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Association of Alkali and Alkaline Earth Cations with Benzo-18-crown-6 and Its Neutral and Negatively Charged Acyclic Analogues in Methanol Solution

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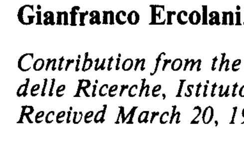
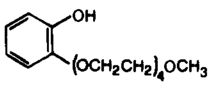
Abstract: The effect of added alkali (Li, Na, K, Rb, and Cs) and alkaline earth (Ca, Sr, and Ba) metal bromides on the acid dissociation of *o*-hydroxyphenyl 3,6,9,12-tetraoxatridecyl ether (ArOH) in MeOH at 25 °C has been investigated spectrophotometrically over a wide range of salt concentration. Except for the Li ion, all the investigated salts increased significantly the apparent acidity of ArOH in a way that could be accounted for by the formation of 1:1 addition compounds of the metal cations with both ArOH and its conjugate base ArO^-. A proper analysis of the experimental data yielded the equilibrium constants for the formation of the associated species. Complexation of the given cations by benzo-18-crown-6 (C) was also studied spectrophotometrically under the same conditions. The set of equilibrium constants here reported constitute a proper basis for a systematic discussion of the ligation properties of sexadentate ligands with oxygen donors belonging to different structural types. The cyclic ligand C binds the cations more strongly than does its open-chain analogue ArOH. The magnitude of the macrocyclic effect is found to be mainly determined by the size of the cation, rather than by its charge. On the other hand, the advantage of the anionic ligand ArO^- over ArOH is highly sensitive to the charge of the cation with little or no dependence upon its size. This suggests that direct contact between the oxide ion and the cation is lacking in the ArO^-M^{z+} species.

In recent work[1] on the template effect of alkali and alkaline earth cations (M^{z+}) on the formation of benzo-18-crown-6 (C) in methanol solution (eq 1), we have obtained evidence for the existence of strong interactions between M^{z+} and the conjugate base of the crown's precursor. In order to evaluate the strength of such interactions we have synthesized the model compound ArOH, in which the reactive CH_2Br end group has been replaced by hydrogen, which is incapable of ring closure. We make the reasonable assumption that the ligation properties are not significantly altered by this structural change. A quantitative study of the effect of M^{z+} on the apparent acidity of ArOH in methanol solution at 25 °C led to the determination of the equilibrium constants of interaction of M^{z+} not only with the anionic ligand ArO^-, but also with the neutral parent compound ArOH. The results of this investigation are now reported, together with the spectrophotometric determination of the equilibrium constants for complex formation of M^{z+} with the macrocyclic ligand C. This work was undertaken with the idea that a systematic comparison of the ligation properties of cyclic vs. acyclic and anionic vs. neutral ligands for several cations would provide better insight into the coordination chemistry of alkali and alkaline earth cations by polyoxygen species.[2]



C

(1)



ArOH

Results

Acyclic Ligands. In order to study the acid dissociation equilibrium of ArOH in methanol, the ratio *I* of the concentration of the base form to that of the acid form was determined spectrophotometrically at increasingly greater concentrations of tetraethylammonium methoxide. Since complete conversion of ArOH to its base form could not be obtained even at the highest base concentrations employed, the specific molar absorbance value was obtained by extrapolation of the apparent ϵ value to infinite methoxide concentration (see Experimental Section). Measurements of the intensity of absorption due to increase of the base form after each addition of titrant were carried out at 296 nm, where the absorption of the acid form is negligible. The results are reported in Figure 1. The excellent linearity of plot A in Figure 1 shows that the concentration equilibrium constant $K = I/[MeO^-]$, which is given by the slope of the line, is independent of base concentration. This indicates an exact cancellation in the ratio of activity coefficients $\gamma_{ArO^-}/\gamma_{MeO^-}$. Remembering that $K = K_a/K_{MeOH}$ and using the literature value[3] of 1.21×10^{-17} for the autoprotolysis of MeOH at 25 °C, a K_a value of 1.1×10^{-15} (pK_a 14.96) is calculated for ArOH.

Although both the shape of the spectrum and the intensity of absorption for the base form of ArOH are unaffected by the presence of the bromides of the alkali cations, the apparent acidity of ArOH is significantly increased by the presence of the above salts, with the exception of the lithium salt. This behavior is illustrated for KBr in Figure 1 (plot B). Sodium, rubidium, and cesium ions provide similar behavior. The ratio of the slope of the line obtained in the presence of added salt over that obtained in its absence is a measure of the increase of apparent acidity (K_{rel}) of ArOH brought out by the added salt. This ratio is clearly independent of base concentration. In order to probe the salt concentration dependence we measured the *I* ratio as a function of salt concentration at constant tetraethylammonium methoxide concentration. K_{rel} values were calculated as the ratio of the quantity *I* measured in the presence of added salt over that measured in its absence. Except from lithium bromide, the de-

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(1) Ercolani, G.; Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1981**, *103*, 2780.

(2) For a comprehensive review on the subject see: Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389.

(3) Koskikallio, J. *Suom. Kemistil.* **1957**, *30*, 111.

(4) See, for instance: Gordon, J. E. "The Organic Chemistry of Electrolyte Solutions"; Wiley: New York, 1975; p 38.

(5) Rochester, C. H.; Rossall, B. *J. Chem. Soc. B* **1967**, 743.

(6) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925.

(7) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In "Coordination Chemistry of Macrocyclic Compounds", Melson, G. A., Ed.; Plenum Press: New York, 1979.

