Thermodynamic and Kinetic Data for Cation–Macrocycle Interaction†

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I. Introduction

The discovery[1-3] that cations and anions form stable complexes with macrocyclic polyethers and polyamines has opened the door to several broad and fruitful areas of chemical investigation. The interest in these macrocycles was stimulated when it was found that certain of them formed stable complexes with alkali and alkaline earth metal ions and that preferential cation complexation resulted when the relative sizes of the cation and ligand cavity were matched.[4] In addition, these synthetic ligands are similar in their structures and reactions to many naturally occurring compounds of the macrocyclic type which are known to exhibit selective cation complexation.[5] A number of macrocyclic compounds having more than one cyclic ring and having donor atoms such as sulfur and phosphorus in place of the well-known oxygen, nitrogen, and oxygen-nitrogen combinations have been synthesized.[6] The synthesis and subsequent study of a large number of these ligands have presented a challenge in interpreting the cation and anion binding data in terms of the observed selectivities and solvation characteristics of the ligands under various experimental conditions. Chiral derivatives of macrocycles can distinguish between enantiomers of optically active organic cations[7-9] and have been used in their separation.[8] Macrocyclic ligands have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid-liquid or solid-liquid phase-transfer reactions, dissolution in apolar solvents of metal and organic salts, preparation of ion-selective electrodes, isotope separations, and in the understanding of some natural processes through mimicry of metalloenzymes.[10]

Understanding the interactions between macrocyclic ligands and ions requires the study of various parameters governing the reactions. Extensive thermodynamic and kinetic data have been collected by various investigators during the past 15 years and several review articles have been published which deal with cation-macrocycle interactions. Those reviews which contain compilations of equilibrium constant (K), enthalpy change (ΔH), entropy change (ΔS), rate constant (k), and activation parameter data ($\Delta X^{\ddagger}$) are listed below together with the major areas of emphasis in each case.

1. Christensen, Eatough, and Izatt, "The Synthesis and Ion Binding of Synthetic Multidentate Macrocyclic Compounds", 1973.[11] The review deals with the synthetic multidentate macrocyclic compounds containing multiple donor atoms and exhibiting ion-binding properties. The article consists, in part, of a compilation of log K, ΔH, and ΔS values for cation-macrocycle interaction published through December 1972.

2. Liesegang and Eyring, "Kinetic Studies of Synthetic Multidentate Macrocyclic Compounds", 1978.[12]

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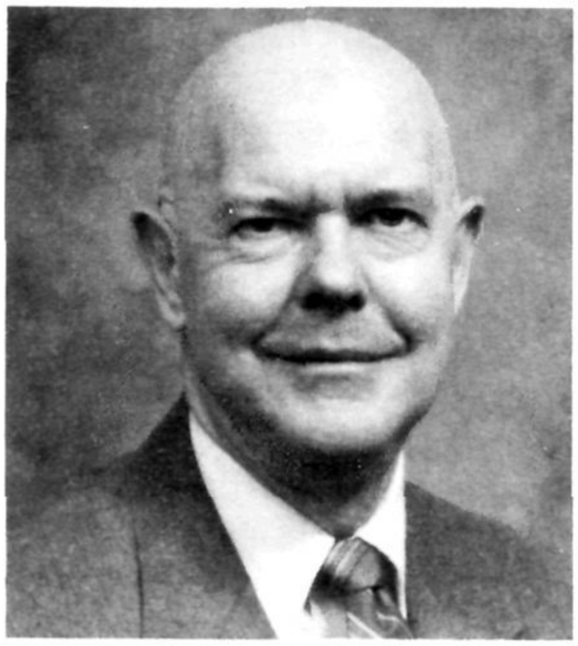
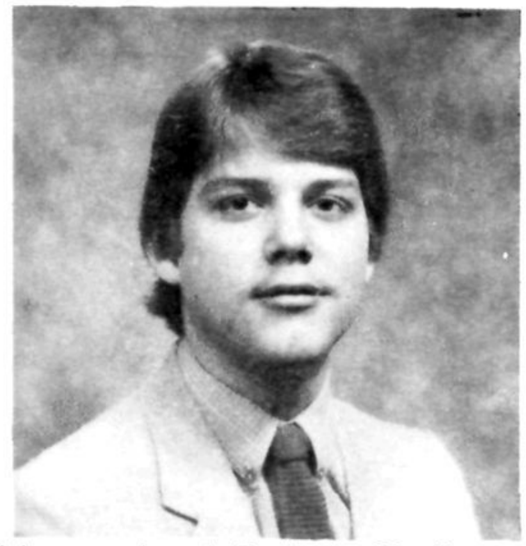


Reed M. Izatt was born in Logan, UT, and received his B.S. degree at Utah State University in 1951. He received his Ph.D. degree in 1954 with Professor W. Conard Fernelius in coordination chemistry at The Pennsylvania State University. After 2 years of postdoctoral work at Carnegie-Mellon University, he joined the Brigham Young University Chemistry Department in 1956. He delivered the Annual Sigma Xi lecture at BYU in 1966 and the Annual BYU Faculty Lecture in 1970 and was BYU Teacher of the Month in October 1974. He received the BYU Karl G. Maeser Research and Creative Arts Award in 1967 and was the recipient of an NIH Career Development Award (1967–1972), the Utah Award (American Chemical Society) in 1971, the Huffman Award (Calorimetry Conference) in 1983, and the Willard Gardner Award of the Utah Academy of Sciences, Arts, and Letters in 1985. He is a member of the Organizing Committee for the annual International Symposium on Macrocyclic Chemistry. His research interests include the design of membrane systems for the carrier-mediated selective separation of cations, calorimetry applied to metal–ligand and nonelectrolyte interactions, and the compilation of thermodynamic data.

Jerald S. Bradshaw was born in Cedar City, UT, and received a B.A. degree in Chemistry at the University of Utah in 1955. After 4 years as an officer in the U.S Navy, he enrolled in a Ph.D. program at UCLA. He received the Ph.D. in 1963 with Professor Donald J. Cram on electrophilic substitution at saturated carbon. He received an NSF postdoctoral fellowship for the 1962–1963 academic year to work with Professor George S. Hammond at California Institute of Technology. After 3 years as a research chemist at Chevron Research in Richmond, CA, he joined the faculty at the Brigham Young University at Provo, UT in 1966. He was named Professor of the Year at BYU in 1975. He was a U.S. National Academy of Science Exchange Professor for the academic year of 1972–1973 and the Summer of 1982 working with Professor Miha Tisler at the University of Ljubljana, Yugoslavia. He also was a visiting professor with Dr. J. F. Stoddart at the University of Sheffield, England in 1978. He was a member of the Advisory Board for the International Society of Heterocyclic Chemistry (1982–1984) and a member of the American Chemical Society. His research interests are the synthesis and cation complexation properties of macrocyclic multidentate compounds, the photochemical reactions of heterocyclic compounds, and the preparation of new polysiloxanes for chromatography uses.



Steven A. Nielsen was born in Redlands, CA. He received his B.A. degree from Brigham Young University in 1984. He will enter medical school in 1985. He has worked with Professors Izatt, Christensen, and Bradshaw on the retrieval and compilation of thermodynamic data.

John D. Lamb was born in Brockville, Ontario, Canada. He received his Ph.D. degree in Inorganic Chemistry in 1978 from Brigham Young University with Professor Reed M. Izatt. His dissertation concerned the characterization of synthetic macrocyclic ligand complexes, their solution stability, cation selectivity patterns, and membrane transport. Thereafter he served as an Associate Research Scientist at Brigham Young University with specific charge over the computer and separations projects. From 1982 to 1984, he worked with the U.S. Department of Energy in Washington, D.C., as Program Manager for Separation and Analysis in the Office of Basic Energy Sciences. He has recently returned to Brigham Young University as Associate Professor of Chemistry. In 1985, he assumes responsibility as Director of Research Administration for Brigham Young University in addition to his faculty assignment. He continues a strong interest in the chemistry of macrocycles and facilitated transport in liquid membranes.

Kinetic data for crown ether– and cryptand–metal complexation through 1976 and some thermodynamic data are included.

3. Lamb, Izatt, Christensen, and Eatough, "Thermodynamics and Kinetics for Cation–Macrocycle Interaction", 1979.[4] A compilation is given of log K, ΔH, and ΔS values for cation–macrocycle interaction through 1976 together with some kinetic data.

4. Poonia and Bajaj, "Coordination Chemistry of Alkali and Alkaline Earth Cations", 1979.[13] Several aspects of coordination complexes of alkali and alkaline earth cations are discussed. Included are some equilibrium constants for the reaction of these cations with macrocyclic ligands.

James J. Christensen was born in Salt Lake City, UT. He obtained B.S. and M.S. degrees from the University of Utah and a Ph.D. degree from Carnegie–Mellon University, all in chemical engineering. He joined the Brigham Young University faculty in 1957 where he is a professor in the Chemical Engineering Department. He has spent short leaves at Du Pont (1959), Dow Chemical Company (1964), Oxford University (1964), Polytechnical Institute at Mexico City (1973), Exxon (1981), and the Bartlesville Energy Technology Center (1981). He was the Annual Sigma Xi Lecturer at BYU in 1966 and delivered the Annual Faculty lecture at BYU in 1970. He has received the following awards: Karl G. Maeser Research and Creative Arts Award (1967), NIH Career Development Award (1967–1972), Utah Award of the American Chemical Society (1976), and Huffman Award of the Calorimetry Conference (1976). His research interests include the development of flow calorimeters capable of operating at elevated temperatures and pressures, the study of the thermodynamics of nonelectrolyte and cation–macrocycle interactions, and the compilation of thermodynamic data.

Debabrata Sen was born in Chittagong (now in Bangladesh). He obtained the M.Sc. (1947), Ph.D. (1952), and D.Sc. (1965) degrees from Calcutta University working with Professor P. Ray. He did postdoctoral work at The Pennsylvania State University and at the University of California (Berkeley). He has worked as a Research Officer, Government of India (1955–1958); Reader in Chemistry, Jadavpur University, Calcutta (1958–1966); and since 1966 has been Professor of Chemistry, Indian Institute of Technology, Kharagpur. He was associated with Brigham Young University as a Visiting Professor (May–Oct 1981); University of Heidelberg, West Germany as a Senior DAAD Fellow (Dec 1981–Feb 1982), and visited various institutes and universities in Novosibirsk, Leningrad, and Moscow in the USSR (Sept–Oct 1984) as a guest of the Institute of Catalysis, Siberian branch of the USSR Academy of Sciences. His research interests and publications are in the fields of synthetic and structural studies of transition-metal complexes, especially with biguanides and on homogeneous catalytic reactions.

5. deJong and Reinhoudt, "Stability and Reactivity of Crown-Ether Complexes", 1980.[14] The article deals mainly with the physical organic aspects of crown-ether chemistry. Numerous log K and a few ΔH and ΔS data for cation–macrocycle interaction are compiled and a discussion is given of these data in relation to organic reactions. The literature up to 1978 is covered.

The present article provides a tabulation of the thermodynamic (Table I) and kinetic (Table IV) data incorporated in publications on the title subject through early 1984. In addition, we have attempted in the text to draw the reader's attention to the various parameters involved in ion–macrocycle interaction such as relative cation/anion and ligand cavity sizes, the number and stereochemical arrangement of ligand binding sites, substitution on the macrocyclic ring(s), solvent effects, macrocyclic effects, and type of bonding. Appropriate examples taken from the tables of data are used to illustrate these parameters. The compounds included in the Review are listed by formula and abbreviation in Charts I–XIII. (Cyclic aza compounds are listed as aza crowns with the nomenclature found in the reference given in parentheses.)

The compilation of log K, ΔH, and $T\Delta S$ values is intended to be exhaustive and includes data for coronand and cryptand complexes with alkali, alkaline earth, transition-metal, and post-transition-metal ions, and organic cations. Nomenclature for the crown-type compounds has been presented and discussed.[15] The abbreviations used in the Tables can be understood by reference to the structures and names given in Charts I–XIII. Equilibrium constants are the most numerous thermodynamic data included in the review. These constants have been determined under a variety of temperature, ionic strength, and solvent conditions and the attempt has been made to provide as much information as possible concerning these conditions for each entry. It is important to note that these data are valid only at the specific experimental conditions given.

Kinetic data are compiled for formation and dissociation of ion–macrocycle complexes. In addition, reference is given to representative kinetic data for reactions of metal–macrocycle complexes which involve aquation, hydrolysis, anion substitution, macrocycle exchange, and reduction potential.

II. Thermodynamics of Cation–Macrocycle Interaction

Table I contains log K, ΔH, and ΔS data for the interaction of macrocycles and related ligands with cations in solution. The method used to determine log K is given in each case. The method used to determine ΔH is given only if it is different than that used to determine log K. In these cases, the method is placed in parentheses immediately after the ΔH value. The medium (solvent, supporting electrolyte) used in each determination, the temperature of measurement, and the literature reference are given, also.

A. Cation–Coronand Complexation

Selective binding of cations in solution is a distinctive feature of the solution chemistry of macrocyclic polyethers. The design and synthesis of new macrocyclic

CHART I

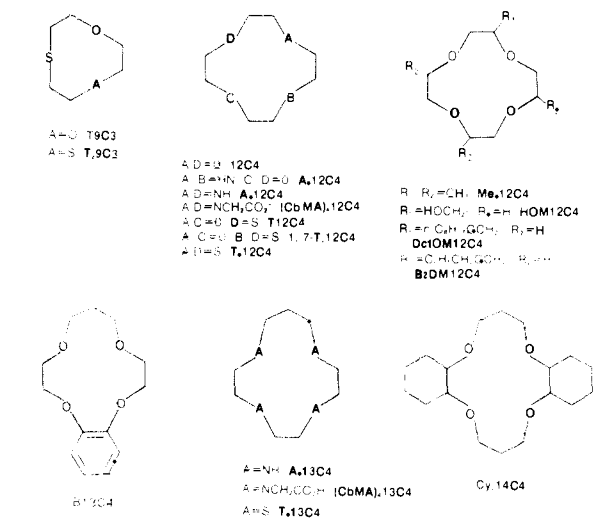
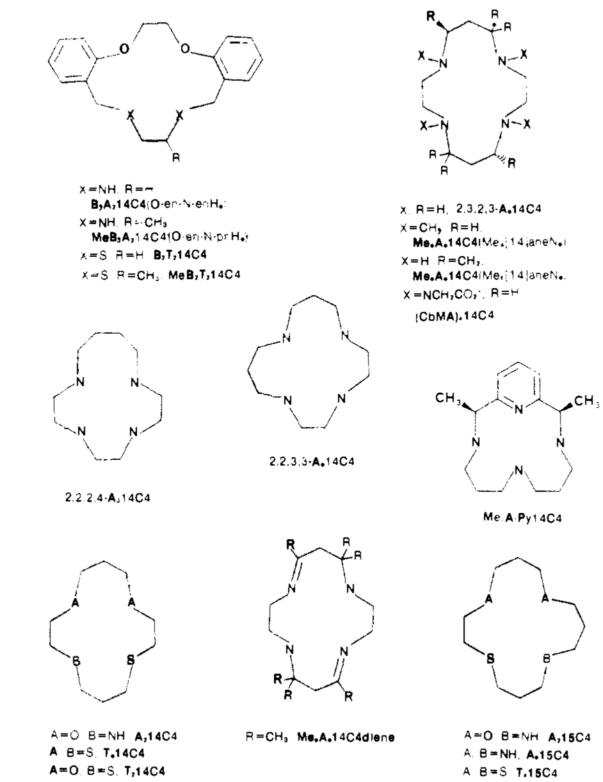


CHART II



ligands with different cavity sizes, donor atom types, ring substituents, etc. have resulted in a large number and variety of compounds. Few of these macrocycles have been studied with respect to their cation complexation properties. However, many of those which have been investigated show unique selective cation complexation behavior. The process of ion–macrocycle association depends on several factors related to characteristic properties of the ligand, reacting ion, and solvent. These energy quantities are depicted in the following Born–Haber cycle where X^- = anion and L

$$\begin{array}{ccc} M^+X^-_{solv} + L & \xrightarrow{K_2} & M^+_{solv} + X^-_{solv} + L \\ \Big\uparrow K_1 & & \Big\downarrow K_3 \\ M^+\cdot L\cdot X^-_{solv} & \xrightarrow[K_4]{} & M^+\cdot L_{solv} + X^-_{solv} \end{array}$$

CHART III

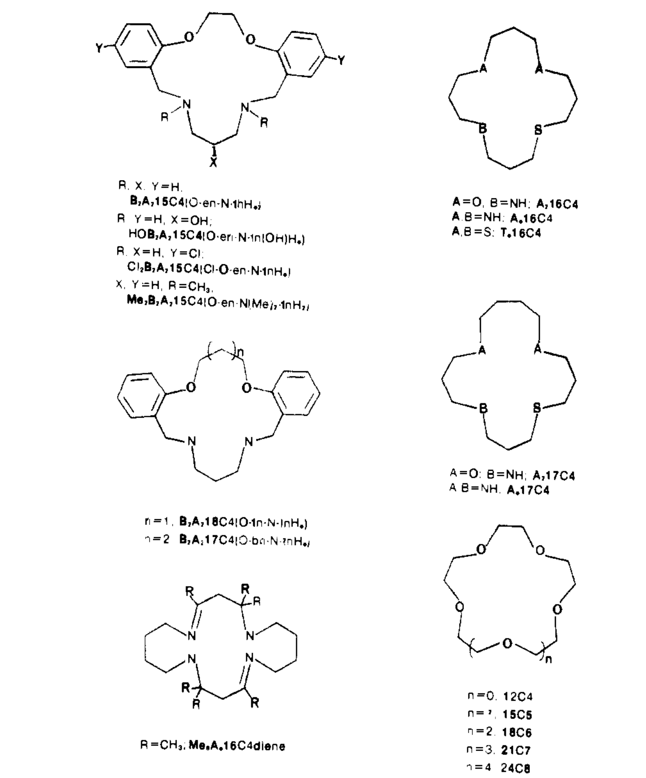
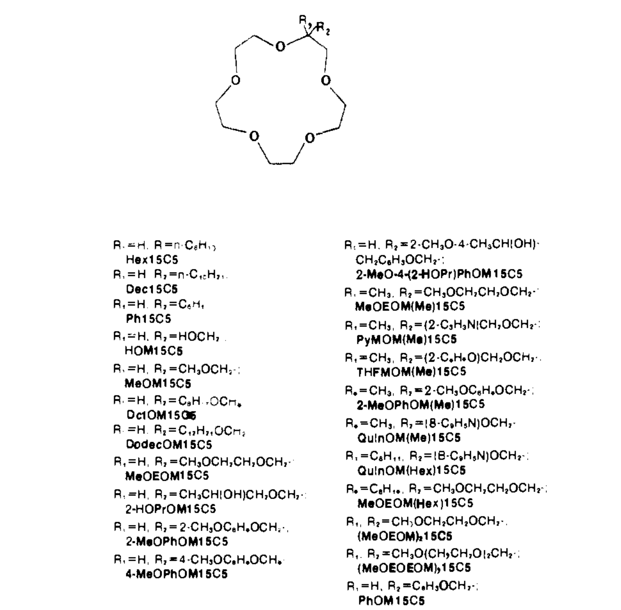


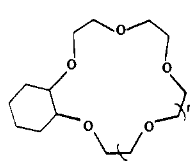
CHART IV



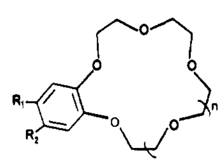
= macrocyclic ligand.

In polar solvents, the equilibrium associated with K_3 predominates over that associated with K_1 whereas in apolar solvents the opposite is the case. An illustration of the importance of the relative solvation energies of M^+ and M^+X^- in determining the cation selectivity of 18C6 is given by Yamabe et al.[89] These workers describe the photoelectron spectra of 18C6 and 12C4 by molecular orbital calculations using the CNDO/2 method for the crown ethers and their cation complexes. The relative stabilities of the Na^+ and K^+ complexes of 18C6 in aqueous solution are explained reasonably by consideration of the hydrated cation and complex indicating the important role of solvation in determining cation selectivity by this crown ether.

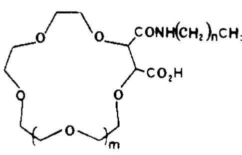
CHART V



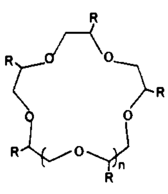
n=1: Cy15C5
n=2: Cy18C6



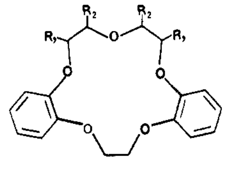
n=1, R_1,R_2=H: B15C5
n=1, R_1=H, R_2=$CH_3C(O)$: AcetoB15C5
n=1, R_1=H, R_2=$CH_3NHCH_2CH(OH)$: AdrB15C5
n=1, R_1=H, R_2=CHO: AldB15C5
n=1, R_1=H, R_2=NH_2: AmB15C5
n=1, R_1=H, R_2=Br: BrB15C5
n=1, R_1=H, R_2=$(CH_3)_3C$: t-BuB15C5
n=1, R_1=H, R_2=CO_2H: HCbB15C5
n=1, R_1=H, R_2=CH_3: MeB15C5
n=1, R_1=H, R_2=NO_2: NitB15C5
n=1, R_1,R_2=NO_2: $(NitB)_2$15C5
n=2, R_1,R_2=H: B18C6
n=2, R_1=H, R_2=$CH_3C(O)$: AcetoB18C6
n=2, R_1=H, R_2=$CH_3HNCH_2CH(OH)$: AdrB18C6
n=2, R_1=H, R_2=CHO: AldB18C6
n=2, R_1=H, R_2=n-$C_4H_9NHC(O)$: n-BuAcetB18C6
n=2, R_1=H, R_2=CH_3: MeB18C6
n=3, R_1,R_2=H: B21C7
n=6, R_1,R_2=H: B30C10



m=1, n=7: Cb(OctAcet)15C5
m=1, n=13: Cb(TetrdecAcet)15C5
m=1, n=17: Cb(OctodecAcet)15C5
m=2, n=3: Cb(BuAcet)18C6
m=2, n=7: Cb(OctAcet)18C6
m=2, n=13: Cb(TetredecAcet)18C6
m=2, n=17: Cb(OctedecAcet)18C6

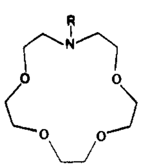


n=1, R=CH_3: $Me_3$15C5
n=2, R=CH_3: $Me_3$18C6

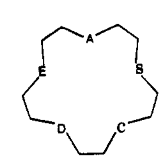


R_6=H, R_7=CH_3:
7, 9-$Me_2B_2$15C5
R_6=CH_3, R_7H:
8, 10-$Me_2B_2$15C5

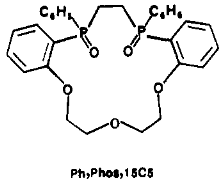
CHART VI



R=H: A15C5
R=CH_3: MeA15C5
R=n-C_4H_9: BuA15C5
R=n-C_8H_{17}: OctA15C5
R=CH_2=$CHCH_2$: AlA15C5
R=$C_6H_5CH_2$-: BzA15C5
R=$HOCH_2CH_2$-: HOEA15C5
R=$CH_3OCH_2CH_2$-: MeOEA15C5
R=$H(OCH_2CH_2)_2$: $H(OE)_2$A15C5
R=$CH_3(OCH_2CH_2)_2$: $Me(OE)_2$A15C5
R=$H(OCH_2CH_2)_3$: $H(OE)_3$A15C5
R=$CH_3(OCH_2CH_2)_3$: $Me(OE)_3$A15C5
R=$CH_3(OCH_2CH_2)_4$: $Me(OE)_4$A15C5
R=$CH_3(OCH_2CH_2)_6$: $Me(OE)_6$A15C5
R=$CH_3(OCH_2CH_2)_7$: $Me(OE)_7$A15C5

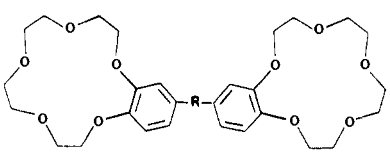


A-C=O, D, E=NH:
1, 4-$A_2$15C5
A, B, D=O, C, E=NH:
1, 7-$A_2$15C5(2.1)
A, B, C, O=O; E=S: T15C5
A, B, C=O; D, E=S:
1, 4-$T_2$15C5
A, B, D=O; C, E=S;
1, 7-$T_2$15C6
A, B, C, D, E=S: $T_5$15C5
A=O; B, E=NH; C, D=S;
4, 13-A_2-7, 10-$T_2$15C5
A=O; B, E=S; C, D=NH;
7, 10-A_2-4, 13-$T_2$15C5

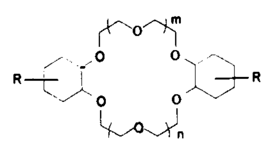


$Ph_2Phos_2$15C5

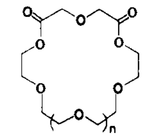
CHART VII



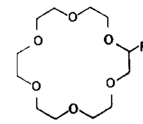
R=CH_2OCH_2: $O(MB15C5)_2$
R=$O_2C(CH_2)_2CO_2$: $E(CbB15C5)_2$
R=C=$N(CN_2)_4$C=N: $Bu(NMB15C5)_2$
R=$O_2C(CH_2)_3CO_2$: $Pent(CbB15C5)_2$
R=$O_2CCH_2CH_2OCH_2CH_2CO_2$: $EOE(CbB15C5)_2$
R=$O_2C(CH_2CH_2O)_2CH_2CH_2CO_2$: $(EO)_2E(CbB15C5)_2$
R=$O_2C(CH_2)_6CO_2$: $Oct(CbB15C5)_2$
R=C=$N(CH_2)_9$N=C: $Non(NMB15C5)_2$
R=C=$N(CH_2)_{10}$N=C: $Dec(NMB15C5)_2$



m, n=1; R=H; $Cy_2$18C6
m, n=1; R=$(CH_3)_3C$-;
$(t-BuCy)_2$18C6
m=1, n=2, R=H; $Cy_2$21C7
m, n=2; R=H; $Cy_2$24C8

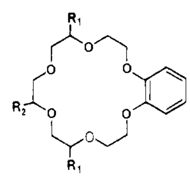


n=1: $K_2$18C6
n=2: $K_2$21C7

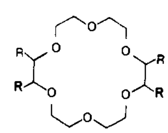


R=n-C_8H_{16}: Oct18C6
R=n-$C_{12}H_{26}$: Dodec18C5
R=C_6H_5: Ph18C5
R=n-$C_8H_{17}OCH_2$: OctOM18C6
R=n-$C_{12}H_{23}OCH_2$: DodecOM18C6

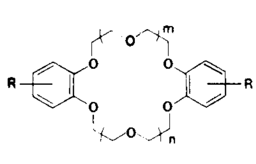
CHART VIII



R_1,R_2=H: B18C6
R_1=CH_3, R_2=H: 8,15-Me_2B18C6
R_1,R_2=CH_3: 8,11,15-Me_3B18C6



R=$C_6H_5CH_2OCH_2$-: $(BzOM)_4$18C6
R=$(C_6H_5)_3COCH_2$-: $(TritOM)_4$18C6
R=$OC(CH_3)_2OCH_2CH$-:
$(DMD)_2$18C6
R=$(CH_3)_2NC(O)$: $(Me_2Acet)_4$18C6
R=$CH_3NHC(O)$: $(MeAcet)_4$18C6
R=^-O_2C: $Cb_4$18C6
R=$CH_3O_2CCH_2NHC(O)$:
$(MeCbMAcet)_4$18C6
R=$^-O_2CCH_2NHC(O)$:
$(CbMAcet)_4$18C6
R=$^-O_2CCHCH_2CH_2CH_2NC(O)$:
$(ProCbe)_4$18C6
R=$C_6H_5CH_2CH(CO_2^-)NHC(O)$
$(PheCbe)_4$18C6
R=$(3-C_8H_6N)CH(CO_2^-)NHC(O)$:
$(TrpCbe)_4$18C6
R=$^-O_2CCH_2CH_2CH(CO_2^-)NHC(O)$:
$(GluCbe)_4$18C6
R=$(2-C_{10}H_6-6-SO_3^-)NHC(O)$:
$(SulNapAcet)_4$18C6
R=$(2-C_{10}H_6-3-CO_2^-)NHC(O)$:
$(CbNapAcet)_4$18C6
R=$(H_2N)_2^+CNH(CH_2)_3$-
$CH(CO_2^-)NHC(O)$: $(ArgCbe)_4$18C6
R=$H_3\overset{+}{N}CH_2CH_2NHC(O)$:
$(enCbe)_4$18C6
R=CH=CHCH=C(CONH_2)CH=$\overset{+}{N}$-
$CH_2CH_2NHC(O)$: $(NicEAcet)_4$18C6



m, n=1; R=H; $B_2$18C6
m,n=1, R=NH_2; $(AmB)_2$18C6
m, n=1, R=Br; $(BrB)_2$18C6
m, n=1; R=$(CH_3)_3C$-; $(t-BuB)_2$18C6
m, n=1; R=CH_3; $(MeB)_2$18C6
m,n=1, R=NO_2; $(NitB)_2$18C6
m=1, n=2, R=H; $B_2$21C7
m=0, n=4, R=H; 1,7-$B_2$24C4
m=1, n=3, R=H; 1,10-$B_2$24C8
m, n=2, R=H; 1,13-$B_2$24C8
m, n=2; R=CH_3; $(MeB)_2$24C8
m=2, n=3, R=H; $B_2$27C9
m, n=3; R=H; $B_2$30C10
m, n=3; R=CH_3; $(MeB)_2$30C10
m,n=8, R=H; $B_4$60C20

1. Relative Cation and Ligand Cavity Sizes

Many K_3 and K_1 values have been determined by using diverse experimental methods. The enhancement of complex stability by a close correspondence between the ionic crystal radius of the metal ion and the radius of the cavity formed by the crown-ether ring has been noted.[11] Full participation of all macrocycle donor atoms with the complexed cation is expected to give the highest possible stability to the resulting complex. The selectivity of 18C6 for certain of the alkali and alkaline earth cations is shown in Figure 1.

