Stability Constants of Complexes of a Series of Metal Cations with 6,7,9,10,17,18,20,21-Octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexa-oxacyclo-octadecin (Dibenzo-18-crown-6) in Aqueous Solutions

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Aqueous stability constants for complex formation of dibenzo-18-crown-6 (dbc) with a series of metal ions have been determined spectrophotometrically by the solubility technique ($M^{n+} = Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, [NH_4]^+, Sr^{2+}, Ba^{2+}, Pb^{2+}$, and La^{3+}). The stability of the complexes is affected by changes in the ionic strength of the solutions and thermodynamic constants have been obtained by extrapolating the experimental values to infinite dilution. The monodissociated ion pairs $[BaCl]^+$ and $[SrCl]^+$ complex more strongly with dbc than the free ions Ba^{2+} and Sr^{2+}. The behaviour of dbc with bivalent metal ions is much more sensitive to their ionic size than in the case of univalent ions. This is explained on the basis of electrostatic considerations.

THE formation of complexes of macrocyclic polyethers with alkali-metal cations has been extensively investigated in recent years and comprehensive reviews of the subject are available.[1-4] Cations in such complexes are held principally by electrostatic forces, *i.e.* ion–dipole interactions,[5,6] and the equilibrium constants of complex formation are strongly affected by the solvent medium.[7,8] For aliphatic ' crown ' ethers the stability constants of their complexes in aqueous solutions have been determined by calorimetric titrations [9] or potentiometrically by using ion-selective electrodes.[10] However, for ' crown ' ether complexes in which aromatic rings adjoin the macrocylic polyether ring values of the aqueous stability constants are not yet available because of severe limitations imposed by the very low solubility of these compounds in water. The only attempts to evaluate the stability constants of their alkali-metal complexes in water were based on measurements in mixed solvents.[11]

In the present study the equilibrium constants of complex formation of dibenzo-18-crown-6 (dbc) † with several uni- and bivalent cations have been determined spectrophotometrically by the solubility technique, which is based on the observation that the solubility of the complexes in water is much higher than that of the parent macrocyclic ethers.

EXPERIMENTAL

Dibenzo-18-crown-6 (dbc) was prepared as described by Pedersen [5] (method X), recrystallised from benzene, purified by selective complex formation with K[SCN] in methanol,[12]

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† 6,7,9,10,17,18,20,21-Octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]-hexa-oxacyclo-octadecin.

[1] C. J. Pedersen and H. K. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16.

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[4] J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351.

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[10] H. K. Frensdorff, *J. Amer. Chem. Soc.*, 1971, **93**, 600.

[11] G. A. Rechnitz and E. Eyal, *Analyt. Chem.*, 1972, **44**, 370.

[12] E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Amer. Chem. Soc.*, 1971, **93**, 7133.

precipitated with water, and repeatedly rinsed with distilled water to remove all traces of K[SCN]. Finally it was recrystallized from pure dioxan.

Salt Solutions.—The salts LiCl, NaCl, KCl, RbCl, CsCl, $[NH_4]Cl$, HCl, $CaCl_2$, $SrCl_2$, $BaCl_2$, $CdCl_2$, $Na[NO_3]$, $K[NO_3]$, $Rb[NO_3]$, $Cs[NO_3]$, $Ag[NO_3]$, $Tl[NO_3]$, $Sr[NO_3]_2$, $Ba[NO_3]_2$, $Pb[NO_3]_2$, and $La[NO_3]_3$ (B.D.H., analytical grade) were used for the preparation of the aqueous solutions in the concentration range 0.02—1.0M. * Two identical solutions were independently prepared for each salt concentration. In order to eliminate any possible discrepancies due to small gravimetric or volumetric errors, their exact concentrations were also conductimetrically verified.