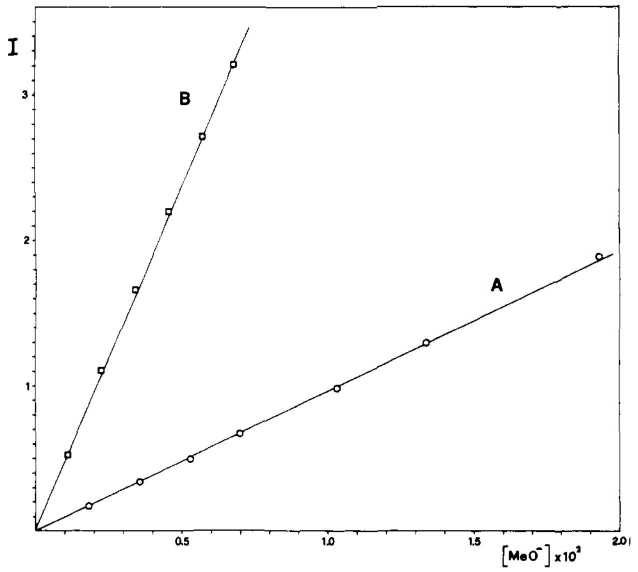
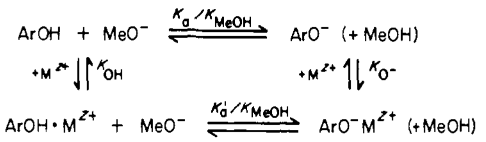


Figure 1. Ionization of ArOH as a function of Et_4NOMe concentration. Plot A: without any added salt. Plot B: in the presence of 4.11×10^{-2} M KBr.

Scheme I



pendence of K_{rel} on salt concentration was well described by the equation

$$K_{rel} = \frac{1 + a[\text{salt}]}{1 + b[\text{salt}]} \qquad (2)$$

where the parameters a and b are a function of the alkali bromide. Numerical values of the parameters were evaluated by a least-squares treatment of the quantity $(K_{rel} - 1)/[\text{salt}]$ vs. K_{rel}, according to eq 3, into which eq 2 can be transformed. How closely eq 2 reproduces the experimental data is shown graphically by the full lines drawn in Figure 2.

$$(K_{rel} - 1)/[\text{salt}] = a - bK_{rel} \qquad (3)$$

The relation between K_{rel} and salt concentration can be rationalized by assuming a 1:1 association of the alkali cations with both ArOH and ArO^-, according to Scheme I where K_{OH} and K_{O^-} are the equilibrium constants for association of the cation with the neutral and negatively charged ligand, respectively, and K_a' is the acidity constant of the cation associated form. From the definition of K_{rel} and from Scheme I one obtains eq 4, where $\gamma_\pm$

$$K_{rel} = \frac{1 + K_{O^-}\gamma_\pm^2[M^+]}{1 + K_{OH}[M^+]} \qquad (4)$$

is the mean ionic activity coefficient. Equation 4 is based on the assumption that coefficients of neutral species are unity, and that $\gamma_{ArOH \cdot M^+} = \gamma_{M^+}$. It is immediately apparent that eq 2 and 4 are coincident if $K_{OH} = b$ and $K_{O^-}\gamma_\pm^2 = a$. Strictly speaking, the term $K_{O^-}\gamma_\pm^2$ is not a constant. In one set of equilibrium experiments the ionic strength varied from above 0.005 to 0.02 M, and in the other one from about 0.01 to 0.025 M. Therefore, the a parameter is a sort of mean concentration equilibrium constant for association of a given cation with the anionic ligand, averaged by the least-squares treatment over the given ranges of ionic strength. In order to evaluate the thermodynamic K_{O^-} values, eq 4 can be rearranged into the linear form

$$(1 + K_{OH}[M^+])K_{rel} = 1 + K_{O^-}\gamma_\pm^2[M^+] \qquad (5)$$

K_{O^-} values were determined as the least-squares slopes of plots

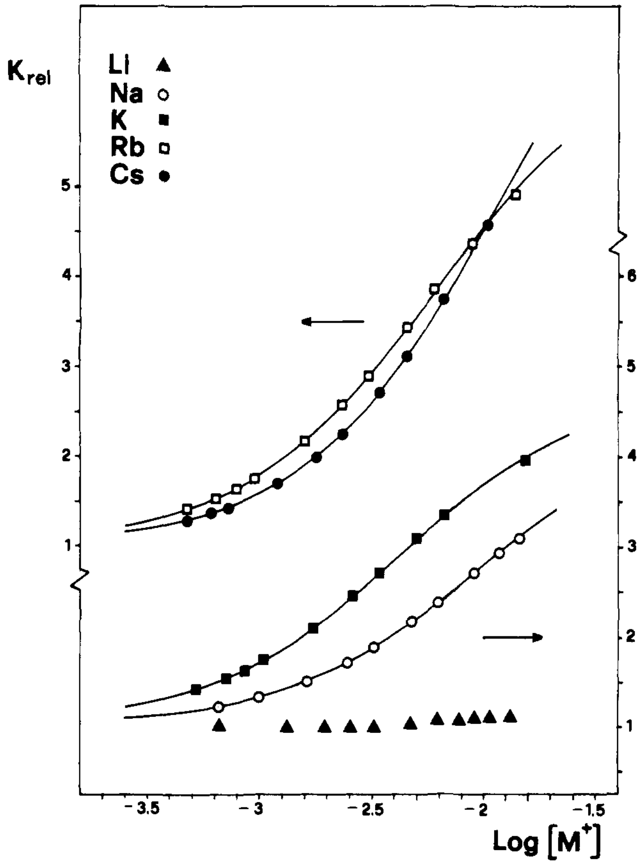


Figure 2. Effect of the alkali bromides on the apparent acidity of ArOH. The points are experimental and the lines are plots of eq 2.

of the quantity on the left (calculated from the experimental data by assuming $K_{OH} = b$) against $\gamma_\pm^2[M^+]$ ($\gamma_\pm^2$ being given by the Debye–Hückel equation adapted to methanol at 25 °C with a value of 6 Å for the adjustable parameter[4]). In all cases the linearity of the plots was good, with correlation coefficients not less than 0.997. The equilibrium constants are listed in Table I.