Cavity radii for the macrocyclic ligands were computed originally from different types of molecular models such as Corey-Pauling-Kolton (CPK) and Fisher-Hirschfelder-Taylor (FHT). X-ray crystallographic studies have made possible the accurate determination of the positions of the interacting atoms and ions in the complexes as well as their dimensions

CHART IX

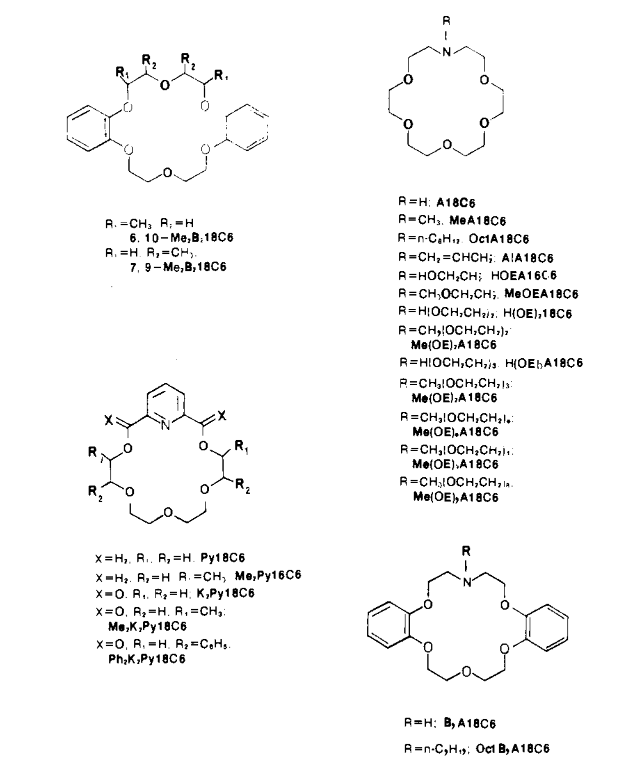


CHART X

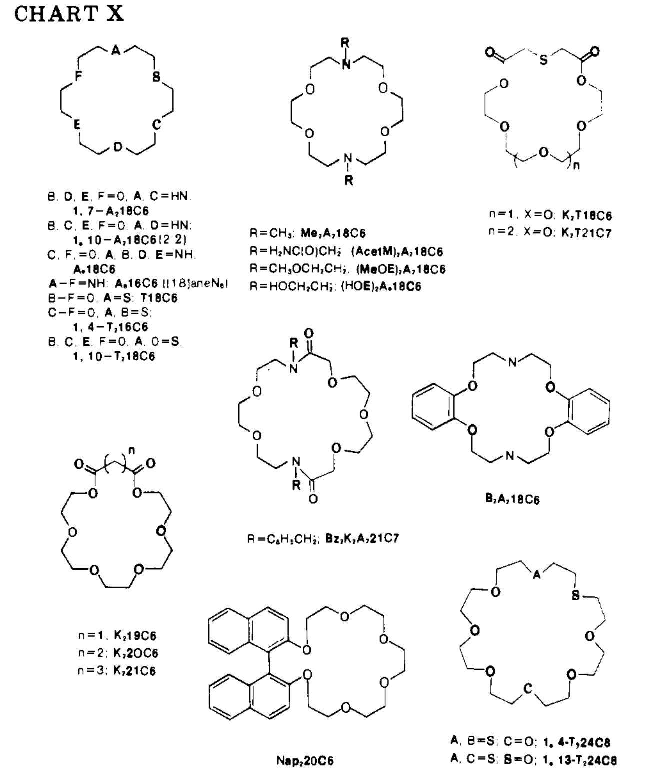


CHART XI

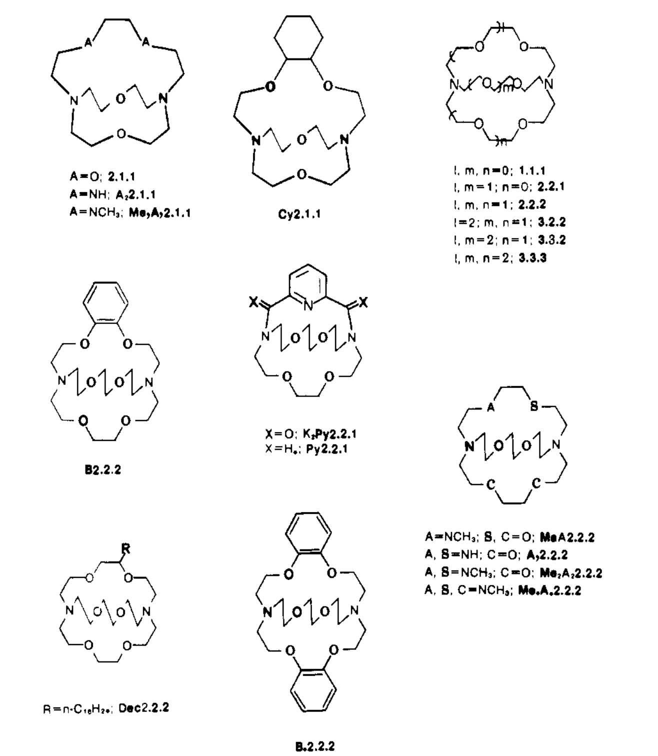
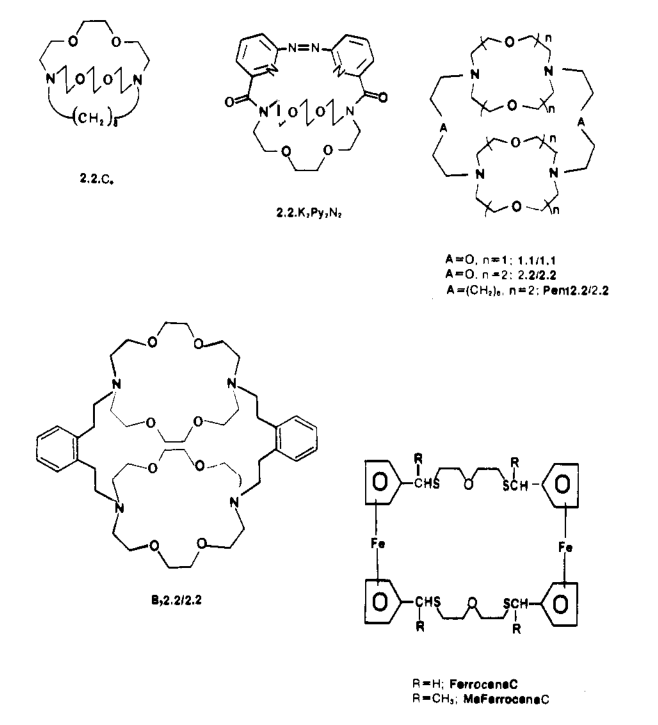


CHART XII

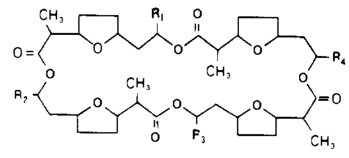


in the free state. The best fit of the X-ray data is found with CPK models.[187] Some representative macrocycle cavity radii are given in parentheses: 15C5 (0.86–0.92 Å), 18C6 (1.34–1.43 Å), 21C7 (1.7 Å).[187] Ionic radii are given in Table II for many of the cations listed in Table I.

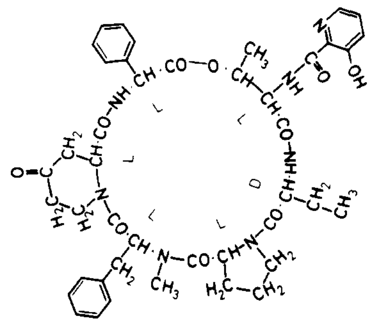
The cation radii listed in Table II are taken from a more comprehensive listing by Shannon[188] which is based on X-ray structural analyses of oxides and fluorides. This set of ionic radii and others valid for nonhydrated cations have been discussed.[189] Marcus[190] has set forth arguments for the use of hydrated cation radii in correlations involving solvated cations. These radii have been calculated for more than 30 ions by using published data of the average distances between the ions and the nearest water molecules, obtained by diffraction and computer simulation methods.

The data in Figure 1 show that for both alkali and alkaline earth metal ions the maximum stability for complexes with 18C6 occurs when the metal ion to ligand cavity ratio is approximately unity as is the case

CHART XIII



R_1-R_4=CH_3: Nonectin
R_1-R_3=CH_3, R_4=C_2H_5: Monectin
R_1, R_3=CH_3; R_2, R_4=C_2H_5: Dinectin
R_1=CH_3, R_2-R_4=C_2H_5: Trinactin



Virginimycin

with K^+ and Ba^{2+}. The greater stability at a ratio of unity is largely due to the enthalpy term indicating a greater electrostatic bond energy for those ions whose dimensions best match those of the ligand cavity.[53,61,115]

In many cases, the stoichiometry of cation–macrocycle interaction has not been investigated thoroughly. An interesting example of complexation behavior possible in the solid state is provided by the RbSCN-$B_2$18C6 complex.[191] The X-ray crystal structure of this complex indicates that the metal is in the macrocycle cavity, but one-third of the cavities are empty. Thus, the complex is 1:1 while the solid-state stoichiometry is 2:3. Other crystal forms may be possible depending on experimental conditions, i.e., solvent, relative solute concentrations, etc. Also, B15C5 forms a 1:2 complex with KI in the solid state,[192] but only 1:1 stoichiometry has been assumed in methanol–water solvents.[119]

The formation of a 1:1 metal ion–coronand complex does not necessarily mean that the metal ion is located within the cavity of the macrocycle. The alkali metal thiocyanates of $B_2$18C6 were reported by Pedersen[193] to have metal to ligand ratios of 1:1, 1:1 and 1:2, and 1:2 and 2:3 for potassium, rubidium, and cesium, respectively. A "sandwich" structure, in which the metal ion is located between two coronand molecules, was suggested as the most probable one for the 1:2 complexes. Similarly, the 2:3 complex can be visualized as two metal ions between three coronand molecules arranged flatwise in three tiers.[193]

The ESR spectrum of spin-labeled B15C5 in ethanol in the presence of NaSCN was similar to that of the present compound, whereas in the presence of KSCN a drastic change of the ESR spectrum was noted when the molar ratio of KSCN-B15C5 was 1:2.[194] The diminished line intensity resulting from spin–spin interaction as SCN^- concentration was increased was interpreted to mean that the stability of the 1:2 KSCN-B15C5 complex was much larger than that of the 1:1 complex. In some cases, the metal ion may have directed bonding orbitals which preclude bonding to all

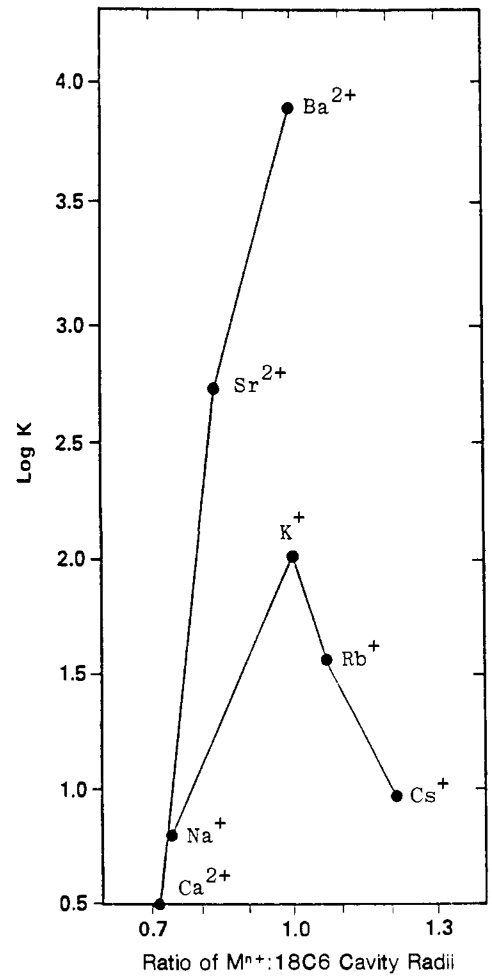


Figure 1. Selectivity of 18C6: log K values for reaction of 18C6 with metal cations in water at 25 °C vs. the ratio of the ionic cation radius to the 18C6 cavity radius.[4] The low K value for Ca^{2+} is reported as <0.5.[11] Reprinted with permission from ref 4. Copyright 1979, Plenum Press.

of the oxygen atoms in the coronands. This was shown in the case of a complex between cobalt chloride and $Cy_2$18C6 where both a sandwich type structure and a chain-type polymer configuration with an alternating array of cobalt cations and cyclic polyether molecules have been proposed.[195]

Comparison of equilibrium constants for a large number of 1:1 cation–macrocycle complexes reveals that log K values for complexes with 15C5 are much lower than those with the ligand 18C6 for all cations studied except Na^+, Li^+, and NH_4^+. On the other hand, the larger coronands $Cy_2$21C7 and $Cy_2$24C8 bind Cs^+ more strongly than do smaller macrocycles and generally are selective for Cs^+ over all other cations.

Extensive work has been done on the reactions of mono- and bivalent cations with two of the isomers of $Cy_2$18C6 in water.[53,115,116] These ligands have high selectivity toward certain cations. For example, the difference in log K values between the Ca^{2+} and Pb^{2+} complexes is 5. Neither isomer has measurable affinity in water for either Cd^{2+} or Zn^{2+}, but both isomers have high affinity for Hg^{2+}.

The "ion-in-the-hole" model has limited usefulness in predicting relative binding capacities of metal cations with polyethers. For example, as the number of ring atoms increases, the macrocycle flexibility increases and it becomes difficult to define the cavity diameter.

TABLE I. Log K, ΔH, and ΔS Values for Cation-Macrocycle Interaction in Solution

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
T9C3	Hg^{2+}	(3)	Cal	−57.82		25	70% MeOH	16
$T_2$9C3	Hg^{2+}	(1)	Cal	−52.01		25	70% MeOH	16
	Hg^{2+}	(2)	Cal	−62.55		25	70% MeOH	16
12C4	H^+	2.2 (1)	Pot			25	MeCN	335
	H^+	0.63 (2)	Pot			25	MeCN	335
	Li^+	~0	NMR			27	H_2O, 0.02 M $LiClO_4$	17
	Li^+	~0	NMR			27	Me_2SO, 0.02 M $LiClO_4$	17
	Li^+	3.40	Cond			25	MeCN (anion = I^-)	18
	Li^+	4.25	NMR	−16.3 (Cal)	27.2	27	MeCN, 0.02 M $LiClO_4$	17
	Li^+	1.62	NMR	−13.4 (Cal)	−14.2	27	Me_2CO, 0.02 M $LiClO_4$ (NMR), 0.5 M $LiClO_4$ (Cal)	17
	Li^+	~0	NMR	−3.3 (Cal)		27	MeOH, 0.02 M $LiClO_4$ (NMR), 0.5 M $LiClO_4$ (Cal)	17
	Li^+	>4 (1)	NMR	−36.8 (Cal)		27	NMe, 0.02 M $LiClO_4$	17
	Li^+	1.6 (2)	NMR	−19.2 (Cal)	−34.3	27	NMe, 0.02 M $LiClO_4$	17
	Li^+	2.93	Pot			25	PC, ? M Et_4NClO_4	19
	Li^+		NMR	−10.9 (Cal)	>41.8	27	Pc, 0.02 M $LiClO_4$	17
	Li^+	0.70	NMR			27	Py, 0.02 M $LiClO_4$	17
	Li^+	~0	NMR			27	TMG, 0.02 M $LiClO_4$	17
	Na^+	3.32	Cond			25	MeCN (anion = BPh_4^-)	18
	Na^+	1.47 (1)	Cal	−12.6	−14.0	25	MeOH	20
	Na^+	2.29 (2)	Cal	−28.0	−50.5	25	MeOH	20
	Na^+	1.41 (1)	ISE			25	MeOH	21
	Na^+	2.20 (2)	ISE			25	MeOH	21
	Na^+	1.7	ISE			25	MeOH	22
	Na^+	3.6 (1)	Polg			25	PC, ? M Et_4NClO_4	19
	Na^+	2.57 (2)	Polg			25	PC, ? M Et_4NClO_4	19
	Na^+	3.5 (1)	Pot			25	PC, ? M Et_4NClO_4	19
	Na^+	2.81 (2)	Pot			25	PC, ? M Et_4NClO_4	19
	K^+	1.59 (1)	Pot	−21.3 (Cal)	−41.3	25	MeOH	20
	K^+	0.56 (2)	Pot			25	MeOH	20
	K^+	1.74	ISE			25	MeOH	22
	K^+	1.58 (1)	ISE			25	MeOH	21
	K^+	0.15 (2)	ISE			25	MeOH	21
	K^+	2.15	Polg			25	PC, ? M Et_4NClO_4	19
	Rb^+	1.69	Polg			25	PC, ? M Et_4NClO_4	19
	Cs^+	1.43	Polg			25	PC, ? M Et_4NClO_4	19
	Mg^{2+}	2.61 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Mg^{2+}	3.6 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ca^{2+}	5.53 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ca^{2+}	3.98 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Sr^{2+}	5.29 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Sr^{2+}	2.62 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ba^{2+}	4.63 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ba^{2+}	3.27 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	La^{3+}	5.00 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	La^{3+}	1.98 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pr^{3+}	5.27 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pr^{3+}	1.82 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Nd^{3+}	5.19 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Nd^{3+}	1.55 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{2+}	8.4 (1 + 2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{3+}	5.17 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{3+}	1.59 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tb^{3+}	5.15 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tb^{3+}	0.94 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Yb^{2+}	8.3 (1 + 2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Yb^{3+}	4.94	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Lu^{3+}	5.00	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	7.68 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	4.02 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tl^+	3.71	Pot			25	PC, 0.1 M Et_4NClO_4	24
	NH_4^+	1.3	Pot			25	MeOH	22
$Me_4$12C4	Li^+	3.46	Cond			25	MeCN	18
	Na^+	1.41	ISE			25	MeOH	11, 25
HOM12C4	Na^+	1.37 (1)	ISE			25	MeOH	21
	Na^+	1.79 (2)	ISE			25	MeOH	21
	K^+	1.43 (1)	ISE			25	MeOH	21
	K^+	<0 (2)	ISE			25	MeOH	21
OctOM12C4	Na^+	1.32 (1)	ISE			25	MeOH	21
	Na^+	1.97 (2)	ISE			25	MeOH	21
	K^+	1.36 (1)	ISE			25	MeOH	21
	K^+	<0 (2)	ISE			25	MeOH	21
BzOM12C4	Na^+	1.35 (1)	ISE			25	MeOH	21
	Na^+	1.98 (2)	ISE			25	MeOH	21
	K^+	1.42 (1)	ISE			25	MeOH	21
	K^+	1.29 (2)	ISE			25	MeOH	21

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
$A_2$12C4	H^+	9.53 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	7.65 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Co^{2+}	5.76	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ni^{2+}	5.91	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	8.16	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Zn^{2+}	6.22	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
$A_4$12C4	H^+	10.91 (1)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	9.90 (2)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.7 (1)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	27, 28
	H^+	9.7 (2)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	27, 28
	H^+	1.73 (3)	Pot			25	H_2O	27
	H^+	0.94 (4)	Pot			25	H_2O	27
	H^+	10.51 (1)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	9.49 (2)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	Cu^{2+}		Cal	−95.0	151 (calcd)	25	H_2O	30, 251
	Cu^{2+}	24.8	Polg	−76.6	215	25	H_2O, μ = 0.20	28, 31–34
	Cu^{2+}	24.8	Pot	−95.0 (Cal)	157	25	H_2O, 0.5 M KNO_3	35
	Zn^{2+}	16.2	Polg	−33.1	197	25	H_2O, μ = 2	32
	Zn^{2+}		Cal	−60.7		25	H_2O	30, 251
	Cd^{2+}	14.3	Polg	−34.3	159	25	H_2O, μ = 0.2	32
	Hg^{2+}	25.5	Polg	−98.7	157.8	25	H_2O, 0.20 M $NaClO_4$	36
	Pb^{2+}	15.9	Polg	−27.6	213	25	H_2O, μ = 0.2	32
(CbMA)$_4$12C4	H^+	11.08 (1)	Pot			25	H_2O, 1 M NaCl	27
	H^+	9.23 (2)	Pot			25	H_2O, 1 M NaCl	27
	H^+	4.24 (3)	Pot			25	H_2O, 1 M NaCl	27
	H^+	4.18 (4)	Pot			25	H_2O, 1 M NaCl	27
	H^+	1.88 (5)	Pot			25	H_2O, 1 M NaCl	27
	H^+	1.71 (6)	Pot			25	H_2O, 1 M NaCl	27
	H^+	9.95 (1)	Pot			80	H_2O, 1 M NaCl	27
	H^+	8.28 (2)	Pot			80	H_2O, 1 M NaCl	27
	H^+	4.22 (3)	Pot			80	H_2O, 1 M NaCl	27
	H^+	3.65 (4)	Pot			80	H_2O, 1 M NaCl	27
	H^+	2.22 (5)	Pot			80	H_2O, 1 M NaCl	27
	H^+	1.30 (6)	Pot			80	H_2O, 1 M NaCl	27
	Na^+	2.52	Pot			25	H_2O, 1 M NaCl	27
	Mg^{2+}	11.03	Pot			20	H_2O, 0.1 M KCl	337
	Ca^{2+}	15.85	Pot			20	H_2O, 0.1 M KCl	337
	Sr^{2+}	12.80	Pot			20	H_2O, 0.1 M KCl	337
	Co^{2+}	18.42	Pot			20	H_2O, 0.1 M KCl	337
	Ni^{2+}	17.25	Pot			20	H_2O, 0.1 M KCl	337
	Cu^{2+}	19.06	Pot			20	H_2O, 0.1 M KCl	337
	Zn^{2+}	18.90	Pot			20	H_2O, 0.1 M KCl	337
	Cd^{2+}	19.08	Pot			20	H_2O, 0.1 M KCl	337
	Pb^{2+}	19.89	Pot			20	H_2O, 0.1 M KCl	337
T12C4	Ag^+	2.71	Cal	−42.80	−91.68	25	H_2O	16
	Ag^+	(1)	Cal	−43.47		25	70% MeOH	16
	Ag^+	3.68 (2)	Cal	−44.10	−77.50	25	70% MeOH	16
	Hg^{2+}	(1)	Cal	−50.21		25	70% MeOH	16
	Hg^{2+}	(2)	Cal	−52.05		25	70% MeOH	16
	Pb^{2+}	0.94	Cal	−24.52	−64.30	25	H_2O	16
1,7-$T_2$12C4	Ag^+	(1)		−70.21		25	70% MeOH	16
	Ag^+	4.26 (2)	Cal	−49.33	−83.96	25	70% MeOH	16
	Hg^{2+}	(1)	Cal	−69.83		25	70% MeOH	16
	Hg^{2+}	(2)	Cal	−62.51		25	70% MeOH	16
$T_4$12C4	Cu^{2+}	3.382	Spec			5	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.39	Spec			15	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.39	Spec	0.46	66.5	25	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.39	Spec			35	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.39	Spec			25	H_2O, 0.1 M $HClO_4$	38
	Cu^{2+}	2.51	Spec			25	80% MeOH, 0.1 M $HClO_4$	38
	Cu^{2+}	2.38	Spec			25	80% MeOH, 0.1 M $HClO_4$	39
	Cu^{2+}	2.44	TJ			25	80% MeOH, 0.1 M $HClO_4$	38
B13C4	Li^+	5 (1)	NMR			25	CH_2Cl_2 (anion = ClO_4^-)	41
	Li^+	1.7 (2)	NMR			25	CH_2Cl_2 (anion = ClO_4^-)	41
	Li^+	2.4 (1)	NMR			25	MeCN (anion = ClO_4^-)	41
	Li^+	~3 (1)	NMR			25	NMe (anion = ClO_4^-)	41
	Li^+	1.26 (2)	NMR			25	NMe (anion = ClO_4^-)	41
$A_4$13C4	H^+	11.30 (1)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.31 (2)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.10 (1)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.10 (2)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.90 (1)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	9.91 (2)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	Cu^{2+}	29.1	Polg	−122	141	25	H_2O, μ = 0.20	33, 34
	Zn^{2+}	15.6	Polg	−32.6	188	25	H_2O, μ = 0.2	32
	Hg^{2+}	25.3	Polg	−103.3	139.3	25	H_2O, 0.20 M $NaClO_4$	36

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
$(CbMA)_4$13C4	Mg^{2+}	6.36	Pot			20	H_2O, 0.1 M KCl	337
	Ca^{2+}	8.06	Pot			20	H_2O, 0.1 M KCl	337
	Sr^{2+}	11.70	Pot			20	H_2O, 0.1 M KCl	337
	Ba^{2+}	7.24	Pot			20	H_2O, 0.1 M KCl	337
	Co^{2+}	14.98	Pot			20	H_2O, 0.1 M KCl	337
	Ni^{2+}	15.75	Pot			20	H_2O, 0.1 M KCl	337
	Cu^{2+}	17.29	Pot			20	H_2O, 0.1 M KCl	337
	Zn^{2+}	14.42	Pot			20	H_2O, 0.1 M KCl	337
	Cd^{2+}	16.54	Pot			20	H_2O, 0.1 M KCl	337
	Pb^{2+}	15.63	Pot			20	H_2O, 0.1 M KCl	337
$T_4$13C4	Cu^{2+}	3.58	Pot			5	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.49	Pot			15	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.44	Pot	−9.9	32.6	25	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.39	Pot			35	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	2.43	Kin			25	80% MeOH, 0.1 M $HClO_4$	38
	Cu^{2+}	2.43	Spec			25	80% MeOH, 0.1 M $HClO_4$	39
	Cu^{2+}	3.44	Spec			25	H_2O, 0.1 M $HClO_4$	38
$Cy_2$14C4	Na^+	2.18	ISE			25	MeOH	11, 25
	K^+	1.30	ISE			25	MeOH	11, 25
$B_2A_2$14C4	H^+	9.19 (1)	Pot			25	95% MeOH, 0.1 M, Me_4NCl	42, 43
	H^+	5.40 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42, 43
	Ni^{2+}	3.7	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Cu^{2+}	8.2	Pot			25	95% MeOH, 0.1 M Me_4NCl	44
$MeB_2A_2$14C4	H^+	9.41 (1)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	6.01 (2)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	9.48 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	H^+	4.98 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Ni^{2+}	3.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
2,3,2,3-$A_4$14C4	H^+	11.82 (1)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.50 (2)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.50 (1)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.30 (2)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.49 (1)	Spec			25	H_2O, 0.1 M NaOH	48
	H^+	11.23 (1)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.15 (2)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.59 (1)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	10.62 (2)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	1.61 (3)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	2.42 (4)	Pot			25	H_2O, 0.5 M KNO_3	45
	Ni^{2+}	23.5	Spec			10	H_2O, μ = 0.1, NaOH	48
	Ni^{2+}	22.2	Spec	−129.7 (Cal)	−8.4	25	H_2O, μ = 0.1, NaOH	48
	Ni^{2+}	21.2	Spec			40	H_2O, μ = 0.1, NaOH	48
	Ni^{2+} (H)^e			−100.8 (Cal)		25	H_2O (pH 14?)	47
	Ni^{2+} (L)^e			−78.2 (Cal)		25	H_2O (pH 14?)	47
	Ni^{2+}	22.2	Polg	−129.7	−8.4	25	H_2O	31, 33, 34, 48
	Zn^{2+}		Cal	−61.9		25	H_2O (pH 14)	251
	Zn^{2+}	15.5	Polg	−31.8	192	25	H_2O	32
	Hg^+	23	Polg	−137.7	−20.5	25	H_2O, 0.20 M $NaClO_4$	36
	Cu^{2+}		Cal	−135.6		25	H_2O (pH 14)	251
2,2,3,3-$A_4$14C4	Ni^{2+} (H)^e			−82.4 (Cal)		25	H_2O (pH 14?)	50
	Ni^{2+} (L)^e			−60.2 (Cal)		25	H_2O (pH 14?)	50
	Cu^{2+}	22.36	Pot	−87.5 (Cal)		25	H_2O, μ = 0.5	46
	Ni^{2+}			−53.6 (Cal)		25	H_2O, μ = 0.5	46
	Ni^{2+}			−36.4 (Cal)		25	H_2O, μ = 0.5	46
2,2,2,4-$A_4$14C4	H^+	10.98 (1)	Pot			25	H_2O, 0.5 M KNO_3	46
	H^+	9.75 (2)	Pot			25	H_2O, 0.5 M KNO_3	46
	H^+	4.86 (3)	Pot			25	H_2O, 0.5 M KNO_3	46
	H^+	2.00 (4)	Pot			25	H_2O, 0.5 M KNO_3	46
Me_2A_3Py14C4	Ni^{2+} (H)^e			−50.2 (Cal)		25	H_2O (pH 14?)	50
	Ni^{2+} (L)^e			−31.8 (Cal)		25	H_2O (pH 14?)	50
$Me_4A_4$14C4	H^+	9.70 (1)	Pot			25	H_2O, 0.5 M KNO_3+	45
	H^+	9.31 (2)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	3.09 (3)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	2.64 (4)	Pot			25	H_2O, 0.5 M KNO_3	45
$Me_6A_4$14C4	H^+	12.6 (1)	Solv Extr			25	H_2O	51
	H^+	10.4 (2)	Pot			25	H_2O	51
	H^+	0.8 (3)	Pot			25	H_2O	51
	H^+	0.8 (4)	Pot			25	H_2O	51
rac	H^+	18.2	Spec			25	H_2O, 0.1 M NaOH	48
	H^+	11.6 (1)	Pot			25	H_2O	11
	H^+	10.7 (2)	Pot			25	H_2O	11
	H^+	2.7 (3)	Pot			25	H_2O	11
	H^+	2.3 (4)	Pot			25	H_2O	11
meso	H^+	11.69 (1)	Spec			25	H_2O, 0.1 M NaOH	48
rac	H^+	11.6 (1)	Spec			25	H_2O, 0.1 M NaOH	48
rac	H^+	18.2	Spec			25	H_2O, 0.1 M NaOH	48

