

- (4) W. A. Lathan, G. R. Pack, and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 6628 (1975).
- (5) P. Kollman in "Modern Theoretical Chemistry", H. F. Schaefer, Ed., Plenum Publishing Co., New York, N.Y., 1976.
- (6) One strong (~30 kcal dissociation energy) charge-transfer complex whose structure has been known for some time is NH_3BH_3 , for which $r(\text{N}-\text{B}) = 1.56 \text{ \AA}$ and the BH_3 group becomes pyramidal. See S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 6084 (1955); E. W. Hughes, *ibid.*, **78**, 502 (1956); E. L. Lippert and W. N. Lipscomb, *ibid.*, **78**, 503 (1956).
- (7) S. J. Harris, S. E. Novick, and W. Klempner, *J. Chem. Phys.*, **61**, 193 (1974).
- (8) C. A. Coulson, "The Shape and Structure of Molecules", Oxford University Press, London, 1974.
- (9) L. C. Allen, *J. Am. Chem. Soc.*, **97**, 6921 (1975).
- (10) M. Tamres, ref 2b, Vol. 1, pp 49-116.
- (11) R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley-Interscience, New York, N.Y., 1969.
- (12) J. L. Lipert, M. W. Hanna, and P. J. Trotter, *J. Am. Chem. Soc.*, **91**, 4035 (1969).
- (13) R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **97**, 7205 (1975).
- (14) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **33**, 1660 (1960).
- (15) S. D. Christian and J. Grundnes, *Nature (London)*, **214**, 1111 (1967).
- (16) J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, **90**, 2239 (1968).
- (17) J. A. Pople in "Computational Methods for Large Molecules and Localized States in Solids", F. Herman, A. D. McLean, and R. K. Nesbet, Ed., Plenum Publishing Co., New York, N.Y., 1973, p 11.
- (18) H. F. Schaefer in "Critical Evaluation of Chemical and Physical Structural Information", D. R. Lide and M. A. Paul, Ed., National Academy of Sciences, Washington, D.C., 1974, pp 591-602.
- (19) J. A. Pople in "Modern Theoretical Chemistry", H. F. Schaefer, Ed., Plenum Publishing Co., New York, N.Y., 1976.
- (20) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana.
- (21) D. B. Neumann, H. Basch, R. Kornegay, L. C. Snyder, J. W. Moskowicz, C. Hornback, and P. Liebmann, POLYATOM, Program No. 199, Quantum Chemistry Program Exchange, University of Indiana.
- (22) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (23) W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970).
- (24) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).
- (25) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
- (26) A. Veillard, *Theor. Chim. Acta.*, **12**, 405 (1968).
- (27) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.
- (28) G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand-Reinhold, New York, N.Y., 1966.
- (29) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **51**, 1580 (1969).
- (30) Value selected by R. D. Nelson, D. R. Lide, and A. A. Maryott, *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand.*, **No. 10** (1967).
- (31) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).
- (32) D. K. Coles, W. E. Good, J. K. Bragg, and A. H. Sharbaugh, *Phys. Rev.*, **82**, 877 (1951).
- (33) R. Trambarulo, S. N. Ghosh, C. A. Burrus, and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953).
- (34) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958).
- (35) J. D. Childs, Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma, 1971.

Calorimetric Titration Study of the Interaction of Several Uni- and Bivalent Cations with 15-Crown-5, 18-Crown-6, and Two Isomers of Dicyclohexo-18-crown-6 in Aqueous Solution at 25 °C and $\mu = 0.1^1$

R. M. Izatt,* R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Ayondet, and J. J. Christensen

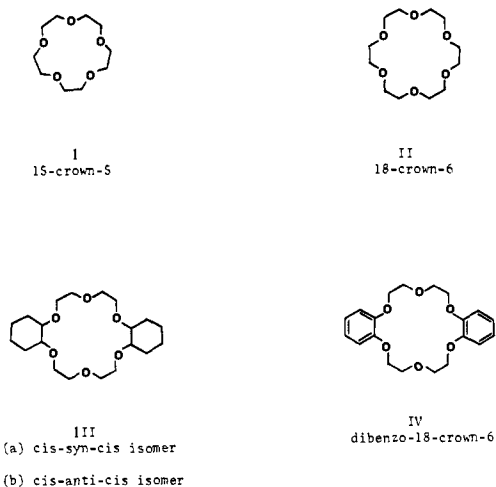
Contribution from the Departments of Chemistry and Chemical Engineering and No. 85 from the Institute for Thermochemical Studies, Brigham Young University, Provo, Utah 84602. Received May 10, 1976

Abstract: Log K , ΔH , and ΔS values for the 1:1 reactions at 25 °C in aqueous solution of several uni- and bivalent cations with 15-crown-5, 18-crown-6, and the cis-syn-cis and cis-anti-cis isomers of dicyclohexo-18-crown-6 have been determined by a calorimetric titration procedure. The marked selectivity toward uni- and bivalent cations shown by 18-crown-6 is not found with 15-crown-5. Ti^+ forms more stable complexes than Rb^+ (same crystal radius) with all three 18-crown-6 ligands. Favorable enthalpy and entropy changes contribute to this result. Ag^+ forms more stable complexes than K^+ (approximately same crystal radius) with only the cis-syn-cis isomer. Unfavorable ΔH and favorable ΔS values characterize formation of this complex. Only NH_4^+ , of the cations studied, forms a more stable complex with 15-crown-5 than with the 18-crown-6 ligands. For the 18-crown-6 set of ligands, cation selectivity, particularly for bivalent metal ions, is enhanced when dicyclohexo groups are present in the cis-syn-cis conformation, but is diminished when these groups are present in the cis-anti-cis conformation.

The selectivity shown by certain cyclic polyethers toward cations is well documented²⁻⁴ and constitutes one of the interesting features which distinguish them from most noncyclic ligands. The demonstration of cation selectivity by these compounds has resulted in much interest in them for possible use in many areas where this property is important,²⁻⁴ e.g., sensing elements in cation selective electrodes, study of biological transport mechanisms, solubilization of salts in solvents of low polarity making possible new organic reactions with increased yields, and development of carrier-membrane systems. The synthesis of macrocyclic compounds for these or other applications requires a knowledge of the effect on cation selectivity of various ligand and cation parameters.²⁻⁷ The present study is one of several designed to examine the effect of these parameters on cation selectivity as measured by the

thermodynamic quantities, log K , ΔH , and ΔS , for complex formation. The compounds included in the present study are I, II, IIIa, and IIIb, and the parameters considered are: (1) ligand ring substitution and cavity size; (2) cation size, charge, and electronic configuration.