At 0.01 M LiBr concentration K_{rel} is only 10% greater than unity which prohibits the assignment of even rough numerical values to K_{O^-} and K_{OH} for lithium. Strictly speaking if $K_{O^-} \approx K_{OH}$ there will be little or no effect on K_{rel} even if K_{O^-} and K_{OH} are very large. However, we believe it more reasonable to conclude that association of lithium ion with both ArOH and ArO^- is too weak to measure under our experimental conditions. This conclusion is consistent with the absence of a significant rate-enhancing effect of 0.05 M LiBr on reaction 1.[1]

Equilibrium measurements with added Ca, Sr, and Ba bromides required a special technique because association with ArO^- is so strong that in their presence neutralization of ArOH by MeO^- is virtually complete. We found the ratio I to be conveniently measurable in a 0.04 M triethylamine/triethylammonium bromide buffer over a wide concentration range of added salts. At zero salt concentration the ratio I was too small for direct measurement. This problem was circumvented by means of an indicator method, which was based on the observation that in the buffer solution an I value of 1.165 for p-nitrophenol (PNPH) could be directly measured. Since the ratio of activity coefficients of compounds of similar structure and charge should be unity to a good approximation in the presence of the same hydrogen ion activity, the following relation holds

$$I^{\text{ArOH}} = \frac{K_a^{\text{ArOH}}}{K_a^{\text{PNPH}}} I^{\text{PNPH}} \qquad (6)$$

from which, using the literature[5] value of 3.16×10^{-12} for K_a^{PNPH}, an I ratio of 4.17×10^{-4} was calculated for ArOH. The experimental data were found to be well correlated by eq 2 (Figure 3), which indicates that interaction of alkaline earth cations with the

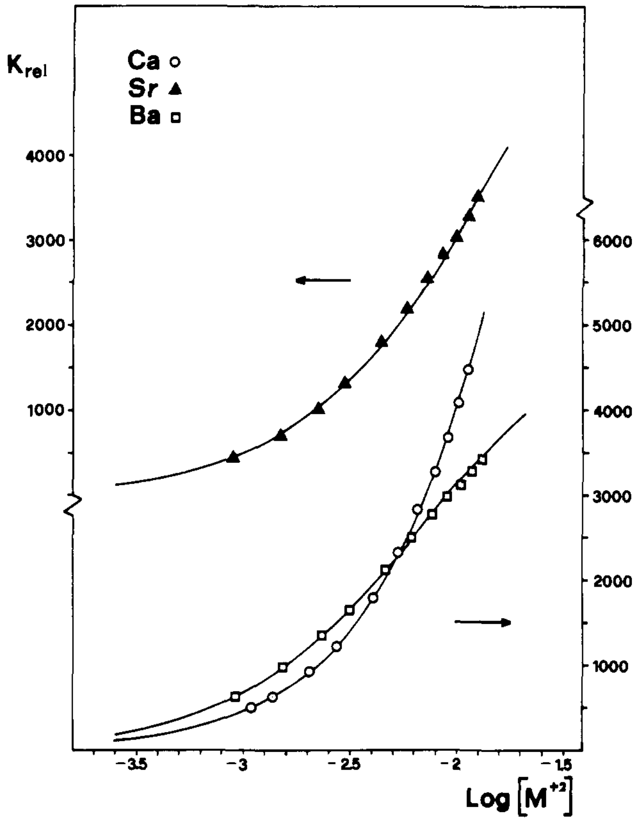


Figure 3. Effect of the alkaline earth bromides on the apparent acidity of ArOH. The points are experimental and the lines are plots of eq 2.

ArOH–ArO$^-$ pair also conforms to Scheme I. It is worth noting that eq 4 does not take into account any possible association of M^{2+} with bromide ion to give positively charged pairs MBr^+. The absence of such complication is further substantiated by the finding that the equilibrium constants for interaction of M^{2+} with the cyclic ligand C are not significantly altered by the presence of the 0.04 M triethylamine–triethylammonium bromide buffer (Experimental Section). Allowance for non-ideal behavior of ionic species leads to an expression for K_{rel}, which differs from eq 4 and its equivalent form of eq 5 solely by the presence of $\gamma_{M^{2+}}$ in place of $\gamma_{\pm}^2$. A least-squares treatment of the experimental data (with $\gamma_{M^{2+}}$ being given by the Debye–Hückel equation) afforded the thermodynamic K_{O^-} values (Table I) with correlation coefficients not less than 0.9985.

Cyclic Ligand. With the sole exception of lithium bromide, which apparently does not interact with C, addition of the alkali and alkaline earth bromides caused small, but measurable, changes of the UV spectrum of C in MeOH solution. In all cases the absorbance changes were found to closely fit the equation

$$(A - A_0)/(A_\infty - A) = K_C[\text{salt}] \qquad (7)$$

where A is the absorbance reading after each addition of the salt, A_0 is the absorbance due to the ligand alone, and A_∞ is the limiting value at high salt concentrations. Equation 7 is consistent with a 1:1 association between C and the cation, whose equilibrium constant $K_C = [CM^{z+}]/[M^{z+}][C]$ is given by the least-squares slope of eq 7. No correction for non-ideal behavior was required because extensive cancellation in the ratio $\gamma_{CM^{z+}}/\gamma_{M^{z+}}$ is likely.

Discussion

K_C, K_{OH}, and K_{O^-} values for the association in methanol at 25 °C of alkali and alkaline earth cations with the multidentate ligands C, ArOH, and ArO$^-$, respectively, are summarized in Table I and plotted in Figure 4 against ionic radii from crystallographic data.[6] These results provide insight into the influence on cation binding of the two fundamental multidentate ligand structural features, namely (1) its being a cyclic molecule and (2) its being an anion. These features will be discussed under separate headings.