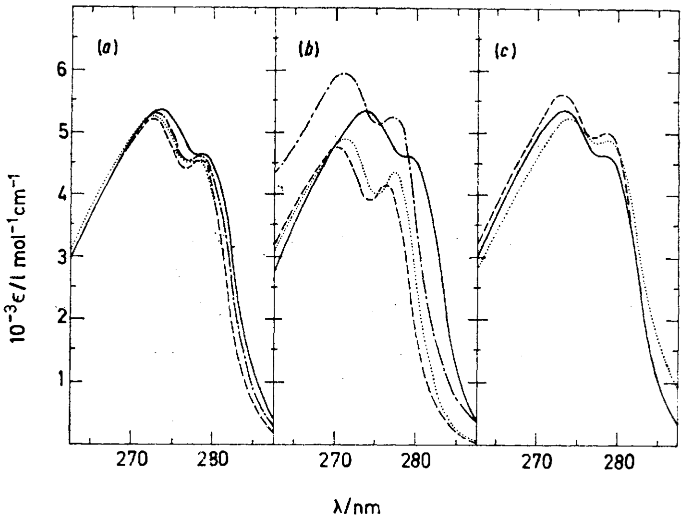

FIGURE 1 Optical-absorption spectra of dbc (——) and its ionic complexes in water: (*a*) K (— — —), Na and Rb (· · ·), and Cs (— · —); (*b*) Sr (— — —), Ba (· · ·), and Pb (— · —); and (*c*) Tl (– – –) and Ag (· · ·)

Solubility Measurements.—Aliquot portions (50 cm^3) of the investigated salt solutions or of distilled water were equilibrated at 25 ± 0.1 °C in the presence of CCl_4 (5 cm^3) and dbc (*ca*. 30 mg) in Erlenmayer flasks (100 cm^3, equipped with ground-joint stoppers). Under vigorous magnetic stirring the equilibration was complete within 4 h. Nevertheless, to avoid any small deviations from equilibrium, stirring was usually stopped after only 16 h, the CCl_4 layer and excess of dbc allowed to settle down, and the clear aqueous solution transferred by decantation into a 1 or 5 cm optical cell and inserted into a thermostatted cell holder of a Cary 15 spectrophotometer. The u.v. absorption spectrum of the solution was recorded against a reference cell containing the salt solution used for the equilibration. At least two independent experiments were conducted to verify each point. Optical densities observed in such parallel experiments were reproducible within 0.001—0.002 units.

Absorption Coefficients.—Aliquot portions (5 cm^3) of a 10^{-3}M solution of dbc in dioxan were diluted in volumetric flasks to 250—500 cm^3 with 1M solutions of the investigated chlorides, 0.2M solutions of the investigated nitrates, or with distilled water. 5 cm Optical cells were used for the determination of the absorbance of the solutions. Absorption coefficients of the complexes and of dbc in water, at the two maxima, were calculated by an iteration procedure in order to introduce small corrections due to incomplete complex formation of dbc.

RESULTS AND DISCUSSION

Spectral Data.—The u.v. absorption spectra of dbc and of its various complexes in water are shown in Figure 1. A small shift in the position of the absorption peak of dbc at 273 nm occurred on complexing with cations, and the absorption maximum at *ca*. 278 nm became more pronounced. Moreover, the intensity of the absorption band was affected by complex formation. The observed changes in the absorption of dbc due to its interaction with cations were not clearly correlated with the stability of the respective complexes. This is understandable since the observed changes reflect mainly deviations from planarity of the aromatic ring and of the oxygen atoms attached to it. The participation of the lone-pair electrons of these oxygen atoms in the resonance of the aromatic system is responsible for the high oscillator strength of such systems. Hence, the sensitivity of the aromatic α band to any small configurational changes.

Stability-constant Determinations.—The equilibrium constant of the complex-formation reaction between metal cations and dbc is given by equation (1) where

$$K = \frac{[M(dbc)]}{[M][dbc]} \cdot \frac{f_{M(dbc)}}{f_M f_{dbc}} \qquad (1)$$

[M(dbc)], [dbc], and [M] denote concentrations of the complex, dbc, and the metal cation and $f_{M(dbc)}$, f_{dbc}, and f_M their respective activity coefficients. In our experiments the initial concentrations of the cations were always several orders of magnitude higher than that of dbc; hence, their initial values and those at equilibrium were virtually identical. The concentration of dbc was kept constant at the saturation level and the concentration of the complex was calculated from the absorption spectrum after subtracting the absorption due to free dbc. It is essential to maintain the concentration of free dbc at the exact saturation level during the experiment. This was facilitated by equilibration of the samples in the presence of CCl_4 saturated with dbc. The solubility

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* 1M = 1 mol dm^{-3}.