A plot^{2,8} of log K for the reaction of dicyclohexo-18-crown-6⁹ (IIIa or IIIb) with uni- and bivalent cations vs. cation radius results in regions of maximum stability for both cation types. Since the thermodynamic quantities for the reaction of these isomers with a given cation usually differ considerably, it is of interest to compare results for them with those for II to learn the effect on complex stability of ligand substitution and isomer conformation. The latter property has been determined for crystalline IIIa and IIIb by x-ray crystallography, their isomers having the cis-syn-cis¹⁰ and cis-anti-cis¹¹ conforma-



tions, respectively. Comparison of results for II with those for I will give information on the effect of cavity diameter on cation selectivity and complex stability. Large conformation changes involving the ligand "wrapping" around the cation such as are reported⁴ for cation complexes of valinomycin, nonactin, and dibenzo-30-crown-10 are not expected in the ligands studied here. However, x-ray data show^{10,12} that the ring of IIIa changes from elliptical to nearly circular upon complexation with Ba^{2+} , and that some "wrapping" occurs in the Na^+ -II crystal.¹³ Also, calculation of the most stable conformations of free 12-crown-4 and of its Li^+ complex shows these conformations to be different.¹⁴

Log K values have been reported previously^{8,15,16} for the reaction of several univalent and bivalent cations with II, IIIa, and IIIb, but not with I. Also, Log K values for the reaction of several univalent and bivalent cations with dibenzo-18-crown-6 (IV) are available.¹⁷ Some ΔH and ΔS data for the reactions of K^+ , Rb^+ , NH_4^+ , Sr^{2+} , and Ba^{2+} with IIIa and IIIb have been reported.⁸ In the present study, additional log K , ΔH , and ΔS values are reported for the reactions of several uni- and bivalent cations with I, II, IIIa and IIIb.

Experimental Section

Materials. The following chemicals were obtained from the indicated suppliers: HCl, NaCl, KCl, CsCl, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (reagent, J. T. Baker); AgNO_3 , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (reagent, Baker and Adamson); $\text{Pb}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (reagent, G. Frederick Smith); Ti_2CO_3 and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (ultrapure, Alpha Inorganics); RbCl (99.9%, Research Inorganics); La_2O_3 (American Potash and Chemical Corp.); $\text{Th}(\text{NO}_3)_4$ (Baker 'Analyzed'); $\text{UO}_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Research Organic/Inorganic Chemical Corp.); $\text{CH}_3\text{NH}_3\text{Cl}$ and NH_4Cl (reagent, Fisher); $\text{Hg}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (reagent, Matheson, Coleman, and Bell); $(\text{CH}_3)_3\text{SI}$ (Eastman).

The preparation and purification of compound I are described in this section. It is included here because 15-crown-5 is difficult to separate from higher boiling polyethylene glycols and water; it is very hygroscopic. Subsequent to the completion of most of this work, 15-crown-5 became available commercially. We have found that most of the commercial material (available from several suppliers) needs purification prior to its use in applications where purity is important. Compound I was carefully distilled twice and stored under vacuum in dry argon atmosphere just before using. The NMR spectrum showed no observable impurities and the infrared spectrum showed no indication whatsoever of hydroxyl bands due to alcohols or water. Compound II was obtained from PCR, Inc. It was dried by placing the melt (50 °C) under vacuum (0.1 Torr) for 24 h, mp 37–38 °C, and used without any further purification. Compound III was obtained as a mixture of isomers from H. K. Frensdorff, E. I. duPont de Nemours and Co. The two isomers were separated and purified using either of two methods of separation which have been described.^{8,18} The elemental analyses and molecular weights of II, IIIa, and IIIb were found to be satisfactory. Careful thermometric titrations of II, IIIa, and IIIb using Pb^{2+} showed all three to be greater than 99% pure.

Each cation solution was prepared by dissolving the appropriate salt in oxygen-free, double distilled water or the metal oxide or carbonate in the stoichiometric amount of acid. The mercuric perchlorate solutions contained 0.100 M HClO_4 to prevent hydrolysis. The mercurous nitrate solution was standardized volumetrically by adding an excess of standard FeSO_4 and then titrating the excess Fe^{2+} with standard $\text{K}_2\text{Cr}_2\text{O}_7$. Mercurous nitrate was used instead of the perchlorate because of the limited solubilities of the mercurous perchlorate complexes of IIIa and IIIb in water. All mercurous solutions were stored over metallic mercury. The following were gravimetrically determined to better than 0.08% in each case: SrCl_2 as SrHPO_4 , BaCl_2 as BaCrO_4 , $\text{Pb}(\text{ClO}_4)_2$ as PbCrO_4 , TiClO_4 as Ti_2CrO_4 , and $\text{Hg}(\text{ClO}_4)_2$ as HgS . It was found that pure Ti_2CO_3 and HgO , after drying, could be as accurately weighed as their solutions could be gravimetrically standardized. Dried NH_4Cl and $\text{CH}_3\text{NH}_3\text{Cl}$ were standardized by precipitation of AgCl and then weighed directly; these solutions were 0.010 M in HCl. The cyclic polyether solutions (about 0.010 M) were prepared by dissolving each ligand in water.

Elemental analyses and molecular weights were performed by M-H-W Laboratories, Garden City, Mich. Infrared spectra were recorded using a Perkin-Elmer 457 double beam spectrometer and were calibrated using a polystyrene film. Proton NMR spectra were recorded at ambient temperatures using a Varian A-60A spectrometer and were calibrated using tetramethylsilane as an internal standard.