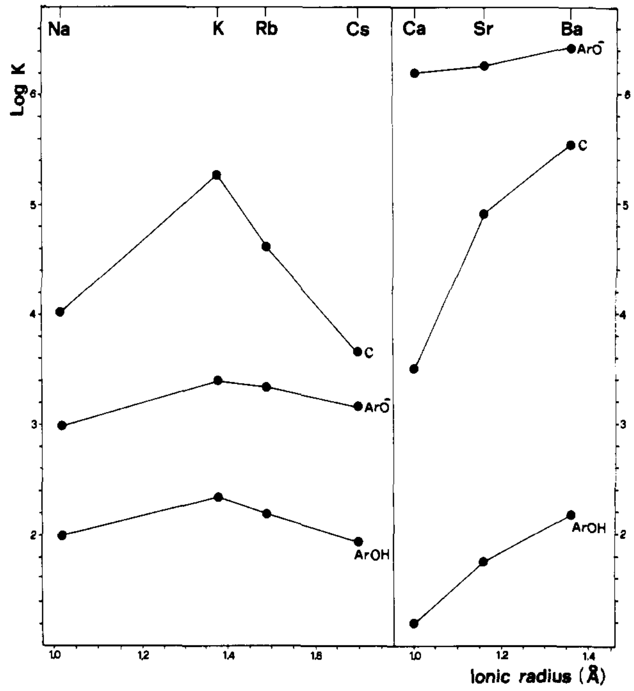


Figure 4. Association of C, ArOH, and ArO$^-$ with alkali and alkaline earth cations.

Table I. Log K Values[a] for Association of C, ArOH, and ArO$^-$ with Alkali and Alkaline Earth Cations in Methanol at 25.0 °C

	log K_C	log K_{OH}	log K_{O^-}	log (K_C/K_{OH})	log (K_{O^-}/K_{OH})
Na^+	4.03	2.00[c]	2.99	2.03	0.99
K^+	5.27[b]	2.34[c]	3.40	2.93	1.06
Rb^+	4.62	2.19	3.34	2.43	1.15
Cs^+	3.66	1.93	3.15	1.73	1.22
Ca^{2+}	3.50	1.20	6.20	2.29	4.99
Sr^{2+}	4.92	1.86	6.26	3.05	4.40
Ba^{2+}	5.35	2.18	6.43	3.18	4.25

[a] Error limits for the log K values can be estimated to be in the range of ±0.02–0.05 for the alkali cations and ±0.04–0.08 for the alkaline earth cations. [b] This value can be compared with the value of 5.20 determined at 22 °C by a polarographic method (Hofmanova, A.; Koryta, J.; Brezina, M.; Mittal, M. L. *Inorg. Chim. Acta* 1978, *28*, 73). [c] These values compare fairly well with the values of 2.19 (Na^+) and 2.08 (K^+) determined by a potentiometric technique under the same conditions.[9]

Acyclic vs. Cyclic Ligand. The data in Table I show that the cyclic polyether interacts about two to three powers of ten more strongly than its acyclic neutral analogue with all cations studied. The magnitude of this macrocyclic effect[2,7] is given by the log (K_C/K_{OH}) values in Table I. For the alkali and alkaline earth cations the effect is a maximum with potassium and barium, respectively. Thus, within each series the advantage of cyclic over acyclic ligand is at a maximum for those cations whose ionic radius is such as to give the best fit[7,8] to the cavity size of the macrocycle. Furthermore, pairs of cations of different charge but like size, namely Na^+ and Ca^{2+} on the one hand and K^+ and Ba^{2+} on the other, show effects whose magnitude differs by less than a factor of 2. We therefore conclude that the macrocyclic effect is determined more by the size of the cation than by its charge.

Another important observation is that the order of complex stability for the two ligands follows the same trends with both the

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(8) Lamb, J. D.; Izzatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475.

(9) Chaput, G.; Jeminet, G.; Juillard, J. *Can. J. Chem.* **1975**, *53*, 224.

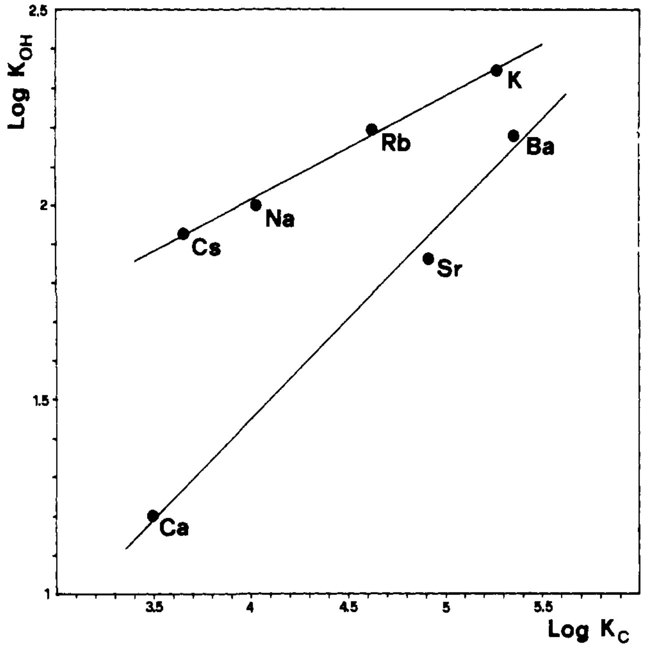


Figure 5. Ligation properties of open chain vs. cyclic sexadentate ligand: log K_{OH} vs. log K_C for complexes with the alkali and alkaline earth cations.

monovalent and divalent cations (Figure 4). This finding is given quantitative expression in the form of a linear free-energy relationship, namely

$$\log K_{OH} = \text{constant} + m \log K_C \tag{8}$$

with an m value of 0.26 for the alkali cations and of 0.51 for the alkaline earth cations (Figure 5). This means that the selectivity of the cyclic ligand compared to that of the acyclic one is considerably greater for alkali than alkaline earth cations. Since the fit of the cation into the macrocycle cavity is a well-recognized factor in determining complex stability,[7,8] it is not surprising that the cyclic ligand is more selective than the acyclic one. What is less easily understood is the greater selectivity of the cyclic ligand toward the monovalent than divalent cations.