of dbc in CCl_4 (5×10^{-3} mol l^{-1}) is much greater than in water (1.28×10^{-5} mol l^{-1}). Accordingly, CCl_4 can serve as a reservoir of dbc. The rate of saturation of the aqueous solution with dbc may be greatly increased when vigorous stirring produces a large water–CCl_4 interface. Indeed, under such conditions the equilibration process was shortened from several days to *ca.* 3—4 h. Moreover, CCl_4 also removes traces of impurities which may remain in the sample or be formed during the equilibration as result of very slow cleavage of the macrocyclic ring. Trace amounts of such impurities dissolved in water would contribute to the overall absorption and vitiate the results. The values of the pertinent activity coefficients must be known in order to calculate the equilibrium constant, K, from equation (1). However, the activity-coefficient term approaches unity in a system in which the activity of a neutral molecule, such as dbc, is not affected by changes in the ionic strength of the solution whereas the activities of the cations and their complexes are affected to the same extent. In such a system, $K_{\text{app.}}\{= [\text{M(dbc)}]/[\text{M}][\text{dbc}]\}$ would be virtually identical to K. Values of $K_{\text{app.}}$ were calculated from the relation $K_{\text{app.}} = (a - a_0)\varepsilon_{\text{dbc}}/[\text{M}]_0 a_0 \varepsilon_{\text{M(dbc)}}$ where a_0 and a denote the absorption of dbc in water and in the salt solution, $\varepsilon_{\text{M(dbc)}}$ and ε_{dbc} are the absorption coefficients of the complex and dbc, and $[\text{M}]_0$ is the initial salt concentration. Values computed from absorptions at 273 nm agreed to within 1—2% with those from absorptions at 278 nm.

TABLE 1

Values of $K_{\text{app.}}$ at various salt concentrations

	Chloride			Nitrate		
Cation	Concentration mol l^{-1}	No. of samples (n)	$K_{\text{app.}} \pm (\sigma/n^{\frac{1}{2}})$ l mol^{-1}	Concentration mol l^{-1}	No. of samples (n)	$K_{\text{app.}} \pm (\sigma/n^{\frac{1}{2}})$ l mol^{-1}
Na$^+$	0.04	4	14.0 ± 1.0	0.04	2	14.7 ± 0.5 *
	0.08	4	14.3 ± 0.2	0.08	2	14.9 ± 0.4 *
	0.10	5	13.5 ± 1.1	0.10	3	14.7 ± 0.4 *
K$^+$	0.04	4	45.3 ± 0.5	0.04	4	47.4 ± 0.6
	0.10	4	44.2 ± 0.4	0.08	4	48.1 ± 0.1
	0.20	4	41.5 ± 0.20	0.10	5	49.0 ± 0.4
	0.50	3	37.5 ± 1.1	0.20	6	50.0 ± 0.1
	1.0	3	26.7 ± 0.1	0.50	4	50.3 ± 0.3
				1.0	4	15.6 ± 0.3
Rb$^+$	0.05	2	11.2 ± 0.1 *			
	0.075	2	11.5 ± 0.5 *			
	0.10	2	9.8 ± 0.4 *			
Cs$^+$	0.1	4	6.3 ± 0.3	0.1	4	6.5 ± 0.2
	0.5	2	4.9 ± 0.3 *			
Ag$^+$				0.05	5	24.0 ± 0.5
				0.10	5	27.4 ± 0.6
[NH$_4$]$^+$	0.2	2	1.6 ± 0.5 *			
	0.5	2	1.5 ± 0.2 *			
Tl$^+$				0.05	2	30.0 ± 0.6 *
				0.10	5	30.4 ± 0.4
				0.20	2	26.8 ± 0.5 *
Sr^{2+}	0.1	3	8.8 ± 0.6	0.1	2	11.4 ± 1.5 *
	1.0	2	10.7 ± 0.5 *			
Ba^{2+}	0.02	2	92.0 ± 0 0.*			
	0.04	2	92.0 ± 0.0 *	0.05	2	105.0 ± 1.0
	0.1	7	94.5 ± 0.6			
	0.2	5	91.6 ± 0.7			
	0.5	5	92.7 ± 0.9			
	1.0	5	85.5 ± 1.2			
Pb^{2+}				0.02	2	74.5 ± 0.0 *
				0.05	2	79.0 ± 1.5 *

*Average deviation.