1,4,7,10,13-Pentaoxacyclopentadecane. One liter of dioxane was placed in a large reaction flask which was fitted with a mechanical stirrer, reflux condenser, gas inlet, and two addition funnels which were adjustable for very slow flow rates. The reflux condenser was fitted with a drying tube containing anhydrous CaCl_2 and NaOH pellets. All reactants and solvents were dried over CaH_2 or anhydrous MgSO_4 and stored over molecular sieves to remove as much water as possible. The reaction was carried out in an inert atmosphere of dry nitrogen. Bis(2-chloroethyl) ether (143 g, 1 mol) was diluted to a volume of 300 ml with dioxane, after which the solution was placed in one of the addition funnels; 140.2 g (1.00 mol) of dry triethylene glycol (Aldrich) was similarly diluted and placed in the other funnel. The dioxane was brought to reflux and some Na-K alloy was cautiously added to the boiling dioxane. The Na-K alloy was prepared by pressing together under dioxane 46.0 g of freshly cut sodium and 78.2 g of freshly cut potassium. Careful and vigorous stirring was maintained throughout the reaction in order to create a fine dispersion of the alloy. The triethylene glycol and bis(2-chloroethyl) ether solutions were slowly added at the same rate of about 4 ml/h. The overall reaction time was about 75 h, during which time the reaction mixture attained a characteristic pale blue color. After all of the reactants had been added, the reaction mixture was cooled to room temperature and wet methanol was added dropwise to destroy the unreacted alkali metal. The solution was filtered and placed in a rotary evaporator to remove the dioxane. Water (200 ml) was added and the remaining solution was extracted with three 300-ml portions of diethyl ether. The ether layers were separated, cooled, combined, dried over anhydrous MgSO_4 , and placed in a rotary evaporator to remove the ether. The resulting liquid was extracted with three 300-ml portions of warm (50 °C) *n*-hexane; the fractions were combined and the hexane was removed. The crude product was distilled a first time in vacuo (2 Torr) in order to remove residual amounts of hexane, dioxane, methanol, water, and unreacted bis(2-chloroethyl) ether. The separation of the product from the glycol could not be easily performed by distillation. The remaining colorless liquid containing small amounts of unreacted glycol was placed in a neutral alumina column (3 × 50 cm) and eluted with *n*-hexane until no more cyclic ether came off the column. The fractions were combined and the hexane was removed. The product was purified a second time by distillation under vacuum to obtain a pure colorless liquid, bp 115–116 °C (1.8 Torr). The yield was 12.1 g (5.5%). Molecular weight measurement by osmometry in benzene at 37 °C gave a value of 221 compared to that of 220.27 calculated for I. The proton NMR spectrum in CCl_4 consisted of a large singlet at δ 3.58. The density and refractive index (sodium D line) at 25 °C were 1.1044 and 1.4628 g/cm^3 , respectively. The infrared spectrum had a unique and easily observed absorption at 981 cm^{-1} which distinguished the cyclic ether from the glycol precursor whose infrared spectrum was very similar. Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_5$: C, 54.53; H, 9.15. Found: C, 54.50; H, 9.26.

Procedure and Calculations. The calorimetric determinations were made at 25 °C using a precision isoperibol titration calorimeter.¹⁹ The

Table I.^a Log *K*, ΔH , and ΔS Values for the 1:1 Reactions in Aqueous Solution at 25 °C and $\mu = 0.1$ of Several Univalent Cations with I, II, and III

Ligand	Cation	Log <i>K</i>	ΔH , kcal/mol	ΔS , cal/(deg mol)
I	Na ⁺	0.70 ± 0.10	-1.50 ± 0.04	-1.8
I	K ⁺	0.74 ± 0.08	-4.1 ± 0.1	-10.4
I	Rb ⁺	0.62 ± 0.10	-1.90 ± 0.01	-3.5
I	Cs ⁺	0.8 ± 0.2	-1.3 ± 0.2	-0.5
I	Ag ⁺	0.94 ± 0.08	-3.23 ± 0.03	-6.5
I	Tl ⁺	1.23 ± 0.04	-4.01 ± 0.05	-7.8
II	Na ⁺	0.80 ± 0.10	-2.25 ± 0.10	-3.7
		<0.3 ^b		
II	K ⁺	2.03 ± 0.10	-6.21 ± 0.01	-11.4
		2.06 ^b		
II	Rb ⁺	1.56 ± 0.02	-3.82 ± 0.11	-5.7
II	Cs ⁺	0.99 ± 0.07	-3.79 ± 0.10	-8.1
		0.8 ^b		
II	Ag ⁺	1.50 ± 0.03	-2.17 ± 0.09	-0.4
		1.6 ^b		
II	Tl ⁺	2.27 ± 0.04	-4.44 ± 0.04	-4.5
IIIa	Li ⁺	0.6 ^b		
IIIa	Na ⁺	1.21 ± 0.09	+0.16 ± 0.04	6.1
		(1.5-1.85) ^b		
IIIa	K ⁺	2.02 ^c	-3.88 ^c	-3.8 ^c
		2.18 ^b		
IIIa	Rb ⁺	1.52 ^c	-3.33 ^c	-4.2 ^c
IIIa	Cs ⁺	0.96 ^c	-2.41 ^c	-3.7 ^c
		1.25 ^b		
IIIa	Ag ⁺	2.36 ± 0.11	0.07 ± 0.01	11.0
		2.3 ^b		
IIIa	Tl ⁺	2.44 ± 0.04	-3.62 ± 0.02	-1.0
IIIa	Hg ₂ ²⁺	1.93 ± 0.09	-2.16 ± 0.10	1.6
IIIa	Hg ₂ L ²⁺	(0.6-1.8) ^d	6.1 ± 0.7 ^e	26
IIIb	Na ⁺	0.69 ± 0.12	-1.57 ± 0.04	-2.1
		(1.2-1.6) ^b		
IIIb	K ⁺	1.63 ^c	-5.07 ^c	-9.6 ^c
		1.78 ^b		
IIIb	Rb ⁺	0.87 ^c	-3.97 ^c	-9.3 ^c
IIIb	Cs ⁺	0.9 ^b		
IIIb	Ag ⁺	1.59 ^c	-2.09 ^c	0.3 ^c
		1.8 ^b		
IIIb	Tl ⁺	1.83 ± 0.02	-4.29 ± 0.03	-6.0
IIIb	Hg ₂ ²⁺	1.57 ± 0.09	-4.34 ± 0.04	-7.4
IIIb	Hg ₂ L ²⁺	1.1 ± 0.4	-5.7 ± 0.4	-14

^a Values are the average of four to six experimental determinations. The uncertainties are given as standard deviations. ^b Reference 15, determined potentiometrically using ion selective electrodes. Reactant concentrations <0.01 M. ^c Reference 8, determined calorimetrically. ^d Log *K* cannot be determined accurately from the calorimetric data. ^e Calculated at log *K* = 1.2.