We believe it unlikely that such free-energy correlations will be of general applicability in the coordination chemistry of alkali and alkaline earth cations with multidentate ligands. In fact, literature data indicate that whereas the stability of complexes with tetra-, penta-, hexa-, and heptaglyme[9] in MeOH solution decreases in the same order K > Cs > Na irrespective of the number of oxygens in the ligand, different orders are observed for the stability of complexes with 15-crown-5 and 21-crown-7.[8]

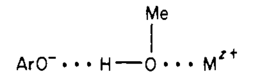
Neutral vs. Negatively Charged Ligand. Table I shows that ArO^- invariably binds cations more strongly than ArOH does, and that the advantage of the former over the latter is much greater with the divalent cations. This is consistent with expectations, since Coulombic interaction of the negative charge of the ligand with the cation is expected to provide an additional driving force for association, and the driving force should be greater with a doubly charged cation. The log (K_{O^-}/K_{OH}) values (Table I), which are the log K values for transfer of a cation from the neutral to the anionic ligand (eq 9), provide a rough measure of the Coulombic effect. However, solvation may also play an important role.

$$\text{ArOH}\cdot\text{M}^{z+} + \text{ArO}^- \xrightleftharpoons{K_{O^-}/K_{OH}} \text{ArO}^-\text{M}^{z+} + \text{ArOH} \tag{9}$$

For the alkali cations, the stabilities of ArO^-M^+ are greater than those of $ArOH\cdot M^+$ by about one power of ten. The two sets of data are roughly parallel (Figure 4) and log (K_{O^-}/K_{OH}) shows only slight cation dependence (Table I). In fact, the small monotonic drop of log (K_{O^-}/K_{OH}) from Cs to Na is just opposite of what would be predicted by the simple consideration that the electrical field in the immediate surroundings of a small ion is more intense than that in the surroundings of a large ion. It is therefore concluded that although Coulombic interaction is an easily recognizable and significant factor, the major driving force for association between ArO^- and the alkali cations is provided by multichelate coordination with the ether oxygens.[10] This is also consistent with the earlier observation[1] that guaiacolate ion, which lacks the polyether side chain, does not appreciably associate with the alkali cations in methanol solution.

The data obtained for the alkaline earth cations show that ArO^- binds these ions four to five orders of magnitude more strongly than does ArOH. Thus, for a divalent cation both coordination with the ether oxygens and cation–anion interaction are significant in determining complex stability with ArO^-. The apparent insensitivity of the stability of ArO^-M^{2+} to the identity of M^{2+} results from the fact that these two factors grade regularly from Ca to Ba, but with opposite trends.

Concerning the structure of ArO^-M^{z+}, contact ion pairing seems to be ruled out by the absence of spectral changes[10] with the possible exception of Ca, which exhibits a weak hypsochromic shift of ca. 2 nm (see Experimental Section). Therefore, ArO^-M^{z+} may exist as solvent-separated ion pairs. One possibility is that the cationic and anionic centers are connected through one hydrogen-bonded cation-coordinated solvent molecule,[11] as shown below



$$\text{ArO}^- \cdots \text{H}{-}\overset{\text{Me}}{\overset{|}{\text{O}}} \cdots \text{M}^{z+}$$

Experimental Section

^1H NMR spectra were taken on a Jeol JNM-C60 HL spectrometer. Gas chromatographic analyses were performed on an Erba G1 instrument fitted with a 2% SE 30 plus 0.4% FFAP on Chromosorb W 60–80 column. Spectrophotometric measurements were carried out in the thermostated cell compartments of either a Beckman DB GT or a Cary 219 instrument; temperature control was within ±0.1 °C. Data were elaborated on a HP 9820 A desk calculator.

Materials. Tetraethylammonium hydroxide (25% in methanol) was from Fluka. AR grade *p*-nitrophenol was from Carlo Erba. Benzo-18-crown-6 and the alkali and alkaline earth bromides were from a previous investigation.[1] Methanol was purified as previously reported.[1] Triethylammonium bromide was prepared by adding 40% HBr in AcOH (Merck) to an ice cold solution of triethylamine (Erba RP freshly distilled over Na) in dry diethyl ether. The crude material was recrystallized from AcOH, washed with diethyl ether, and dried at 120 °C under vacuum for several hours.

***o*-Hydroxyphenyl 3,6,9,12-tetraoxatridecyl ether (ArOH)** was prepared according to the following scheme.

$$\text{HO(CH}_2\text{CH}_2\text{O)}_4\text{H} \xrightarrow[\text{1. Na, benzene}]{\text{2. CH}_3\text{I}} \text{HO(CH}_2\text{CH}_2\text{O)}_4\text{CH}_3 \xrightarrow{\text{PBr}_3\text{, pyridine}} \text{Br(CH}_2\text{CH}_2\text{O)}_4\text{CH}_3 \xrightarrow{\text{catechol, KOH}} \text{ArOH}$$

Monomethylation of tetraethylene glycol (Fluka) was carried out in a dry 500-mL three-necked round-bottomed flask, fitted with a mechanical stirrer, reflux condenser, and dropping funnel. The apparatus was protected from moisture and CO_2 with guard tubes. Sodium–dry benzene (300 mL) and sodium wire (7.0 g, 0.304 mol) were placed in the flask, and tetraethylene glycol (56 g, 0.289 mol) was added dropwise at room temperature over 40 min under vigorous stirring. After the dissolution of sodium was complete, CH_3I (45 g, 0.317 mol) was added dropwise

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(10) The situation is quite different from that observed in 99% aqueous Me_2SO solution (Illuminati, G.; Mandolini, L.; Masci, B., presented at the Fourth International Symposium on Physical Organic Chemistry, York, U. K., September 4–8, 1978, and unpublished results) where the stability of complexes between the alkali cations and ArO^- and other phenoxide ions follows the order $Li^+ > Na^+ > K^+ \geq Rb^+ \geq Cs^+$, indicating the dominating role of electrostatic interactions. Furthermore, association of the above cations with the oxide chromophore causes significant hypsochromic shifts in the UV spectra, the magnitude of which closely parallels the stability order. This suggests the associated species to be described as tight ion pairs in Me_2SO solution.