It is evident from Table 1 that $K_{\text{app.}}$ depends on the counter ion and on the ionic strength of the solution. The derivation of true equilibrium constants must, therefore, be based on extrapolation of the experimental results to infinite dilution. Semi-logarithmic plots of $K_{\text{app.}}$ against $I^{\frac{1}{2}}$ and of $K_{\text{app.}}$ against molality, m, were reasonably linear for fairly dilute solutions. The use of the latter plot seems however, to be more justified. Effects due to changes in activity of the ionic species should nearly cancel at the lower concentration range and effects due to salting out or salting in of dbc * must be considered in order to account for the observed changes. An exponential dependence of the solubility of neutral species on the molality of the electrolyte was suggested by Setchenow.[13] Accordingly, one may expect a proportionality between log $K_{\text{app.}}$ and molality. Indeed, the semilogarithmic plot of $K_{\text{app.}}$ against m in Figure 2 is linear up to 0.5 mol kg^{-1} of KCl. In the case of K[NO$_3$], a linear dependence was only maintained in the 0.04—0.1 mol kg^{-1} range. The gradients of these two lines are opposite in sign and the lines converge † at the

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* The presence of an electrolyte may affect the solubility of free dbc. However, computations of $K_{\text{app.}}$ were based on the saturation concentration of dbc in water.

† Uncertainties in the extrapolation derived with $(\Sigma\sigma^2/n)^{1/2}$ are ±1.4% for KCl and ±1.8% for K[NO$_3$].

[13] G. N. Lewis and M. Randall, ' Thermodynamics,' revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961, p. 584.

ordinate. Their common intercept yields $K(K^+) = 46.6 \pm 0.8$ mol l^{-1}. Values of the equilibrium constants, K, for other alkali-metal cations were similarly obtained.

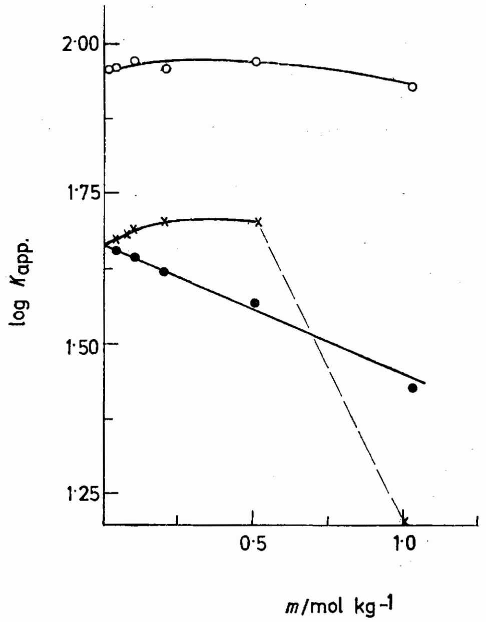

FIGURE 2 Plots of log $K_{app.}$ against molality for (●), KCl, (■), $K[NO_3]$, and (○), $BaCl_2$ solutions

The extrapolated results, together with values from the literature for other ' crown ' ethers, are summarized in Table 2.

TABLE 2

Complex formation constants in water at 25 °C for the 18-crown-6 ethers

Cation	Ionic radius (Å)	K/l mol^{-1}				
		dbc	Dicyclohexyl-18-crown-6 [a]		Cyclohexyl-18-crown-6 [b]	18-crown-6 [b]
			Isomer A	Isomer B		
Li^+	0.68	<1	4		<5	
Na^+	0.97	14.6 ± 1.0	30—70	15—40	6.3	<2
Ag^+	1.26	26 ± 2.0 [c]	170	63	50—80	40
K^+	1.33	46.5 ± 0.8	150	60	80	112
Rb^+	1.47	12.0 ± 1.1	33	7.6		
Tl^+	1.47	31.8 ± 1.3	290	70		
Cs^+	1.67	6.8 ± 0.8	18	8	6.3	6.3
$[NH_4]^+$	1.43	*ca.* 2	25	6.3	12.5	12.5
Ca^{2+}	0.99	<1	1	*ca.* 1		
Sr^{2+}	1.12	10 ± 1.5 [d]	1 750	430		
Ba^{2+}	1.34	*ca.* 90	3 700	1 900		
$[BaCl]^+$		*ca.* 140				
Pb^{2+}	1.20	77 ± 2.5 [e]	9 500	28 000		
La^{3+}	1.14	<1				

[a] From refs. 9 and 10. [b] From ref. 10. [c] $K_{app.}$ in 0.05—0.1M-$Ag[NO_3]$. [d] $K_{app.}$ in 0.1—1.0M-$SrCl_2$. [e] $K_{app.}$ in 0.02—0.05M-$Pb[NO_3]_2$.