calorimeter description, general experimental procedure, and method of calculating *K* and ΔH values from the calorimetric data are available.²⁰⁻²⁴

Results and Discussion

No measurable heat other than heat of dilution was found for the mixing of Ca²⁺ or Hg²⁺ with I, or of UO₂²⁺, Cd²⁺, Co²⁺, La³⁺, Th⁴⁺, (CH₃)₃S⁺, or H⁺ with IIIa; and, consequently, no attempt was made to calculate *K* values for these systems. Although it had been claimed that II forms a complex with uranyl nitrate in the solid state, a crystal structure also showed the absence of interaction between II and the uranyl ion.²⁵ It should be remembered that a negligible heat of reaction can indicate that log *K* is small and/or the enthalpy change is near zero. The calorimetric data used to calculate the thermodynamic quantities reported here are available.¹ Log *K* values reported by others for the systems studied are given in the appropriate tables. Agreement between these values and those determined in the present study is good considering the differences in experimental methods and procedures which are involved. Log *K*, ΔH , and ΔS values for the 1:1 reactions of several univalent metal ions with I, II, IIIa, and IIIb are given in Table I together with available literature values and the log

K values are plotted vs. cation radius²⁶ in Figure 1. Included in Figure 1 are data from Shchori et al.¹⁷ for the reaction of these metal ions with IV.

Complexation Selectivity toward M⁺, 15-Crown-5. In Figure 1, lines are drawn connecting the data points for the alkali metal ions. A distinctive feature of the plot is the absence of selectivity by I toward these cations. This behavior is in marked contrast to that of the three 18-crown-6 ligands where peak selectivity is seen with K⁺ always forming the most stable complex. Except in the case of K⁺, the ΔH and ΔS values are comparable for the alkali metal ions, and in all cases the ΔH and ΔS values compensate each other resulting in nearly identical log *K* values for each M⁺-I system. The log *K* values for both the Ag⁺ and Tl⁺ complexes with I are larger than would be expected based on the affinities of I for alkali metal ions (K⁺, Rb⁺) of comparable radii.

The 15-crown-5 ligands, in comparison to the 18-crown-6 ligands, possess significantly poorer ligating properties. Larger cations such as K⁺ and Rb⁺ are too large to be effectively accommodated within the 15-crown-5 ligand. A smaller cation such as Na⁺ more closely fits into the ligand, but the higher solvation energy of the sodium ion works against its coordination. Hence, the selectivity of the 15-crown-5 ligands is far

less marked. Furthermore, the overall ligating power is reduced owing to the fewer number of donor atoms (five instead of six). It would be anticipated that both the cation selectivity and ligating ability of the 15-crown-5 ligands in less polar organic solvents should increase significantly.

Complexation Selectivity toward M^+ , 18-Crown-6 Ligands.

Peak selectivity toward the alkali metal ions is seen in Figure 1 for each of the 18-crown-6 ligands with the K^+ complex being most stable in each case. This observation is consistent with x-ray data which show that K^+ fits nicely into the crown-6 cavity in the crystal.¹³ Also, K^+ has nearly the same ionic radius (1.33 Å)²⁶ as Ba^{2+} (1.34 Å),²⁶ which is known to lie in the center of the Ba^{2+} -IIIa complex.¹⁰ The observed peaks for the three ligands would also be seen if ΔH were plotted vs. cation radius as the change in $\log K$ parallels the change in ΔH (Table I) for this series of cations with each crown-6 ligand. It is interesting that, taken alone, the change in ΔS in the series Na^+ , K^+ , Rb^+ , Cs^+ would result in a nearly opposite order of $\log K$ values for each of these ligands. Thus ΔH and ΔS compensate each other with ΔH being the dominant quantity in determining the magnitude of $\log K$.

$\log K$ values for the post-transition series cations, Tl^+ and Ag^+ , lie above the lines connecting the alkali metal ions (Figure 1) in all cases except for the Ag^+ -II and Ag^+ -IV systems. The $\log K$ values for the Tl^+ -crown-6 complexes are from 0.42 to 0.96 $\log K$ unit larger than would be expected based on the corresponding $\log K$ values for Rb^+ , which has the same crystal radius (1.47 Å)²⁶ as Tl^+ . The data in Table I show that both the ΔH and ΔS values contribute to the greater $\log K$ value in the case of the reaction of Tl^+ with each of the three crown-6 ligands. The greater stabilities of the Tl^+ complexes probably reflect the greater polarizability of Tl^+ compared to Rb^+ and thus greater covalent contribution to the bonding. The same result might be expected for Ag^+ interaction with these ligands; however, the data in Figure 1 show that only in the case of IIIa is $\log K$ markedly larger than that expected from the curves for the alkali metal ions. The larger $\log K$ value, in this case, is primarily a result of a favorable ΔS value, ΔH being nearly zero. Comparison of the $\log K$, ΔH , and ΔS values for the reaction of Ag^+ with II and IIIb show these quantities to be nearly identical for the two reactions. Compared to Tl^+ and the alkali metal cations, the ΔH values are smaller than might be expected, perhaps due to the peculiar stereochemical requirements²⁷ of Ag^+ .

Eisenman and Krasne²⁸ conclude, based on ΔG values for cation interaction with nonactin, valinomycin, hexadecavalinomycin, and dicyclohexo-18-crown-6, that it is the general rule for Tl^+ and Ag^+ to show excess binding energy with macrocyclic compounds having carbonyl and ether oxygen donor atoms. They point out that these cations have energies of hydration larger than those of alkali metal ions of comparable radii and that this is also the case with the energy of solvation of these ions by the carbonyl group of the solvent propylene carbonate. These effects are attributed to the greater polarizabilities of these cations and the subsequently greater covalent character of the bonds they form with the donor oxygen atoms. It would be expected that these effects would result in more negative ΔH values and this is consistent with our results for Tl^+ , where ΔH values are always larger than those for Rb^+ , but not for Ag^+ where the ΔH values are much less than those for K^+ , and the ΔS terms make substantial contributions to the stabilities of the complexes.