(11) Similarly bridged ion pairs have been observed in the solid state and proposed in solution of hydroxylic solvents. See, for instance: Furberg, S.; Mostad, A. *Acta Chem. Scand.* **1962**, *16*, 1627, Ginsburg, H.; Guibe, F.; Nee, G. *Bull. Soc. Chim. Fr.* **1972**, 4590. Grunwald, E.; Highsmith, S.; Ting-Po, I. In "Ions and Ion Pairs in Organic Reactions", Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2.

Table II. Dissociation of ArOH in Methanol at 25.0 °C

no added salt				in the presence of 4.11 × 10^{-2} M KBr			
V,[a] μL	[MeO^-]	A[b]	I[c]	V,[d] μL	[MeO^-]	A[b]	I[c]
25	1.79 × 10^{-3}	0.248	0.171	25	1.08 × 10^{-3}	0.591	0.532
50	3.55 × 10^{-3}	0.422	0.337	50	2.23 × 10^{-3}	0.885	1.103
75	5.28 × 10^{-3}	0.550	0.499	75	3.38 × 10^{-3}	1.044	1.657
100	6.97 × 10^{-3}	0.656	0.671	100	4.54 × 10^{-3}	1.142	2.202
150	1.03 × 10^{-2}	0.792	0.984	125	5.68 × 10^{-3}	1.205	2.724
200	1.34 × 10^{-2}	0.881	1.298	150	6.81 × 10^{-3}	1.246	3.207
300	1.93 × 10^{-2}	0.976	1.890				

[a] Volume of 0.150 M Et_4NOMe added to 2.00 mL of 4.60 × 10^{-4} M ArOH. [b] Absorbance readings at 296 nm. Cell path 10.0 mm. [c] Calculated as $A'/(c\epsilon - A')$. A' is the absorbance corrected for dilution and c the initial ArOH concentration. [d] Volume of a solution containing 0.150 M Et_4NOMe and 4.11 × 10^{-2} M KBr added to 3.00 mL of a solution containing 4.11 × 10^{-2} M KBr and 4.60 × 10^{-4} M ArOH.

Table III. Effect of Cesium Bromide on the Dissociation of ArOH in Methanol at 25.0 °C

V,[a] μL	[Cs^+]	A[b]	I[c]
0	0	0.600	0.417
20	4.83 × 10^{-4}	0.711	0.540
25	6.03 × 10^{-4}	0.735	0.570
30	7.23 × 10^{-4}	0.756	0.598
50	1.20 × 10^{-3}	0.833	0.710
75	1.78 × 10^{-3}	0.901	0.827
100	2.35 × 10^{-3}	0.957	0.940
150	3.48 × 10^{-3}	1.035	1.140
200	4.56 × 10^{-3}	1.084	1.308
300	6.64 × 10^{-3}	1.133	1.570
500	1.04 × 10^{-2}	1.147	1.906

[a] Volume of solution containing 7.30 × 10^{-2} M CsBr and 4.80 × 10^{-3} M Et_4NOMe added to 3.00 mL of a solution containing 5.47 × 10^{-4} M ArOH and 4.80 × 10^{-3} M Et_4NOMe. [b] Absorbance readings at 296 nm. Cell path 10.0 mm. [c] Calculated as $A'/(c\epsilon - A')$. A' is the absorbance corrected for dilution and c the initial total ArOH concentration.

Table IV. Effect of Barium Bromide on the Dissociation of ArOH in Methanol at 25.0 °C

V,[a] μL	[Ba^{2+}][b]	A[c]	I[d]
0	0		4.17 × 10^{-4} [e]
30	8.91 × 10^{-4}	0.356	0.264
50	1.49 × 10^{-3}	0.491	0.408
75	2.24 × 10^{-3}	0.606	0.564
100	2.98 × 10^{-3}	0.680	0.689
150	4.44 × 10^{-3}	0.772	0.888
200	5.87 × 10^{-3}	0.824	1.041
250	7.26 × 10^{-3}	0.851	1.151
300	8.61 × 10^{-3}	0.869	1.246
350	9.93 × 10^{-3}	0.873	1.303
400	1.12 × 10^{-2}	0.878	1.367
450	1.24 × 10^{-2}	0.881	1.427

[a] Volume of solution containing 0.103 M $BaBr_2$, 4.00 × 10^{-2} M Et_3N, and 4.00 × 10^{-2} M Et_3NHBr added to 3.00 mL of a solution containing 4.57 × 10^{-4} M ArOH, 4.00 × 10^{-2} M Et_3N, and 4.00 × 10^{-2} M Et_3NHBr. [b] Corrected for the fraction of Ba^{2+} sequestered by ArO^-. [c] Absorbance readings at 296 nm. Cell path 10.0 mm. [d] Calculated as $A'/(c\epsilon - A')$. A' is the absorbance corrected for dilution and c the initial total ArOH concentration. [e] Calculated according to eq 6 (see text).