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
meso	Ni^{2+}	23.06	Spec			10	H_2O, μ = 0.1, NaOH	48
meso	Ni^{2+}	21.90	Spec	−117.6 (Cal)	34	25	H_2O, μ = 0.1, NaOH	48
meso	Ni^{2+}	21.02	Spec			40	H_2O, μ = 0.1, NaOH	48
	Cu^{2+}	20 (blue, complex)	Pot			25	H_2O, μ = 0.1	51
	Cu^{2+}	28 (red, complex)	Pot			25	H_2O, μ = 0.1	51
	Cu^{2+}	20	Spec			25	H_2O (blue complex)	11
	Cu^{2+}	28	Spec			25	H_2O (red complex)	11
$Me_6A_414C4diene$	Zn^{2+}	9.9	Polg			10	H_2O, μ = 0.1, $NaClO_4$	49
	Zn^{2+}	9.5	Polg	−42.7	37.7	25	H_2O, μ = 0.1, $NaClO_4$	49
	Zn^{2+}	9.4	Polg			30	H_2O, μ = 0.1, $NaClO_4$	49
	Zn^{2+}	9.2	Polg			35	H_2O, μ = 0.1, $NaClO_4$	49
	Zn^{2+}	8.9	Polg			50	H_2O, μ = 0.1, $NaClO_4$	49
$(CbMA)_414C4$	H^+	11.56 (1)	Pot			25	H_2O, 1 M NaCl	27
	H^+	10.18 (2)	Pot			25	H_2O, 1 M NaCl	27
	H^+	4.05 (3)	Pot			25	H_2O, 1 M NaCl	27
	H^+	3.38 (4)	Pot			25	H_2O, 1 M NaCl	27
	H^+	2.17 (5)	Pot			25	H_2O, 1 M NaCl	27
	H^+	1.42 (6)	Pot			25	H_2O, 1 M NaCl	27
	H^+	10.11 (1)	Pot			80	H_2O, 1 M NaCl	27
	H^+	9.50 (2)	Pot			80	H_2O, 1 M NaCl	27
	H^+	4.02 (3)	Pot			80	H_2O, 1 M NaCl	27
	H^+	3.29 (4)	Pot			80	H_2O, 1 M NaCl	27
	H^+	1.90 (5)	Pot			80	H_2O, 1 M NaCl	27
	H^+	10.15 (2)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.07 (1)	Pot			20	H_2O, 1 M KCl	27
	H^+	9.75 (2)	Pot			20	H_2O, 1 M KCl	27
	H^+	4.31 (3)	Pot			20	H_2O, 1 M KCl	27
	H^+	3.46 (4)	Pot			20	H_2O, 1 M KCl	27
	Na^+	1.64	Pot			25	H_2O, 1 M NaCl	27
	Mg^{2+}	3.02	Pot			20	H_2O, 0.1 M KCl	337
	Ca^{2+}	3.48	Spec			25	H_2O (pH 10.4), 0.25 M NaCl	29
$(CbMA)_414C4$	Ca^{2+}	9.48	Pot			20	H_2O, 0.1 M KCl	337
	Sr^{2+}	6.15	Pot			20	H_2O, 0.1 M KCl	337
	Ba^{2+}	4.32	Pot			20	H_2O, 0.1 M KCl	337
	Co^{2+}	15.00	Pot			20	H_2O, 0.1 M KCl	337
	Ni^{2+}	15.26	Pot			20	H_2O, 0.1 M KCl	337
	Cu^{2+}	18.60	Pot			20	H_2O, 0.1 M KCl	337
	Zn^{2+}	15.81	Pot			20	H_2O, 0.1 M KCl	337
	Cd^{2+}	15.53	Pot			20	H_2O, 0.1 M KCl	337
	Pb^{2+}	14.73	Pot			20	H_2O, 0.1 M KCl	337
T_414C4	Cu^{2+}	4.54	Pot			5	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	4.44	Pot			15	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	4.34	Pot	−17.7	23.4	25	H_2O, 0.1 M $HClO_4$	37, 38
	Cu^{2+}	4.22	Pot			35	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	4.3	Pot			5	H_2O, 0.010 M $HClO_4$	37
	Cu^{2+}	4.4	Pot			5	H_2O, 0.025 M $HClO_4$	37
	Cu^{2+}	4.4	Pot			5	H_2O, 0.050 M $HClO_4$	37
	Cu^{2+}	4.5	Pot			5	H_2O, 0.100 M $HClO_4$	37
	Cu^{2+}	5.0	Pot			5	H_2O, 0.500 M $HClO_4$	37
	Cu^{2+}	4.2	Pot			15	H_2O, 0.010 M $HClO_4$	37
	Cu^{2+}	4.3	Pot			15	H_2O, 0.025 M $HClO_4$	37
	Cu^{2+}	4.3	Pot			15	H_2O, 0.050 M $HClO_4$	37
	Cu^{2+}	4.4	Pot			15	H_2O, 0.100 M $HClO_4$	37
	Cu^{2+}	4.9	Pot			15	H_2O, 0.500 M $HClO_4$	37
	Cu^{2+}	4.1	Pot	−13.96	7.6	25	H_2O, 0.010 M $HClO_4$	37
	Cu^{2+}	4.2	Pot	−15.59	6.6	25	H_2O, 0.025 M $HClO_4$	37
	Cu^{2+}	4.2	Pot	−16.14	6.4	25	H_2O, 0.050 M $HClO_4$	37
	Cu^{2+}	4.3	Pot	−17.51	5.7	25	H_2O, 0.100 M $HClO_4$	37
	Cu^{2+}	4.8	Pot	−20.27	5.6	25	H_2O, 0.500 M $HClO_4$	37
	Cu^{2+}	4.0	Pot			35	H_2O, 0.010 M $HClO_4$	37
	Cu^{2+}	4.1	Pot			35	H_2O, 0.025 M $HClO_4$	37
	Cu^{2+}	4.1	Pot			35	H_2O, 0.050 M $HClO_4$	37
	Cu^{2+}	4.2	Pot			35	H_2O, 0.100 M $HClO_4$	37
	Cu^{2+}	4.7	Pot			35	H_2O, 0.500 M $HClO_4$	37
	Cu^{2+}	3.48	Kin			25	80% MeOH, 0.10 M $HClO_4$	38
	Cu^{2+}	3.48	Spec			25	80% MeOH, 0.10 M $HClO_4$	38, 39
B_2A_215C4	H^+	9.69 (1)	Pot			25	H_2O, 0.1 M KCl	42
	H^+	7.63 (2)	Pot			25	H_2O, 0.1 M KCl	42
	H^+	9.96 (1)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	8.01 (2)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	9.42 (1)	Pot			25	90% MeOH, 0.1 M Me_4NCl	42
	H^+	6.50 (2)	Pot			25	90% MeOH, 0.1 M Me_4NCl	42
	H^+	9.81 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42, 43
	H^+	6.82 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42, 43
	Ni^{2+}	5.1	Pot			25	H_2O, 0.1 M KCl	42
	Ni^{2+}	5.4	Pot			25	H_2O, 1 M KCl	42

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Ni^{2+}	5.2	Pot			25	90% MeOH, 0.1 M Me_4NCl	42
	Ni^{2+}	5.4	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Cu^{2+}	7.2	Pot			25	95% MeOH, 0.1 M Me_4NCl	44
HOB_2A_215C4	H^+	9.45 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	H^+	6.49 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Ni^{2+}	5.4	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
$Cl_2B_2A_215C4$	H^+	9.36 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	H^+	6.29 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Ni^{2+}	4.8	Pot			25	95% MeOH, 0.1 M Me_4NCl	42, 44
	Cu^{2+}	6.8	Pot			25	95% MeOH, 0.1 M Me_4NCl	44
$Me_2B_2A_215C4$	H^+	10.14 (1)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	7.92 (2)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	9.64 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	H^+	6.61 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Ni^{2+}	<4	Pot			25	H_2O, 1.0 M KCl	42
	Ni^{2+}	<4	Pot			25	95% MeOH, 1.0 M Me_4NCl	42
2,3,3,3-A_415C4	H^+	11.40 (1)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.30 (2)	Polg			15	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.20 (1)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	10.10 (2)	Polg			25	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.00 (1)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	9.90 (2)	Polg			35	H_2O, μ = 0.20, $NaClO_4$	32
	H^+	11.08 (1)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	10.38 (2)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	5.28 (3)	Pot			25	H_2O, 0.5 M KNO_3	45
	H^+	3.60 (4)	Pot			25	H_2O, 0.5 M KNO_3	45
	Cu^{2+}	24.4	Polg			25	H_2O, μ = 0.2	32
	Cu^{2+}		Cal	−110.9	95 (calcd)	25	H_2O (pH 14)	30, 251
	Zn^{2+}		Cal	−69.0		25	H_2O	30
	Zn^{2+}	15.0	Polg	−34.3	172	25	H_2O, μ = 0.2	32
	Hg^{2+}	23.7	Polg	−103.3	106.7	25	H_2O, 0.20 M $NaClO_4$	36
2,3,2,4-A_415C4	H^+	11.04 (1)	Pot	−46.4	16.7	25	H_2O, 0.5 M KNO_3	52
	H^+	10.47 (2)	Pot	−51.5	8.4	25	H_2O, 0.5 M KNO_3	52
	H^+	3.98 (3)	Pot	−27.2	−4.6	25	H_2O, 0.5 M KNO_3	52
	H^+	3.41 (4)	Pot	−30.5	−10.9	25	H_2O, 0.5 M KNO_3	52
T_415C4	Cu^{2+}	3.35	Pot			5	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.29	Pot			15	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.39	Kin			25	H_2O, 0.1 M $HClO_4$	38
	Cu^{2+}	3.17	Pot	−13.7	15.1	25	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.11	Pot			35	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	3.17	Spec			25	H_2O, 0.1 M $HClO_4$	38
	Cu^{2+}	2.33	Kin			25	80% MeOH, 0.1 M $HClO_4$	38
	Cu^{2+}	2.36	Spec			25	80% MeOH, 0.1 M $HClO_4$	39
A_416C4	H^+	10.73 (1)	Pot	−46.4	14.6	25	H_2O, 0.5 M KNO_3	52
	H^+	9.85 (2)	Pot	−47.7	8.4	25	H_2O, 0.5 M KNO_3	52
	H^+	6.83 (3)	Pot	−42.7	−3.8	25	H_2O, 0.5 M KNO_3	52
	H^+	3.96 (4)	Pot	−33.5	−10.9	25	H_2O, 0.5 M KNO_3	52
B_2A_216C4	H^+	9.95 (1)	Pot			25	H_2O, 0.1 M KCl	42
	H^+	7.71 (2)	Pot			25	H_2O, 0.1 M KCl	42
	H^+	10.14 (1)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	8.07 (2)	Pot			25	H_2O, 1.0 M KCl	42
	H^+	10.07 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42, 43
	H^+	7.09 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42, 43
	Ni^{2+}	5.2	Pot			25	H_2O, 0.1 M KCl	42
	Ni^{2+}	5.5	Pot			25	H_2O, 1.0 M KCl	42
	Ni^{2+}	5.8	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Cu^{2+}	7.7	Pot			25	95% MeOH, 0.1 M Me_4NCl	44
T_416C4	Cu^{2+}	2.27	Pot			5	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	2.23	Pot			15	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	2.20	Pot	−6.0	22.2	25	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	2.16	Pot			35	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	2.20	Spec			25	H_2O, 0.1 M $HClO_4$	38
	Cu^{2+}	0.95	Kin			25	80% MeOH, 0.1 M $HClO_4$	38
	Cu^{2+}	0.95	Spec			25	80% MeOH, 0.1 M $HClO_4$	39
	Cu^{2+}	1.04	Spec			25	80% MeOH, 0.1 M $HClO_4$	38
A_417C4	H^+	11.20 (1)	Pot	−43.5	20.5	25	H_2O, 0.5 M KNO_3	52
	H^+	10.13 (2)	Pot	−46.4	11.3	25	H_2O, 0.5 M KNO_3	52
	H^+	7.96 (3)	Pot	−45.6	0.0	25	H_2O, 0.5 M KNO_3	52
	H^+	6.30 (4)	Pot	−45.6	−9.6	25	H_2O, 0.5 M KNO_3	52
B_2A_217C4	H^+	9.56 (1)	Tit			25	95% MeOH	43
	H^+	7.98 (2)	Tit			25	95% MeOH	43
	H^+	9.63 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	H^+	8.10 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Ni^{2+}	3.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	42
	Cu^{2+}	7.2	Pot			25	95% MeOH, 0.1 M Me_4NCl	44

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
15C5	H^+	4.1	Pot			25	MeCN	335
	H_3O^+	4.45	Pot			25	MeCN	335
	Li^+	~0	NMR			27	H_2O, 0.02 M $LiClO_4$	17
	Li^+	~0	NMR			27	Me_2SO, 0.02 M $LiClO_4$	17
	Li^+	3.60	Cond			25	MeCN (anion = I^-)	18
	Li^+	>4	NMR	-21.3 (Cal)	>6.3	27	MeCN, 0.02 M $LiClO_4$	17
	Li^+	3.59	NMR	-19.7 (Cal)		27	Me_2CO, 0.02 M $LiClO_4$ (NMR), 0.5 M $LiClO_4$ (Cal)	17
	Li^+		NMR	-19.2 (Cal)	4.2	27	Me_2CO, 0.5 M $LiClO_4$	17
	Li^+	1.23	NMR	-11.3 (Cal)	-14.2	27	MeOH, 0.02 M $LiClO_4$	17
	Li^+	>4	NMR	-43.5 (Cal)		27	NMe, 0.02 M $LiClO_4$	17
	Li^+	4.26	Cond			25	PC	52a
	Li^+	>4	NMR	-16.7 (Cal)	>20.9	27	PC, 0.02 M $LiClO_4$	17
	Li^+	2.48	NMR			27	Py, 0.02 M $LiClO_4$	17
	Li^+	~0	NMR			27	TMG, 0.02 M $LiClO_4$	17
	Li^+		Cal	0		25	MeOH	61
	Na^+	0.70	Cal	-6.28	-7.5	25	H_2O	53
	Na^+	0.67	IEM			25	H_2O	20a
	Na^+	0.70	Elec			25	H_2O	54
	Na^+	0.79	ISE			25	H_2O	55
	Na^+	0.44	NMR			25	H_2O	57
	Na^+	4.86	Spec			25	Diox	336
	Na^+	1.97	NMR			25	DMF	57
	Na^+	1.31	NMR			25	Me_2SO	57
	Na^+	5.24	Pot			10	MeCN	58
	Na^+	4.9	Pot	-24.1	15.1	25	MeCN	58
	Na^+	5.28	Cond			25	MeCN (anion = BPh_4^-)	18
	Na^+	>4	NMR			25	MeCN	57
	Na^+	4.81	Pot			40	MeCN	58
	Na^+	1.49	ISE			25	20% MeOH	55
	Na^+	1.71	ISE			25	40% MeOH	55
	Na^+	2.21	ISE			25	60% MeOH	55
	Na^+	2.65	ISE			25	80% MeOH	55
	Na^+	2.97	ISE			25	90% MeOH	55
	Na^+	2.97	ISE			25	90% MeOH	59, 60
	Na^+	3.48	Cal	-20.9	-3.37	25	MeOH	61
	Na^+	3.30	Cal	-22.6	-12.6	25	MeOH	67
	Na^+	3.14 (1)	Pot	-23.01 (Cal)	-17.27	25	MeOH	20
	Na^+	2.4 (2)				25	MeOH	20
	Na^+	3.25	ISE			25	MeOH	55
	Na^+	3.30 (1)	ISE			25	MeOH	21
	Na^+	1.44 (2)	ISE			25	MeOH	21
	Na^+	3.24	ISE			25	MeOH	22
	Na^+	3.27	Pot			25	MeOH	62
	Na^+	3.31	Pot			25	MeOH	63
	Na^+	>4(1)	NMR			25	NMe	57
	Na^+	1.6 (2)	NMR			25	NMe	57
	Na^+	3.7	Cond			25	PC	52a
	Na^+	2.68	NMR			25	Py	57
	Na^+	>4	NMR			25	THF	57
	K^+	0.74	Cal	-17.2	-43.5	25	H_2O	53
	K^+	0.74	Elec			25	H_2O	54
	K^+	0.76	IEM			25	H_2O	20a
	K^+	2.98	Cond			25	MeCN (anion = BPh_4^-)	18
	K^+	3.77 (1)	Cal	-32.2	-35.9	25	MeOH	61
	K^+	2.71 (2)	Cal	-33.9	-61.8	25	MeOH	61
	K^+	3.35 (1)	Cal	-32.6	-45	25	MeOH	67
	K^+	2.65 (2)	Cal	-36.8	-73	25	MeOH	67
	K^+	3.1 (1)	ISE			25	MeOH	64
	K^+	2.9 (2)	ISE			25	MeOH	64
	K^+	3.61 (1)	Pot	-32.22 (Cal)	-39.31	25	MeOH	20
	K^+	1 (2)	Pot			25	MeOH	20
	K^+	3.34 (1)	ISE			25	MeOH	21
	K^+	2.21 (2)	ISE			25	MeOH	21
	K^+	3.43	ISE			25	MeOH	22
	K^+	3.3-3.6	Pot			25	MeOH	62
	K^+	3.34	Pot			25	MeOH	63
	K^+	3.41	Cond			25	PC	52a
	Rb^+	0.62	Cal	-7.95	-14.6	25	H_2O	53
	Rb^+	3.04	Cond			25	PC	52a
	Cs^+	0.8	Cal	-5.4	-2.1	25	H_2O	53
	Cs^+	0.79	IEM			25	H_2O	20a
	Cs^+	2.62	Cal	-31.9	-57	25	MeOH	67
	Cs^+	2.18	Cal	-49.0	-122	25	MeOH	61
	Cs^+	2.69	Cond			25	PC	52a
	Mg^{2+}		Cal	0		25	MeOH	61
	Ca^{2+}	2.18	Cal	-6.07	21.3	25	MeOH	61
	Ca^{2+}	2.55 (1)	Cal	-11.7	9.5	25	MeOH	67

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Ca^{2+}	2.1 (2)	Cal	20.1	108	25	MeOH	67
	Ca^{2+}	2.36	ISE			25	MeOH	22
	Sr^{2+}	1.95	Cal	−3.8	25	25	H_2O	53
	Sr^{2+}	2.63	Cal	−19.6	−15.5	25	MeOH	61
	Ba^{2+}	1.71	Cal	−4.77	16.7	25	H_2O	53
	La^{3+}	6.27	Pot			25	PC, 0.1 M Et_4NClO_4	65
	La^{3+}	6.49 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	La^{3+}	3.69 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pr^{3+}	6.22	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Nd^{3+}	6.55 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Nd^{3+}	2.10 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{3+}	6.11	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Tb^{3+}	5.96 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tb^{3+}	1.70 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Dy^{3+}	5.66	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Er^{3+}	5.53	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Yb^{3+}	5.53	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Lu^{3+}	5.83 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Lu^{3+}	2.06 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Ag^+	0.94	Cal	−13.51	−27.2	25	H_2O	53
	Ag^+	3.62	Cal	−27.53	−23.0	25	MeOH	61
	Ag^+	5.67	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Hg^{2+}	1.68	Cal	−15.06	−16.7	25	H_2O	53
	Tl^+	1.23	Cal	−16.77	−32.6	25	H_2O	53
	Tl^+	5.29 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tl^+	1.45 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	1.85	Cal	−13.63	−10.46	25	H_2O	53
	Pb^{2+}	16.55 (1 + 2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	NH_4^+	1.71	Cal	−1.0	29.3	25	H_2O	53
	NH_4^+	3.03	ISE			25	MeOH	22
	Cu^{2+}			0		25	MeOH	61
Cb(OctAcet)15C5	Na^+	3.4	ISE			25	90% MeOH, 0.1 M NMe_4Cl	334
	Na^+	3.4	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
	K^+	3.0	ISE			25	90% MeOH, 0.1 M NMe_4Cl	334
	K^+	2.9	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
	Rb^+	2.6	ISE			25	90% MeOH, 0.1 M NMe_4Cl	334
	Rb^+	2.7	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
Cb(TetraAcet)15C5	Na^+	4.4	ISE			25	90% MeOH, 0.1 M NMe_4Cl	334
	Na^+	4.2	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
	K^+	3.0	ISE			25	90% MeOH, 0.1 M NMe_4Cl	334
	K^+	2.9	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
	Rb^+	2.6	ISE			25	90% MeOH, 0.1 M NMe_4Cl	334
	Rb^+	2.7	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
Cb(OctadecAcet)15C5	K^+	2.9	Pot			25	90% MeOH, 0.1 M NMe_4Cl	334
Cy15C5	Li^+	<1.0	Pot			25	H_2O	11, 25
	Na^+	<0.3	Pot			25	H_2O	11, 25
	Na^+	3.71	ISE			25	MeOH	11, 25
	Na^+	3.42	Pot			25	MeOH	63
	K^+	0.6	ISE			25	H_2O	11, 25
	K^+	3.58 (1)	ISE			25	MeOH	11, 25
	K^+	1.88 (2)	ISE			25	MeOH	11, 25
	K^+	3.30	Pot			25	MeOH	63
	Cs^+	2.78 (1)	Pot			25	MeOH	11, 25
	Cs^+	1.91 (2)	Pot			25	MeOH	11, 25
Hex15C5	Na^+	3.15	Pot			25	MeOH	63
	K^+	3.19	Pot			25	MeOH	63
Dec15C5	Na^+	3.18	Pot			25	MeOH	63
	K^+	3.15	Pot			25	MeOH	63
Ph15C5	Na^+	3.34	Pot			25	MeOH	63
	K^+	3.38	Pot			25	MeOH	63
HOM15C5	Na^+	2.75	ISE			25	90% MeOH	66
MeOM15C5	Na^+	2.74	ISE			25	90% MeOH	66
OctOM15C5	Na^+	3.13	Pot			25	MeOH	63
	K^+	2.95 (1)	Pot			25	MeOH	63
	K^+	2.55 (2)	Pot			25	MeOH	63
DodecOM15C5	Na^+	3.14	Pot			25	MeOH	63
	K^+	3.09 (1)	Pot			25	MeOH	63
	K^+	2.41 (2)	Pot			25	MeOH	63
MeOEOM15C5	Na^+	2.83	ISE			25	90% MeOH	59, 60, 66
2-HOPrOM15C5	Na^+	2.82	ISE			25	90% MeOH	66
2-MeOPhOM15C5	Na^+	2.97	ISE			25	90% MeOH	66
	Na^+	3.24	Cal	−22.3	−12.9	25	MeOH	67
	K^+	3.32 (1)	Cal	−32.6	−46	25	MeOH	67
	K^+	2.53 (2)	Cal	−36.8	−75	25	MeOH	67
4-MeOPhOM15C5	Na^+	2.56	ISE			25	90% MeOH	66
	Na^+	2.90	Cal	−22.6	−20	25	MeOH	67

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	K^+	3.17 (1)	Cal	−33.8	−53	25	MeOH	67
	K^+	2.77 (2)	Cal	−31.0	−51	25	MeOH	67
	Cs^+	2.63 (1)	Cal	−32.6	−59	25	MeOH	67
	Cs^+	2.37 (2)	Cal	13.4	90	25	MeOH	67
2-MeO-4-(2HOPr)PhOM15C5	Na^+	2.93	ISE			25	90% MeOH	66
MeOEOM(Me)15C5	Na^+	3.87	Pot			25	MeOH	62a
	K^+	3.42	Pot			25	MeOH	62a
PyMOM(Me)15C5	Na^+	3.58	Pot			25	MeOH	62
	K^+	3.08	Pot			25	MeOH	62
THFMOM(Me)15C5	Na^+	4.02	Pot			25	MeOH	62
	K^+	3.49	Pot			25	MeOH	62
2-MeOPhOM(Me)15C5	Na^+	3.79	Pot			25	MeOH	62
	K^+	3.35	Pot			25	MeOH	62
QuinOM(Me)15C5	Na^+	4.87	Pot			25	MeOH	62
	K^+	3.56	Pot			25	MeOH	62
QuinOM(Hex)15C5	Na^+	4.85	Pot			25	MeOH	62
	K^+	3.41	Pot			25	MeOH	62
MeOEOM(Hex)15C5	Na^+	3.90	Pot			25	MeOH	62
	K^+	3.29	Pot			25	MeOH	62
$(MeOEOM)_2$15C5	Na^+	3.84	Pot			25	MeOH	62
	K^+	3.44	Pot			25	MeOH	62
$(MeOEOEOM)_2$15C5	Na^+	3.86	Pot			25	MeOH	62
	K^+	3.98	Pot			25	MeOH	62
PhOM15C5	Na^+	3.07 (1)	ISE			25	MeOH	21
	Na^+	1.94 (2)	ISE			25	MeOH	21
	K^+	3.16 (1)	ISE			25	MeOH	21
	K^+	1.27 (2)	ISE			25	MeOH	21
$Me_5$15C5 (mixed isomers)	Na^+	3.34	Pot			25	MeOH	63
	K^+	2.85	Pot			25	MeOH	63
B15C5	Li^+	3.77	Cond			25	PC	68
	Na^+	0.40	Elec			25	H_2O	54
	Na^+	2.80	NMR			25	MeCN	71
	Na^+	1.6	NMR			25	DMF	57
	Na^+	0.98	Spec			25	99% Me_2SO	72
	Na^+	1.1	NMR			25	Me_2SO	57
	Na^+	>4	NMR			25	MeCN	57
	Na^+	4.55	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Na^+	3.54	Cond			25	Me_2CO	69
	Na^+	0.72	Cal	−7.40	−10.9	25	20% MeOH	73
	Na^+	1.17	Cal	−11.0	−14.6	25	40% MeOH	73
	Na^+	1.64	Cal	−15.8	−21.7	25	60% MeOH	73
	Na^+	1.99	Cal	−16.0	−15.5	25	70% MeOH	73
	Na^+	2.26	Cal	−34.8	−73.6	25	80% MeOH	73
	Na^+	3.05	ISE			25	MeOH	64
	Na^+	3.37	Cond			25	MeOH	74
	Na^+	2.87	Pot			25	MeOH	340
	Na^+	>4 (1)	NMR			25	NME	57
	Na	0.8 (2)	NMR			25	NME	57
	Na^+	4.35	Cond			25	PC	68
	Na^+	2.6	NMR			25	Py	57
	Na^+	>4	NMR			25	THF	57
	K^+	0.38	Cal	−9.7	−25.5	25	H_2O	73
	K^+	0.38	Elec			25	H_2O	54
	K^+	1.29	NMR			25	99% Me_2SO	72
	K^+	3.40	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	1.20	Cal	−7.5	−2.1	25	20% MeOH	73
	K^+	1.92	Cal	−10.5	1.7	25	40% MeOH	73
	K^+	1.5 (1)	Cal			25	70% MeOH	73
	K^+	2.65 (2)	Cal	−58.2 (1 + 2)	−115.5	25	70% MeOH	73
	K^+	2.2 (1)	Cal			25	80% MeOH	73
	K^+	2.60 (2)	Cal	−64.9 (1 + 2)	−125.5	25	80% MeOH	73
	K^+	2.8 (1)				25	MeOH	64
	K^+	3.15 (2)				25	MeOH	64
	K^+	2.78	Cond	−26.4	−35.4	25	PC	68
	K^+	0.97	Pot			25	50% THF/H_2O	11
	Rb^+	1.23	NMR			25	99% Me_2SO	72
	Rb^+	2.90	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	1.8 (1)	Cal			25	70% MeOH	73
	Rb^+	1.97 (2)	Cal	−50.2 (1 + 2)	−98.3 (1 + 2)	25	70% MeOH	73
	Rb^+	2.38	Cond			25	PC	68
	Rb^+	0.46	Pot			25	50% THF	11
	Cs^+	1.13	NMR			25	99% Me_2SO	72
	Cs^+	3.10	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	1.70	Cal	−10.2	−1.7	25	70% MeOH	73
	Cs^+	1.91	Cond			25	MeOH	74
	Cs^+	2.03	Cond			25	MeOH	68

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Ba^{2+}	2.60	NMR			25	MeCN	71
	Tl^+	5.20	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	3.00	Polg			22	MeOH, 0.05 M Bu_4NClO_4	70
	Pb^{2+}	2.04	Cal	−21.37	−32.6	25	70% MeOH	73
	NH_4^+	2.30 (1)	NMR			25	MeCN	71
	NH_4^+	2.00 (2)	NMR			25	MeCN	71
AcetoB15C5	Na^+	3.09	Cond			25	Me_2CO	69
AdrB15C5	Na^+	2.94	Pot			25	MeOH	340
	K^+	2.63 (1)	Pot			25	MeOH	340
	K^+	3.41 (2)	Pot			25	MeOH	340
AldB15C5	Na^+	3.05	Cond			25	Me_2CO	69
AmB15C5	Na^+	3.91	Cond			25	Me_2CO	69
BrB15C5	Na^+	3.31	Cond			25	Me_2CO	69
t-BuB15C5	Mg^{2+}	6.72	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ca^{2+}	6.05	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Sr^{2+}	5.55 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Sr^{2+}	5.05 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ba^{2+}	5.35 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ba^{2+}	5.05 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	23
	La^{3+}	3.26 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	La^{3+}	2.65 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Ce^{3+}	3.62	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pr^{3+}	3.60	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Nd^{3+}	3.75	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{2+}	10.8 (1 + 2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{3+}	3.45	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Gd^{3+}	3.02	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tb^{3+}	2.85	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Dy^{3+}	2.90	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Ho^{3+}	2.80	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Er^{3+}	2.82	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tm^{3+}	2.81	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Yb^{2+}	8.4 (1 + 2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Yb^{3+}	2.80	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Lu^{3+}	2.80	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tl^+	4.13 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tl^+	2.22 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	7.85 (1)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	6.54 (2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
E(CbB15C5)	K^+	6.46	Cond			25	THF	211
Pent(CbB15C5)	K^+	7.11	Cond			25	THF	211
Oct(CbB15C5)	K^+	6.78	Cond			25	THF	211
EOE(CbB15C5)	K^+	7.81	Cond			25	THF	211
	NH_4^+	4.87	Cond			25	THF	211
$(EO)_2E(CbB15C5)$	K^+	7.51	Cond			25	THF	211
	NH_4^+	4.78	Cond			25	THF	211
HCbB15C5	Na^+	3.21	Cond			25	Me_2CO	69
MeB15C5	Na^+	3.60	Cond			25	Me_2CO	69
	Na^+	4.28	Spec			25	Diox	336
$O(MeB15C5)_2$	Na^+	4.67	Spec			25	Diox	336
NitB15C5	Na^+	2.65	Cond			25	Me_2CO	69
$(Nit)_2B15C5$	Na^+	2.18	Cond			25	Me_2CO	69
B_215C5	Na^+	2.2	ISE			25	MeOH	64
	K^+	2.0 (1)	ISE			25	MeOH	64
	K^+	3.21 (2)	ISE			25	MeOH	64
rac-7,9-Me_2B_215C5	Na^+	1.9	ISE			25	MeOH	64
	K^+	1.4 (1)	ISE			25	MeOH	64
	K^+	3.17 (2)	ISE			25	MeOH	64
meso-7,9-Me_2B_215C5	Na^+	2.1	ISE			25	MeOH	64
rac-6,10-Me_2B_215C5	Na^+	1.1	ISE			25	MeOH	64
	K^+	0.9 (1)	ISE			25	MeOH	64
	K^+	3.1 (2)	ISE			25	MeOH	64
meso-6,10-Me_2B_215C5	Na^+	1.5	ISE			25	MeOH	64
	K^+	1.4 (1)	ISE			25	MeOH	64
	K^+	3.27 (2)	ISE			25	MeOH	64
$Bu(NCB15C5)_2$	K^+	5.57	Kin			23	MeOH, 0.15 M LiCl	332
	Rb^+	5.76	Kin			23	MeOH, 0.15 M LiCl	332
$Non(NCB15C5)_2$	K^+	5.73	Kin			23	MeOH, 0.15 M LiCl	332
	Rb^+	5.72	Kin			23	MeOH, 0.15 M LiCl	332
$Dec(NCB15C5)_2$	K^+	5.08	Kin			23	MeOH, 0.15 M LiCl	332
	Rb^+	5.38	Kin			23	MeOH, 0.15 M LiCl	332
A15C5	Na^+	2.06	ISE			25	MeOH	76
	K^+	2.72	ISE			25	MeOH	76
	NH_4^+	3.05	Pot			25	MeOH	75
MeA15C5	NH_4^+	3.2	Pot			25	MeOH	75
BuA15C5	Na^+	2.62	ISE			25	90% MeOH	59, 60