Interestingly, the affinities of dbc towards alkali-metal cations are similar to those of its aliphatic analogues. Complex formation of dbc with protons was too small to be measured and no indication was obtained for the formation of Co^{2+} and Cd^{2+} complexes. The values of $K(K^+)$ and $K(Rb^+)$ are of the same order of magnitude as those estimated by Rechnitz and Ayal[11] on the basis of their measurements in water—tetrahydrofuran mixtures. These investigators assumed that, providing sufficient water is present to meet the hydration requirements of the ions involved, the complex-formation equilibria in the solvent mixture and pure water will be identical. Such an assumption may be, of course, used only as an approximation, especially since the presence of the organic solvent may affect the extent of ion association in the solution. The value of $K([NH_4]^+)$ is much smaller than that of $K(Rb^+)$, though their ionic radii are very similar. The low value of $K([NH_4]^+)$ may be due to the dispersion of charge between the four hydrogen atoms of $[NH_4]^+$, which will hinder its interaction with the polyether ring.[14] The affinity of $[NH_4]^+$ towards aliphatic analogues of dbc does not show, however, such a deviation. Apparently the ether oxygen atoms of these more flexible rings may adjust to the special requirements of the tetrahedral ion.

Complex Formation of $BaCl_2$ *with* dbc.—As may be seen from Figure 2, the plot of $K_{app.}$ for the barium complex against molality differs from that obtained for the KCl system, *i.e.* a broad maximum is noted at 0.1—0.5 mol kg^{-1}. Strontium(II) seems to behave in a similar fashion. At first glance, such behaviour of the bivalent metal salts could be attributed to a very small salting-in effect in conjunction with some other small effects at higher concentrations. However, this did not seem to be very plausible in view of the strong salting out of dbc caused by the addition of the non-complexing $CaCl_2$. An alternative scheme, which accounts for the experimental results, is based on the assumption that two different complex-formation reactions occur simultaneously, namely with free Ba^{2+} ions and with $[BaCl]^+$ ion pairs. Indeed, one can calculate from the association constant (log $K_{ass.}$ −0.13) reported in the literature[15] that only at high dilutions will the univalent ion pair $[BaCl]^+$ dissociate completely into Ba^{2+} and Cl^-.

Experiments in which various amounts of HCl were

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[14] P. B. Chock, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 1939.

[15] G. McDougall and C. W. Davies, *J. Chem. Soc.*, 1935, 1416.

added to the $BaCl_2$ solutions were conducted in order to check this hypothesis. Protonation of dbc is negligible and a salting-in effect was not observed when dbc was dissolved in 0.2—1.0M-HCl solutions. Thus addition of HCl provides a simple way of following effects due to a shift to the right of equilibrium (2). Results of such

$$Ba^{2+} + Cl^- \rightleftharpoons [BaCl]^+ \qquad (2)$$

experiments (Table 3) demonstrate that $K_{app.}$ increases significantly with increasing concentration of HCl in $BaCl_2$ solutions. From equations (3)—(6) one can derive (7). Gradients of plots of $K_{app.}[BaCl_2]_0$ against

$$Ba^{2+} + dbc \overset{K'}{\rightleftharpoons} [Ba(dbc)]^{2+} \text{ (I)} \qquad (3)$$

$$[BaCl]^+ + dbc \overset{K''}{\rightleftharpoons} BaCl(dbc)]^+ \text{ (II)} \qquad (4)$$

$$[Ba^{2+}]_e + [BaCl^+]_e = [BaCl_2]_0 \qquad (5)$$

$$BaCl_2 + dbc \overset{K_{app.}}{\rightleftharpoons} \text{(I)} + \text{(II)} \qquad (6)$$

$$K_{app}[BaCl_2]_0 = K'[BaCl_2]_0 + (K'' - K')[BaCl^+] \qquad (7)$$

$[BaCl^+]$ at constant $[BaCl_2]_0$ should yield $(K'' - K')$ and their intercepts divided by $[BaCl_2]_0$ should yield K'. It must be noted that extrapolation to infinite dilution is still required to convert the thus derived K' and K'' into true equilibrium constants.