Table V. Spectrophotometric Determination of the Association Constants between Benzo-18-crown-6 and Na^+ in Methanol at 25.0 °C

V,[a] μL	[Na^+][b]	A[c]
0	0	0.766
5	3.01 × 10^{-5}	0.798
10	7.69 × 10^{-5}	0.816
20	1.90 × 10^{-4}	0.833
30	3.13 × 10^{-4}	0.842
40	4.42 × 10^{-4}	0.845
50	5.71 × 10^{-4}	0.848
60	7.01 × 10^{-4}	0.850
70	8.32 × 10^{-4}	0.852
∞	∞	0.860

[a] Volume of a solution containing 0.106 M NaBr and 1.046 × 10^{-4} M C added to 8.00 mL of 1.046 × 10^{-4} M C. [b] Corrected for the fraction of Na^+ sequestered by C by means of the equation $[Na^+] = [Na^+]_{tot} - [C]_{tot}(A - A_0)/(A_\infty - A_0)$. [c] Absorbance readings at 267 nm. Cell path 40.0 mm.

over 15 min to the well-stirred mixture, which was eventually heated at 50 °C with stirring for 2 h to ensure complete reaction. The mixture was then transferred into a separatory funnel, the upper benzenic phase was discarded, and the lower thick layer was taken up with $CHCl_3$ and filtered free from any precipitated sodium iodide. The clear filtrate was shaken with water and then separated. The aqueous solution containing the unreacted starting material was discarded. The $CHCl_3$ extracts were dissolved in water, and the resulting solution was repeatedly extracted with small portions of CCl_4 which selectively extracts the dimethyl derivative. The crude tetraethylene glycol monomethyl ether which was obtained in 49% yield upon evaporation of the aqueous phase was distilled in vacuo to give the pure product, bp 110–120 °C (1 mm Hg). The purity of the product was determined to be >99% by GLC, and its structure was confirmed by ^1H NMR.

Treatment of the above product with PBr_3 and dry pyridine[12] gave 1-bromo-3,6,9,12-tetraoxatridecane in 27% yield. This compound was reacted with excess catechol in KOH/EtOH according to a previously reported procedure.[12] Elution of the crude product from alumina with EtOAc gave the pure title compound in 59% yield which had a ^1H NMR spectrum consistent with the proposed structure. Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 59.76; H, 8.15.

Equilibrium Measurements. Equilibrium measurements involving the ArOH–ArO^- pair were carried out spectrophotometrically at 25.0 °C in 10-mm quartz cuvettes. The substrate concentration in the cuvette was in the order of 5 × 10^{-4} M and calculated amounts of the proper reagent were dispensed in small aliquots by means of an "Agla" mycrosyringe with care being taken to minimize contamination by atmospheric CO_2. After each addition the absorbance value at 296 nm was recorded with allowance being made for thermal equilibration. When required, minor corrections due either to consumption of MeO^- or sequestration of metal cation were carried out. Typical runs are reported in Tables II, III, and IV.

Since complete dissociation of ArOH could not be attained even in the presence of the alkali bromides, the specific molar absorbance of the base form in the presence of the different counterions was obtained as the intercept of plots of $1/\epsilon_{app}$ vs. $1/[MeO^-]$, which showed good linearity in all cases. The molar extinction coefficient of the base form in the presence of alkaline earth bromides could be measured directly, owing to the strong acidity-enhancing effects of these salts. For each cation the spectral data of the base form of ArOH, namely λ_{max}(nm), $10^{-3}\epsilon_{max}$, and $10^{-3}\epsilon_{296}$ ($M^{-1}cm^{-1}$), are listed below in the given order: Et_4N^+, 292, 4.13, 3.79; Li^+, 292, 3.99, 3.66; Na^+, 292, 4.00, 3.67; K^+, 292, 4.00, 3.67; Rb^+, 292, 3.99, 3.66; Cs^+, 292, 3.99, 3.66; Ca^{2+}, 290, 4.03, 3.39; Sr^{2+}, 292, 4.25, 3.86; Ba^{2+}, 292, 4.12, 3.77.

The absorbance changes due to addition of the alkali bromides in the presence of excess Et_4NOMe were translated into values of the ratio I, using a mean value of 3.73 × 10^3 M^{-1} cm^{-1} for ϵ_{296}. For each run the Et_4NOMe concentration (M), a and b values, and correlation coefficient resulting from a least-squares treatment of the experimental data according to eq 3 are reported in the given order: Na^+, 4.8 × 10^{-3}, 467, 103, 0.997; 9.6 × 10^{-3}, 412, 96, 0.9990; K^+, 4.9 × 10^{-3}, 1180, 205, 0.9941; 9.6 × 10^{-3}, 1120, 230, 0.9994; Rb^+, 4.8 × 10^{-3}, 1090, 162, 0.9993; 9.5 × 10^{-3}, 933, 148, 0.9991; Cs^+, 4.8 × 10^{-3}, 722, 82, 0.9991; 9.5 × 10^{-3},

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(12) Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1977**, *99*, 7709.

632, 88, 0.9997. For the experiments in the presence of the alkaline earth bromides, the ϵ_{296} values of the associated forms were used. In all cases the concentration of the buffer components was $[Et_3N] = [Et_3NHBr] = 4 \times 10^{-2}$ M. A least-squares treatment of the data as above gave the following a and b values and correlation coefficients in the given order: Ca^{2+}, 4.69×10^5, 16, 0.9893; Sr^{2+}, 5.34×10^5, 73, 0.9994; Ba^{2+}, 7.78×10^5, 152, 0.9998.

Equilibrium measurements involving the cyclic ligand C were carried out by measuring the absorbance changes of a dilute (1.42×10^{-5}–1.05×10^{-4} M) solution of C upon addition of increasing amounts of metal bromide. In order to improve sensitivity a 40 mm cuvette was used and different wavelengths were chosen for the various salts. These were 267 nm for Na^+, 283 nm for K^+, 283 nm for Rb^+, 275 nm for Cs^+, 280 nm for Ca^{2+}, 280 nm for Sr^{2+}, and 234 nm for Ba^{2+}. A typical run is reported in Table V. The absorbance readings in each run were treated according to eq 7 by a least-squares procedure. Two independent sets of measurements were carried out for the alkali bromides. In the case of the alkaline earth bromides a second set of experiments was carried out in the presence of the 0.04 M triethylamine–triethylammonium bromide buffer in order to demonstrate the lack of substantial interactions of the alkaline earth cations with the buffer components (see Results section). Log K_C values reported in Table I refer only to measurements carried out in the absence of buffer. For each cation K_C values and correlation coefficients are given in that order—data in parentheses refer to equilibrium measurements in the presence of the buffer: Na, 1.18×10^4, 0.9991; 0.97×10^4, 0.9969; K^+, 2.15×10^5, 0.9980; 1.56×10^5, 0.9893; Rb^+, 4.25×10^4, 0.9988; 4.07×10^4, 0.9906: Cs^+, 4.21×10^3, 0.9974; 4.93×10^3, 0.9927; Ca^{2+}, 3.13×10^3, 0.9942; (3.43×10^3, 0.9919); Sr^{2+}, 8.23×10^4, 0.9983; (6.58×10^4, 0.9928); Ba^{2+}, 2.25×10^5, 0.9981; (1.48×10^5, 0.9884).