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Na^+	3.22	Cal	−17.36	3.4	25	MeOH	67
	K^+	2.99	Cal	−26.6	−32.0	25	MeOH	67
	Ca^{2+}	2.83 (1)	Cal	−13.8	7.9	25	MeOH	67
	Ca^{2+}	2.8 (2)	Cal	14.6	103	25	MeOH	67
OctA15C5	Na^+	2.91	ISE			25	MeOH	76
	K^+	3.05	ISE			25	MeOH	76
AlA15C5	Na^+	2.82	ISE			25	90% MeOH	59
BzA15C5	Na^+	2.48	ISE			25	90% MeOH	59
HOEA15C5	Na^+	3.92	ISE			25	MeOH	76
	K^+	3.67	ISE			25	MeOH	76
MeOEA15C5	Na^+	3.66	ISE			25	90% MeOH	59, 60
	Na^+	4.33 (1)	Cal	−26.74	−6.8	25	MeOH	67
	Na^+	2.30 (2)	Cal	−2.1	37	25	MeOH	67
	K^+	4.20 (1)	Cal	−38.0	−47.0	25	MeOH	67
	K^+	2.19 (2)	Cal	−2.51	34	25	MeOH	67
	Cs^+	2.79	Cal	−32.9	−57.0	25	MeOH	67
	Ca^{2+}	3.78 (1)	Cal	−10.8	36.2	25	MeOH	67
	Ca^{2+}	2.71 (2)	Cal	7.5	77	25	MeOH	67
	NH_4^+	3.15	ISE			25	90% MeOH	75
$H(OE)_2A15C5$	Na^+	4.68	ISE			25	MeOH	76
	K^+	4.42	ISE			25	MeOH	76
$Me(OE)_2A15C5$	Na^+	4.16	ISE			25	90% MeOH	59, 60
	NH_4^+	3.2	ISE			25	90% MeOH	75
$H(OE)_3A15C5$	Na^+	4.34	ISE			25	MeOH	76
	K^+	4.77	ISE			25	MeOH	76
$Me(OE)_3A15C5$	Na^+	4.32	ISE			25	MeOH	76
	K^+	4.85	ISE			25	MeOH	76
	NH_4^+	3.4	ISE			25	90% MeOH	75
$Me(OE)_4A15C5$	NH_4^+	3.5	ISE			25	90% MeOH	75
$Me(OE)_5A15C5$	NH_4^+	3.5	ISE			25	90% MeOH	75
$Me(OE)_8A15C5$	NH_4^+	3.05	ISE			25	90% MeOH	75
1,4-$A_2$15C5	H^+	9.20 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	6.30 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Co^{2+}	4.90	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ni^{2+}	5.05	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	8.86	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Zn^{2+}	5.04	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
1,7-$A_2$15C5 (2.1)	H^+	8.76 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	H^+	8.04 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	H^+	9.26 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	8.12 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	La^{3+}	7.08	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	La^{3+}	14.4	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Pr^{3+}	7.94	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Pr^{3+}	14.5	Pot			25	PC, 0,1 M Et_4NClO_4	65
	Nd^{3+}	7.86	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Sm^{3+}	7.00	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Sm^{3+}	14.9	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Eu^{3+}	8.59	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Eu^{3+}	14.6	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Gd^{3+}	7.67	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Tb^{3+}	8.29	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Dy^{3+}	8.96	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Dy^{3+}	15.2	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Ho^{3+}	8.81	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Er^{3+}	8.70	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Er^{3+}	14.8	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Y^{3+}	8.66	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Tm^{3+}	9.46	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Yb^{3+}	15.4	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Co^{2+}	5.05	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Co^{2+}	5.22	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ni^{2+}	3.73	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ni^{2+}	4.05	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	7.17	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	8.15	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	4.37	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Cu^{2+}	4.49	Spec			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Zn^{2+}	5.34	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ag^+	5.85	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ag^+	5.17	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	79
	Ag^+	7.61 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	3.60 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	13.3	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Zn^{2+}	5.19	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	6.46	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	8.72 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Cd^{2+}	3.27 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Hg^{2+}	16.65	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Pb^{2+}	5.85	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Pb^{2+}	3.57	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Pb^{2+}	7.87 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	3.49 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	7.86 (1)	Spec			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	4.22 (2)	Spec			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	8.64 (1)	Spec			25	PC, 0.01 M Et_4NClO_4	81
	Pb^{2+}	3.66 (2)	Spec			25	PC, 0.01 M Et_4NClO_4	81
T15C5	Ag^+	5.0 (1)	Cal	−39.20	−35.10	25	H_2O	16
	Ag^+	2.45 (2)	Cal	−14.52	−1.83	25	H_2O	16
	Hg^{2+}	(1 + 2)	Cal	−70.58		25	H_2O	16
	Tl^+	0.80	Cal	−32.2	−92.7	25	H_2O	16
	Pb^{2+}	1.65	Cal	−21.51	−40.58	25	H_2O	16
1,4-$T_2$15C5	Ag^+	(1)	Cal	−50.71		25	H_2O	16
	Ag^+	3.31 (2)	Cal	−23.4	−15.16	25	H_2O	16
	Hg^{2+}	(1)	Cal	−47.36		25	H_2O	16
	Hg^{2+}	5.1 (2)	Cal	−32.59	−11	25	H_2O	16
	Tl^+	<0.6	Cal			25	H_2O	16
	Pb^{2+}	1.21	Cal	−23.8	−56.86	25	H_2O	16
1,7-$T_2$15C5	Ag^+	(1)	Cal	−69.33		25	H_2O	16
	Ag^+	2.7 (2)	Cal	−4.2	37.9	25	H_2O	16
	Hg^{2+}	(1)		−67.36		25	H_2O	16
	Hg^{2+}	2.91 (2)	Cal	−20.9	−14.5	25	H_2O	16
	Tl^+	<0.2	Cal			25	H_2O	16
	Pb^{2+}	1.62	Cal	−31.8	−75.7	25	H_2O	16
4,13-A_2-7,10-$T_2$15C5	H^+	8.60 (1)	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 84
	H^+	7.55 (2)	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 84
	Co^{2+}	5.42	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82, 84
	Ni^{2+}	7.98	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82, 84
	Cu^{2+}	11.55	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82, 84
	Ag^+	8.95	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82
	Ag^+	12.21 (Ag_2L)	Pot			25	H_2O, 0.1 M $NaClO_4$	82
	Ag^+	14.15 (AgHL)	Pot			25	H_2O, 0.1 M $NaClO_4$	82
	Zn^{2+}	5.09	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82, 84
	Cd^{2+}	6.53	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82
	Pb^{2+}	5.67	Pot			25	H_2O, 0.1 M $NaClO_4$	77, 82, 84
7,10-A_2-4,13-$T_2$15C5	H^+	8.86 (1)	Cal	−33.85	55.73	25	H_2O, 0.1 M $NaClO_4$	82, 83, 85
	H^+	5.21 (2)	Cal	−40.92	37.74	25	H_2O, 0.1 M $NaClO_4$	82, 83, 85
	Co^{2+}	5.22	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Ni^{2+}	8.06	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Cu^{2+}	13.26	Cal	−52.47	77.45	25	H_2O, 0.1 M $NaClO_4$	82, 83, 85
	Ag^+	9.91	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Ag^+	15.22 (AgHL)	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Ag^+	12.6 (Ag_2L)	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Zn^{2+}	4.43 (1)	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Zn^{2+}	3.48 (2)	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Cd^{2+}	7.13	Pot			25	H_2O, 0.1 M $NaClO_4$	82, 83
	Pb^{2+}	6.78	Cal	−39.83	−4.01	25	H_2O, 0.1 M $NaClO_4$	82, 83, 85
	Cu^{2+}	4.35	Pot			5	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	4.27	Pot			15	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	4.18	Pot	−12.6	37.7	25	H_2O, 0.1 M $HClO_4$	37, 38
	Cu^{2+}	4.12	Pot			35	H_2O, 0.1 M $HClO_4$	37
	Cu^{2+}	2.99	Kin			25	80% MeOH, 0.1 M $HClO_4$	38
	Cu^{2+}	2.99	Spec			25	80% MeOH, 0.1 M $HClO_4$	39
	Cu^{2+}	4.18	Spec			25	80% MeOH, 0.1 M $HClO_4$	38
$Ph_2Phos_2$15C5	Mg^{2+}	2.88	Cond			22	MeCN	86
18C6	H^+	3.282	Cond			25	DCE	123
	H^+	6.5	Pot			25	MeCN	335
	H^+	6.3	Pot			25	PC	335
	H_3O^+	6.4	Pot			25	MeCN	335
	Li^+	3.73	Cond			25	MeCN (anion = I^-)	18
	Li^+	~0	NMR			27	H_2O, 0.02 M $LiClO_4$	17
	Li^+	~0	NMR			27	Me_2SO, 0.02 M $LiClO_4$	17
	Li^+	2.34	NMR	~0 (Cal)	44.8	27	MeCN, 0.02 M $LiClO_4$	17
	Li^+	1.50	NMR	−14.6 (Cal)	−20.5	27	Me_2CO, 0.02 M $LiClO_4$ (NMR), 0.5 M $LiClO_4$ (Cal)	17
	Li^+	1.51	NMR			27	Me_2CO, 0.02 M LiI	17
	Li^+	~0	NMR	−11.7 (Cal)		27	MeOH, 0.02 M $LiClO_4$ (NMR), 0.5 M $LiClO_4$ (Cal)	17
	Li^+	>4	NMR	~12.6 (Cal)	>0	27	NMe, 0.02 M $LiClO_4$	17
	Li^+	2.69	NMR	−15.9 (Cal)	−2.5	27	PC	17
	Li^+	0.62	NMR			27	Py	17
	Li^+	~0	NMR			27	TMG	17
	Na^+	0.8	Cal	−9.41	−15.5	25	H_2O	53
	Na^+	0.82	IEM			25	H_2O	20a

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Na^+	1.80	ISE			25	H_2O	55
	Na^+	0.82	NMR			25	H_2O	57
	Na^+	0.80	?			25	H_2O	89
	Na^+	<0.3	ISE			25	H_2O	11, 25
	Na^+	4.54, 4.55	Spec			25	Diox	336
	Na^+	2.31	NMR			25	DMF	57
	Na^+	1.41	NMR			25	Me_2SO	57
	Na^+	1.43	ISE			25	Me_2SO	90a
	Na^+	3.8	NMR			25	MeCN	57
	Na^+	4.55	ISE			25	MeCN	90a
	Na^+	4.7	Pot			10	MeCN	58
	Na^+	4.8	Pot	1.6	96.3	25	MeCN	58
	Na^+	4.8	Pot			40	MeCN	58
	Na^+	>4	NMR			25	Me_2CO	57
	Na^+	2.18	ISE			25	20% MeOH	55
	Na^+	2.47	ISE			25	40% MeOH	55
	Na^+	2.81	ISE			25	60% MeOH	55
	Na^+	2.76	Cal	−20.45	−15.9	25	70% MeOH	73
	Na^+	3.25	ISE			25	80% MeOH	55
	Na^+	3.66	Cal	−27.8	−23.1	25	90% MeOH	91, 92
	Na^+	3.73	ISE			25	90% MeOH	55
	Na^+	4.33	Cal	−33.9	−30.9	25	99% MeOH	92
	Na^+	4.36	Cal	−35.1	−34.4	25	MeOH	61, 91, 92
	Na^+	4.38	Cal	−31.38	−21.76	25	MeOH	20
	Na^+	4.46	Cond			25	MeOH	74
	Na^+	4.32	Elec			25	MeOH	54
	Na^+	4.35	ISE			25	MeOH	55
	Na^+	4.35	ISE			25	MeOH	22
	Na^+	4.32	ISE			25	MeOH	11, 25
	Na^+	>4	NMR			25	NMe	57
	Na^+	5.68	Cond			25	PC	52a
	Na^+	5.25	ISE			25	PC	90a
	Na^+	>4	NMR			25	PC	57
	Na^+	>3	NMR			25	Py	57
	Na^+	>4	NMR			25	THF	57
	Na^+	4.34	ISE			21.5	MeOH	114
	K^+	2.03	Cal	−26.0	−47.7	25	H_2O	53
	K^+	2.06	IEM			25	H_2O	20a
	K^+	2.15	Pot	−23.43 (Cal)	−37.63	25	H_2O	20
	K^+	2.03				25	H_2O	89
	K^+	2.06	Pot			25	H_2O	11, 25
	K^+	5.99	Spec			25	Spec	336
	K^+	3.28	Cond			25	Me_2SO	93
	K^+	3.21	ISE			25	Me_2SO	90a
	K^+	5.72	Cond			25	MeCN	93
	K^+	5.70	ISE			25	MeCN	90a
	K^+	4.33	Cal	−40.5	−53.1	25	70% MeOH	73
	K^+	5.35	Cal	−49.3	−62.6	25	90% MeOH	92
	K^+	6.05	Cal	−55.3	−69.6	25	99% MeOH	92
	K^+	6.10	ISE			23	MeOH	114
	K^+	6.08	ISE			24	MeOH	114
	K^+	6.06	Cal	−56.1	−72.2	25	MeOH	61, 92
	K^+	6.08	Cond			25	MeOH	93
	K^+	6.20	Cond			25	MeOH	74
	K^+	6.1	Elec			25	MeOH	54
	K^+	5.93	ISE			25	MeOH	64
	K^+	6.08	ISE			25	MeOH	22
	K^+	6.18	Pot	−53.14 (Cal)	−60.37	25	MeOH	20
	K^+	6.10	ISE			25	MeOH	11, 25
	K^+	6.24	Cond			25	PC	52a
	K^+	6.32	ISE			25	PC	90a
	Rb^+	1.56	Cal	−16.0	−23.8	25	H_2O	53
	Rb^+	3.46	Cal	−38.76	−64.0	25	70% MeOH	73
	Rb^+	5.32	ISE			23	MeOH	114
	Rb^+	5.32	Cal	−50.6	−67.8	25	MeOH	61
	Rb^+	5.73	Cond			25	MeOH	74
	Rb^+	5.35	ISE			25	MeOH	114
	Rb^+	5.32	Cond			25	PC	52a
	Cs^+	0.99	Cal	−15.85	−33.9	25	H_2O	53
	Cs^+	0.98	IEM			25	H_2O	20a
	Cs^+	0.8	ISE			25	H_2O	11, 25
	Cs^+	3.95 (1)	NMR			25	DMF	94
	Cs^+	0.39 (2)	NMR			25	DMF	94
	Cs^+	3.04 (1)	NMR			25	DMSO	94
	Cs^+	0.0 (2)	NMR			25	DMSO	94
	Cs^+	>4 (1)	NMR			25	MeCN	94

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Cs^+	0.57 (2)	NMR			25	MeCN	94
	Cs^+	5.30 (1)	NMR			25	Me_2CO	94
	Cs^+	1.53 (2)	NMR			25	Me_2CO	94
	Cs^+	2.84	Cal	−33.8	−59.0	25	70% MeOH	73
	Cs^+	4.70	ISE			22	MeOH	114
	Cs^+	4.79 (1)	Cal	−47.2	−66.7	25	MeOH	61
	Cs^+	2.06 (2)	Cal	−13.9	−7.2	25	MeOH	61
	Cs^+	4.49	Cond			25	MeOH	74
	Cs^+	4.62 (1)	Pot			25	MeOH	11, 25
	Cs^+	1.30 (2)	ISE			25	MeOH	11, 25
	Cs^+	4.03	NMR	−69.96	157.3	25	$MeNH_2$	95
	Cs^+	4.48	Cond			25	PC	52a
	Cs^+	4.52	ISE			25	PC	90a
	Cs^+	4.18 (1)	NMR			25	PC	94
	Cs^+	1.04 (2)	NMR			25	PC	94
	Cs^+	≥6.7 (1)	NMR			−38	Py	98
	Cs^+	3.07 (2)	NMR			−38	Py	98
	Cs^+	≥6 (1)	NMR			−29	Py	98
	Cs^+	2.79 (2)	NMR			−29	Py	98
	Cs^+	≥6 (1)	NMR			−18	Py	98
	Cs^+	2.64 (2)	NMR			−18	Py	98
	Cs^+	≥6 (1)	NMR			−1	Py	98
	Cs^+	2.34 (2)	NMR			−1	Py	98
	Cs^+	≥6 (1)	NMR			12	Py	98
	Cs^+	2.08 (2)	NMR			12	Py	98
	Cs^+	≥5 (1)	NMR			24	Py	98
	Cs^+	1.9 (2)	NMR			24	Py	98
	Cs^+	5.7 (1)	NMR			25	Py	94
	Cs^+	1.87 (2)	NMR			25	Py	94
	Cs^+	1.89 (2)	NMR	−24.3 (2)	−44.8 (2)	25	Py	98
	Ca^{2+}	<0.5	Cal			25	H_2O	53
	Ca^{2+}	0.48	IEM			25	H_2O	20a
	Ca^{2+}	1.8	Pot			25	H_2O	87
	Ca^{2+}	2.51	Cal	−17.86	−11.7	25	70% MeOH	73
	Ca^{2+}	3.86	Cal	−11.5	35.4	25	MeOH	61
	Ca^{2+}	3.90	ISE			25	MeOH	22
	Sr^{2+}	2.8	Pot			25	H_2O	87
	Sr^{2+}	2.72	Cal	−15.1	1.25	25	H_2O	53
	Sr^{2+}	5.0	Cal	−31.3	−10.5	25	70% MeOH	73
	Sr^{2+}	>5.5	Cal	−36.0		25	MeOH	61
	Ba^{2+}	3.87	Cal	−31.7	−33.0	25	H_2O	53
	Ba^{2+}	6.0	Cal	−44.58	−35.5	25	70% MeOH	73
	Ba^+	6.56	Cal	−43.2	−19.4	25	90% MeOH	92
	Ba^+	7.03	Cal	−43.4	−11.1	25	99% MeOH	92
	Ba^+	7.04	Cal	−43.55	−11.3	25	MeOH	61, 92
	La^{3+}	4.4	Cal	−36.2	−37.3	25	MeCN (anion = NO_3^-)	100
	La^{3+}	3.29	Cal	11.76	102	25	MeOH	101
	La^{3+}	8.75	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Ce^{3+}	4.5	Cal	−43.0	−55.6	25	MeCN (anion = NO_3^-)	100
	Ce^{3+}	3.57	Cal	10.63	104	25	MeOH	101
	Pr^{3+}	3.7	Cal	−44.0	−76.9	25	MeCN (anion = NO_3^-)	100
	Pr^{3+}	2.63	Cal	18.66	113	25	MeOH	101
	Pr^{3+}	8.60	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Nd^{3+}	3.5	Cal	−36.2	−54.3	25	MeCN (anion = NO_3^-)	100
	Nd^{3+}	2.44	Cal	19.96	114	25	MeOH	101
	Sm^{3+}	2.03	Cal	15.36	90.4	25	MeOH	101
	Sm^{3+}	8.10	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Eu^{3+}	2.7	Cal	−12.8	8.7	25	MeCN (anion = NO_3^-)	100
	Eu^{3+}	1.84	Cal	12.8	78.2	25	MeOH	101
	Gd^{3+}	1.32	Cal	15.61	77.6	25	MeOH	101
	Dy^{3+}	7.90	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Er^{3+}	7.67	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Yb^{3+}	7.50	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Ag^+	1.50	Cal	−9.07	−1.7	25	H_2O	53
	Ag^+	1.60	Pot			25	H_2O	11, 25
	Ag^+	8.08	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ag^+	6.21	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	79
	Ag^+	4.58	Cal	−38.3	−40.7	25	MeOH	61, 102
	Ag^+	4.57	ISE			25	MeOH	90a
	Ag^+	10.18 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	3.33 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	7.10	ISE			25	PC	90a
	Ag^{3+}	7.05	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Cd^{2+}	5.59	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cd^{2+}	5.31	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	7.83 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Cd^{2+}	3.58 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Hg^{2+}	2.42	Cal	−19.6	−19.7	25	H_2O	53
	Tl^+	2.27	Cal	−18.57	−18.8	25	H_2O	53
	Tl^+	2.2	Pot	−22	−34.7	25	H_2O, 0.10 M $NaClO_4$, (pH 2)	103
	Tl^+	4.85	Fluor			25	EtOH	180
	Tl^+	4.6	Fluor			25	MeOH	180
	Tl^+	5.26	ISE			25	MeOH	90a
	Tl^+	7.13	ISE			25	PC	90a
	Pb^{2+}	4.27	Cal	−21.6	9.2	25	H_2O	53
	Pb^{2+}	4.4	Pot	−13	40.6	25	H_2O, 0.10 M $NaClO_4$, (pH 2)	103
	Pb^{2+}	7.01	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Pb^{2+}	6.90	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Pb^{2+}	6.5	Cal	−38.4	−4.6	25	70% MeOH	73
	Pb^{2+}	9.48 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	2.82 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	3.66 (2)	Spec			25	PC, 0.01 M Et_4NClO_4	81
	NH_4^+	1.23	Cal	−9.79	−9.2	25	H_2O	53
	NH_4^+	1.23	?			25	H_2O	89
	NH_4^+	1.1	ISE			25	H_2O	11, 25
	NH_4^+	4.27	Cal	−38.8	−48.5	25	MeOH	104, 105
	NH_4^+	4.14	ISE			25	MeOH	22
	$NH_2NH_3^+$	4.21	Cal	−43.6	−65.7	25	MeOH	104, 105
	$CH_3NHNH_3^+$	3.41	Cal	−39.7	−68.0	25	MeOH	105
	$HONH_3^+$	3.99	Cal	−37.7	−50.2	25	MeOH	104, 105
	$CH_3NH_3^+$	4.25	Cal	−44.8	−59.8	25	MeOH	104, 105
	$C_2H_5NH_3^+$	3.99	Cal	−44.6	−73.3	25	MeOH	104, 105
	$(CH_3)_2NH_2^+$	1.76	Cal	−27.9	−60.7	25	MeOH	104, 105
	c-$PrNH_3^+$	3.90	Cal	−42.3	−67.4	25	MeOH	104, 105
	$CH_2{=}CHCH_2NH_3^+$	4.02	Cal	−44.0	−70.8	25	MeOH	105
	n-$C_3H_7NH_3^+$	3.97	Cal	−42.1	−64.1	25	MeOH	104, 105
	n-$C_3H_7NH_3^+$	3.90	Cal	−41.2	−63.6	25	MeOH	105
	n-$C_3H_7NH_3^+$	6.36	Spec			26.6	C_6H_6	106
	i-$C_3H_7NH_3^+$	3.56	Cal	−40.4	−67.3	25	MeOH	105
	i-$C_3H_7NH_3^+$	6.21	Spec			26.6	C_6H_6	106
	$C_4H_9NH_2^+$	1.98	Cal	−30.8	−65.3	25	MeOH	104, 105
	n-$C_4H_9NH_3^+$	7.75	Spec			6	C_6H_6	106
	n-$C_4H_9NH_3^+$	6.36	Spec			26.6	C_6H_6	106
	n-$C_4H_9NH_3^+$	5.99	Spec			35	C_6H_6	106
	sec-$C_4H_9NH_3^+$	7.18	Spec			6	C_6H_6	106
	sec-$C_4H_9NH_3^+$	5.85	Spec			26.6	C_6H_6	106
	sec-$C_4H_9NH_3^+$	5.49	Spec			35	C_6H_6	106
	t-$C_4H_9NH_3^+$	6.98	Spec			6	C_6H_6	106
	t-$C_4H_9NH_3^+$	5.66	Spec			26.6	C_6H_6	106
	t-$C_4H_9NH_3^+$	5.30	Spec			35	C_6H_6	106
	t-$C_4H_9NH_3^+$	2.90	Cal	−32.5	−53.1	25	MeOH	104, 105
	n-$C_5H_{11}NH_3^+$	6.36	Spec			26.6	C_6H_6	106
	sec-$C_5H_{11}NH_3^+$	5.91	Spec			26.6	C_6H_6	106
	t-$C_5H_{11}NH_3^+$	5.35	Spec			26.6	C_6H_6	106
	n-$C_3H_6(C_2H_5)NH_3^+$	4.93	Spec			26.6	C_6H_6	106
	$C_2H_5OC(O)CH_2NH_3^+$	3.84	Cal	−38.5	−55.6	25	MeOH	105
	$C_2H_5OC(O)CH(CH_3)NH_3^+$	3.28	Cal	−34.5	−52.9	25	MeOH	105
	$PhCH(CH_3)NH_3^+$	3.84	Cal	−39.8	−60.1	25	MeOH	105
	morpholinium	2.05	Cal	−28.6	−56.6	25	MeOH	105
	$^+H_3N(CH_2)_2NH_3^+$	3.05 (1)	Cal	−49.4	−108.1	25	MeOH	105
	$^+H_3N(CH_2)_2NH_3^+$	3.75 (2)	Cal	−44.4	−75.8	25	MeOH	105
	$^+H_3N(CH_2)_3NH_3^+$	3.20 (1)	Cal	−51.9	−112.3	25	MeOH	105
	$^+H_3N(CH_2)_3NH_3^+$	3.79 (2)	Cal	−38.5	−57.6	25	MeOH	105
	$^+H_3N(CH_2)_4NH_3^+$	3.51 (1)	Cal	−41.9	−73.0	25	MeOH	105
	$^+H_3N(CH_2)_4NH_3^+$	3.47 (2)	Cal	−49.0	−98.3	25	MeOH	105
	$^+H_3N(CH_2)_5NH_3^+$	3.1 (1)	Cal	−46.9	−98.3	25	MeOH	105
	$^+H_3N(CH_2)_5NH_3^+$	3.7 (2)	Cal	−44.8	−82.8	25	MeOH	105
	$^+H_3N(CH_2)_6NH_3^+$	3.3 (1)	Cal	−44.8	−87.0	25	MeOH	105
	$^+H_3N(CH_2)_6NH_3^+$	3.9 (2)	Cal	−41.4	−64.6	25	MeOH	105
	$PhNH_3^+$	3.80	Cal	−39.9	−61.7	25	MeOH	105, 107, 108
	2-$CH_3PhNH_3^+$	2.86	Cal	−31.7	−51.9	25	MeOH	105, 107, 108
	4-$CH_3PhNH_3^+$	3.82	Cal	−41.5	−66.1	25	MeOH	105, 108
	2,6-$(CH_3)_2PhNH_3^+$	2.00	Cal	−23.6	−40.7	25	MeOH	105, 107
	3,5-$(CH_3)_2PhNH_3^+$	3.74	Cal	−37.9	−55.7	25	MeOH	105, 108
	PhN_2^+	4.44	Spec			50	DCE	109
	PhN_2^+	4.782	Spec			50	DCE	110, 111
	PhN_2^+	2.50	Cal	−35.2	−70.1	25	MeOH	107
	PhN_2^+	2.37	Cal	−58.5	−151.5	25	MeOH	108
	PhN_2^+	2.46	Spec			15	MeOH	112
	4-$FPhN_2^+$	2.52	Cal	−35.8	−71.5	25	MeOH	107
	4-$ClPhN_2^+$	4.74	Spec			50	DCE	109
	4-$ClPhN_2^+$	4.888	Spec			50	DCE	110, 111

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	4-ClPhN$_2^+$	2.62	Cal	−36.2	−71.5	25	MeOH	107
	3-ClArN$_2^+$	2.71	Spec			15	MeOH	112
	4-CNArN$_2^+$	3.15	Spec			15	MeOH	112
	3-CNPhN$_2^+$	5.27	Spec			50	DCE	110
	2-CH$_3$PhN$_2^+$	3.34	Spec			50	DCE	109
	2-CH$_3$PhN$_2^+$	3.97	Spec			15	DCE	112
	3-CH$_3$PhN$_2^+$	4.29	Spec			50	DCE	109
	3-CH$_3$PhN$_2^+$	4.53	Spec			50	DCE	110
	4-CH$_3$PhN$_2^+$	4.40	Spec			50	DCE	109
	4-CH$_3$PhN$_2^+$	4.39	Spec			50	DCE	110
	4-CH$_3$PhN$_2^+$	5.10	Spec			15	DCE	112
	4-CH$_3$PhN$_2^+$	2.30	Cal	−35.9	−77.1	25	MeOH	107
	4-CH$_3$PhN$_2^+$	2.26	Cal	−41.9	−97.5	25	MeOH	108
	4-CH$_3$PhN$_2^+$	2.39	Spec			15	MeOH	112
	4-CF$_3$PhN$_2^+$	2.85	Cal	−37.2	−70.1	25	MeOH	107
	2,6(CH$_3$)$_2$PhN$_2^+$	2.01	Spec			15	DCE	112
	4-NO$_2$PhN$_2^+$	3.02	Cal	−35.1	−60.3	25	MeOH	107
	4-NO$_2$ArN$_2^+$	3.10	Spec			15	MeOH	112
	3-CH$_3$OArN$_2^+$	2.63	Spec			15	MeOH	112
	3-CH$_3$OPhN$_2^+$	4.78	Spec			50	DCE	110
	4-CH$_3$OPhN$_2^+$	2.56	Spec			15	Me$_2$CO	112
	4-CH$_3$OPhN$_2^+$	3.23	Spec			15	CH$_2$Cl$_2$	112
	4-CH$_3$OPhN$_2^+$	3.45	Spec			15	CHCl$_3$	112
	4-CH$_3$OPhN$_2^+$	4.67	Spec			15	DCE	112
	4-CH$_3$OPhN$_2^+$	1.87	Spec			15	Diox	112
	4-CH$_3$OPhN$_2^+$	2.01	Cal	−33.9	−75.7	25	MeOH	107
	4-CH$_3$OPhN$_2^+$	2.09	Spec			15	MeOH	112
	4-CH$_3$OPhN$_2^+$	2.27	Spec			15	THF	112
	2-CH$_3$C(O)PhN$_2^+$	−∞	Spec			50	DCE	109
	3-CH$_3$C(O)PhN$_2^+$	5.06	Spec			50	DCE	109
	3-CH$_3$C(O)PhN$_2^+$	5.02	Spec			50	DCE	110
	4-CH$_3$C(O)PhN$_2^+$	5.05	Spec			50	DCE	109
	4-(CH$_3$)$_3$CPhN$_2^+$	4.28	Spec			50	DCE	109
	4-(CH$_3$)$_2$NPhN$_2^+$	1.56	Spec			15	MeOH	112
Cb(OctAcet)18C6	Na$^+$	4.2	Pot			25	90% MeOH, 0.1 M NMe$_4$Cl	334
Cy18C6	Li$^+$	<0.7	ISE			25	H$_2$O	11, 25
	Na$^+$	0.8	ISE			25	H$_2$O	11, 25
	Na$^+$	4.09	ISE			25	MeOH	11, 25
	K$^+$	1.90	ISE			25	H$_2$O	11, 25
	K$^+$	5.89	ISE			25	MeOH	11, 25
	Cs$^+$	0.8	ISE			25	H$_2$O	11, 25
	Cs$^+$	4.30 (1)	ISE			25	MeOH	11, 25
	Cs$^+$	1.52 (2)	ISE			25	MeOH	11, 25
	Ag$^+$	1.7–1.9	Pot			25	H$_2$O, from 3 to 0.3 mM Ag$^+$	11, 25
	NH$_4^+$	1.1	ISE			25	H$_2$O	11, 25
cis-anti-cis-Cy$_2$18C6	H$^+$	8.3	Cond			25	DCE	113
	Na$^+$	1.2–1.6	ISE			25	H$_2$O, from 8 to 1 mM Na$^+$	11, 25
	Na$^+$	0.69	Cal	−6.57	−8.8	25	H$_2$O	53
	Na$^+$	1.7	Cal	−10.5	−2.5	25	Me$_2$SO	11
	Na$^+$	~4.5	Cal	~−36.0	~−34.7	25	EtOH	11
	Na$^+$	3.68	ISE			25	MeOH	11, 25
	K$^+$	1.63	Cal	−21.2	−40	25	H$_2$O	53, 115, 116
	K$^+$	1.78	ISE			25	H$_2$O	11, 25
	K$^+$	2.7	Cal	−32.2	−56.5	25	Me$_2$SO	11
	K$^+$			−43.9	−43.9	25	MeOH	11
	K$^+$	5.38	ISE			25	MeOH	11, 25
	Rb$^+$	0.87	Cal	−16.6	−38.9	25	H$_2$O	53, 115
	Cs$^+$	0.9	Cal			25	H$_2$O	115
	Cs$^+$	0.9	ISE			25	H$_2$O	11, 25
	Cs$^+$	3.49	ISE			25	MeOH	11, 25
	Sr^{2+}	2.64	Cal	−13.2	6.3	25	H$_2$O	53, 115
	Ba^{2+}	3.27	Cal	−25.9	−24.3	25	H$_2$O	53, 115
	Ag$^+$	1.59	Cal	−8.74	1.3	25	H$_2$O	11, 53, 115
	Ag$^+$	1.8	ISE			25	H$_2$O	11, 25
	Hg$_2^{2+}$	1.57 (1)	Cal	−18.15	−31.0	25	H$_2$O	53
	Hg$_2^{2+}$	1.1 (2)	Cal	−23.8	−58.5	25	H$_2$O	53
	Hg^{2+}	2.60	Cal	−10.66	13.8	25	H$_2$O	53
	Tl$^+$	1.83	Cal	−17.9	−25	25	H$_2$O	53
	Pb^{2+}	4.43	Cal	−17.6	25.9	25	H$_2$O	53
	NH$_4^+$	0.80	Cal	−14.26	−32.6	25	H$_2$O	11, 53, 115
	NH$_4^+$	0.80	ISE			25	H$_2$O	11, 25
	CH$_3$NH$_3^+$	0.66	Cal	−3.76	0	25	H$_2$O	53
cis-syn-cis-Cy$_2$18C6	H$^+$	>9	Spec			25	CHCl$_3$	117
	H$^+$	8.6	Cond			25	DCE	113
	H$^+$	2.939	Cond			25	DCE	123
	H$^+$	8.2	Pot			25	MeCN	335

