Tetrahedron Letters No. 25, pp 2109 - 2112, 1975. Pergamon Press. Printed in Great Britain.

COMPLEXATION OF ZEISE'S SALT ($KPtCl_3.C_2H_4$) BY CROWN ETHERS

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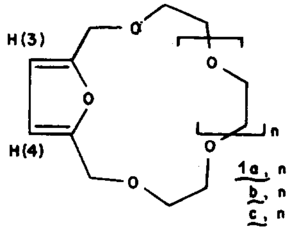
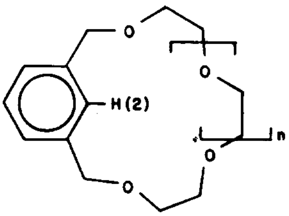
(Received in UK 5 May 1975; accepted for publication 8 May 1975)

Several methods have been used to correlate the structure and complexing ability of crown ethers[1]. The complexing ability is expressed as a (relative) complexation constant, which has been determined either directly in polar solvents or indirectly by partition of the complex between two different liquid phases (the so-called "extraction method"). Both methods have their disadvantages. The first method provides complexation constants in polar solvents; however, crown ethers are mainly used to dissolve salts in apolar solvents. The second has the disadvantage that the value of the complexation constant is obscured by unknown partition coefficients of crown ether, complex and salt.

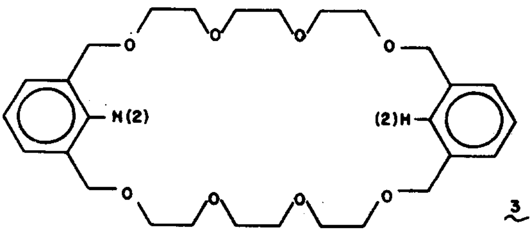
We here report a method by which the formation of a complex in apolar solvents can be directly measured by means of PMR spectroscopy. Crown ethers (CE) of types 1 - 3[2] were stirred in



1a, n=1
b, n=2
c, n=3



2a, n=1
b, n=2
c, n=3
d, n=4
e, n=5
f, n=6



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deuterochloroform (0.04 M) with two equivalents of crystalline Zeise's salt ($KPtCl_3$. ethylene)[3]. Equilibrium was reached within several minutes; the undissolved Zeise's salt was filtered off and subsequently the PMR spectra of the mixtures were measured.

$$CE + KPtCl_3.C_2H_4 \rightleftarrows [CE.K]^{\oplus} [PtCl_3.C_2H_4]^{\ominus}$$

The degree of complexation was calculated from the ratio of the integral in the PMR spectra of the ethylene protons to that of the benzylic protons of the crown ethers. The results are given in the Table. The degree of complexation was independent of the initial crown ether concentration in the range of concentrations studied (0.01 to 0.1 M).

TABLE

Complexation of Crown Ethers with $KPtCl_3.C_2H_4$ in $CDCl_3$.

Crown ether	Ring size	Maximum % of complex	(a) $\Delta\delta_{\text{benzylic } CH_2}$	(a,b) $\Delta\delta_{\text{Arom.}}$
1a	15	50	+ 0.042	+ 0.101
1b	18	100	+ 0.026	- 0.009
1c	24	100	+ 0.049	+ 0.043
2a	15	7	- 0.009	- 0.046
2b	18	87	- 0.111	- 0.137
2c	21	100	- 0.026	+ 0.085
2d	24	100	+ 0.017	+ 0.160
2e	27	100	+ 0.068	+ 0.238
2f	30	100	+ 0.045	+ 0.163
3	30	30	+ 0.095	+ 0.183

(a) The chemical shift difference given (Δδ, ppm) is defined as the particular chemical shift in the equilibrium mixture (max. % of complex) minus the chemical shift of the same proton(s) in the free crown ether.

(b) H(3,4) for 1a - 1c, H(2) for 2a - 2f and 3

We found that the chemical shifts of the benzylic protons and the aryl protons in the crown ethers (especially H(2) in **2** and **3**) were influenced by complexation[4,5]. When instead of an excess, variable amounts of Zeise's salt were added (ratios of added Zeise's salt to crown ether from 0 to 2.0, see Fig. 1) a linear relationship between Δδ and the percentage of complexation was observed in the whole range from free crown ether to maximum complexation (see Figs. 1 and 2). This indicates that complexes of only one type of stoichiometry are formed. The formation of other transitory complexes would certainly be expected to disrupt this linear relationship in view of the sensitivity of the chemical shift towards the structure of the complex. Since the ratio of Zeise's salt to crown ether in solution never exceeded the value of 1.0, even in the presence of an excess of Zeise's salt, we conclude that complexation occurs via the formation of a 1 : 1 complex. In solution the exchange of free and complexed crown ether is fast on the PMR time scale; even at -40 °C we found only one singlet for the benzylic and aromatic H(2) protons.