Homogeneous Catalysis of the Electrochemical Reduction of Dioxygen by a Macrocyclic Cobalt(III) Complex

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Abstract: The rotating ring–disk electrode was used to examine the reduction of dioxygen to hydrogen peroxide as catalyzed by the macrocyclic cobalt complex, *trans*-$[Co([14]aneN_4)(OH_2)_2]^{3+}$. Two different mechanisms were identified that depended on the ratio of dioxygen to cobalt. With excess cobalt, a well-characterized μ-peroxo complex, *trans*-$[(Co([14]aneN_4)(OH_2))_2O_2]^{4+}$, is formed at potentials where the initial Co(III) complex is reduced. At more negative potentials the μ-peroxo complex is reduced to H_2O_2 and $[Co([14]aneN_4)(OH_2)_2]^{2+}$ which re-enters the catalytic cycle. With excess dioxygen, the initial product of the reaction between the Co(II) complex and dioxygen is very rapidly further reduced to form a new complex thought to be *trans*-$[Co([14]aneN_4)(OH_2)(O_2H)]^{2+}$, a new, end-bonded, hydroperoxide complex. The hydroperoxide complex is further reduced at more negative potentials to yield H_2O_2 and $[Co([14]aneN_4)(OH_2)_2]^{2+}$. The rate of reaction of $[Co([14]aneN_4)(OH_2)_2]^{2+}$ with dioxygen proved too fast to measure with the rotating ring–disk electrode. The related complex, $[Co(Me_6[14]4,11\text{-diene }N_4)(OH_2)_2]^{3+}$, also catalyzes the reduction of dioxygen and at a much more positive potential but at a somewhat lower rate.

Several reports in the recent literature have described the use of transition-metal complexes as catalysts for the electrochemical reduction of dioxygen.[1-5] Among the goals of such studies is the development of catalysts that function at graphite or other inexpensive electrodes while approaching (or, conceivably, even exceeding) the catalytic activity of the platinum cathodes presently utilized in fuel cells. The use of catalysts that are confined to electrode surfaces has much to recommend it[1-5] but there are associated difficulties in carrying out kinetic and mechanistic studies with such small quantities of catalysts. The concentrations of catalyst present on the surface are often not known precisely and instability of catalyst coatings can introduce added uncertainties.

In recent studies of the catalytic activity of a highly active, dimeric cofacial porphyrin complex of cobalt(II) attached to graphite electrodes it was argued that a key intermediate in the catalytic mechanism is a peroxo-bridged dicobalt(III) complex.[5] Detailed information on the electrochemical behavior of such species is lacking and we sought to learn more about the properties and electrochemical reactivity of this class of reactants by studying some examples based on water-soluble macrocyclic complexes. We began with the cobalt(III) complex of 1,4,8,11-tetraazacyclotetradecane, $[Co([14]aneN_4)(OH_2)_2]^{3+}$,[6] because it has been well characterized,[7] its redox chemistry has been explored,[8] and the cobalt(II) complex is known to exhibit a high reactivity toward dioxygen.[9]

A particularly attractive feature of this complex was the recent demonstration by Endicott and co-workers[9b] that its reaction with dioxygen leads to the formation of a binuclear μ-peroxo-bridged complex with a structure rather similar to that proposed by Collman et al.[5] It is of interest to determine the factors that affect

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(1) (a) H. Behret, W. Clauberg, and G. Sandstede, *Ber. Bunsenges. Phys. Chem.*, **81**, 54-60 (1977); (b) H. Behret, W. Clauberg, and G. Sandstede, *ibid.*, **83**, 139-147 (1979); (c) H. Behret, W. Clauberg, and G. Sandstede, *Z. Phys. Chem.* (*Wiesbaden*), **113**, 97-116 (1978).

(2) (a) J. Zagal, P. Bindra, and E. Yeager, *J. Electrochem. Soc.*, **127**, 1506-1517 (1980); (b) J. Zagal, R. Y. Sen, and E. Yeager, *ibid.*, **83**, 207-213 (1977).

(3) (a) A. Bettelheim and T. Kuwana, *Anal. Chem.*, **51**, 2257-2260 (1979); (b) A. Bettelheim, R. J. H. Chan, and T. Kuwana, *J. Electroanal. Chem.*, **110**, 93-102 (1980).

(4) A. J. Appelby and M. Savy, *Electrochim. Acta*, **21**, 567-574 (1976).

(5) J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, and F. C. Anson, *J. Am. Chem. Soc.*, **102**, 6027-6036 (1980).

(6) Ligand abbreviations are based on conventions described by G. A. Melson in "Chemistry of Macrocyclic Compounds", G. A. Melson, Ed., Plenum Press, New York, 1979, Chapter 1, p 1.

(7) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 4, 1102-1108 (1965).

(8) J. F. Endicott and B. Durham in "Chemistry of Macrocyclic Compounds", G. A. Melson, Ed., Plenum Press, New York, 1979, Chapter 6, p 415 ff.

(9) (a) G. McLendon and M. Mason, *Inorg. Chem.*, **17**, 362-365 (1978). (b) C. L. Wong, J. A. Switzer, B. P. Balakrishnan, and J. F. Endicott, *J. Am. Chem. Soc.*, **102**, 5511-5518 (1980).

0002-7863/81/1503-7489$01.25/0