TABLE 3

Values of $K_{app.}$ (l mol^{-1}) for $BaCl_2$–dbc complexes at various HCl concentrations

[HCl]/M	0	0.2	0.6	1.0		
		$K_{app.} \pm (\sigma/n^{\frac{1}{2}})$			K'	K''
$[BaCl_2]_0 = 0.453$M	92.0 ± 0.5	97.5 ± 3.5	108 ± 2	123 ± 6	83.9	133
$[BaCl_2]_0 = 0.10$M	94.5 ± 0.6	99.0 ± 1.8	116 ± 2	132 ± 6	81.0	146.6

A value of $K_{ass.} = 0.74$ l mol^{-1} cited in the literature[15] was used for the calculation of $[BaCl^+]$ at various HCl concentrations. (The concentration of the neutral ion pairs, $BaCl_2$, was assumed to be negligible.) Values of K' and K'' derived from the plots in Figure 3 are in Table 3. The agreement of the experimental results with those predicted by equation (7) is very satisfactory * and seems to provide convincing evidence that the assumptions underlying its derivation are correct. The broad maximum in the $BaCl_2$ curve in Figure 2 may thus be attributed to compensating effects due to changes in ionic association and salting out.

The fact that complex formation of dbc with the univalent $[BaCl]^+$ ion pair is favoured over that with Ba^{2+} ions calls for some comment. The ion–dipole interactions responsible for the complex-formation reaction with dbc are undoubtedly weaker in the case of the univalent ion pair $[BaCl]^+$ than the bivalent Ba^{2+}. Nevertheless, the former species seem to be favoured. This apparently must be attributed to their weaker hydration (complex formation involves replacement of water molecules by dbc). A different net effect can be anticipated in some cases, *e.g.* when neutral ion pairs compete with free ions. The sharp decrease of $K_{app.}$ for potassium in 1M-$K[NO_3]$ (*cf.* Figure 2) is perhaps such a situation.

Barely Soluble Complexes.—The present method is based on the assumption that the solubility of complexed dbc is higher, or at least comparable, to that of free dbc. This assumption is not always true. The solubility in water of complexes of dbc with $HgCl_2$ and $Hg[ClO_4]_2$ was very low and in their presence dbc was completely removed from the solution. Lead(II) nitrate yielded a more soluble complex (*ca.* 5×10^{-5} mol l^{-1}) and the value of $K(Pb^{2+})$ was estimated on the basis of experiments in which low concentrations of this salt (<0.05M) were used and the saturation point had not been attained. A similar limitation applies to the $Ba[NO_3]_2$ complex, whose solubility in water was also *ca.* 5×10^{-5} mol l^{-1}.

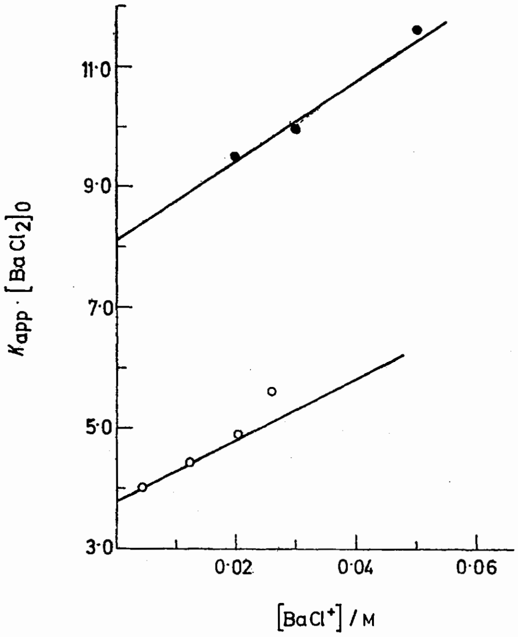

FIGURE 3 $K_{app.}[BaCl_2]_0$ as function of the calculated $[BaCl^+]$ in the HCl solutions: $[BaCl_2]_0 = 0.0456$ (○) and 0.10M (●)

Selectivity of dbc.—It is evident from the semilogarithmetic plot of K against r in Figure 4 that the dependence of the stability constants of the complexes on their ionic radii is much more pronounced for the bi- than for the uni-valent ions. A similar phenomenon was also noted for the aliphatic 'crown' ethers[9] and for the

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* Concentrations of the ionic species instead of their activities in the mixed solutions were used in the computations of $[BaCl^+]$.