$\log K$ data for the 1:1 reaction of Hg_2^{2+} with IIIa and IIIb (Table I) are nearly identical with those for the reaction of K^+ with these respective ligands. Comparison of ΔH and ΔS values for the 1:1 Hg_2^{2+} -IIIa and -IIIb interactions with those for K^+ interactions with these ligands show generally similar values, with ΔH being somewhat lower but compensated by ΔS in each case. The Hg_2^{2+} -IIIa and -IIIb systems have the

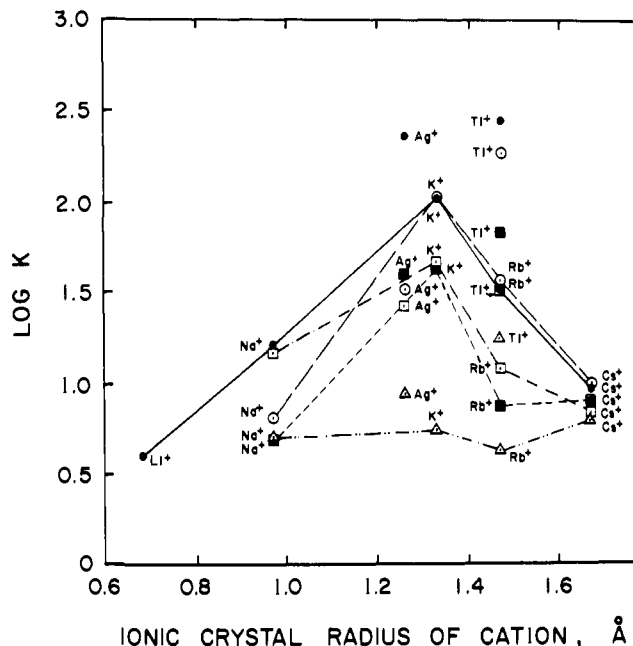


Figure 1. Plot of $\log K$ for the reaction $M^+ + L = ML^+$ vs. cation crystal radius: L = I (Δ), II (\circ), IIIa (\bullet), IIIb (\blacksquare), IV (\square).

unusual, but not unexpected feature that 1:2 (Hg_2^{2+} :L) complexes form. Analysis of the thermometric titration data indicates unequivocally that two reactions are occurring in solution. Unfortunately, the values of ΔH_2 and $\log K_2$ are highly correlated for both IIIa and IIIb, especially in the former case where the minimum in the error function used in determining $\log K_2$ was so broad that only a range of values could be obtained. Fortunately, the five other correlations were small enough that ΔH_1 and $\log K_1$ could be determined with reasonable certainty for both ligands. All reasonable values of $\log K_2$ yielded distinctly endothermic values for ΔH_2 during the reaction with IIIa and distinctly exothermic values for ΔH_2 during the reaction with IIIb. Calculations showed that the weak interaction of Hg_2^{2+} with NO_3^- could be neglected. Although the difference in the values of ΔG are not large, the large differences between the respective ΔH_2 and ΔS_2 values for the two systems suggest that there may be interesting structural or other features involved in the complexation. Models show that two molecules of IIIa could comfortably coordinate to the $Hg(I)$ dimer with all four cyclohexyl groups oriented away from each other. However, ligand-ligand steric interactions could alter the structural conformations and relative stability of the Hg_2^{2+} (IIIb)₂ complex.

$\log K$, ΔH , and ΔS data for the interaction of NH_4^+ with I, II, IIIa, and IIIb and $CH_3NH_3^+$ with IIIa and IIIb, are given together with literature data in Table II. The respective $\log K$ value for the reaction of NH_4^+ (ionic radius = 1.48 Å)²⁹ with each of the crown-6 ligands is lower than that for the reaction of Rb^+ (ionic radius = 1.47 Å)²⁶ with the same ligand, the difference being greatest (0.33 $\log K$ unit) for 18-crown-6 and least (0.07 $\log K$ unit) for the cis-anti-cis isomer, IIIb. A considerably larger difference (0.78 $\log K$ unit) is reported¹⁷ between the $\log K$ values for the reaction of NH_4^+ and Rb^+ with IV, the value for NH_4^+ being the lowest. For the cis-anti-cis isomer, IIIb, $\log K$, ΔH , and ΔS values of the NH_4^+ -IIIb system are similar to those for the Rb^+ -IIIb system. For the two remaining 18-crown-6 ligands (II and IIIa), the stability of the NH_4^+ complex is lower than that of the Rb^+ complex in each case. The lowered stability is a result, primarily, of less favorable ΔH values which are only partially compensated by more favorable ΔS values.

$\log K$ for the reaction of NH_4^+ with I is considerably larger

Table II. Log *K*, ΔH , and ΔS Values for the 1:1 Reaction in Aqueous Solution at 25 °C and $\mu = 0.1$ of NH_4^+ and CH_3NH_3^+ with I, II, IIIa, and IIIb

Reaction ligand	Cation	Log <i>K</i>	ΔH , kcal/mol	ΔS , cal/(deg mol)
I	NH_4^+	1.71 ± 0.16	-0.24 ± 0.04	7.0
II	NH_4^+	1.23 ± 0.06	-2.34 ± 0.08	-2.2
		1.1 ^a		
IIIa	NH_4^+	1.33 ^b	-2.16^b	-1.2 ^b
	CH_3NH_3^+	0.82 ± 0.11	-0.77 ± 0.03	1.2
IIIb	NH_4^+	0.80 ^b	-3.41^b	-7.8 ^b
		0.80 ^a		
	CH_3NH_3^+	0.66 ± 0.10	-0.90 ± 0.06	0

^a Reference 15. ^b Reference 8.

Table III. Log *K*, ΔH , and ΔS Values for the 1:1 Reactions in Aqueous Solution at 25 °C and $\mu = 0.1$ of Several Bivalent Cations with I, II, and III^a

Ligand	Cation	Log <i>K</i>	ΔH , kcal/mol	ΔS , cal/(deg mol)
I	Sr^{2+}	1.95 ± 0.08	-0.9 ± 0.1	6
I	Ba^{2+}	1.71 ± 0.06	-1.14 ± 0.10	4.0
I	Pb^{2+}	1.85 ± 0.03	-3.26 ± 0.03	-2.5
I	Hg^{2+}	1.68 ± 0.07	-3.6 ± 0.3	-4
II	Ca^{2+}	<0.5		
II	Sr^{2+}	2.72 ± 0.02	-3.61 ± 0.02	0.3
II	Ba^{2+}	3.87 ± 0.02	-7.58 ± 0.01	-7.9
II	Pb^{2+}	4.27 ± 0.02	-5.16 ± 0.01	2.2
II	Hg^{2+}	2.42 ± 0.03	-4.69 ± 0.03	-4.7
IIIa	Sr^{2+}	3.24 ^b	-3.68^b	2.5 ^b
IIIa	Ba^{2+}	3.57 ^b	-4.92^b	-0.2 ^b
	Pb^{2+}	4.95 ± 0.04^c	-5.58 ± 0.01	3.9
		5.29 ± 0.10^d	-5.48 ± 0.02	3.0
IIIa	Hg^{2+}	2.75 ± 0.05	-0.71 ± 0.01	10.2
IIIb	Sr^{2+}	2.64 ^b	-3.16^b	1.5 ^b
IIIb	Ba^{2+}	3.27 ^b	-6.20^b	-5.8 ^b
IIIb	Pb^{2+}	4.43 ± 0.05	-4.21 ± 0.02	6.2
IIIb	Hg^{2+}	2.60 ± 0.03	-2.55 ± 0.04	3.3