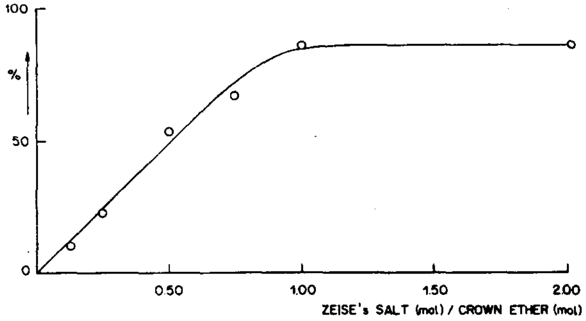

FIGURE 1

RELATIONSHIP BETWEEN [ZEISE's SALT]/[CROWN ETHER] RATIO AND % COMPLEX FORMATION FOR **2b**

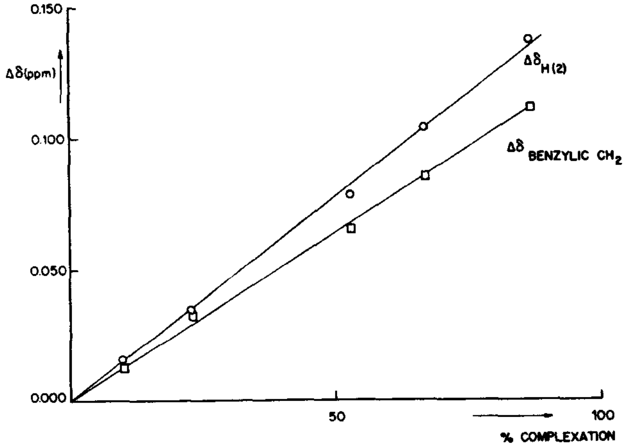

FIGURE 2

RELATIONSHIP BETWEEN CHEMICAL SHIFT DIFFERENCE

Δδ AND % COMPLEXATION OF CROWN ETHER **2b** WITH ZEISE's SALT

We have compared the results of our method with those from an "extraction method" using anilinium or ammonium hexafluorophosphates[6]. With protonated amines we found a gradual increase of complexation with increasing ring size of the crown ether (5 - 60 %), whereas the Zeise's salt method clearly shows whether or not a particular cation (e.g. K^+) can be accommodated within the cavity of the crown ether (compare **2a** (7 %) and **2c** - **f** (100 %)).

So far we have studied the complexation of *Zeise's salt* with crown ethers, but the technique is obviously also applicable to similar salts by variation of either the cation or the anion or both. Apart from being a useful analytical tool for studying complexation of the cation, complexation with Zeise's salt allows us to perform reactions of the *anion* in apolar solvents e.g. displacement of the ethylene by pyridine, which occurs instantaneously.

Further studies in these two directions are in progress.

REFERENCES

(1) C.J. Pedersen, *J. Amer. Chem. Soc.* **89**, 7017 (1967); J.J. Christensen, D.J. Eatough and R.M. Izatt, *Chem. Revs.* **74**, 351 (1974).

(2) D.N. Reinhoudt and R.T. Gray, *Tetrahedron Letters* **1975**, 000

(3) The use of such a salt has the following advantages: (i) The anion contains protons that can be directly monitored by PMR. (ii) Zeise's salt is almost insoluble in $CDCl_3$ (<0.01 g/l) in the absence of crown ethers. (iii) Solutions of crown ether - Zeise's salt complexes are coloured (yellow).

(4) The absorptions due to the protons in the polyether ring are hardly affected by complexation, suggesting little conformational differences between the free and complexed crown ether.

(5) Upon complexation the ^{13}CMR chemical shifts are also influenced ($\Delta\delta \leq 1$ ppm); similar differences have been reported recently for complexes of dibenzo-18-crown-6 with potassium iodide (*C.D. Hall and T. Pooner*, *Texas A & M NMR Newsletter* **1974**, 22).

(6) L.R. Sousa, D.H. Hoffman, L. Kaplan and D.J. Cram, *J. Amer. Chem. Soc.* **96**, 7100 (1974).