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	H_3O^+	8.3	Pot			25	MeCN	335
	Li^+	0.6	ISE			25	H_2O	11, 25
	Na^+	1.21	Cal	0.67	25.5	25	H_2O	53
	Na^+	1.5–1.85	Pot			25	H_2O, from 8 to 1 mM Na^+	11, 25
	Na^+	4.81	Spec			25	Diox	336
	Na^+	4.08	ISE			25	MeOH	11, 25
	K^+	2.02	Cal	−16.2	−15.9	25	H_2O	53, 115, 116
	K^+	2.18	ISE			25	H_2O	11, 25
	K^+	6.01	ISE			25	MeOH	11, 25
	Rb^+	1.52	Cal	−13.9	−17.6	25	H_2O	53, 115
	Rb^+	1.47	Cal	−14.5	−21	25	H_2O	116
	Cs^+	0.96	Cal	−10.1	−15.5	25	H_2O	53, 115, 116
	Cs^+	3.45	NMR			25	DMF	95
	Cs^+	2.20	NMR			25	Me_2SO	95
	Cs^+	1.25	ISE			25	H_2O	11, 25
	Cs^+	>4	NMR			25	Me_2CO	95
	Cs^+	>4	NMR			25	MeCN	95
	Cs^+	4.61 (1)	ISE			25	MeOH	11, 25
	Cs^+	0.59 (2)	ISE			25	MeOH	11, 25
	Cs^+	~4	NMR			25	PC	95
	Cs^+	>5	NMR			25	Py	95
	Sr^{2+}	3.24	Cal	−15.4	10.5	H_2O	53, 115	n
	Ba^{2+}	3.57	Cal	−20.6	−0.84	25	H_2O	53, 115
	Ag^+	2.36	Cal	0.3	46.0	25	H_2O	53, 115
	Ag^+	2.3	Pot			25	H_2O	11, 25
	Hg_2^{2+}	1.93 (1)	Cal	−9.03	6.7	25	H_2O	53
	Hg_2^{2+}	0.6–1.8 (2)	Cal	25.5	109	25	H_2O	53
	Hg^{2+}	2.75	Cal	−3.0	42.7	25	H_2O	53
	Tl^+	2.44	Cal	−15.1	−4.2	25	H_2O	53
	Pb^{2+}	4.95	Cal	−23.3	16.3	25	H_2O	53
	NH_4^+	1.33	Cal	−9.0	−5.0	25	H_2O	53, 115
	NH_4^+	1.4	ISE			25	H_2O	11, 25
	$CH_3NH_3^+$	0.82	Cal	−3.2	5.0	25	H_2O	53
trans-anti-trans-$Cy_2$18C6	Na^+	2.52	ISE			24.5	MeOH	114
	K^+	3.26	ISE			19	MeOH	114
	Rb^+	2.73	ISE			22	MeOH	114
	Cs^+	2.27	ISE			19.5	MeOH	114
trans-syn-trans-$Cy_2$18C6	Na^+	2.99	ISE			21	MeOH	114
	K^+	4.14	ISE			22.5	MeOH	114
	Rb^+	3.42	ISE			23	MeOH	114
	Cs^+	3.00	ISE			19	MeOH	114
$Cy_2$18C6 (mixture of isomers)	H^+	~6	Cond			25	$CHCl_3$	117
	Li^+	<2	Polg			25	MeOH	215
	Li^+	<2	Polg			25	EtOH	215
	Li^+	<2	Polg			25	PrOH	215
	Na^+	4.41, 4.44	Spec			25	Diox	336
	Na^+	4.21	Polg			25	MeOH	215
	Na^+	4.70	Polg			25	EtOH	215
	Na^+	4.90	Polg			25	PrOH	215
	K^+	5.73, 5.75	Spec			25	Diox	336
	K^+	5.97	Polg			25	MeOH	215
	K^+	6.58	Polg			25	EtOH	215
	K^+	7.24	Polg			25	PrOH	215
	K^+	6.60	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	5.40	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	4.25	Polg			25	MeOH	215
	Cs^+	5.1	Polg			25	EtOH	215
	Cs^+	5.76	Polg			25	PrOH	215
	Cs^+	5.10	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	3.45	NMR			25	DMF	94
	Cs^+	2.20	NMR			25	Me_2SO	94
	Cs^+	>4	NMR			25	MeCN	94
	Cs^+	>4	NMR			25	Me_2CO	94
	Cs^+	~4	NMR			25	PC	94
	Cs^+	>5	NMR			25	Pyr	94
	Tl^+	7.40	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	5.20	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
(t-BuCy)$_2$18C6	Li^+	<0.6	Cond			25	H_2O	11
	Na^+	1.42	Cond			25	H_2O	11
	K^+	2.08	Cond			25	H_2O	11
	Cs^+	0.9	Cond			25	H_2O	11
	Rb^+	1.53	Cond			25	H_2O	11
	NH_4^+	1.28	Cond			25	H_2O	11
$K_2$18C6	Na^+	2.5	Cal	−9.5	16	25	MeOH	118, 119
	K^+	2.79	Cal	−24.6	−29.0	25	MeOH	118, 119
	Rb^+	2.09	Cal	−29.3	−58	25	MeOH	119

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Cs^+	2.55	Cal	−6.4	27.5	25	MeOH	119
	Ba^{2+}	3.1	Cal	−1.9	53	25	MeOH	118, 119
	Ag^+	2.50	Cal	−6.4	26.4	25	MeOH	102, 119
Oct18C6	Na^+	3.91	Spec			25	MeOH	63
	K^+	5.03	Spec			25	MeOH	63
Dodec18C6	Na^+	3.93	Spec			25	MeOH	63
	K^+	5.28	Spec			25	MeOH	63
Ph18C6	Na^+	4.17	Spec			25	MeOH	63
	K^+	5.56	Spec			25	MeOH	63
OctOM18C6	Na^+	3.88	Spec			25	MeOH	63
	K^+	5.36	Spec			25	MeOH	63
DodecOM18C6	Na^+	3.83	Spec			25	MeOH	63
	K^+	5.37	Spec			25	MeOH	63
$(BzOM)_4$18C6	t-$BuNH_3^+$	4.30	NMR			?	$CDCl_3$	120
$(TritOM)_4$18C6	t-$BuNH_3^+$	<4.0	NMR			?	$CDCl_3$	120
$(DMD)_4$18C6	Na^+	3.59	ISE			?	MeOH	120
	K^+	4.48	ISE			?	MeOH	120
	Rb^+	4.66	ISE			?	MeOH	120
	t-$BuNH_3^+$	<1.5	NMR			?	$CDCl_3$	120
	$PhCH_2NH_3^+$	6.18	NMR			?	$CDCl_3$	120
$(Me_2Acet)_4$18C6	K^+	1.9	ISE			25	H_2O, Buff 0.1 M, pH 7.0	121
	NH_4^+	<0.70	ISE			25	H_2O, Buff 0.1 M pH 7.0	121
$(MeAcet)_4$18C6	K^+	1.3	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$Cb_4$18C6	K^+	5.5	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	NH_4^+	3.5	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$CH_3NH_3^+$	2.9	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$CH_3CH_2NH_3^+$	2.4	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$(CH_3)_2CHNH_3^+$	1.6	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$CH_3(CH_2)_3NH_3^+$	2.3	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$(CH_3)_3CNH_3^+$	1.6	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5CH_2NH_3^+$	2.8	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5CH_2CH_2NH_3^+$	2.5	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5CH_2CH_2NH_2^+CH_3$	1.4	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH_2CH_2NH_3^+$	2.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH_2CH_2CH_2NH_3^+$	2.5	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH_2CH(CH_3)NH_3^+$	1.6	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH(C_6H_5)CH_2NH_3^+$	2.74	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$(CH_3)_2NH_2^+$	<0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH_2CH_2NH_2^+CH_3$	1	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH_2CH_2NH^+(CH_3)_2$	0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5CH_2CH_2N^+(CH_3)_3$	<0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	adrenaline(1+)	1.8	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	ephedrine(1+)	1.3	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$H_3N^+CH_2CO_2Me$	2.8	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	guanidinium	1.65	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	Histaminium	3.8	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	imidazolium	1	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	noradrenaline(1+)	2.72	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	norephedrine(1+)	2	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	phenylalaninium	1.5	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	serotoninium	2.51	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	tryptaminium	2.51	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_2NH_3^+$	4.6 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_3NH_3^+$	3.8 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_4NH_3^+$	3.23 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_6NH_3^+$	3.08 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_8NH_3^+$	<2.95 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$(CH_3)_2NH^+(CH_2)_2NH_3^+$	4.40	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$(CH_3)_2NH^+(CH_2)_3NH_3^+$	3.61	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(MeCbMAcet)_4$18C6	K^+	1.3	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(CbMAcet)_4$18C6	K^+	2.81	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	NH_4^+	1.5	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3NCH_2CH_2NH_3^+$	2.20 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(ProCba)_4$18C6	NH_4^+	1.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(PheCba)_4$18C6	NH_4^+	2.18	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(TrPCba)_4$18C6	K^+	4.74	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	NH_4^+	2.64	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$CH_3NH_3^+$	2.0	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$CH_3CH_2NH_3^+$	1.8	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5CH_2NH_3^+$	2.18	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5(CH_2)_2NH_3^+$	2	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HO(CH_2)_2NH_3^+$	2.18	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$C_6H_5CH(OH)CH_2NH_3^+$	2.18	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_2NH_3^+$	4 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_3NH_3^+$	3.23 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	$^+H_3N(CH_2)_4NH_3^+$	2.8 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$Nic^+EtNH_3^+$	3.36	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$Nic^+BuNH_3^+$	2.6	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(GluCba)_4$18C6	K^+	4.43	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	NH_4^+	2.40	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_2NH_3^+$	2.9 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_3NH_3^+$	2.63 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_4NH_3^+$	2.26 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(SulNapAcet)_4$18C6	K^+	3	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	NH_4^+	1.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_4NH_3^+$	2.18 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_6NH_3^+$	2.40 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^+H_3N(CH_2)_6NH_3^+$	2.65 (1:1?)	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(CbNapAcet)_4$18C6	K^+	3.23	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$HOCH_2CH_2NH_3^+$	1.81	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(ArgCba)_4$18C6	K^+	2.58	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^-O_3S(CH_2)_2NH_3^+$	<0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^-O_2C(CH_2)_3NH_3^+$	<0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
	$^-O_2C(CH_2)_5NH_3^+$	<0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(enCba)_4$18C6	K^+	1.3	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$(NicEAcet)_4$18C6	K^+	~0.7	ISE			25	H_2O, buffer 0.1 M, pH 7.0	121
$Me_6$18C6 (mixed isomers)	Na^+	2.94	Spec			25	MeOH	63
	K^+	3.86	Spec			25	MeOH	63
B18C6	Na^+	2.5	Cond			25	DMF	338
	Na^+	1.70	NMR			25	99% Me_2SO	72
	Na^+	4.9	Cond			25	MeCN	338
	Na^+	4.90	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Na^+	4.72	Cond			25	Me_2CO	69
	Na^+	4.35	Pot			25	MeOH	340
	Na^+	4.03	Spec			25	MeOH	122
	Na^+	4.5	Cond			25	MeOH	338
	Na^+	5.3	Cond			25	PC	338
	K^+	3.6	Cond			25	DMF	338
	K^+	2.8	Cond			25	Me_2SO	338
	K^+	2.85	Spec			25	99% Me_2SO	72
	K^+	5.3	Cond			25	MeCN	338
	K^+	5.30	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	5.10	Cond			25	Me_2CO	69
	K^+	5.05	Pot			25	MeOH	340
	K^+	5.2	ISE			25	MeOH	64
	K^+	5.20	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	K^+	5.27	Spec			25	MeOH	122
	K^+	5.7	Cond			25	MeOH	338
	K^+	5.4	Cond			25	PC	338
	Rb^+	3.2	Spec			25	DMF	338
	Rb^+	2.6	Spec			25	Me_2SO	338
	Rb^+	2.49	Spec			25	99% Me_2SO	72
	Rb^+	4.4	Cond			25	MeCN	338
	Rb^+	4.40	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	4.62	Spec			25	MeOH	122
	Rb^+	5.1	Cond			25	MeOH	338
	Rb^+	4.5	Cond			25	PC	338
	Cs^+	2.8	Spec			25	DMF	338
	Cs^+	2.4	Spec			25	Me_2SO	338
	Cs^+	2.25	Spec			25	99% Me_2SO	72
	Cs^+	3.8	Cond			25	MeCN	338
	Cs^+	4.05	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	3.66	Spec			25	MeOH	122
	Cs^+	4.1	Cond			25	MeOH	338
	Cs^+	3.6	Cond			25	PC	338
	Ca^{2+}	3.50	Spec			25	MeOH	122
	Sr^{2+}	4.92	Spec			25	MeOH	122
	Ba^{2+}	5.35	Spec			25	MeOH	122
	Tl^+	5.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	4.60	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	n-$C_3H_7NH_3^+$	5.09	Spec			26.6	C_6H_6	106
	i-$C_3H_7NH_3^+$	5.16	Spec			26.6	C_6H_6	106
	n-$C_4H_9NH_3^+$	6.36	Spec			6	C_6H_6	106
	n-$C_4H_9NH_3^+$	5.18	Spec			26.6	C_6H_6	106
	n-$C_4H_9NH_3^+$	4.78	Spec			35	C_6H_6	106
	sec-$C_4H_9NH_3^+$	6.11	Spec			6	C_6H_6	106
	sec-$C_4H_9NH_3^+$	4.88	Spec			26.6	C_6H_6	106
	sec-$C_4H_9NH_3^+$	4.50	Spec			35	C_6H_6	106
	t-$C_4H_9NH_3^+$	6.28	Spec			6	C_6H_6	106
	t-$C_4H_9NH_3^+$	5.00	Spec			26.6	C_6H_6	106

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	$t\text{-}C_4H_9NH_3^+$	4.62	Spec			35	C_6H_6	106
	$n\text{-}C_5H_{11}NH_3^+$	5.24	Spec			26.6	C_6H_6	106
	$sec\text{-}C_5H_{11}NH_3^+$	4.92	Spec			26.6	C_6H_6	106
	$t\text{-}C_5H_{11}NH_3^+$	4.66	Spec			26.6	C_6H_6	106
	$n\text{-}C_3H_6(C_2H_5)NH_3^+$	3.98	Spec			26.6	C_6H_6	106
8,15-Me_2B18C6	Na^+	3.76	Cond			25	MeOH	74
	K^+	4.39	Cond			25	MeOH	74
	Rb^+	3.90	Cond			25	MeOH	74
	Cs^+	3.38	Cond			25	MeOH	74
8,11,15-Me_3B18C6	Na^+	3.53	Cond			25	MeOH	74
	K^+	3.91	Cond			25	MeOH	74
	Rb^+	3.37	Cond			25	MeOH	74
	Cs^+	2.99	Cond			25	MeOH	74
AcetoB18C6	$n\text{-}C_4H_9NH_3^+$	4.79	Spec			26.6	C_6H_6	106
	$sec\text{-}C_4H_9NH_3^+$	4.55	Spec			26.6	C_6H_6	106
	$t\text{-}C_4H_9NH_3^+$	4.68	Spec			26.6	C_6H_6	106
AdrB18C6	Na^+	4.35	Pot			25	MeOH	340
	K^+	5.05	Pot			25	MeOH	340
AldB18C6	Na^+	4.59	Cond			25	Me_2CO	69
	K^+	4.89	Cond			25	Me_2CO	69
N-BuAcetB18C6	Na^+	4.51	Cond			25	Me_2CO	69
	K^+	4.75	Cond			25	Me_2CO	69
MeB18C6	Na^+	5.09	Cond			25	Me_2CO	69
	Na^+	4.30, 4.36	Spec			25	Diox	336
	K^+	5.58	Cond			25	Me_2CO	69
	K^+	5.193, 5.190, 5.23	Spec			25	Diox	336
NitB18C6	Na^+	4.67	Cond			25	Me_2CO	69
	K^+	4.80	Cond			25	Me_2CO	69
$B_2$18C6	H^+	2.32	Cond			25	$CHCl_3$ ion pair with Br^-	117
	H^+	3.7	Pot			25	MeCN	335
	H_3O^+	3.4	Pot			25	MeCN	335
	Li^+	0	Spec			25	H_2O	124
	Li^+	3.0	Cond			25	DMF	125
	Li^+	3.26	Cond			25	PC	125
	Na^+	1.16	Spec			25	H_2O	124
	Na^+	1.1	Sol			25	H_2O	90a
	Na^+	3.857	Cond			10	DME	126
	Na^+,BPh_4^-	3.791	Cond			10	DME	126
	Na^+	3.728	Cond			20	DME	126
	Na^+,BPh_4^-	3.684	Cond			20	DME	126
	Na^+	3.66 interpolated	Cond	−16.3	16.3	30	DME	126
	Na^+,BPh_4^-	3.62 interpolated	Cond	−14.2	22.6	30	DME	126
	Na^+	3.559	Cond			40	DME	126
	Na^+,BPh_4^-	3.535	Cond			40	DME	126
	Na^+	2.8	NMR			25	DMF	128
	Na^+	3.34	Cond			25	DMF	125
	Na^+	3.25	NMR			29	DMF	131
	Na^+	2.69	Cond			30	DMF	11
	Na^+	3.30	Cond			25	Me_2SO	125
	Na^+	1.93	ISE			25	Me_2SO	90a
	Na^+	5.13	Pot			10	MeCN	58
	Na^+	5.00	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Na^+	5.00	Pot	−14.3	47.7	25	MeCN	58
	Na^+	4.85	ISE			25	MeCN	90a
	Na^+	5.04	Cond			25	MeCN	11
	Na^+	4.9	Pot			40	MeCN	58
	Na^+	4.5	Cal	−31.2	−18.8	25	MeOH	127
	Na^+	4.36	Elec			25	MeOH	54
	Na^+	4.36	ISE			25	MeOH	11, 25
	Na^+	4.4	Sol			25	MeOH	90a
	Na^+	4.36	Spec			25	MeOH	63
	Na^+	6.3	Pot	−35		5–65	NBnz, 0.01 M Bu_4NPh_4B	129
	Na^+	3.88	Cond			25	PC	125
	Na^+	5.20	ISE			25	PC	90a
	K^+	1.67	Spec			25	H_2O	124
	K^+	1.6	Sol			25	H_2O	90a
	K^+	5.46	Sol			25	BuOH (anion = picrate)	133
	K^+	3.54	Cond			25	DMF	125
	K^+	3.64	NMR			29	DMF	131
	K^+	3.26	Sol			25	DMF (anion = Cl^-)	133
	K^+	3.15	ISE			25	DMF (anion = ClO_4^-)	133
	K^+	2.5	Cal	−23.0	−36.7	25	Me_2SO	11
	K^+	2.52	Cond			25	Me_2SO	93

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	K^+	3.41	Cond			25	Me_2SO	125
	K^+	2.46	ISE			25	Me_2SO	90a
	K^+	4.83	Cond			25	MeCN	11, 93
	K^+	4.81	ISE			25	MeCN	90a
	K^+	4.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	5.00	ISE			25	MeOH	11, 25
	K^+	5.1	Cal	−40.04	−36.66	25	MeOH	127
	K^+	5.08	Cond			25	MeOH	93
	K^+	5.00	Elec			25	MeOH	54
	K^+	4.8	ISE			25	MeOH	64
	K^+	5.05	ISE			25	MeOH	90a
	K^+	5.00	Spec			25	MeOH	63
	K^+	4.60	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	K^+	6.0	Pot			5–65	NBnz, 0.01 M Bu_4NPh_4B	129
	K^+	5.08	Cond			25	PC	125
	K^+	5.13	ISE			25	PC	90a
	K^+	5.41	Sol			25	*i*-PrOH (anion = picrate)	133
	K^+	1.87	Pot			25	50% THF/H_2O	11
	Rb^+	1.08	Spec			25	H_2O	124
	Rb^+	3.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	3.54	Cond			25	DMF	125
	Rb^+	2.89	NMR			25	DMF	131
	Rb^+	3.37	Cond			25	Me_2SO	125
	Rb^+	4.23	Sol			25	MeOH	90a
	Rb^+	3.76	Cond			25	PC	125
	Rb^+	3.91	ISE			25	PC	90a
	Rb^+	1.35	Pot			25	50% THF/H_2O	11
	Cs^+	0.83	Spec			25	H_2O	124
	Cs^+	1.48	NMR			25	DMF	94
	Cs^+	3.48	Cond			25	DMF	125
	Cs^+	2.35	NMR			25	DMF	131
	Cs^+	1.34	NMR			25	Me_2SO	94
	Cs^+	3.31	Cond			25	Me_2SO	125
	Cs^+	3.55 (1)	ISE			25	MeOH	11, 25
	Cs^+	2.92 (2)	ISE			25	MeOH	11, 25
	Cs^+	3.50	Pot			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	1.54	NMR			25	MeCN	94
	Cs^+	3.59	ISE			25	MeCN	90a
	Cs^+	>3	NMR			25	Me_2CO	94
	Cs^+	3.55	Cond			25	PC	125
	Cs^+	3.31	ISE			25	PC	90a
	Cs^+	~3	NMR			25	PC	94
	Cs^+	3.85 (1)	NMR			25	Py	94
	Cs^+	2.36 (2)	NMR			25	Py	94
	Ca^{2+}	0	Spec			25	H_2O	124
	Sr^{2+}	1.0	Spec			25	H_2O	124
	Sr^{2+}	3.55	Kin			−15	MeOH, 0.05 M $LiClO_4$	130
	Ba^{2+}	~1.95	Spec			25	H_2O	124
	Ba^{2+}	4.28	Cal	−21.2	11.1	25	MeOH	127
	$BaCl^+$	~2.15	Spec			25	H_2O	124
	La^{3+}	0	Spec			25	H_2O	124
	Ag^+	1.41	Spec			25	H_2O	124
	Ag^+	1.5	Sol			25	H_2O	90a
	Ag^+	4.04	Sol, ISE			25	MeOH	90a
	Ag^+	5.82	ISE			25	PC	90a
	Tl^+	1.50	Spec			25	H_2O	124
	Tl^+	1.5	Sol			25	H_2O	90a
	Tl^+	2.45	NMR			29	DMF	131
	Tl^+	4.90	Polg			22	MeCN, 0.025 M Bu_4NClO_4	70
	Tl^+	4.00	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Tl^+	3.92	Sol, ISE			25	MeOH	90a
	Tl^+	3.80	ISE			25	MeOH	90a
	Tl^+	4.98	Pot			25	PC	24
	Tl^+	5.05	ISE			25	PC	90a
	Pb^{2+}	1.89	Spec			25	H_2O	124
	Pb^{2+}	9.74	Pot			25	PC	24
	NH_4^+	~0.30	Spec			25	H_2O	124
meso-6,10-$Me_2B_2$18C6	Na^+	3.56	ISE			25	MeOH	64
	K^+	4.13	ISE			25	MeOH	64
rac-6,10-$Me_2B_2$18C6	Na^+	3.77	ISE			25	MeOH	64
	K^+	4.37	ISE			25	MeOH	64
meso-7,9-$Me_2B_2$18C6	Na^+	2.79	ISE			25	MeOH	64
	K^+	3.42	ISE			25	MeOH	64
rac-7,9-$Me_2B_2$18C6	Na^+	3.03	ISE			25	MeOH	64
	K^+	4.04	ISE			25	MeOH	64

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
syn-$(AmB)_2$18C6	Na^+	3.031	Cond			10	DMF	126
	Na^+	2.860	Cond			20	DMF	126
	Na^+	2.76	Cond			30	DMF	126
	Na^+	2.544	Cond			40	DMF	126
$(BrB)_2$18C6	H^+	5.86	Spec	−27.6	−96.1	25	$CHCl_3$	117
$(t\text{-}BuB)_2$18C6	Na^+	5.36	Polg			25	PC, ? M Et_4NClO_4	132
	Na^+	5.41	Pot			25	PC, 0.1 M Et_4NClO_4	132
	K^+	5.38	ISE	−27.6	−96.1	25	*n*-BuOH (anion = picrate)	133
	K^+	3.30	Sol			25	DMF (anion = Cl^-)	133
	K^+	2.67	ISE			25	Me_2SO	133
	K^+	4.94	Sol			25	MeCN (anion = Cl^-)	133
	K^+	4.90	Sol			25	MeCN (anion = Br^-)	133
	K^+	5.15	ISE			25	MeCN (anion = picrate)	133
	K^+	5.23	Sol			25	Me_2CO (anion = Br^-)	133
	K^+	5.62	ISE			25	*i*-PrOH	133
	K^+	5.18	Sol			25	MeOH (anion = IO_3^-)	133
	K^+	5.32	Sol			25	PC (anion = Cl^-)	133
	Mg^{2+}	<1	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ca^{2+}	6.86	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Sr^{2+}	7.82	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ba^{2+}	7.66	Pot			25	PC, 0.1 M Et_4NClO_4	23
	La^{3+}	5.14	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Ce^{3+}	4.95	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Pr^{3+}	4.79	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Nd^{3+}	4.58	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Sm^{3+}	4.00	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Gd^{3+}	3.62	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Tb^{3+}	3.50	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Dy^{3+}	3.40	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Ho^{3+}	3.29	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Er^{3+}	3.16	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Tm^{3+}	2.94	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Yb^{3+}	2.57	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Lu^{3+}	2.51	Pot			25	PC, 0.1 M Et_4NClO_4	132
	Sm^{3+}	3.97	Polg			25	PC, 0.1 M Et_4NClO_4	132
	Sm^{2+}	7.60	Polg			25	PC, 0.1 M Et_4NClO_4	132
	Yb^{3+}	2.68	Polg			25	PC, 0.1 M Et_4NClO_4	132
	Yb^{2+}	7.31	Polg			25	PC, 0.1 M Et_4NClO_4	132
	Tl^+	4.98	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	9.74	Pot			25	PC, 0.1 M Et_4NClO_4	24
$(MeB)_2$18C6	Na^+	3.69	Spec			25	Diox	336
	Na^+	5.10	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	5.01, 5.05, 4.98	Spec			25	Diox	336
	K^+	4.80	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	4.37	NMR			25	MeOH	83
	K^+	5.00	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Rb^+	4.00	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	3.40	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	5.00	Polg			22	MeCN, 0.025 M Bu_4NClO_4	70
	Ti^+	3.80	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
syn-$(NitB)_2$18C6	Na^+	1.99	Cond			30	DMF	126
A18C6	Na^+	2.77	ISE			25	MeOH	76
	K^+	4.18	ISE			25	MeOH	76
	K^+	3.90	ISE			25	MeOH	11, 25
	Ag^+	3.3	Pot			25	H_2O	11, 25
	NH_4^+	3.55	ISE			25	90% MeOH	75
MeA18C6	NH_4^+	4.05	ISE			25	90% MeOH	75
OctA18C6	Na^+	3.51	ISE			25	MeOH	76
	K^+	4.65	ISE			25	MeOH	76
A1A18C6	Na^+	3.10	ISE			25	90% MeOH	59
HOEA18C6	Na^+	4.75	ISE			25	MeOH	76
	K^+	5.49	ISE			25	MeOH	76
MeOEA18C6	Na^+	4.18	ISE			25	90% MeOH	59
	Na^+	5.6 (1)	Cal	−31.1	2.8	25	MeOH	67
	Na^+	2.7 (2)	Cal	−5.9	32	25	MeOH	67
	K^+	5.35	Cal	−51.8	−71	25	MeOH	67
	Cs^+	4.24 (1)	Cal	−44.9	−69.3	25	MeOH	67
	Cs^+	2.10 (2)	Cal	−3.8	28	25	MeOH	67
	Ca^{2+}	4.83 (1)	Cal	−13.3	48	25	MeOH	67
	Ca^{2+}	3.45 (2)	Cal	3.1	76	25	MeOH	67
	NH_4^+	4.2	ISE			25	90% MeOH	75
$H(OE)_2$A18C6	Na^+	4.34	ISE			25	MeOH	76
	K^+	5.88	ISE			25	MeOH	76
$Me(OE)_2$A18C6	Na^+	5.7 (1)	Cal	−28.0	15	25	MeOH	67
	Na^+	3.7 (2)	Cal	−1.8	65	25	MeOH	67
	K^+		Cal	−52.5		25	MeOH	67