cryptates.[16] Such behaviour is due to the fact that the free energy of complex formation in water, $-\Delta F_{M(dbc)}$, is given by the difference between the free energies of the complex and of the hydrated ions (both large numbers). The thermodynamic consequences are illustrated in Figure 5. For the hydrated ion (II) the gradient is *ca.* 4 times steeper than that of (I) (because the free energy of hydration is proportional to e^2/r). On the other hand, the positions of the dipoles in the macrocyclic rings are essentially fixed in space with respect to the centre of the complexed ion. Thus, for a point-charge model, the electrostatic ion–dipole interactions in the complex should be independent of the ionic radius, providing it can be accommodated within the ring (up to r_M in Figure 5). For real ions such an approximation does not hold true, but nevertheless the effect of ionic size must be rather small. This is particularly true for the bivalent ions because of their higher charge density. In consequence, values of $\Delta F_{M(dbc)}$ for univalent ions will become negative at a broader range of ionic radii than for the bivalent ions, while at r_M the value of the free energy for (II) is greater than that for (I). Thus, $K(Ba^{2+}) > K(K^+)$, but $K(Ca^{2+}) < K(Na^+)$.

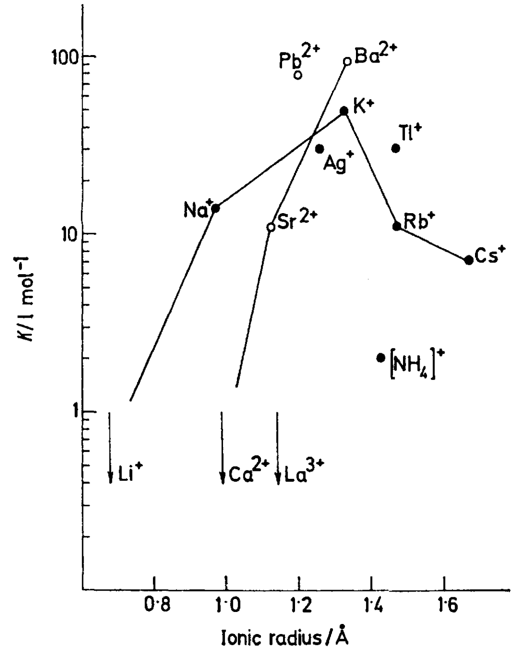

FIGURE 4 Equilibrium constants of complex formation in water as a function of ionic radius

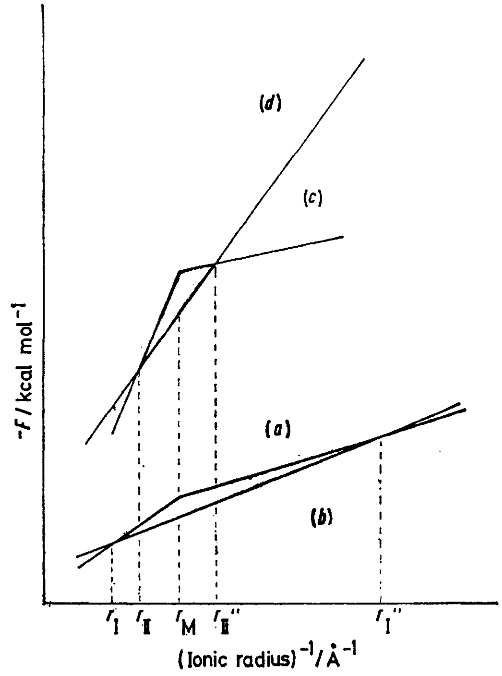

FIGURE 5 Representation of free energies of ions as a function of the ionic radius: (*a*) and (*c*), complexed (I) and (II); (*b*) and (*d*), hydrated (I) and (II)

This type of behaviour should be even more pronounced for tri- than for bi-valent ions. Indeed, no complex formation of dbc with La^{3+} was detected in water, though its ionic radius (1.14 Å) is about the same as for Sr^{2+} (1.12 Å). In organic solvents, complexes of lanthanoids with dbc were observed.[17] Strong complexing in water of some of the lanthanoids (ionic radii from 0.9 to 1.14 Å) may be expected for smaller 'crown' ethers (*e.g.* 15-crown-5). This proposition will be the object of a separate investigation.

[4/1853 *Received, 10th September,* 1974]

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[16] B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Letters*, 1969, 2889; C. Kappenstein, *Bull. Soc. chim. France*, 1974, 89.

[17] A. Cassol, A. Seminaro, and G. Depaoli, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1163; R. B. King and P. R. Heckley, *J. Amer. Chem. Soc.*, 1974, **96**, 3118.