^a Values are the average of four to six experimental determinations. The uncertainties are given as standard deviations. ^b Reference 8. ^c Value from direct titration of IIIa with $\text{Pb}(\text{ClO}_4)_2$. Values lie outside optimum range of calorimetric titration method and may be low, see text. ^d Value from competing reaction of $\text{Hg}(\text{ClO}_4)_2$ and $\text{Pb}(\text{ClO}_4)_2$ for IIIa, see text.

than that for the reaction of NH_4^+ with II. This result is unexpected, since the trend is opposite to that found (Table I) for the reaction of all metallic cations thus far studied with these ligands. For example, the data in Table I show log *K* values of 0.62 and 1.56 for the 1:1 reactions of Rb^+ with I and II, respectively. Compared to Rb^+ , the greater stability of the NH_4^+ -I complex is almost entirely due to a threefold more favorable entropy change, the difference between the ΔH values for the reactions of NH_4^+ and Rb^+ with I (1.66 kcal/mol) being almost identical with that for the reaction of these cations with II (1.52 kcal/mol).

Ammonium ion has two distinctive features which may be important in understanding the above stability trend. First, it has the capability of hydrogen bonding, a property not shared with the metallic cations. Second, it consists of a tetrahedral arrangement of protons about the central nitrogen atom which could lead to distinctive stereochemical requirements. The smaller 15-crown-5 may offer more favorable circumstances for binding NH_4^+ than 18-crown-6. Support for this idea has come from several recent studies. Goldberg³⁰ reports hydrogen bonding and nitrogen-to-oxygen polar interactions to be important components in the structure of a *tert*-butylammonium ion-cyclic polyether complex. Eisenman and Krasne²⁸ attribute the greater affinity of NH_4^+ for nonactin than for valinomycin to the existence of a tetrahedral arrangement of oxygen atoms in the former compared to an octahedral arrangement of oxygen atoms in the latter. Finally, ab initio

calculations^{31,32} show a preference by NH_4^+ for a tetrahedral arrangement of donor atoms, a situation which is not necessary for the alkali metal ions.

Substitution of a CH_3 group for H on NH_4^+ results in a marked decrease of 1.39 and 2.51 kcal/mol, respectively, in the ΔH values for formation of the IIIa and IIIb complexes compared to the corresponding NH_4^+ complexes. The change in ΔS values from NH_4^+ to CH_3NH_3^+ is toward a more stable complex in each case, thus compensating in part for the large decrease in the ΔH values. The log *K* value for formation of the CH_3NH_3^+ complex is lower in each case than that for formation of the corresponding NH_4^+ complex.

The decreased stability of the CH_3NH_3^+ complexes compared to the corresponding NH_4^+ complexes is in agreement with the prediction of Pullman and Armbruster.³¹ These authors have conducted an ab initio calculation of the interaction of H_2O molecules with NH_4^+ and CH_3NH_3^+ and calculate that the methyl group has a destabilizing effect on the binding ability of the cation. This effect results in a lengthening of the N...O distance, which might be expected to result in smaller ΔH values compared to NH_4^+ . Indeed, the log *K* and ΔH data for the NH_4^+ and CH_3NH_3^+ systems studied here follow these trends.

Complexation Selectivity toward M^{2+} . Log *K*, ΔH , and ΔS data for the reaction of several bivalent cations with I, II, IIIa, and IIIb are given together with literature data in Table III and the log *K* values are plotted vs. cation crystal radius²⁶ in

Figure 2. Two sets of $\log K$, ΔH , and ΔS values are given in Table III for the reaction of Pb^{2+} with IIIa. The lower $\log K$ value (4.95) is calculated from data obtained by direct titration of IIIa with $\text{Pb}(\text{ClO}_4)_2$. This value lies outside the optimum range for determination of K by the calorimetric titration method.³³ The higher $\log K$ value (5.29) was calculated from data obtained by titrating a solution of IIIa containing $\text{Hg}(\text{ClO}_4)_2$ with $\text{Pb}(\text{ClO}_4)_2$. The equilibrium constant for this reaction was in the range for accurate determination by the calorimetric titration procedure and is considered the more reliable value for the reaction of Pb^{2+} with IIIa. The most striking feature of Figure 2 is the sharp stability peak for all three crown-6 ligands at about the cation radius of Pb^{2+} . Compensation of ΔH and ΔS values for the reaction of a given cation with a given ligand is found. The $\log K$ and ΔH values generally parallel each other as was found for univalent metal ion interaction with the crown-6 ligands.

The cation selectivity pattern is markedly changed in the case of the M^{2+} -I systems with $\log K$ values for $\text{M}^{2+} = \text{Sr}^{2+}$, Ba^{2+} , Pb^{2+} , and Hg^{2+} being nearly the same. The peak at Sr^{2+} is consistent with the smaller cavity size of I. A large selectivity difference between I and II for univalent cations was also noted (Figure 1).

Comparison of the $\log K$ values in Figures 1 and 2 for the reaction of univalent and bivalent cations with the three crown-6 compounds shows cation selectivity by these ligands to be much more pronounced in the case of the bivalent cations where $\log K$ for formation of the Ba^{2+} -ligand complexes are much larger than those for formation of the corresponding K^+ complexes. However, small univalent cations form more stable complexes with these ligands than do bivalent cations, i.e., $\text{Na}^+ > \text{Ca}^{2+}$. A similar finding has been reported¹⁷ for the reactions in aqueous solution of univalent and bivalent cations with IV.