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Cs^+	4.34	Cal	−49.4	−83	25	MeOH	67
	Ca^{2+}	4.23 (1)	Cal	−11.6	42.0	25	MeOH	67
	Ca^{2+}	3.08 (2)	Cal	4.6	74	25	MeOH	67
	NH_4^+	4.75	ISE			25	90% MeOH	75
$H(OE)_3A18C6$	Na^+	4.26	ISE			25	MeOH	76
	K^+	5.69	ISE			25	MeOH	76
$Me(OE)_3A18C6$	Na^+	4.28	ISE			25	MeOH	76
	K^+	5.96	ISE			25	MeOH	76
	NH_4^+	4.6	ISE			25	90% MeOH	75
$Me(OE)_4A18C6$	NH_4^+	4.4	ISE			25	90% MeOH	75
$Me(OE)_5A18C6$	NH_4^+	4.05	ISE			25	90% MeOH	75
$Me(OE)_8A18C6$	NH_4^+	3.6	ISE			25	90% MeOH	75
B_2A18C6	K^+	3.20	Pot			25	MeOH	11, 25
$OctB_2A18C6$	K^+	4.10	Pot			25	MeOH	11, 25
Py18C6	Na^+	4.09	Cal	−22.76	2.0	25	MeOH	61, 102
	K^+	5.35	Cal	−38.1	−25.4	25	MeOH	61, 102
	Rb^+	4.56	Cal	−36.4	−34.8	25	MeOH	61
	Ca^{2+}	5.26	Cal	−12.1	60.0	25	MeOH	61
	Ba^{2+}	>5.5	Cal	−32.3		25	MeOH	61, 102
	Cu^{2+}	4.63	Cal	−7.03	65.1	25	MeOH	61
	Ag^+	>5.5	Cal	−34.85		25	MeOH	61, 102
	Ag^+	2.58 (2)	Cal	10.8	85.6	25	MeOH	61
(*S*,*S*)-$Me_2Py18C6$	(*S*)-$TryOMe^+$	2.29	Cal	−14.4	−4.3	25	MeOH	9
	(*R*)-$TryOMe^+$	2.43	Cal	−14.4	−1.9	25	MeOH	9
$K_2Py18C6$	Na^+	4.29	Cal	−25.9	−4.8	25	MeOH	102, 119
	K^+	4.66	Cal	−38.9	−41.3	25	MeOH	102, 119
	Rb^+	4.24	Cal	−37.95	−46.1	25	MeOH	119
	Ba^{2+}	4.34	Cal	−25.2	−1.6	25	MeOH	102, 119
	Ag^+	4.88	Cal	−32.76	−16.5	25	MeOH	102, 119
	Ag^+	5.15	Cal	−34.3	−16.5	25	MeOH	9
	NH_4^+	2.93	Cal	−32.4	−53	25	MeOH	119
	NH_4^+	3.29	Cal	26.0	−24.2	25	MeOH	9
(*S*,*S*)-$Me_2K_2Py18C6$	Ag^+	5.01	Cal	−37.5	−30.0	25	MeOH	9
	(*S*)-$TryOMe^+$	1.76	Cal	−19.2	−30.6	25	MeOH	9
	(*R*)-$TryOMe^+$	1.73	Cal	−17.2	−24.7	25	MeOH	9
	(*S*)-$NapEtNH_3^+$	2.06	Cal	−26.4	−49.3	25	MeOH	9
	(*R*)-$NapEtNH_3^+$	2.47	Cal	−27.6	−45.2	25	MeOH	9
	(*S*)-$AlaOMe^+$	1.78	Cal	−14.6	−14.8	25	MeOH	9
	(*R*)-$AlaOMe^+$	2.02	Cal	−14.8	−10.9	25	MeOH	9
	NH_4^+	2.81	Cal	−26.2	−33.9	25	MeOH	9
(*S*,*S*)-$Ph_2K_2Py18C6$	Ag^+	5.01	Cal	−35.6	−23.5	25	MeOH	9
	(*S*)-$TryOMe^+$	2.00	Cal	−16.65	−17.6	25	MeOH	9
	(*R*)-$TryOMe^+$	1.96	Cal	−15.36	−14.0	25	MeOH	9
	(*S*)-$AlaOMe^+$	1.84	Cal	−14.0	−11.8	25	MeOH	9
	(*R*)-$AlaOMe^+$	1.85	Cal	−13.8	−10.9	25	MeOH	9
	NH_4^+	2.72	Cal	−23.0	−25.1	25	MeOH	9
1,7-A_218C6	H^+	9.59 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	8.01 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Co^2	3.26	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ni^{2+}	3.21	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	7.40	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Zn^{2+}	4.26	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
1,10-A_218C6 (2.2)	H^+	9.08 (1)	Pot	−36.0 (Cal)	53.1	25	H_2O, 0.1 M Me_4NClO_4	99
	H^+	7.94 (2)	Pot	−39.7 (Cal)	18.4	25	H_2O, 0.1 M Me_4NClO_4	99
	H^+	9.20 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	H^+	8.02 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	H^+	9.30 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	8.15 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	9.245 (1)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	H^+	8.23 (2)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	H^+	9.28 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	H^+	7.97 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Li^+	1.07	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Na^+	4.30	Cond			25	MeCN	90
	K^+	4.32	Cond			25	MeCN	90
	K^+	2.04	Pot			25	MeOH	11, 25
	Rb^+	3.37	Cond			25	MeCN	90
	Cs^+	2.48	Cond			25	MeCN	90
	Ca^+	1.8	Pot			25	H_2O, 0.1 M Me_4NCl	99
	Ca^{2+}	4.04	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Sr^{2+}	2.57	Pot	−10.9 (Cal)	13.0	25	H_2O, 0.1 M Me_4NCl	99
	Sr^{2+}	5.60	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ba^{2+}	2.98	Pot	−12.6 (Cal)	15.1	25	H_2O, 0.1 M Me_4NCl	99
	La^{3+}	6.18	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Co^{2+}	≥3.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Co^{2+}	≤2.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Co^{2+}	3.25	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ni^{2+}	≥2.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ni^{2+}	≤2.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ni^{2+}	3.43	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	6.18	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	7.59	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Cu^{2+}	3.00	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Cu^{2+}	3.30	Spec			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Cu^{2+}	8.77	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ag^+	7.8	Pot			25	H_2O	11, 25
	Ag^+	7.8	Pot	−38.3 (Cal)	21	25	H_2O, 0.1 M Me_4NCl	99
	Ag^+	7.90	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ag^+	8.08	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ag^+	6.21	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	79
	Ag^+	10.18 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	3.33 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Zn^{2+}	4.31	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Zn^{2+}	3.19	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Zn^{2+}	≥2.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Cd^{2+}	5.31	Pot			25	H_2O, 0.1 M Et_4NO_3	77
	Cd^{2+}	5.25	Pot	−2.9 (cal)	90	25	H_2O, 0.1 M Me_4NCl	99
	Cd^{2+}	5.59	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cd^{2+}	7.18	Pot			25	95% MeOH, 0.1 M Me_4NNO_3	87
	Cd^{2+}	7.83 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Cd^{2+}	3.58 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Hg^{2+}	17.85	Pot	−71.8 (Cal)	102	25	H_2O, 0.1 M Me_4NCl	99
	Pb^{2+}	6.90	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Pb^{2+}	7.01	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Pb^{2+}	4.22	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Pb^{2+}	9.48 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	2.82 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	11.64 (1)	Spec			25	PC, 0.01 M Et_4NClO_4	81
	Pb^{2+}	3.66 (2)	Spec			25	PC, 0.01 M Et_4NClO_4	81
Me_2A_218C6	H^+	9.28 (1)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	6.70 (2)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Na^+	3.26	Pot			25	95% MeOH, 0.01 M Me_4NBr	134, 172
	Na^+	3.7	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	4.38	Pot			25	95% MeOH, 0.01 M Me_4NBr	134, 172
	K^+	5.3	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Rb^+	4.3	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	4.4	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Sr^{2+}	6.1	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ba^{2+}	6.7	Pot			25	95% MeOH, 0.01 M Me_4NBr	134, 172
$(AcetM)_2A_218C6$	H^+	6.684 (1)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	H^+	5.40 (2)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Na^+	<2	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	K^+	<2	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Mg^{2+}	<2	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ca^{2+}	5.65	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cu^{2+}	7.38	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ag^+	6.25	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cd^{2+}	8.60	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Pb^{2+}	10.70	Pot			25	H_2O, 0.5 M $LiClO_4$	88
$(HOE)_2A_218C6$	H^+	8.702 (1)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	H^+	7.47 (2)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Na^+	<2	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	K^+	<2	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Mg^{2+}	<2	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ca^{2+}	4.08	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cu^{2+}	6.60	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ag^+	7.27	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cd^{2+}	7.96	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Pb^{2+}	9.20	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Pb^{2+}	4.22	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
$(MeOE)_2A_218C6$	H^+	8.540 (1)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	H^+	7.43 (2)	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Ag^+	7.25	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Cd^{2+}	5.01	Pot			25	H_2O, 0.5 M $LiClO_4$	88
	Pb^{2+}	8.39	Pot			25	H_2O, 0.5 M $LiClO_4$	88
$(Me)(R)A_218C6$	Na^+	3.35	Pot			25	95% MeOH, 0.1 M Me_4NBr	134
	K^+	4.80	Pot			25	95% MeOH, 0.1 M Me_4NBr	134
B_2A_218C6	K^+	1.63	ISE			25	H_2O	11, 25
A_418C6	H^+	9.67 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	H^+	8.85 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Co^{2+}	9.68	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Ni^{2+}	12.49	Pot			25	H_2O, 0.1 M Et_4NClO_4	26

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Cu^{2+}	15.50	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
	Zn^{2+}	10.90	Pot			25	H_2O, 0.1 M Et_4NClO_4	26
$A_6$18C6([18]aneN_6)	K^+	~0.8	Pot			35	H_2O. 0.2 M $NaClO_4$	135
	Ca^{2+}	2.5	Pot	−28	−50	35	H_2O, 0.2 M $NaClO_4$	135
	Sr^{2+}	3.2	Pot			25	H_2O, 0.2 M $NaClO_4$	135
	La^{3+}	5.7	Pot			25	H_2O, 0.2 M $NaClO_4$	135
	Co^{2+}	18.9	Pot			35	H_2O, 0.2 M $NaClO_4$	135
	Ni^{2+}	19.6	Pot			35	H_2O, 0.2 M $NaClO_4$	135
	Cu^{2+}	21.6	Pot	−96	92	25	H_2O, 0.2 M $NaClO_4$	135
	Zn^{2+}	17.8	Pot	−52	167	25	H_2O, 0.2 M $NaClO_4$	135
	Cd^{2+}	17.9	Pot	−59	142	25	H_2O, 0.2 M $NaClO_4$	135
	Hg^{2+}	29.1	Polg	−176	20	25	H_2O, 0.2 M $NaClO_4$	135
	Pb^{2+}	14.1	Pot	−56	84	25	H_2O, 0.2 M $NaClO_4$	135
T18C6	Na^+	2.57	Cal	−20.9	−20.8	25	MeOH	61
	K^+	3.61	Cal	−37.7	−57.3	25	MeOH	61
	Rb^+	2.99	Cal	−36.0	−63	25	MeOH	135a
	Ba^{2+}	3.4	Cal	−25.5	−20.5	25	MeOH	61
	Ag^+	>5.5	Cal	−51.5		25	MeOH	61
1,4-$T_2$18C6	Ag^+	3.0 (1)	Cal	−65.7	−168	25	H_2O	16
	Hg^{2+}	(2)	Cal	−118.8		25	H_2O	16
	Tl^+	1.38	Cal	−30.5	−76.1	25	H_2O	16
	Pb^{2+}	2.63	Cal	−36.94	−73.57	25	H_2O	16
1,10-$T_2$18C6	K^+	1.15	Pot			25	MeOH	11
	Ag^+	4.34	Pot			25	H_2O	11, 25
	Ag^+		Cal	−69.9		25	H_2O	16
	Hg^{2+}		Cal	−74.48		25	H_2O	16
	Tl^+	0.93 (1)	Cal	−46.0	−136.6	25	H_2O	16
	Pb^{2+}	3.13 (1)	Cal	−88.7	−237	25	H_2O	16
K_2T18C6	Ag^+	3.05	Cal	−29.2	−39.4	25	MeOH	102, 119
$K_2$19C6	Na^+	1.8	Cal	−4.6	19	25	MeOH	118, 119
	K^+	2.55	Cal	−33.1	−62.2	25	MeOH	118, 119
	Ba^{2+}	1.41	Cal	−20.4	−41.5	25	MeOH	118, 119
$K_2$20C6	Na^+	1.7	Cal	−4.2	19	25	MeOH	119
	K^+	1.94	Cal	−23.4	−41.5	25	MeOH	119
	Rb^+	1.74	Cal	−29.3	−65	25	MeOH	119
$Nap_2$20C6	Tl^+	0.56	NMR			29	DMF	131
$K_2$21C6	K^+	1.71	Cal	−20.5	−36	25	MeOH	119
	Rb^+	1.63	Cal	−27.6	−62	25	MeOH	119
	Cs^+	1.02	Cal	−48.1	−142	25	MeOH	119
21C7	H^+	5.3	Pot			25	MeCN	335
	Na^+	1.73	Cal	−43.4	−112	25	MeOH	61
	Na^+	2.54	ISE			25	MeOH	22
	K^+	4.22	Cal	−35.94	−39.7	25	MeOH	61
	K^+	4.35	ISE			25	MeOH	22
	K^+	4.41	ISE			25	MeOH	11, 25
	Rb^+	4.86	Cal	−40.4	−42.5	25	MeOH	61
	Cs^+	5.01	Cal	−46.77	−61.0	25	MeOH	61
	Cs^+	5.02	ISE			25	MeOH	11, 25
	Ca^{2+}	2.80	ISE			25	MeOH	22
	Sr^{2+}	1.77	Cal	−29.7	−65.7	25	MeOH	61
	Ba^{2+}	5.44	Cal	−28.5	8.6	25	MeOH	61
	Ag^+	2.46	Cal	−28.9	−49.7	25	MeOH	61
	NH_4^+	3.27	ISE			25	MeOH	22
	PHN_2^+	5.789	Spec			50	DCE	110, 111
	4-$ClphN_2^+$	5.188	Spec			50	DCE	110, 111
	3-$CH_3PhN_2^+$	5.56	Spec			50	DCE	110
	4-$CH_3PhN_2^+$	5.49	Spec			50	DCE	110
	3-$CH_3OPhN_2^+$	5.85	Spec			50	DCE	110
$Cy_2$21C7	Cs^+	1.9	ISE			25	H_2O	11, 25
$K_2$21C7	K^+	2.32	Cal	−27.0	−46.3	25	MeOH	119
	Rb^+	2.27	Cal	−41.3	−94.9	25	MeOH	119
	Ba^{2+}	1.73	Cal	−34.9	−84	25	MeOH	119
B21C7	K^+	1.94	Spec			25	99% Me_2SO	72
	Rb^+	2.66	Spec			25	99% Me_2SO	72
	Cs^+	2.53	Spec			25	99% Me_2SO	72
$B_2$21C7	H^+	2.9	Pot			25	MeCN	335
	Na^+	~-∞	NMR			30	DMF	136
	Na^+	~-∞	NMR			30	Me_2SO	136
	Na^+	2.28	NMR			30	Me_2CO	136
	Na^+	2.78	NMR			30	MeCN	136
	Na^+	2.40	ISE			25	MeOH	11, 25
	Na^+	3.14	NMR			30	NMe	136
	Na^+	2.56	NMR			30	Py	136
	K^+	4.30	ISE			25	MeOH	11, 25
	Cs^+	2.78	NMR			30	DMF	136
	Cs^+	2.84	NMR	−43	−88	30	DMF	136

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Cs^+	2.51	NMR			40	DMF	136
	Cs^+	2.43	NMR			50	DMF	136
	Cs^+	2.06	NMR			60	DMF	136
	Cs^+	1.93	NMR			70	DMF	136
	Cs^+	1.72	NMR			30	Me_2SO	136
	Cs^+	4.11	NMR			20	MeCN	136
	Cs^+	3.95	NMR	−34	−38	30	MeCN	136
	Cs^+	3.73	NMR			40	MeCN	136
	Cs^+	3.41	NMR			60	MeCN	136
	Cs^+	3.15	NMR			75	MeCN	136
	Cs^+	4.52	NMR			10	Me_2CO	136
	Cs^+	4.19.	NMR			20	Me_2CO	136
	Cs^+	3.93	NMR	−46	−78	30	Me_2CO	136
	Cs^+	3.64	NMR			40	Me_2CO	136
	Cs^+	3.36	NMR			55	Me_2CO	136
	Cs^+	4.14	NMR			20	MeOH	136
	Cs^+	3.96	NMR	−27.7	−15	30	MeOH	136
	Cs^+	3.83	NMR			40	MeOH	136
	Cs^+	3.68	NMR			50	MeOH	136
	Cs^+	3.54	NMR			60	MeOH	136
	Cs^+	4.20 (1)	ISE			25	MeOH	11, 25
	Cs^+	1.9 (2)	ISE			25	MeOH	11, 25
	Cs^+	4.40	NMR			15	NMe	136
	Cs^+	4.14	NMR	−32	−26	30	NMe	136
	Cs^+	3.81	NMR			45	NMe	136
	Cs^+	3.66	NMR			60	NMe	136
	Cs^+	3.39	NMR			75	NMe	136
	Cs^+	3.21	NMR			90	NMe	136
	Cs^+	4.12	NMR			20	PC	136
	Cs^+	3.80	NMR	−47	−80	30	PC	136
	Cs^+	3.47	NMR			40	PC	136
	Cs^+	3.25	NMR			50	PC	136
	Cs^+	3.16	NMR			60	PC	136
	Cs^+	4.27	NMR	−30.2	−18	30	Py	136
	Cs^+	4.07	NMR			40	Py	136
	Cs^+	3.89	NMR			50	Py	136
	Cs^+	3.78	NMR			60	Py	136
	Cs^+	3.57	NMR			75	Py	136
	Cs^+	3.39	NMR			90	Py	136
	Tl^+	2.18	NMR			30	DMF	136
	Tl^+	0.63	NMR			30	Me_2SO	136
	Tl^+	>5	NMR			30	MeCN	136
	Tl^+	4.71	NMR			30	Me_2CO	136
	Tl^+	3.97	NMR			30	MeOH	136
	Tl^+	>5	NMR			30	NMe	136
$Bz_2K_2A_221C7$	H^+	5.24	Volt			22	NBnz, 0.01 M Bu_4N-π(3)-1,2-dicarbollylcobaltate(III)	137
	Li^+	7.19	Volt			22	NBnz, 0.01 M Ph_4AsPh_4B	137
	Na^+	5.46	Volt			22	NBnz, 0.01 M Ph_4AsPh_4B	137
	Mg^{2+}	11.96 (1 + 2)	Volt			22	NBnz 0.01 M Ph_4AsPh_4B	137
	Ca^{2+}	18.31 (1 + 2)	Volt			22	NBnz, 0.01 M Ph_4AsPh_4B	137
	Sr^{2+}	16.92 (1 + 2)	Volt			22	NBnz, 0.01 M Ph_4AsPh_4B	137
	Ba^{2+}	15.59 (1 + 2)	Volt			22	NBnz, 0.01 M Ph_4AsPh_4B	137
K_2T21C7	K^+	2.09	Cal	−16.1	−13.9	25	MeOH	119
	Rb^+	2.52	Cal	−23.0	−28.8	25	MeOH	119
	Cs^+	1.91	Cal	−12.7	−5.9	25	MeOH	119
24C8	Na^+	2.35	ISE			25	MeOH	22
	K^+	3.53	ISE			25	MeOH	22
	K^+	3.48	ISE			25	MeOH	11, 25
	Cs^+	4.15	ISE			25	MeOH	11, 25
	Ca^{2+}	2.66	ISE			25	MeOH	22
	NH_4^+	2.63	ISE			25	MeOH	22
Cy_224C8	Cs^+	1.9	ISE			25	H_2O	11, 25
	PhN_2^+	4.528	Spec			50	DCE	110, 111
	4-ClPhN_2^+	4.312	Spec			50	DCE	110, 111
	3-$CH_3PhN_2^+$	4.17	Spec			50	DCE	110
	4-$CH_3PhN_2^+$	4.26	Spec			50	DCE	110
	3-$CH_3OPhN_2^+$	4.55	Spec			50	DCE	110
1,7-B_224C8	Na^+	2.55	Pot			25	MeOH	138
	K^+	3.85	Pot			25	MeOH	138
	Rb^+	4.2	Pot			25	MeOH	138
1,10-B_224C8	Na^+	2.15	Pot			25	MeOH	138
	K^+	3.45	Pot			25	MeOH	138
	Rb^+	3.8	Pot			25	MeOH	138
1,13-B_224C8	H^+	3.2	Pot			25	MeCN	335
	Na^+	∼-∞	NMR			30	DMF	136

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Na^+	~-∞	NMR			30	Me_2SO	136
	Na^+	4.00	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Na^+	2.95	NMR			30	MeCN	136
	Na^+	1.54	Cal	−32.4	−79.0	25	70% MeOH	73
	Na^+	1.54	Elec			25	70% MeOH	54
	Na^+	2.25	Pot			25	MeOH	138
	Na^+	3.74	NMR			30	NMe	136
	Na^+	4.16	Cond	−37.7	−46.0	25	PC	52a, 333
	Na^+	2.89	NMR			30	Py	136
	K^+	3.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	2.42	Cal	−35.7	−73.6	25	70% MeOH	73
	K^+	2.42	Elec			25	70% MeOH	54
	K^+	3.6	Pot			25	MeOH	138
	K^+	3.57	Cond	−35.3	−49.4	25	MeOH	333
	K^+	3.49	ISE			23	MeOH	11, 25
	K^+	3.20	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	K^+	3.73	Cond	−34.5	−44.4	25	PC	52a, 333
	Rb^+	3.40	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	2.55	Cal	−36.5	−73.6	25	70% MeOH	73
	Rb^+	3.86	Cond	−39.4	−57.7	25	MeOH	333
	Rb^+	3.85	Pot			25	MeOH	138
	Rb^+	3.55	Cond	−32.9	−42.3	25	PC	52a, 333
	Cs^+	2.10	NMR	−25.6	−43	30	DMF	136
	Cs^+	1.61	NMR			30	Me_2SO	136
	Cs^+	3.94	NMR	−34.0	−36	30	MeCN	136
	Cs^+	3.80	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	3.71	NMR	−47	−84	30	Me_2CO	136
	Cs^+	2.48	Cal	−37.34	−77.8	25	70% MeOH	73
	Cs^+	3.84	Cond	−36.8	−49.0	25	MeOH	333
	Cs^+	3.78	Pot			25	MeOH	11, 25
	Cs^+	3.60	NMR	−41	−67	30	MeOH	136
	Cs^+	5.4	Pot			5-65	NBnz, 0.01 M Bu_4NBPh_4	129
	Cs^+	4.11	NMR	−26.2	−7	30	NMe	136
	Cs^+	3.46	Cond	−32.3	−42.3	25	PC	52a, 333
	Cs^+	3.25	NMR	−34	−48	30	PC	136
	Cs^+	4.00	NMR	−25.0	−6	30	Py	136
	Cs^+	2.65	NMR			0	DMF	136
	Cs^+	2.46	NMR			10	DMF	136
1,13-$B_2$24C8	Cs^+	2.32	NMR			20	DMF	136
	Cs^+	2.10	NMR			30	DMF	136
	Cs^+	2.02	NMR			40	DMF	136
	Cs^+	1.89	NMR			50	DMF	136
	Cs^+	4.50	NMR			5	MeCN	136
	Cs^+	3.94	NMR			30	MeCN	136
	Cs^+	3.77	NMR			40	MeCN	136
	Cs^+	3.57	NMR			50	MeCN	136
	Cs^+	3.45	NMR			60	MeCN	136
	Cs^+	3.19	NMR			75	MeCN	136
	Cs^+	4.37	NMR			5	Me_2CO	136
	Cs^+	4.15	NMR			15	Me_2CO	136
	Cs^+	3.71	NMR			30	Me_2CO	136
	Cs^+	3.37	NMR			40	Me_2CO	136
	Cs^+	3.07	NMR			55	Me_2CO	136
	Cs^+	4.04	NMR			10	MeOH	136
	Cs^+	3.85	NMR			20	MeOH	136
	Cs^+	3.65	NMR			30	MeOH	136
	Cs^+	3.36	NMR			40	MeOH	136
	Cs^+	3.11	NMR			50	MeOH	136
	Cs^+	2.86	NMR			65	MeOH	136
	Cs^+	4.26	NMR			20	NMe	136
1,13-$B_2$24C8	Cs^+	4.11	NMR			30	NMe	136
	Cs^+	3.91	NMR			45	NMe	136
	Cs^+	3.68	NMR			60	NMe	136
	Cs^+	3.52	NMR			75	NMe	136
	Cs^+	3.37	NMR			90	NMe	136
	Cs^+	3.56	NMR			20	PC	136
	Cs^+	3.25	NMR			30	PC	136
	Cs^+	3.12	NMR			40	PC	136
	Cs^+	3.09	NMR			50	PC	136
	Cs^+	2.78	NMR			60	PC	136
	Cs^+	2.70	NMR			70	PC	136
	Cs^+	4.00	NMR			30	Py	136
	Cs^+	3.76	NMR			45	Py	136
	Cs^+	3.60	NMR			60	Py	136
	Cs^+	3.44	NMR			75	Py	136
	Cs^+	3.27	NMR			90	Py	136
	Tl^+	1.16	NMR			30	DMF	136

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Tl^+	<1.00	NMR			30	Me_2SO	136
	Tl^+	4.81	NMR			30	MeCN	136
	Tl^+	4.80	Polg			22	MeCN, 0.05 M Bu_2NClO_4	70
	Tl^+	4.15	NMR			30	Me_2CO	136
	Tl^+	3.19	NMR			30	MeOH	136
	Tl^+	3.40	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Tl^+	>5	NMR			30	NMe	136
	Tl^+	1.64	NMR			30	Py	136
$(MeB)_2$24C8	Na^+	4.10	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	3.90	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	3.50	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Rb^+	3.90	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	3.90	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	5.00	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	3.30	Polg			22	MeOH, 0.05 M Bu_4NClO_4	70
1,4-$T_2$24C8	Ag^+	4.5 (1)	Cal	−59.8	−115	25	H_2O	16
	Ag^+	5.0 (2)	Cal	−8.8	−66	25	H_2O	16
	Hg^{2+}		Cal	−57.3		25	H_2O	16
	Tl^+		Cal	0		25	H_2O	16
	Pb^{2+}		Cal	0		25	H_2O	16
1,13-$T_2$24C8	Ag^+	(1)	Cal	−57.7		25	H_2O	16
	Hg^{2+}	(1)	Cal	−56.5		25	H_2O	16
	Tl^+		Cal	0		25	H_2O	16
	Pb^{2+}		Cal	0		25	H_2O	16
$B_2$27C9	Na^+	1.50	Cal	−49.1	−135.9	25	70% MeOH	73
	K^+	2.86	Cal	−39.7	−78.6	25	70% MeOH	73
	Cs^+	2.89	NMR			−10	DMF	136
	Cs^+	2.78	NMR			0	DMF	136
	Cs^+	2.58	NMR			10	DMF	136
	Cs^+	2.33	NMR			20	DMF	136
	Cs^+	2.20	NMR	−30	−57	30	DMF	136
	Cs^+	2.05	NMR			40	DMF	136
	Cs^+	4.24	NMR			9	MeCN	136
	Cs^+	4.17	NMR			17	MeCN	136
	Cs^+	3.89	NMR			30	MeCN	136
	Cs^+	3.63	NMR			45	MeCN	136
	Cs^+	3.30	NMR			63	MeCN	136
	Cs^+	3.09	NMR			77	MeCN	136
	Cs^+	4.43	NMR			20	Me_2CO	136
	Cs^+	4.24	NMR	−61	−120	30	Me_2CO	136
	Cs^+	3.88	NMR			40	Me_2CO	136
	Cs^+	3.62	NMR			50	Me_2CO	136
	Cs^+	3.22	NMR			55	Me_2CO	136
	Cs^+	1.42	Cal	−25.69	−59.0	25	70% MeOH	73
	Cs^+	3.74	NMR			25	MeOH	136
	Cs^+	3.52	NMR	−21	−22	30	MeOH	136
	Cs^+	3.46	NMR			40	MeOH	136
	Cs^+	3.32	NMR			50	MeOH	136
	Cs^+	3.22	NMR			59	MeOH	136
	Cs^+	4.29	NMR	−31	−19	30	NMe	136
	Cs^+	4.24	NMR			40	NMe	136
	Cs^+	4.14	NMR			50	NMe	136
	Cs^+	3.81	NMR			61	NMe	136
	Cs^+	3.48	NMR			75	NMe	136
	Cs^+	3.46	NMR			90	NMe	136
	Cs^+	<4	NMR			12	PC	136
	Cs^+	3.64	NMR	−47	−86	30	PC	136
	Cs^+	3.27	NMR			40	PC	136
	Cs^+	3.18	NMR			46	PC	136
	Cs^+	2.95	NMR			57	PC	136
	Cs^+	2.84	NMR			64	PC	136
	Cs^+	4.15	NMR	−38	−30	30	Py	136
	Cs^+	3.93	NMR			48	Py	136
	Cs^+	3.78	NMR			56	Py	136
	Cs^+	3.61	NMR			68	Py	136
	Cs^+	3.35	NMR			82	Py	136
	Cs^+	3.08	NMR			98	Py	136
B30C10	K^+	1.25	Spec			25	99% Me_2SO	72
	Rb^+	1.57	Spec			25	99% Me_2SO	72
	Cs^+	1.38	Spec			25	99% Me_2SO	72
$B_2$30C10	H^+	3.6	Pot			25	MeCN	335
	Li^+	<0	Spec			25	MeOH	139
	Na^+	3.60	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Na^+	2.0	ISE			25	MeOH	11, 25
	Na^+	2.1	Spec	−17		25	MeOH	139

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Na^+	2.114	Spec	−16.7		25	MeOH, 0.15 M LiCl	11
	Na^+	6.6	Pot			5–65	NBnz, 0.01 M Bu_4NPh_4B	129
	K^+	4.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	3.90	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	K^+	4.60	ISE			25	MeOH	11, 25
	K^+	4.6	Spec	−48		25	MeOH, 0.15 M LiCl	139
	K^+	4.568	Spec	−48.1		25	MeOH, 0.15 M LiCl	11
	K^+	1.35	Pot			25	50% THF/H_2O	11
	Rb^+	4.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	4.6	Spec	−53		25	MeOH	139
	Rb^+	4.643	Spec	−53.1		25	MeOH, 0.15 M LiCl	11
	Rb^+	1.56	Pot			25	50% THF/H_2O	11
	Cs^+	3.39	NMR	−21.5	−6.4	30	MeCN (anion = SCN^-)	140, 141
	Cs^+	3.50	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Cs^+	4.04	NMR			30	Me_2CO (anion = picrate)	141
	Cs^+	3.99	NMR			30	Me_2CO (anion = SCN^-)	140, 141
	Cs^+	4.05	NMR			30	Me_2CO (anion = 0.0025 M BPh_4^-)	141
	Cs^+	3.96	NMR	−56.4	−110	30	Me_2CO (anion = 0.005 M BPh_4^-)	140, 141
	Cs^+	4.230	Spec	−46.9		25	50% MeOH, 0.15 M LiCl	11
	Cs^+	4.2	Spec	−47		25	MeOH	139
	Cs^+	4.18	NMR	−53.2	−95.5	30	MeOH (anion = SCN^-)	140, 141
	Cs^+	4.30	NMR	−33.3	−27.9	30	NMe (anion = ClO_4^-)	140, 141
	Cs^+	4.41	NMR	−33.2	−24.8	30	Py (anion = BPh_4^-)	140, 141
	Mg^{2+}	2.89	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Cs^{2+}	5.23	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Sr^{2+}	7.67	Pot			25	PC, 0.1 M Et_4NClO_4	23
	Ba^{2+}	9.33	Pot			25	PC, 0.1 M Et_4NClO_4	23
	La^+	4.29	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Ce^{3+}	4.10	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pr^{3+}	4.12	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Nd^{3+}	4.10	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{3+}	8.3 (1 + 2)	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Sm^{3+}	3.75	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Gd^{3+}	3.53	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tb^{3+}	4.07	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Er^{3+}	4.48	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Yb^{2+}	7.5	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Yb^{3+}	4.76	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Lu^{3+}	4.80	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Tl^+	5.60	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	4.4	Fluor			25	MeOH	180
	Tl^+	4.5	Spec	−46		25	MeOH	139
	Tl^+	4.10	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Tl^+	4.505	Spec	−46.0		25	MeOH, 0.015 M Bu_4NClO_4	11
	Tl^+	5.35	Pot			25	PC, 0.1 M Et_4NClO_4	24
	Pb^{2+}	11.45	Pot			25	PC, 0.1 M Et_4NClO_4	24
	NH_4^+	2.4	Spec	−23		25	MeOH	139
	NH_4^+	2.431	Spec	−23.0		25	MeOH, 0.15 M LiCl	11
$(MeB)_230C10$	Na^+	3.60	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	4.80	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	K^+	4.70	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Rb^+	4.90	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Rb^+	4.65	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
	Cs^+	3.80	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
$(MeB)_230C10$	Tl^+	5.70	Polg			22	MeCN, 0.05 M Bu_4NClO_4	70
	Tl^+	4.20	Polg			22	MeOH, 0.025 M Bu_4NClO_4	70
B_260C20	K^+	3.90	ISE			25	MeOH	11, 25
2.1.1	H^+	11.84	Pot			1.2	H_2O	142
	H^+	11.17	Pot			25	H_2O	142
	H^+	10.64 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	7.85 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	11.32 (1)	Pot	37.2 (Cal)	92.2	25	H_2O, 0.1 M Et_4NClO_4	77, 143
	H^+	8.14 (2)	Pot	−33.4 (Cal)	43.9	25	H_2O, 0.1 M Et_4NClO_4	77, 143
	H^+	12.65 (1)	Pot	−42.2 (Cal)	99.9	25	MeOH, 0.05 M Et_4NClO_4	143
	H^+	8.46 (2)	Pot	58.1 (Cal)	−32.6	25	MeOH, 0.05 M Et_4NClO_4	143
	H^+	10.48 (1)	Pot			25	H_2O, 0.25 M Me_4NCl	154
	H^+	7.86 (2)	Pot			25	H_2O, 0.25 M Me_4NCl	154
	H^+	11.59 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	H^+	7.12 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	H^+	11.00 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	6.56 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Li^+	5.5	Pot	−21.3 (Cal)	33.5	25	H_2O, 0.05 M Me_4NBr, pH 12	87, 134, 144
	Li^+		Cal	−21.8		25	H_2O, piperdine HCl buffer, μ = 0.1 M, pH 11.4	155
	Li^+	6.99	EMF			25	DMF, 0.1 M Et_4NClO_4	145
	Li^+	5.84	EMF			25	DMSO, 0.1 M Et_4NClO_4	145

