4N HCl was added to the eluate in order to obtain a 1N HCl, which was concentrated to a small volume at room temp., before the last traces of water were removed in a desiccator over conc H_2SO_4 and solid KOH. In all cases the percentage of residual K was smaller than 0.2%. The trichloro(ethylene)platinum(II) salts were thus obtained in 80–90% yield. The elemental analyses of the Rb and Cs salts were satisfactory: Rb 21.0% (calc. 19.7%), Cs 28.6% (calc. 28.5%). The sodium salt could not be obtained analytically pure owing to decomposition.

Synthesis of 18,20 - *dimethyl* - 3,6,9,12,15 - *pentaoxo* - 19 - *thiabicyclo*(15.3.0) - *eicosa* 17,20, *diene* 19,19-*dioxide* (7). A soln of 330 mg (1.0 mmol) of **4b** and 410 mg (2.4 mmol) *m*-perchlorobenzoic acid in 50 ml dichloromethane was refluxed for 2 hr. The mixture was cooled to −25° and the crystalline material was filtered off. The filtrate was concentrated to a small volume and subsequently filtered over alumina. Elution with dry THF gave 75 mg of 7 (20%).

Complexation of crown ethers 1–4 *with trichloro(ethylene)platinum(II) salts in deuterochloroform*

(a) *At various ratios of salt to crown ether.* Solns of 0.05 mmol crown ether in 0.5 ml $CDCl_3$ were mixed with 0.125, 0.25, 0.50, 0.75, 1.00 and 2.00 equivs of $MPtCl_3 \cdot C_2H_4 \cdot H_2O$. Subsequently the PMR spectra were recorded and the percentage of complex was determined from the ratio of the intensities of the ethylene protons to those of the benzylic protons. From the plots of $\Delta\delta$ vs the percentage complexation the equilibrium value was calculated.

(b) *With excess of salt.* A soln of 0.05 mmol crown ether in 0.5 ml $CDCl_3$ was mixed with two equivs of salt. The PMR spectra were recorded at 1-min intervals. In all cases the maximum value of complexation was reached within the first interval.

Competition experiments

(a) *Titration method.* To a soln of 0.05 mmol complex of crown ether A in 0.5 ml $CDCl_3$ (prepared from 0.05 mmol of crown ether A and 2 equivs of Zeise's salt) a soln of 0.05 mmol crown ether B

Table 7. Titration of complexes of crown ethers **2b** and **2d** with Zeise's salt

No. of Experiment	Ratio[a] [2d]/[2b]	2d		2b		K_{2d}/K_{2b}
		δ_{H_2}	$\Delta\delta_{H_2}$[b]	δ_{H_2}	$\Delta\delta_{H_2}$[b]	
1	0	-	-	7.584	-0.163	-
1	0.86	7.534	+0.075	7.613	-0.114	0.71
1	0.95	7.537	+0.072	7.613	-0.114	0.66
1	1.05	7.521	+0.062	7.626	-0.101	0.66
2	1.32	7.512	+0.053	7.638	-0.095	0.57
2	1.72	7.521	+0.062	7.619	-0.108	0.56
2	1.96	7.534	+0.075	7.609	-0.118	0.65
2	∞	7.596	+0.137	-	-	-

a. In the equilibrium mixtures 90 % complexation of 2b and 2d was detected.

b. $\Delta\delta = \delta_{observed} - \delta_{free\ crown\ ether}$

Table 8. Competition experiment of crown ethers **2b** and **2c** with Zeise's salt

No.	Σ% of Compl. Crown ethers	2c		2b				K_{2c}/K_{2b}
		δ_{H_2}	$\Delta\delta_{H_2}$	δ_{H_2}	$\Delta\delta_{H_2}$	δ_{CH_2}	$\Delta\delta_{CH_2}$	
1	-	7.515	-	7.774	-	4.633	-	-
2	11	7.521	+0.006	7.697	-0.017	4.616	-0.017	0.65
3	27	7.538	+0.023	7.665	-0.049	4.593	-0.040	0.94
4	34	7.544	+0.029	7.652	-0.062	4.590	-0.043	0.83
5	75	7.580	+0.065	7.590	-0.124	4.545	-0.088	-[a]
6	87	7.583	+0.068	7.583	-0.131	4.535	-0.098	-[a]

a. Owing to small differences in chemical shifts the resulting value of K_{2c}/K_{2b} becomes very inaccurate.

in 0.5 ml $CDCl_3$ was added in five equal portions. After each addition the PMR spectrum of the mixture was recorded.

The results of the titration experiments of crown ethers **2b/2d** are given in Table 7.

(b) *Competition method.* Samples of equimolar mixtures of crown ethers were equilibrated with 0.125, 0.25, 0.50, 0.75, 1.00 and 2.00 equivs of Zeise's salt. From the chemical shift differences the ratios of complexed to free crown ether were calculated.

The results of the competition experiment of crown ethers **2b/2c** with Zeise's salt are given in Table 8.

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