In Figure 2, we have chosen to draw the line between points to include the post-transition cations, Hg^{2+} and Pb^{2+} . Certainly, the correlation between $\log K$ and cation radius using all bivalent cations is better than was the case with univalent cations (Figure 1); however, it is possible that Pb^{2+} lies above a curve with its maximum between Sr^{2+} and Ba^{2+} . This situation would be consistent with that found in the case of Tl^+ (Figure 1). Support for this idea comes from a theoretical treatment of M^{n+} interaction with 18-crown-6,^{34,35} which suggests that maximum stability for both univalent and bivalent cation interaction with 18-crown-6 should occur at the same cation radius in a plot similar to that in Figure 2. If this were the case for the plots in Figures 1 and 2, one would expect the experimental points for K^+ and Ba^{2+} to lie to the right of the maximum. The value for Pb^{2+} would fall above the curve and arguments similar to those advanced in the case of Tl^+ explain the greater stability of its complex relative to that expected for an alkaline earth cation of the same size. The crystal radius of Pb^{2+} is 1.20 Å compared to 1.12 Å for Sr^{2+} and 1.34 Å for Ba^{2+} .²⁶ The ΔH values for formation of Pb^{2+} complexes with II, IIIa, and IIIb are more favorable than the corresponding ΔH values in the cases of Sr^{2+} and Ba^{2+} , except for the Ba^{2+} -IIIb system. The corresponding ΔS values all favor formation of the Pb^{2+} complexes over the Sr^{2+} or Ba^{2+} complexes and the $\log K$ values are higher for formation of the Pb^{2+} complex in all cases. Thus, the situation with Pb^{2+} appears to be analogous to that of Tl^+ , which was discussed earlier; both $d^{10} s^2$ ions have the same unique behavior.

Mercury(II) and Sr^{2+} have nearly identical crystal radii (1.10 and 1.12 Å, respectively) and Sr^{2+} forms the more stable complex with each of the three crown-6 ligands, although the stability difference in the case of IIIb is insignificant. The greater stability of Sr^{2+} in the case of II is a result of a more favorable entropy change, which more than compensates for a less favorable enthalpy change. The reverse is true for the IIIa

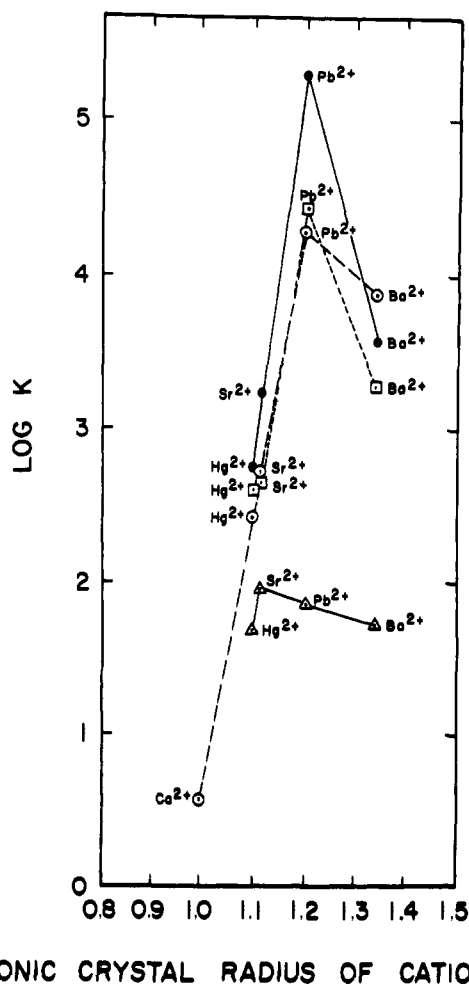


Figure 2. Plot of $\log K$ for the reaction $\text{M}^{2+} + \text{L} = \text{ML}^{2+}$ vs. cation crystal radius: L = I (Δ), II (\odot), IIIa (\bullet), IIIb (\square).

and IIIb systems, with the greater stability of the Sr^{2+} complex in each case resulting from a more favorable enthalpy change which is only partially cancelled by a less favorable entropy change. Comparisons between Sr^{2+} and Hg^{2+} are generally analogous to those discussed earlier for the K^+ and Ag^+ pair, suggesting that similar causes underlie the observations in the two sets of cations. It is noteworthy that the Ag^+ -IIIa and Hg^{2+} -IIIa reactions have small enthalpy changes (near zero), but distinctly positive entropy changes; the entropies of reaction are the principal driving forces for the reactions of these d^{10} ions. The only other metal ion-cyclic polyether system which is entropy driven is the reaction of Na^+ with IIIa.

Effect of Substitution on Complexation Selectivity. The effect on $\log K$ of the substitution of cyclohexo groups on 18-crown-6 is quite different for the two isomers considered as seen in Figures 1 and 2. With the exception of Ba^{2+} , the $\log K$ values for the reaction of the bivalent cations with IIIb follow those of 18-crown-6 quite closely, while the $\log K$ values for IIIa are consistently higher. With the exceptions of Na^+ and Ag^+ the opposite is true in the case of the univalent cations in that the 18-crown-6 and IIIa curves are similar. Thus, substitution of the dicyclohexo groups in the cis-syn-cis conformation (IIIa) enhances the selectivity of the 18-crown-6 ligand for bivalent cations, but has no effect on its selectivity for univalent cations. On the other hand, substitution in the cis-anti-cis conformation (IIIb) results in diminished stability for complexes with univalent cations, but little stability change in the case of bivalent cations. These stability trends are consistent with the cavity in the cis-syn-cis isomer being better defined and less suscep-

tible to conformational changes, which is consistent with the expected effect of the cyclohexo groups on ring rigidity.

The log K values in Table III for the reactions of Sr^{2+} , Ba^{2+} , and Pb^{2+} with II, IIIa, and IIIb are much larger than the corresponding values for the reactions of these metal ions with IV.¹⁷ In addition, the Pb^{2+} -IV complex is reported to be less stable than the Ba^{2+} -IV complex, which is the opposite trend to that seen in Table III for II, IIIa, and IIIb. The results of Shchori et al.¹⁷ with IV suggest that the effect of substitution of two benzo groups on II is to markedly lower complex stability for bivalent, but not univalent (Figure 1) metal ions and to reverse the Pb^{2+} , Ba^{2+} stability order. On the other hand, the data in Figure 2 generally show trends opposite to these for IIIa and IIIb when compared with II.