TABLE I (Continued)

ligand	cation	log K°	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Li^+	8.47	EMF			25	EtOH, 0.1 M Et_4NClO_4	145
	Li^+	>10	EMF			25	MeCN, 0.1 M Et_4NClO_4	145
	Li^+	7.58	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Li^+	7.93	Pot			25	95% MeOH, 0.1 M Me_4NBr	87
	Li^+	8.04	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	Li^+	>6.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Li^+	6.43	EMF			25	NMP, 0.1 M Et_4NPic	145
	Li^+	12.4	Ag^+ISE			25	PC	147
	Li^+	12.87	Pot			25	PC, 0.1 M $LiClO_4$	79
	Na^+	3.2	Pot	−22.6 (Cal)	12	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Na^+	2.8	Pot			25	H_2O, 0.1 M Bu_4NClO_4	148
	Na^+	5.23	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Na^+	4.63	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Na^+	4.3	Pot			25	Me_2SO, 0.1 M Bu_4NClO_4	148
	Na^+	7.09	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Na^+	>9	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Na^+	9.57	Pot			10	MeCN	58
	Na^+	9.09	Pot	−53.8	−7.0	25	MeCN	58
	Na^+	8.62	Pot			40	MeCN	58
	Na^+	9.8	Pot			25	MeCN, 0.1 M Bu_4NClO_4	148
	Na^+	6.08	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Na^+	6.53	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Na^+	6.1	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Na^+	6.7	Pot			25	MeOH 0.1 M Bu_4NClO_4	148
	Na^+	5.06	Pot			25	NMP, 0.1 M Et_4NPic	145
	Na^+	4.5	Pot			25	Me_4U, 0.1 M Bu_4NClO_4	148
	Na^+	8.8	Ag^+ISE			25	PC	147
	K^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	K^+	<4	NMR			?	Me_2CO	149
	K^+	<2.5	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	K^+	1.0	NMR			?	DMF	149
	K^+	-∞	NMR			?	Me_2SO	149
	K^+	<2.0	Pot			25	Me_2SO, 0.1 M Et_4NCO_4	145
	K^+	≤2.6	Pot			25	EtOH, 0.1 M Et_4NPic	145
	K^+	2.84	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	K^+	2.8	NMR			?	MeCN	149
	K^+	2.26	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	K^+	2.3	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	2.46	Pot			25	NMP, 0.1 M Et_4NPic	145
	K^+	3.3	Ag^+ ISE			25	PC	147
	K^+	2.5	NMR			?	Py	149
	Rb^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Rb^+	<2.0	Pot			25	95% MeOH, 0.1 M Me_4NBr	134
	Rb^+	1.9	Pot			25	MeOH, 0.1 M Me_4NBr	134
	Rb^+	<2.2	Ag^+ ISE			25	PC	147
	Cs^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Cs^+	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Cs^+	<2.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Mg^{2+}	2.5	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Mg^{2+}	4.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	2.50	Pot	−0.4 (Cal)	46.4	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Ca^{2+}	3.2	Kin	21.3	134	25	H_2O, piperidine HCl, pH 11.5, μ = 0.1	157
	Ca^{2+}	2.30	Kin	−1.3	46	25	H_2O, 0.1 M piperidine HCl, pH 11.5	150
	Ca^{2+}		Cal	−1.7		25	H_2O, piperidine HCl, μ = 0.1 M, pH 11.4	155
	Ca^{2+}	3.08	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Ca^{2+}	4.34	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	4.5	Pot			25	95% MeOH, 0.1 M Me_4NBr	87
	Ca^{2+}	5.43	Ag^+ ISE			25	MeOH	152
	Ca^{2+}	8.6	Ag^+ ISE			25	PC	147
	Sr^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Sr^{2+}	2.90	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ba^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Ba^{2+}	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Sm^{3+}	6.8	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Ho^{3+}	6.21	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Tm^{3+}	6.8	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Yb^{3+}	6.51	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Lu^{3+}	6.55	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Co^{2+}	≤4.7	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ni^{2+}	≤4.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	7.78 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	7.51 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	4.08	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Cu^{2+}	≤7.3	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ag^+	11.13	Pot	−71.5	−25	25	H_2O	151
	Ag^+	8.52	Pot			25	H_2O, 0.1 M Et_4NClO_4	77

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Ag^+	8.62	Pot	−98.5	−165	25	DFM, 0.1 M Et_4NClO_4	145, 151
	Ag^+	6.17	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Ag^+	5.45	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	79
	Ag^+	9.70	Pot			25	EtOH, 0.1 M Et_4NClO_4	145
	Ag^+	7.70	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Ag^+	10.61	Pot	−102.9	−142	25	MeOH, 0.1 M Et_4NClO_4	146, 151
	Ag^+	10.30	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	7.64	Pot			25	NMP, 0.1 M Et_4NPic	145
	Ag^+	14.44	Ag^+ ISE			25	PC, 0.1 M Et_4NClO_4	145, 147
	Ag^+	15.00	Pot			25	PC, 0.1 M Et_4NClO_4	79
	Zn^{2+}	≤5.3	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	≤5.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	≤7.7	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Hg^{2+}	15.97	Pot			25	H_2O, 0.1 M Et_4NClO_4	78
	Hg^{2+}	18.71 (B_{111})	Pot			25	H_2O, 0.1 M Et_4NClO_4	78
	Pb^{2+}	7.93	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Pb^{2+}	3.68	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Pb^{2+}	8.18 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	4.04 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	7.01 (1)	Spec			25	PC, 0.01 M Et_4NClO_4	81
	Pb^{2+}	4.29 (2)	Spec			25	PC, 0.01 M Et_4NClO_4	81
$A_2$2.1.1	H^+	10.25 (1)	Pot			25	H_2O^d	153
	H^+	9.55 (2)	Pot			25	H_2O^d	153
	Li^+	1.6	Pot			25	H_2O^d	153
	Mg^{2+}	1.9	Pot			25	H_2O^d	153
	Ni^{2+}	7.8	Pot			25	H_2O^d	153
	Cu^{2+}	17.9	Pot			25	H_2O^d	153
	Ag^+	11.5	Pot			25	H_2O^d	153
	Zn^{2+}	11.3	Pot			25	H_2O^d	153
	Cd^{2+}	16.3	Pot			25	H_2O^d	153
	Tl^+	<1.0	Pot			25	H_2O^d	153
$Me_2A_2$2.1.1	H^+	11.18 (1)	Pot			25	H_2O^d	153
	H^+	9.75 (2)	Pot			25	H_2O^d	153
	H^+	2.42 (3)	Pot			25	H_2O^d	153
	Li^+	3.8	Pot			25	H_2O^d	153
	Li^+	>3.8	Pot			25	95% MeOH^d	153
	Li^+	>4.0	Pot			25	MeOH^d	153
	Na^+	<1.0	Pot			25	H_2O^d	153
	Mg^{2+}	2.4	Pot			25	H_2O^d	153
	Ca^{2+}	2.2	Pot			25	H_2O^d	153
	Co^{2+}	9.9	Pot			25	H_2O^d	153
	Ni^{2+}	10.0	Pot			25	H_2O^d	153
	Cu^{2+}	16.0	Pot			25	H_2O^d	153
	Ag^+	12.7	Pot			25	H_2O^d	153
	Zn^{2+}	11.2	Pot			25	H_2O^d	153
	Cd^{2+}	12.4	Pot			25	H_2O^d	153
	Hg^{2+}	26.6	Pot			25	H_2O^d	153
	Tl^+	3.9	Pot			25	H_2O^d	153
2.2.1	H^+	11.78	Pot			1.2	H_2O	142
	H^+	10.91	Pot			25	H_2O	142
	H^+	10.53 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	7.50 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	11.02 (1)	Pot	−35.1 (Cal)	93.2	25	H_2O, 0.1 M Et_4NClO_4	77, 143
	H^+	7.74 (2)	Pot	−17.1 (Cal)	90.7	25	H_2O, 0.1 M Et_4NClO_4	77, 143
	H^+	10.75 (1)	Pot			25	H_2O, 0.25 M Me_4NCl	154
	H^+	7.68 (2)	Pot			25	H_2O, 0.25 M Me_4NCl	154
	H^+	10.97 (1)	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	H^+	7.31 (2)	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	H^+	10.42 (1)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	6.60 (2)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	11.53 (1)	Pot	−55.6 (Cal)	33.8	25	MeOH, 0.05 M Et_4NClO_4	143
	H^+	9.48 (2)	Pot	−58.9 (Cal)	−16.3	25	MeOH, 0.05 M Et_4NClO_4	143
	Li^+	2.50	Pot	0.0 (Cal)	47.7	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Li^+	3.58	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Li^+	2.77	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Li^+	5.38	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Li^+	10.33	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Li^+	4.18	Pot			25	95% MeOH, 0.1 M Me_4NBr	134
	Li^+	4.46	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Li^+	5.38	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	Li^+	>5.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Li^+	3.48	Pot			25	NMP, 0.1 M Et_4NPic	145
	Li^+	9.6	Ag^+ ISE			25	PC	147
	Na^+	5.40	Pot	−22.38 (Cal)	25.9	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Na^+	5.4	Pot			25	H_2O, 0.1 M Bu_4NClO_4	148
	Na^+	7.93	Pot			25	DMF, 0.1 M Et_4NClO_4	145

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Na^+	6.98	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Na^+	6.9	Pot			25	Me_2SO, 0.1 M Bu_4NClO_4	148
	Na^+	7.24	Pot			25	Me_2SO, 0.1 M $NaClO_4$	79
	Na^+	10.20	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Na^+	12.4	Pot			25	MeCN, 0.1 M Bu_4NClO_4	148
	Na^+	8.84	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Na^+	9.35	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Na^+	9.65	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	Na^+	9.3	Pot			25	MeOH, 0.1 M Bu_4NClO_4	148
	Na^+	>8.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Na^+	6.55	Pot			25	NMP, 0.1 M Et_4NPic	145
	Na^+	12.1	Ag^+ ISE			25	PC	147
	Na^+	12.78	Pot			25	PC, 0.1 M $NaClO_4$	79
	Na^+	7.1	Pot			25	Me_4U, 0.1 M Bu_4NClO_4	148
	K^+	3.95	Pot	−28.5 (Cal)	−19.7	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	K^+	6.66	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	K^+	5.97	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	K^+	8.56	Pot			25	EtOH, 0.1 M Et_4NPic	145
	K^+	7.45	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	K^+	8.54	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	K^+	>7.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	8.54	Cond	−59.9		25	MeOH	156
	K^+	6.11	Pot			25	NMP, 0.1 M Et_4NPic	145
	K^+	9.9	Ag^+ ISE			25	PC	147
	Rb^+	2.55	Pot	−22.6 (Cal	−27.2	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Rb^+	5.35	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Rb^+	4.64	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Rb^+	6.88	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Rb^+	5.80	Pot			25	95% MeOH, 0.1 M Me_4NBr	134
	Rb^+	>6.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Rb^+	6.74	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	Rb^+	5.55	Pot			25	NMP, 0.1 M Et_4NPic	145
	Rb^+	7.0	Ag^+ ISE			25	PC	147
	Cs^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Cs^+	3.61	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Cs^+	3.23	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Cs^+	4.47	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Cs^+	3.90	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Cs^+	~5.0	Pot			25	MeOH, 0.05 M Et_4NClO_4	134
	Cs^+	4.33	Pot			25	MeOH, 0.01 M Me_4NBr	146
	Cs^+	3.87	Pot			25	NMP, 0.1 M Et_4NPic	145
	Cs^+	4.9	Ag^+ ISE			25	PC	147
	Mg^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Mg^{2+}	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	6.8	Kin	−29.7	29	25	H_2O, piperidine HCl, pH 11.5, μ = 0.1	157
	Ca^{2+}	6.95	Pot	−12.1 (Cal)	92.0	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Ca^{2+}	6.86	Kin	−5.4	113	25	H_2O, 0.1 M piperidine HCl, pH 11.5	150
	Ca^{2+}	6.67	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Ca^{2+}	9.61	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	9.92	Ag^+ ISE			25	MeOH	152
	Ca^{2+}	11.5	Ag^+ ISE			25	PC	147
	Sr^{2+}	7.35	Pot	−25.5 (Cal)	54.8	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Sr^{2+}	10.65	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Sr^{2+}	11.04	Pot			25	MeOH	152
	Ba^{2+}	6.30	Pot	−26.4 (Cal)	32.2	25	H_2O, 0.05 M Me_4NBr, pH 12 (ΔH, ref 144)	134, 144
	Ba^{2+}	9.70	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ba^{2+}	10.62	Pot			25	MeOH	152
	La^{3+}	6.59	Pot			25	H_2O, 0.25 M Me_4NCl	154
	La^{3+}	8.26	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	La^{3+}	18.6	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Pr^{3+}	6.58	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Pr^{3+}	9.31	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Pr^{3+}	18.7	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Nd^{3+}	9.86	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Sm^{3+}	6.76	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Sm^{3+}	9.70	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Sm^{3+}	19.0	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Eu^{2+}	10.2	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Eu^{2+}	9.31	Volt	−36.8	54	25	H_2O	158
	Eu^{3+}	5.94	Volt	7.9	140	25	H_2O	158
	Eu^{3+}	6.8	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Eu^{3+}	10.57	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Eu^{3+}	19.0	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Gd^{3+}	6.7	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Gd^{3+}	10.14	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Tb^{3+}	6.6	Pot			25	H_2O, 0.25 M Me_4NCl	154

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Tb^{3+}	10.26	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Dy^{3+}	10.45	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Dy^{3+}	19.0	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Ho^{3+}	10.86	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Er^{3+}	6.60	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Er^{3+}	10.78	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Er^{3+}	19.2	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Y^{3+}	10.34	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Tm^{3+}	6.88	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Tm^{3+}	11.61	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Yb^{3+}	12.00	Pot			25	MeOH, 0.05 M Et_4NClO_4	65
	Yb^{3+}	19.1	Pot			25	PC, 0.1 M Et_4NClO_4	65
	Co^{2+}	5.40	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Co^{2+}	5.92	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ni^{2+}	4.28	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	7.56 (1)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	5.14 (2)	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	2.7	Cal	−17.9	−8.4	25	Me_2SO	159
	Cu^{2+}	2.5	Kin			25	Me_2SO	159
	Cu^{2+}	3.77	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Cu^{2+}	8.71	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ag^+	10.6	Pot			25	H_2O, 0.1 M Me_4NBr	134
	Ag^+	10.6	Pot			25	H_2O, 0.1 M Bu_4NClO_4	148
	Ag^+	11.82	Pot	−51.0	54	25	H_2O	151
	Ag^+	10.60	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ag^+	12.43	Pot			25	H_2O, 0.1 M Et_4NClO_4	78
	Ag^+	12.43	Pot	−88.7	−14	25	DMF, 0.1 M Et_4NClO_4	151
	Ag^+	12.41	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Ag^+	9.61	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Ag^+	8.2	Pot			25	Me_2SO, 0.1 M Bu_4NClO_4	148
	Ag^+	9.73	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	79
	Ag^+	13.84	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Ag^+	11.24	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Ag^+	9.7	Pot			25	MeCN, 0.1 M Bu_4NClO_4	148
	Ag^+	14.64	Pot	−80.8	8	25	MeOH, 0.1 M Et_4NClO_4	146, 151
	Ag^+	13.3	Pot			25	MeOH, 0.1 M Bu_4NClO_4	148
	Ag^+	14.30 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	5.20 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	10.45	Pot			25	NMP, 0.1 M Et_4NPic	145
	Ag^+	18.50	ISE			25	PC, 0.1 M Et_4NClO_4	145, 147
	Ag^+	18.80	Pot			25	PC, 0.1 M Et_4NClO_4	79
	Ag^+	10.5	Pot			25	Me_4U, 0.1 M Bu_4NClO_4	148
	Zn^{2+}	5.41	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	10.04	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	11.30	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Hg^{2+}	19.97	Pot			25	H_2O, 0.1 M Et_4NClO_4	78
	Tl^+	6.8	Kin			25	H_2O	160
	Pb^{2+}	13.12	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Pb^{2+}	8.37	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Pb^{2+}	15.11 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	4.96 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	16.34 (1)	Spec			25	PC, 0.1 M Et_4NClO_4	81
	Pb^{2+}	3.73 (2)	Spec			25	PC, 0.1 M Et_4NClO_4	81
py2.2.1	Na^+	4.89	Spec			25	H_2O	277
	K^+	4.78	Spec			25	H_2O	277
K_2py2.2.1	Na^+	4.58	Spec			25	H_2O	277
	K^+	5.25	Spec			25	H_2O	277
2.2.2	H^+	10.66	Cond			1.2	H_2O	142
	H^+	9.86	Cond			25	H_2O	142
	H^+	10.00 (1)	Pot	−35.1 (Cal)	73.1	25	H_2O, 0.1 M Et_4NClO_4	77, 143
	H^+	7.53 (2)	Pot	−18.8 (Cal)	83.2	25	H_2O, 0.1 M Et_4NClO_4	77, 143
	H^+	9.95 (1)	Pot			25	H_2O, 0.25 M Me_4NCl	154
	H^+	7.59 (2)	Pot			25	H_2O, 0.25 M Me_4NCl	154
	H^+	9.71 (1)	Pot	−45.2	34.3	25	H_2O, 0.1 M Me_4NCl	99
	H^+	7.31 (2)	Pot	−18.8	76.6	25	H_2O, 0.1 M Me_4NCl	99
	H^+	9.8 (1)	Kin			25	H_2O, 0.1 M piperidine HCl	150
	H^+	7.4 (2)	Kin			25	H_2O, 0.1 M piperidine HCl	150
	H^+	9.60 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	7.28 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	10.05 (1)	Pot			25	H_2O, 0.1 M Me_4NCl	87
	H^+	7.15 (2)	Pot			25	H_2O, 0.1 M Me_4NCl	87
	H^+	9.85 (1)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	6.64 (2)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	10.72 (1)	Pot	−51.8 (Cal)	30.9	25	MeOH, 0.05 M Et_4NClO_4	143
	H^+	9.03 (2)	Pot	−53.9 (Cal)	−8.4	25	MeOH, 0.05 M Et_4NClO_4	143
	Li^+	1.25	Cal	−5.86	4.2	25	H_2O	161

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Li^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Li^+	<1.4	CyVol			25	H_2O, 0.01 M Et_4NClO_4	162
	Li^+	<1.0	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Li^+	<1.0	CyVolt			25	Me_2SO, 0.1 M Et_4NClO_4	162
	Li^+	≤2.3	Pot			25	EtOH, 0.1 M Et_4NClO_4	145
	Li^+	6.97	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Li^+	1.8	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Li^+	~1	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Li^+		Cal	0.71	52.3	25	MeOH	161
	Li^+	2.6	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Li^+	2.97	Pot			25	NMP, 0.1 M Et_4NPic	145
	Li^+	6.9	Ag^+ ISE			25	PC	147
	Na^+		Cal	−31.88		25	H_2O	161
	Na^+	3.9	Pot	−31.0 (Cal)	−29.3	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Na^+	4.11	Pot	−31.0 (Cal)	−25.1	25	H_3O, 0.1 M Me_4NCl	99
	Na^+	3.9	CyVol			25	H_2O, 0.01 M Et_4NClO_4	162
	Na^+	3.9	Pot			25	H_2O, 0.1 M Bu_4NClO_4	148
	Na^+		Cal	−39.96		25	DMF	339
	Na^+	5.83	Pot			25	DMF	163
	Na^+	6.17	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Na^+		Cal	−44.64		25	Me_2SO	339
	Na^+	5.3	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Na^+	4.9	ISE			25	Me_2SO	163
	Na^+	5.4	Pot			25	Me_2SO, 0.1 M Bu_4NClO_4	148
	Na^+	5.4	CyVolt			25	Me_2SO, 0.1 M Et_4NClO_4	162
	Na^+	5.28	Pot			25	Me_2SO, 0.1 M $NaClO_4$	79
	Na^+	8.57	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Na^+	>7	Cond			25	MeCN	90
	Na^+	10.68	ISE			25	MeCN	163
	Na^+	9.63	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Na^+	10.9	Pot			25	MeCN, 0.1 M Bu_4NClO_4	148
	Na^+	7.21	Pot	−44.4 (Cal)	−11.0	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Na^+	7.4	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Na^+		Cal	−44.64	2.1	25	MeOH	161
	Na^+	>8.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Na^+	7.9	CyVol			25	MeOH, 0.05 M Et_4NClO_4	162
	Na^+	7.98	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	Na^+	7.8	Pot			25	MeOH, 0.1 M Bu_4NClO_4	148
	Na^+	5.82	Pot			25	NMP, 0.1 M Et_4NPic	145
	Na^+	10.1	ISE			25	PC	163
	Na^+	10.25	Pot			25	PC	163
	Na^+	10.5	Ag^+ ISE			25	PC	147
	Na^+	10.83	Pot			25	PC, 0.1 M $NaClO_4$	79
	Na^+	5.6	Pot			25	Me_4U, 0.1 M Bu_4NClO_4	148
	K^+	5.3	Cal	−48	−58.9	25	H_2O	144
	K^+		Cal	−48.4		25	H_2O	161
	K^+	5.4	Kin			25	H_2O	160
	K^+	5.4	Pot	−47.7 (Cal)	−59.0	25	H_2O, 0.05M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	K^+	5.58	Pot	−46.0 (Cal)	−48.1	25	H_2O, 0.1 M Me_4NCl	99
	K^+	5.4	CyVol			25	H_2O, 0.01 M Et_4NClO_4	162
	K^+		Cal	−54.52		25	DMF	339
	K^+	7.98	EMF			25	DMF, 0.1 M Et_4NClO_4	145
	K^+	7.89	Pot	−53.0 (Cal)	−27	25	DMF, 0.1 M Et_4NClO_4	151
	K^+		Cal	−61.17		25	Me_2SO	339
	K^+	6.95	ISE			25	Me_2SO	163
	K^+	7.11	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	K^+	6.0	CyVol			25	Me_2SO, 0.1 M Et_4NClO_4	162
	K^+	6.92	Pot	−60.8	−71	25	Me_2SO, 0.1 M Et_4NClO_4	151
	K^+	10.50	Pot			25	EtOH, 0.1 M Et_4NPic	145
	K^+	>7	Cond			25	MeCN	90
	K^+	10.46	ISE			25	MeCN	163
	K^+	10.71	Pot	−74.1 (Cal)	−44	25	MeCN, 0.1 M Et_4NClO_4	151
	K^+	11.3	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	K^+	5.6	Pot			25	H_2O, 0.1 M Et_4NClO_4	166
	K^+	6.0	Pot			25	5% MeCN, 0.1 M Et_4NClO_4	166
	K^+	6.5	Pot			25	10% MeCN, 0.1 M Et_4NClO_4	166
	K^+	7.1	Pot			25	20% MeCN, 0.1 M Et_4NClO_4	166
	K^+	7.7	Pot			25	30% MeCN, 0.1 M Et_4NClO_4	166
	K^+	8.1	Pot			25	40% MeCN, 0.1 M Et_4NClO_4	166
	K^+	8.6	Pot			25	50% MeCN, 0.1 M Et_4NClO_4	166
	K^+	8.9	Pot			25	60% MeCN, 0.1 M Et_4NClO_4	166
	K^+	9.2	Pot			25	70% MeCN, 0.1 M Et_4NClO_4	166
	K^+	9.7	Pot			25	80% MeCN, 0.1 M Et_4NClO_4	166
	K^+	10.3	Pot			25	90% MeCN, 0.1 M Et_4NClO_4	166
	K^+	10.9	Pot			25	95% MeCN, 0.1 M Et_4NClO_4	166
	K^+	11.4	Pot			25	MeCN, 0.1 M Et_4NClO_4	166

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	K^+	9.75	Pot	−79.5 (Cal)	−80.3	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	K^+		Cal	−71.29	−36.4	25	MeOH	161
	K^+	>7.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	10.41	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	K^+	10.8	Pot			25	MeOH, 0.05 M Et_4NClO_4	162
	K^+	~8.4	Pot			25	NMP, 0.1 M Et_4NPic	145
	K^+	10.73	Pot			25	PC	163
	K^+	11.2	Ag^+ ISE			25	PC	147
	K^+	11.10	Pot	−69.2	−20	25	PC, 0.1 M Et_4NClO_4	151
	K^+	0.4	Spec	−34	−155	−50	THF	165
	Rb^+		Cal	−49.25		25	H_2O	161
	Rb^+	4.35	Pot	−49.4 (Cal)	−82.8	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Rb^+	4.06	Pot	−49.4 (Cal)	−87.4	25	H_2O, 0.1 M Me_4NCl	99
	Rb^+	4.3	CyVol			25	H_2O, 0.01 M Et_4NClO_4	162
	Rb^+			−55.40 (Cal)		25	DMF	339
	Rb^+	6.78	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Rb^+			59.16 (Cal)		25	DMSO	339
	Rb^+	5.85	Pot			25	DMSO, 0.1 M Et_4NClO_4	145
	Rb^+	5.7	CyVolt			25	DMSO, 0.1 M Et_4NClO_4	162
	Rb^+	9.28	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Rb^+	>7	Cond			25	MeCN	90
	Rb^+		Cal	−74.85	−79.1	25	MeOH	161
	Rb^+	8.40	Pot	−82.0 (Cal)	−114.6	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Rb^+	>6.0	Pot			25	MeOH, 0.05 M Me_4NBr	134
	Rb^+	8.98	Pot			25	MeOH, 0.05 M Et_4NClO_4	146
	Rb^+	7.28	Pot			25	NMP, 0.1 M Et_4NPic	145
	Rb^+	9.0	Ag^+ ISE			25	PC	147
	Rb^+	4.6	Spec	−8.8	−105	−50	THF	165
	Cs^+	1.44	Cal	−21.7	−45.2	25	H_2O	161
	Cs^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Cs^+	<1.4	CyVol			25	H_2O, 0.01 M Et_4NClO_4	162
	Cs^+		Cal	−30.96		25	DMF	339
	Cs^+	2.16	NMR			25	DMF	167
	Cs^+	2.16	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Cs^+	1.40	Cal	−35.6	−92.5	25	DMSO	339
	Cs^+	1.45	NMR			25	DMSO	167
	Cs^+	1.4	CyVol			25	DMSO, 0.1 M Et_4NClO_4	162
	Cs^+	4.17	Pot			25	EtOH, 0.1 M Et_4NPic	145
	Cs^+	4.54	Cond			25	MeCN	90
	Cs^+	4.57	NMR			25	MeCN	167
	Cs^+	4.57	Pot			25	MeCN, 0.1 M Et_4NClO_4	145
	Cs^+	4.03	NMR			25	Me_2CO	167
	Cs^+	3.54	Pot	−49.8 (Cal)	−99.2	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Cs^+		Cal	−49.92	−83.3	25	MeOH	161
	Cs^+	4.4	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Cs^+	~4.4	Pot			25	NMP, 0.1 M Et_4NPic	145
	Cs^+	3.97	NMR			25	PC	167
	Cs^+	4.2	Ag^+ ISE			25	PC	147
	Cs^+	>5	NMR			25	Py	167
	Cs^+	8.0	Spec			−50	THF	165
	Mg^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Mg^{2+}	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	4.4	Pot	−0.8 (Cal)	81.6	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Ca^{2+}	4.57	Pot	−0.8 (Cal)	84.5	25	H_2O, 0.1 M Me_4NCl	99
	Ca^{2+}	4.45	Kin	−2.1	79	25	H_2O, piperidine HCl	150
	Ca^{2+}	4.40	Kin	−2.9	75	25	H_2O, piperidine HCl, pH 11.5, μ = 0.1 M	157
	Ca^{2+}	3.84	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Ca^{2+}	7.60	Pot	−27.6 (Cal)	52.7	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Ca^{2+}	7.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ca^{2+}	8.14	Ag^+ ISE			25	MeOH	152
	Ca^{2+}	10.8	Ag^+ ISE			25	PC	147
	Sr^{2+}	8.0	Pot	−43.1 (Cal)	8	25	H_2O, 0.05 M Me_4NBr pH 10.4 (ΔH, ref 144)	134, 144
	Sr^{2+}	8.26	Pot	−44.4 (Cal)	9.2	25	H_2O, 0.1 M Me_4NCl	99
	Sr^{2+}	11.5	Pot	−59.0 (Cal)	21.9	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Sr^{2+}	11.75	Pot			25	MeOH	152
	Sr^{2+}	12.90	Spec			−15	MeOH	130
	Ba^{2+}	9.5	Pot	−59.0 (Cal)	−16.7	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Ba^{2+}	9.7	Pot	−59.8 (Cal) p	−15.5	25	H_2O, 0.1 M Me_4NCl	99
	Ba^{2+}	12	Pot	−84.1 (Cal)	−53.3	25	95% MeOH, 0.01 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	La^{3+}	6.45	Pot			25	H_2O, 0.25 M Me_4NCl	154
	La^{3+}	9.4	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	La^{3+}	12.91	Pot	−54.5	64	25	PC	170
	Ce^{3+}	8.4	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ce^{3+}	14.20	Pot	−76.5	15	25	PC	170
	Pr^{3+}	6.37	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Pr^{3+}	15.88	Pot	−94.5	−28	25	PC	170