References and Notes

- (1) Supported by National Science Foundation Grant GP-33536X and National Institutes of Health Grant GM 18811. Taken in part from the M.S. Thesis (1973) of B.L.H. and the Ph.D. Dissertation (1976) of R.E.T., Brigham Young University.
- (2) R. M. Izatt, D. J. Eatough, and J. J. Christensen, *Struct. Bonding*, **16**, 161 (1973).
- (3) J. M. Lehn, *Struct. Bonding*, **16**, 1 (1973).
- (4) Y. A. Ovchinnikov, V. T. Ivanov, and A. M. Shkrob, "Membrane-Active Complexones", Elsevier, New York, N.Y., 1974.
- (5) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem.*, **11**, 16 (1972).
- (6) C. Kappenstein, *Bull. Soc. Chim. Fr.*, 89 (1974).
- (7) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971).
- (8) R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, *J. Am. Chem. Soc.*, **93**, 1619 (1971).
- (9) Nomenclature is that proposed for these compounds by C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
- (10) N. K. Dalley, D. E. Smith, R. M. Izatt, and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, 90 (1972).
- (11) D. E. Fenton, M. Mercer, and M. R. Truter, *Biochem. Biophys. Res. Commun.*, **48**, 10 (1972).
- (12) N. K. Dalley, J. S. Smith, S. B. Larson, J. J. Christensen, and R. M. Izatt, *J. Chem. Soc., Chem. Commun.*, 43 (1975).
- (13) M. R. Truter, *Struct. Bonding*, **16**, 71 (1973).
- (14) A. Pullman, C. Giessner-Prettre, and Y. V. Kruglyak, *Chem. Phys. Lett.*, **35**, 156 (1975).
- (15) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).
- (16) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
- (17) E. Shchori, N. Nae, and J. Jagur-Grodzinski, *J. Chem. Soc., Dalton Trans.*, 2381 (1975).
- (18) R. M. Izatt, B. L. Haymore, J. S. Bradshaw, and J. J. Christensen, *Inorg. Chem.*, **14**, 3132 (1975).
- (19) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *Rev. Sci. Instrum.*, **36**, 779 (1965).
- (20) L. D. Hansen, R. M. Izatt, D. J. Eatough, T. E. Jensen, and J. J. Christensen, in *Anal. Calorimetry, Proc. Symp. 3rd*, 7-16 (1974).
- (21) L. D. Hansen, R. M. Izatt, and J. J. Christensen, in "New Developments in Titrimetry", J. Jordan, Ed., Marcel Dekker, New York, N.Y., 1974.
- (22) L. D. Hansen, T. E. Jensen, S. Mayne, D. J. Eatough, R. M. Izatt, and J. J. Christensen, *J. Chem. Thermodyn.*, **7**, 919 (1975).
- (23) J. J. Christensen, D. J. Eatough, J. Ruckman, and R. M. Izatt, *Thermochim. Acta*, **3**, 203 (1972).
- (24) D. J. Eatough, J. J. Christensen, and R. M. Izatt, *Thermochim. Acta*, **3**, 219, 233 (1972).
- (25) R. M. Costes, G. Folcher, N. Keller, P. Plurien, and P. Rigny, *Inorg. Nucl. Chem. Lett.*, **11**, 469 (1975); **11**, 13 (1976); G. Bombieri, G. DePaoli, A. Cassol, and A. Immirzi, *Inorg. Chim. Acta*, **18**, L23 (1976).
- (26) L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 155 (1952); R. Shannon and C. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).
- (27) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley-Interscience, New York, N.Y., 1972.
- (28) G. Eisenman and S. J. Krasne in *MTP Int. Rev. Sci., Biochem. Ser.*, **2**, 27-59 (1975).
- (29) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960.
- (30) I. Goldberg, *Acta Crystallogr., Sect. B*, **31**, 2592 (1975).
- (31) A. Pullman and A. M. Armbruster, *Int. J. Quantum Chem.*, **8S**, 169 (1974).
- (32) A. Pullman and A. M. Armbruster, *Chem. Phys. Lett.*, **36**, 558 (1975).
- (33) J. J. Christensen, D. P. Wrathall, and R. M. Izatt, *Anal. Chem.*, **40**, 175 (1968); J. J. Christensen, D. P. Wrathall, J. O. Oscarson, and R. M. Izatt, *Anal. Chem.*, **40**, 1713 (1968).
- (34) L. D. Hansen, R. M. Izatt, R. E. Terry, and J. J. Christensen, manuscript in preparation.
- (35) R. M. Izatt, L. D. Hansen, D. J. Eatough, J. S. Bradshaw, and J. J. Christensen, *Jerusalem Symp., Quantum Chem. Biochem.*, in press.

Calorimetric Titration Study of the Interaction of Some Uni- and Bivalent Cations with Benzo-15-crown-5, 18-Crown-6, Dibenzo-24-crown-8, and Dibenzo-27-crown-9 in Methanol-Water Solvents, at 25 °C and $\mu = 0.1^1$

R. M. Izatt,* R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen

Contribution from the Departments of Chemistry and Chemical Engineering and No. 77 from the Institute for Thermochemical Studies, Brigham Young University, Provo, Utah 84602. Received May 10, 1976

Abstract: The interaction between Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Sr^{2+} , and Pb^{2+} and the cyclic polyethers benzo-15-crown-5, 18-crown-6, dibenzo-24-crown-8, and dibenzo-27-crown-9 in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ solvents has been studied using a calorimetric titration procedure. Log β_i , ΔH_i , and ΔS_i values are calculated in those instances where sufficient amounts of heat were produced. Complexes having 1:1 metal-ligand stoichiometry resulted with these ligands except for the Rb^+ and K^+ -benzo-15-crown-5 systems at 70 and 80 wt % CH_3OH , which were found to be 1:2. As the cyclic polyether ring size increases, the ΔS values for the 1:1 reaction of a given cation become more negative, suggesting increased ligand conformational change upon complex formation.

Following the initial observation of Pedersen² that certain cyclic polyethers selectively complex cations, extensive research has been conducted on the ability of compounds of this class to complex univalent and bivalent metal ions.³ A striking result

of this work was the observation that in aqueous solution certain of the cyclic polyethers (e.g., 18-crown-6) show marked cation selective behavior, while others (e.g., 15-crown-5⁴ and dicyclohexo-24-crown-8⁵) do not. Also, stoichiometry other