TABLE I (Continued)

ligand	cation	log K[a]	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Sm^{3+}	5.94	Pot			25	H_2O, 0.25 Me_4NCl	154
	Sm^{3+}	15.99	Pot	−96.3	−17	25	PC	170
	Eu^{2+}	10.48	Kin	−51.3	8	25	H_2O	158
	Eu_2^+	13.0	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Eu^{3+}	3.37	Kin	16.7	121	25	H_2O	158
	Eu^{3+}	5.90	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Tb^{3+}	16.58	Pot	−104.3	−9	25	PC	170
	Ho^{3+}	6.2	Pot			25	H_2O, 0.25 M Me_4NCl	154
	Yb^{3+}	17.56	Pot	−106.6	−24	25	PC	170
	Co^{2+}	≤2.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Co^{2+}	≤4	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Ni^{2+}	≤3.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ni^{2+}	≤4.5	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Cu^{2+}	6.81	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cu^{2+}	≤6	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Cu^{2+}	2.68	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Ag^+	9.6	Pot			25	H_2O, 0.1 M Me_4NBr	134
	Ag^+	9.6	Pot			25	H_2O, 0.1 M Bu_4NClO_4	148
	Ag^+	9.6	Pot	−53.6 (Cal)	4.2	25	H_2O, 0.1 M Me_4NCl	99
	Ag^+	9.53	Pot			25	H_2O, 0.1 M Et_4NClO_4	171
	Ag^+	9.85	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Ag^+		Cal	−65.61		25	DMF	339
	Ag^+	10.03	Pot	−56.4 (Cal)	−3	25	DMF, 0.1 M Et_4NClO_4	151
	Ag^+	10.07	Pot			25	DMF, 0.1 M Et_4NClO_4	145
	Ag^+	9.77	Pot			25	DMF	163
	Ag^+			−51.42 (Cal)		25	Me_2SO	339
	Ag^+	7.15	Pot	−47.8 (Cal)	−24	25	Me_2SO, 0.1 M Et_4NClO_4	151
	Ag^+	7.30	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	145
	Ag^+	7.0	Pot			25	Me_2SO	163
	Ag^+	7.2	Pot			25	Me_2SO, 0.1 M Bu_4NClO_4	148
	Ag^+	7.15	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	79
	Ag^+	11.51	Pot			25	EtOH, 0.1 M Et_4NClO_4	145
	Ag^+	6.3	Pot			25	HMPT, 0.1 M Et_4NClO_4	151
	Ag^+	8.55	Pot			25	5% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.21	Pot			25	10% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.03	Pot			25	20% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.03	Pot			25	30% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.08	Pot			25	40% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.15	Pot			25	50% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.22	Pot			25	60% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.30	Pot			25	70% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.45	Pot			25	80% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.75	Pot			25	90% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.87	Pot			25	95% MeCN, 0.1 M Et_4NClO_4	171
	Ag^+	8.99	Pot			25	MeCN, 0.1 M Et_4NClO_4	145, 171
	Ag^+	9.3	Pot			25	MeCN, 0.1 M Bu_4NClO_4	148
	Ag^+	8.9	Pot			25	MeCN	145, 163
	Ag^+	8.92	Pot	−54.4 (Cal)	−11	25	MeCN, 0.1 M Et_4NClO_4	151
	Ag^+	12.20	Pot	−85.8 (Cal)	−54	25	MeOH, 0.1 M Et_4NClO_4	146, 151
	Ag^+	11.95	Pot			25	MeOH	163
	Ag^+	12.3	Pot			25	MeOH	148
	Ag^+	12.00 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	3.25 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Ag^+	9.17	Pot			25	NMP, 0.1 M Et_4NPic	145
	Ag^+	16.3	Pot			25	PC, 0.1 M Et_4NClO_4	145, 147
	Ag^+	16.29	Pot	−99.5 (Cal)	−17	25	PC, 0.1 M Et_4NClO_4	151
	Ag^+	16.33	Pot			25	PC, 0.1 M Et_4NClO_4	79
	Ag^+	16.54	Pot			25	PC	163
	Ag^+	9.5	Pot			25	Me_4U, 0.1 M Bu_4NClO_4	148
	Zn^{2+}	≤2.5	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Zn^{2+}	≤4	Pot			25	95% MeOH, 0.1 M Me_4NCl	87
	Cd^{2+}	6.8	Pot	2.1 (Cal)	138.1	25	H_2O, 0.1 M Me_4NCl	99
	Cd^{2+}	7.10	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Cd^{2+}	10.41	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Hg^{2+}	18.2	Pot	−66.7 (Cal)	124.7	25	H_2O, 0.1 M Me_4NCl	99
	Tl^+	6.4	Kin			25	H_2O	160
	Tl^+	6.3	Pot			25	H_2O, 0.1 M Me_4NBr	134
	Tl^+	5.5	Pot	−55.2 (Cal)	−61.9	25	H_2O, 0.1 M Me_4NCl	99
	Tl^+	6.4	CyVol			25	H_2O, 0.01 M Et_4NClO_4	162
	Tl^+	7.7	Pot	−66.1	−75	25	DMF, 0.1 M Et_4NClO_4	151
	Tl^+	6.3	Pot			25	DMSO, 0.1 M Et_4NClO_4	151
	Tl^+	6.1	CyVolt			25	Me_2SO, 0.1 M Et_4NClO_4	162
	Tl^+	5.32	Pot			25	HMPT	151
	Tl^+	12.30	ISE			25	MeCN	163
	Tl^+	10.05	Pot			25	MeOH	163
	Tl^+	10.1	CyVol			25	MeOH, 0.05 M Et_4NClO_4	162

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Tl^+	11.94	Pot			25	PC	163
	Tl^+	11.78	Pot			25	PC, 0.1 M Et_4NClO_4	151
	Pb^{2+}	12.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Pb^{2+}	12.36	Pot	−57.7 (Cal)	42.3	25	H_2O, 0.1 M Me_4NCl	99
	Pb^{2+}	12.72	Pot			25	H_2O, 0.1 M Et_4NClO_4	77
	Pb^{2+}	7.23	Pot			25	Me_2SO, 0.1 M Et_4NClO_4	78
	Pb^{2+}	14.84 (1)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	4.79 (2)	Pot			25	MeOH, 0.05 M Et_4NClO_4	80
	Pb^{2+}	16.00 (1)	Spec			25	PC, 0.01 M Et_4NClO_4	81
	Pb^{2+}	5.20 (2)	Spec			25	PC, 0.01 M Et_4NClO_4	81
B2.2.2	H^+	10.49	Pot			1.2	HMPT	142
	H^+	9.69	Pot			25	HMPT	142
	Li^+	2.19	Ag^+ ISE			25	MeOH, 0.02 M Et_4NClO_4	173
	Na^+	7.4	Pot			25	95% MeOH	172
	Na^+	7.50	Ag^+ ISE	−39.7 (Cal)	−10	25	MeOH, 0.02 M Et_4NClO_4	173
	K^+	9.05	Pot			25	95% MeOH	172
	K^+	9.21	Ag^+ ISE	−65.3 (Cal)	43	25	MeOH, 0.02 M Et_4NClO_4	173
	Rb^+	7.19	Ag^+ ISE	−57.7 (Cal)	56	25	MeOH, 0.02 M Et_4NClO_4	173
	Cs^+	2.98	Ag^+ ISE			25	MeOH, 0.02 M Et_4NClO_4	173
	Cs^+	2.99	Cal	−31.8	50	25	MeOH	173
	Cs^+	2.9	NMR	−4.06	41.4	25	MeOH	168
	Cs^+	1.70	NMR			25	DMF	167
	Cs^+	3.55	NMR			25	MeCN	167
	Cs^+	3.54	NMR			25	Me_2CO	167
	Cs^+	3.17	NMR			25	PC	167
	Cs^+	3.76	NMR			25	Py	167
	Ca^{2+}	7.19	Ag^+ ISE			25	MeOH	152
	Sr^{2+}	10.52	Ag^+ ISE			25	MeOH	152
	Ba^{2+}	11.05	Pot			25	95% MeOH	172
	Ba^{2+}	11.05	Ag^+ ISE			25	MeOH	152
$B_2$2.2.2	H^+	9.5	Pot			25	H_2O	169
	Li^+	2.0	Ag^+ ISE			25	MeOH	174
	Na^+	3.44	Pot			25	H_2O	169
	Na^+	7.3	Pot			25	95% MeOH	172
	Na^+	7.37	Pot			25	MeOH	169
	Na^+	7.60	Ag^+ ISE			25	MeOH	174
	K^+	4.35	Pot			25	H_2O	169
	K^+	8.6	Pot			25	95% MeOH	172
	K^+	8.74	Ag^+ ISE			25	MeOH	174
	K^+	8.60	Pot			25	MeOH	169
	Rb^+	5.91	Ag^+ ISE			25	MeOH	174
	Cs^+	2.61	Ag^+ ISE			25	MeOH	174
	Ca^{2+}	5.94	Ag^+ ISE			25	MeOH	152
	Sr^{2+}	9.05	Ag^+ ISE			25	MeOH	152
	Ba^{2+}	5.65	Pot			25	H_2O	169
	Ba^{2+}	8.5	Pot			25	95% MeOH	172
	Ba^{2+}	8.87	Pot			25	MeOH	169
	Ag^+	8.90	Pot			25	H_2O	169
	Ag^+	11.78	Pot			25	MeOH	169
	Tl^+	4.61	Pot			25	H_2O	169
	Tl^+	7.9	Pot			25	MeOH	169
Dec2.2.2	Li^+	2.0	Ag^+ ISE			25	MeOH	174
	Na^+	7.0	Ag^+ ISE			25	MeOH	174
	K^+	9.42	Ag^+ ISE			25	MeOH	174
	Rb^+	7.61	Ag^+ ISE			25	MeOH	174
	Cs^+	3.21	Ag^+ ISE			25	MeOH	174
MeA2.2.2	H^+	10.55 (1)	Pot			25	H_2O[d]	153
	H^+	8.57 (2)	Pot			25	H_2O[d]	153
	H^+	2.55 (3)	Pot			25	H_2O[d]	153
	Li^+	1.5	Pot			25	H_2O	153
	Li^+	4.0	Pot			25	95% MeOH[d]	153
	Na^+	3.2	Pot			25	H_2O[d]	153
	K^+	4.2	Pot			25	H_2O[d]	153
	Rb^+	3.0	Pot			25	H_2O[d]	153
	Cs^+	<2.0	Pot			25	H_2O[d]	153
	Mg^{2+}	1.9	Pot			25	H_2O[d]	153
	Ca^{2+}	4.6	Pot			25	H_2O[d]	153
	Sr^{2+}	7.4	Pot			25	H_2O[d]	153
	Ba^{2+}	9.0	Pot			25	H_2O[d]	153
	Co^{2+}	5.2	Pot			25	H_2O[d]	153
	Ni^{2+}	5.0	Pot			25	H_2O[d]	153
	Cu^{2+}	9.7	Pot			25	H_2O[d]	153
	Ag^+	10.8	Pot			25	H_2O[d]	153
	Zn^{2+}	6.3	Pot			25	H_2O[d]	153
	Cd^{2+}	9.7	Pot			25	H_2O[d]	153
	Hg^{2+}	21.7	Pot			25	H_2O[d]	153

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	Tl^+	6.3	Pot			25	H_2O^d	153
	Pb^{2+}	14.1	Pot			25	H_2O^d	153
$A_2$2.2.2	H^+	10.19 (1)	Pot			25	H_2O^d	153
	H^+	8.08 (2)	Pot			25	H_2O^d	153
	H^+	3.76 (3)	Pot			25	H_2O^d	153
	Li^+	<1.0	Pot			25	H_2O^d	153
	Na^+	<1.0	Pot			25	H_2O^d	153
	K^+	1.5	Pot			25	H_2O^d	153
	Rb^+	<1.0	Pot			25	H_2O^d	153
	Ag^+	8.7	Pot			25	H_2O^d	153
	Cd^{2+}	12.7	Pot			25	H_2O^d	153
	Tl^+	4.2	Pot			25	H_2O^d	153
$Me_2A_2$2.2.2	H^+	10.01 (1)	Pot			25	H_2O^d	153
	H^+	8.92 (2)	Pot			25	H_2O^d	153
	H^+	2.75 (2)	Pot			25	H_2O^d	153
	Li^+	2.4	Pot			25	H_2O^d	153
	Li^+	<4.0	Pot			25	$MeOH^d$	153
	Li^+	3.8	Pot			25	95% $MeOH^d$	153
	Na^+	2.5	Pot			25	H_2O^d	153
	Na^+	<5.0	Pot			25	$MeOH^d$	153
	K^+	2.7	Pot			25	H_2O^d	153
	K^+	<5.0	Pot			25	$MeOH^d$	153
	Rb^+	2.3	Pot			25	H_2O^d	153
	Rb^+	<4.0	Pot			25	$MeOH^d$	153
	Cs^+	<2.0	Pot			25	H_2O^d	153
	Cs^+	3.8	Pot			25	$MeOH^d$	153
	Mg^{2+}	2.6	Pot			25	H_2O^d	153
	Ca^{2+}	4.3	Pot			25	H_2O^d	153
	Sr^{2+}	6.1	Pot			25	H_2O^d	153
	Ba^{2+}	6.7	Pot			25	H_2O^d	153
	Co^{2+}	4.9	Pot			25	H_2O^d	153
	Ni^{2+}	5.1	Pot			25	H_2O^d	153
	Cu^{2+}	12.7	Pot			25	H_2O^d	153
	Ag^+	11.5	Pot			25	H_2O^d	153
	Zn^{2+}	6.0	Pot			25	H_2O^d	153
	Cd^{2+}	12.0	Pot			25	H_2O^d	153
	Hg^{2+}	24.9	Pot			25	H_2O^d	153
	Tl^+	5.5	Pot			25	H_2O^d	153
	Pb^{2+}	15.3	Pot			25	H_2O^d	153
$Me_4A_4$2.2.2	H^+	9.68 (1)	Pot			25	H_2O^d	153
	H^+	9.37 (2)	Pot			25	H_2O^d	153
	H^+	5.65 (3)	Pot			25	H_2O^d	153
	H^+	2.26 (4)	Pot			25	H_2O^d	153
	Li^+	3.5	Pot			25	95% $MeOH^d$	153
	Li^+	<4	Pot			25	$MeOH^d$	153
	Na^+	4.2	Pot			25	$MeOH^d$	153
	K^+	1.7	Pot			25	H_2O^d	153
	K^+	<5.0	Pot			25	$MeOH^d$	153
	Rb^+	<4.0	Pot			25	$MeOH^d$	153
	Cs^+	3.3	Pot			25	$MeOH^d$	153
	Ca^{2+}	1.5	Pot			25	H_2O^d	153
	Sr^{2+}	1.5	Pot			25	H_2O^d	153
	Ba^{2+}	3.7	Pot			25	H_2O^d	153
	Co^{2+}	5.2	Pot			25	H_2O^d	153
	Ni^{2+}	5.7	Pot			25	H_2O^d	153
	Cu^{2+}	12.5	Pot			25	H_2O^d	153
	Ag^+	13.0	Pot			25	H_2O^d	153
	Zn^{2+}	6.8	Pot			25	H_2O^d	153
	Cd^{2+}	10.7	Pot			25	H_2O^d	153
	Hg^{2+}	26.1	Pot			25	H_2O^d	153
	Tl^+	4.1	Pot			25	H_2O^d	153
	Pb^{2+}	15.5	Pot			25	H_2O^d	153
2.2.C_8	H^+	9.92 (1)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	6.60 (2)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Li^+	<2.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Na^+	3.00	Pot			25	95% MeOH, 0.01 M Me_4NBr	134, 172
	Na^+	3.5	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	4.35	Pot			25	95% MeOH, 0.01 M Me_4NBr	134, 172
	K^+	5.2	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Rb^+	3.4	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Cs^+	2.7	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Ba^{2+}	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134, 172
cis-2.2.$K_2Py_2N_2$	Cu^{2+}	2.46	Spec			30	H_2O, 3.3% EtOH	175
	Pb^{2+}	2.42	Spec			30	H_2O, 3.3% EtOH	175
trans-2.2.$K_2Py_2N_2$	Pb^{2+}	2.58	Spec			30	H_2O, 3.3% EtOH	175

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
3.2.2	H^+	8.50 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	7.33 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	9.14 (1)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	H^+	6.55 (2)	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Li^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Li^+	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Li^+	2.3	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Na^+	1.65	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Na^+	4.57	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Na^+	4.8	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	2.2	Pot	−12.6 (Cal)	0	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	K^+	7.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	K^+	>7.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Rb^+	2.05	Pot	−17.6 (Cal)	−19.7	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Rb^+	7.30	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Rb^+	>6.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Cs^+	1.8	Cal	−23	−41	25	H_2O	144
	Cs^+	2.0	Pot	−22.6 (Cal)	−41.4	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Cs^+	7.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Cs^+	>6.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Mg^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Mg^{2+}	<2.0	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ca^{2+}	~2.0	Pot	0.67 (Cal)	40.2	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Ca^{2+}	4.74	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Sr^{2+}	3.4	Pot	−13.8 (Cal)	18.4	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Sr^{2+}	7.06	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
	Ba^{2+}	6.0	Pot	−25.9 (Cal)	28.0	25	H_2O, 0.05 M Me_4NBr, pH 10.4 (ΔH, ref 144)	134, 144
	Ba^{2+}	10.40	Pot			25	95% MeOH, 0.01 M Me_4NBr	134
3.3.2	H^+	8.16 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	7.31 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Li^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Na^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Na^+	3.2	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	K^+	6.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Rb^+	<0.7	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Rb^+	6.15	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Cs^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Cs^+	>6.0	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Mg^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Ca^{2+}	~2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Sr^{2+}	~2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Ba^{2+}	3.5	Pot			25	H_2O, 0.05 M Me_4NBr	134
3.3.3	H^+	7.70 (1)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	H^+	6.96 (2)	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Li^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Na^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Na^+	2.7	Pot			25	MeOH, 0.01 M Me_4NBr	134
	K^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	K^+	5.4	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Rb^+	<0.5	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Rb^+	5.7	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Cs^+	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Cs^+	5.9	Pot			25	MeOH, 0.01 M Me_4NBr	134
	Mg^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Ca^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
	Sr^{2+}	<2.0	Pot			25	H_2O, 0.05 M Me_4NBr	134
1.1/1.1	Na^+	1.7	ISE			25	H_2O	176
	Na^+	4.3 (1)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Na^+	1.5 (2)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Na^+	4.5	ISE			25	MeOH	11, 176, 176a
	K^+	1.1	ISE			25	H_2O	176
	K^+	5.8	ISE			25	MeOH	11, 176, 176a
	Rb^+	1.0	ISE			25	H_2O	176
	Rb^+	6.2	ISE			25	MeOH	11, 176, 176a
	Cs^+	1.45	ISE			25	H_2O	176
	Cs^+	<6.0	ISE			25	MeOH	11, 176, 176a
	Ca^{2+}	6.53	Pot			25	H_2O	176
	Sr^{2+}	6.97	Pot			25	H_2O	176
	Ba^{2+}	8.0	Pot			25	H_2O	176
	Ag^+	6.0	ISE			25	H_2O	11
	Ag^+	>9.5	ISE			25	MeOH	11
	Ag^+	>6.0	ISE			25	MeOH	11
2.2/2.2	Na^+	<1.5	ISE			25	H_2O	176
	Na^+	3.6 (1)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
	Na^+	3.2 (2)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	K^+	~1.5	ISE			25	H_2O	176
	K^+	4.8 (1)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	K^+	3.9 (2)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Rb^+	~1.5	ISE			25	H_2O	176
	Rb^+	3.7 (1)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Rb^+	3.3 (2)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Cs^+	4.4 (1)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Cs^+	3.0 (2)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Ca^{2+}	4.0	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Sr^{2+}	3.5	ISE			25	H_2O	176
	Sr^{2+}	5.5 (1)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Sr^{2+}	5.5 (2)	ISE			25	95% MeOH, 0.1 M Et_4NBr	176
	Ba^{2+}	4.4	ISE			25	H_2O	176
	Ba^{2+}	6.7 (1)	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
	Ba^{2+}	6.3 (2)	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
Pent2.2/2.2	Na^+	3.2 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Na^+	1.5 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	K^+	4.0 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	K^+	3.2 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Rb^+	3.5 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Rb^+	3.0 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Cs^+	3.5 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Cs^+	2.5 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
$B_22.2/2.2$	Na^+	3.0 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Na^+	2.9 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	K^+	3.6 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	K^+	2.7 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Rb^+	3.0 (1)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Rb^+	2.8 (2)	ISE			25	95% MeOH, 0.1 M NEt_4Br	176
	Ca^{2+}	3.6	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
	Sr^{2+}	4.9 (1)	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
	Sr^{2+}	5 (2)	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
	Ba^{2+}	5.9 (1)	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
	Ba^{2+}	6 (2)	ISE			25	95% MeOH, 0.1 M NMe_4Br	176
valinomycin	Li^+	<0.7	Spec			25	MeOH	5, 178
	Na^+	0.67	Spec			25	MeOH	5, 178
	Na^+	1.08	Pot			25	MeOH	5, 178
	K^+	6.3	Cond			25	EtOH	5, 178
	K^+	6.07	Spec	−8.9 (Cal)	−2.16	25	EtOH	5
	K^+	1.0	Spec			25	50% MeOH	178
	K^+	1.97	Spec			25	70% MeOH	178
	K^+	3.67	Spec			25	90% MeOH	178
	K^+		Cal	−19		25	MeOH	179
	K^+	>3.9	Pot			25	MeOH	178
	K^+	4.43	Cond			25	MeOH	5, 178
	K^+	4.79	Fluor			25	MeOH	180
	K^+	4.90	Spec			25	MeOH	5, 178
	Rb^+	6.46	Cond			25	EtOH	5
	Rb^+	5.12	Fluor			25	MeOH	180
	Rb^+	5.26	Spec			25	MeOH	5, 178
	Cs^+	5.81	Cond			25	EtOH	5
	Cs^+	4.32	Fluor			25	MeOH	180
	Cs^+	4.41	Spec			25	MeOH	5, 178
	Mg^{2+}	<0.7	Spec			25	MeOH	5
	Ca^{2+}	2.70	Spec			25	MeOH	5
	Sr^{2+}	2.23	Spec			25	MeOH	5
	Ba^{2+}	3.34	Spec			25	MeOH	5
	Ag^+	3.90	Spec			25	MeOH	5, 178
	Tl^+	4.62	Fluor			25	EtOH	180
	Tl^+	4.4	Fluor			25	MeOH	180
	Tl^+	3.73	Spec			25	MeOH	5, 178
	NH_4^+	1.67	Spec			25	MeOH	5, 178
	$(NH_2)_2CNH_2^+$	0.40	Spec			25	MeOH	5, 178
enniatin B	Li^+	1.28	Spec			25	MeOH	5, 178
	Na^+	3.11	Cond			25	EtOH	178
	Na^+	3.41	ORD			25	EtOH	178
	Na^+	2.38	Pot			25	MeOH	178
	Na^+	2.41	Spec			25	MeOH	5, 178
	K^+	3.57	Cond			25	EtOH	17
	K^+	3.81	ORD			25	EtOH	178
	K^+	1.161	Spec			25	50% MeOH	178
	K^+	1.64	Spec			25	70% MeOH	178
	K^+	2.45	Spec			25	90% MeOH	178
	K^+	2.919	Spec			25	MeOH	178

TABLE I (Continued)

ligand	cation	log K^a	method[b]	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium[c]	ref
	K^+	2.924	Pot			25	MeOH	178
	Rb^+	2.74	Spec			25	MeOH	178
	Cs^+	2.34	Spec			25	MeOH	178
	Mg^{2+}	1.2	Spec			25	MeOH	5
	Ca^{2+}	3.0	Spec			25	MeOH	5
	Sr^{2+}	2.65	Spec			25	MeOH	5
	Ba^{2+}	2.93	Spec			25	MeOH	5
	Mn^{2+}	0.6	Spec			25	MeOH	5
	Tl^+	2.7	Spec			25	MeOH	178
	Tl^+	<3	Fluor			25	MeOH	180
	NH_4^+	1.92	Spec			25	MeOH	178
cyclo-(Pro-Gly)$_3$	Li^+	2.26	CD			20	80% MeOH	181
	Na^+	0.34	CD			20	H_2O	181
	Na^+	2.04	CD			20	80% MeOH	181
	K^+	1.46	CD			20	80% MeOH	181
	Mg^{2+}	5.00 (1)	CD			20	MeCN	181
	Mg^{2+}	2.81 (2)	CD			20	MeCN	181
	Ca^{2+}	2.11	CD			20	H_2O	181
	Ca^{2+}	5.04	CD			20	MeCN	181
	Ca^{2+}	3.15	CD			20	80% MeOH	181
	Ba^{2+}	2.62	CD			20	80% MeOH	181
nonactin	Na^+	3.27	Cal	−27.4	−29.4	25	EtOH	183
	Na^+	3.3	Osm			30	EtOH	183
	Na^+	3.97	Polg			22	MeCN, 0.025 M Bu_4NClO_4	182
	Na^+	2.7	Fluor			25	MeOH	180
	Na^+	2.71	Cal	−11.1	14.6	25	MeOH	183
	Na^+	2.3	Osm			30	MeOH	183
	Na^+	7.3	Pot			20	Nbnz	129
	K^+	5.26	Cal	−52.2	−74.4	25	EtOH	183
	K^+	4.6	Osm			30	EtOH	183
	K^+	4.43	Polg			22	MeCN, 0.025 M Bu_4NClO_4	182
	K^+	3.9	Fluor			25	MeOH	180
	K^+	4.49	Cal	−43.6	−60.3	25	MeOH	183
	K^+	3.6	Osm			30	MeOH	183
	Rb^+	3.87	Polg			22	MeCN, 0.025 M Bu_4NClO_4	182
	Rb^+	3.81	Fluor			25	MeOH	180
	Rb^+	3.5	Osm			30	MeOH	183
	Cs^+	2.59	Polg			22	MeCN, 0.025 M Bu_4NClO_4	182
	Cs^+	3.23	Fluor			25	MeOH	180
	Cs^+	2.86	Osm			30	MeOH	183
	Ba^{2+}	2.3	Osm			30	EtOH	183
	Ba^{2+}	1.6	Osm			30	MeOH	183
	Tl^+	4.15	NMR			25	MeOH	180
monactin	Na^+	3.5	Osm			30	EtOH	183
	Na^+	4.28	Polg			22	MeCN	182
	Na^+	2.7	Fluor			25	MeOH	180
	Na^+	2.5	Osm			30	MeOH	183
	K^+	4.5	Osm			30	EtOH	183
	K^+	4.78	Polg			22	MeCN	182
	K^+	4.4	Fluor			25	MeOH	180
	K^+	4.04	Osm			30	MeOH	183
	Rb^+	4.0	Fluor			25	MeOH	180
	Rb^+	3.5	Osm			30	MeOH	183
	Cs^+	3.6	Fluor			25	MeOH	180
	Cs^+	3.04	Osm			30	MeOH	183
	Ba^{2+}	2.2	Osm			30	MeOH	183
	Tl^+	4.57	Fluor			25	MeOH	180
dinactin	Na^+	3.6	Osm			30	EtOH	183
	Na^+	4.44	Polg			22	MeCN	182
	Na^+	2.9	Fluor			25	MeOH	180
	Na^+	2.9	Osm			30	MeOH	183
	K^+	5.24	Polg			22	MeCN	182
	K^+	4.7	Fluor			25	MeOH	180
	K^+	3.7	Osm			30	MeOH	183
	Rb^+	3.5	Fluor			25	MeOH	180
	Rb^+	3.6	Osm			30	MeOH	183
	Cs^+	3.5	Fluor			25	MeOH	180
	Cs^+	3.2	Osm			30	MeOH	183
	Ba^{2+}	2.1	Osm			30	MeOH	183
	Tl^+	4.85	Fluor			25	MeOH	180
trinactin	Na^+	3.5	Osm			30	EtOH	183
	K^+	5.44	Polg			22	MeCN	182
	Rb^+	3.9	Osm			30	MeOH	183
	Cs^+	3.3	Osm			30	MeOH	183

TABLE I (Continued)

ligand	cation	log K^a	method^b	ΔH, kJ/mol	ΔS, J/(K mol)	T, °C	medium^c	ref
monensin	Na^+	4.9	Fluor			25	MeOH	180
	K^+	4.5	Fluor			25	MeOH	180
	Rb^+	4.2	Fluor			25	MeOH	180
	Cs^+	3.7	Fluor			25	MeOH	180
	Tl^+	4.42	Fluor			25	MeOH	180
virginiamycin	H^+	7.80	Spec			25	30% H_2O in MeOH	184
	Mg^{2+}	3.10	Spec			25	30% H_2O in MeOH	184
	Ca^{2+}	2.50	Spec			25	30% H_2O in MeOH	184, 185
	Mn^{2+}	2.15	Spec			25	40% H_2O in MeOH	184, 185
	Ni^{2+}	5.05	Spec			25	40% H_2O in MeOH	184, 185
ferrocene C	Na^+	2.40	Spec			25	CH_2Cl_2	186
	K^+	2.11	Spec			25	CH_2Cl_2	186
Meferrocene C	Li^+	2.31	Spec			25	CH_2Cl_2	186
	Na^+	2.42	Spec			25	CH_2Cl_2	186
	K^+	1.96	Spec			25	CH_2Cl_2	186

^{a}Reactions: The log K values are for 1:1 interactions unless consecutive reactions occur. Interactions of the 1:1 type are either of the cation–ligand type (cation–L, no further designation) or of the cation–protonated-ligand type (indicated by MHL, etc., placed in parentheses following the log K value). Two kinds of consecutive reactions have been reported. The most numerous kinds are those in which either protons interact consecutively with the macrocycle or macrocycles interact consecutively with the cation. These interactions are indicated by (1), (2), etc., placed after the log K value. The second and less common kind of consecutive reaction is that in which cations interact consecutively with the macrocycle to form M_2L species. Where these occur, the second reaction is indicated by placing the reaction product (M_2L, etc.) in parentheses after the log K value. ^{b}Methods: CD = circular dichroism, Cal = calorimetry, Cond = conductivity, CyVol = cyclic voltammetry, Elec = electrophoresis, Fluor = fluorescent spectra, Int = interpolated, IEM = ion exchange membrane, ISE = ion selective electrode, Kin = kinetic (calculated from kinetic data), NMR = nuclear magnetic resonance spectroscopy, ORD = optical rotatory dispersion, OSM = osmometry, Polg = polarography, Pot = potentiometry, Sol = solubility, Spec = spectrophotometric, Volt = convolution potential sweep voltammetry. ^{c}Solvents: C_6H_6 = benzene, Diox = 1,4-dioxane, DCE = 1,2-dichloroethane, DME = dimethoxyethane, DMF = dimethylformamide, Me_2SO = dimethyl sulfoxide, EtOH = ethanol, Form = formamide, HMPT = hexamethylphosphorotriamide, *i*-PrOH = isopropyl alcohol, MeCN = acetonitrile, Me_2CO = acetone, $MeNH_2$ = methylamine, MeOH = methanol, *n*-BuOH = *n*-butyl alcohol, NMe = nitromethane, NMP = *N*-methylpropionamide, NBnz = nitrobenzene, PC = propylene carbonate, Py = pyridine, *t*-BuOH = *tert*-butyl alcohol, THF = tetrahydrofuran, TMG = tetramethylguanidine, TMU = tetramethyluracil, Me_4U = tetramethylurea. ^{d}[NMe_4Cl] or [NMe_4NO_3] variable, μ = 0.1 M. ^{e}H = high spin, L = low spin.

TABLE II. **Radii (Å) of Some Representative Cations**[188,189]

cation	radius, Å	cation	radius, Å	cation	radius, Å
Li^+	0.76	Ba^{2+}	1.35	Cu^{2+}	0.77
Na^+	1.02	Eu^{2+}	1.17	Zn^{2+}	0.74
K^+	1.38	Mn^{2+}	0.67 (L)^a	Cd^{2+}	0.95
Rb^+	1.52		0.83 (H)^a	Pb^{2+}	1.19
Cs^+	1.67	Fe^{2+}	0.61 (L)^a	Hg^{2+}	1.19
Ag^+	1.15		0.78 (H)^a	La^{3+}	1.03
Tl^+	1.50	Co^{2+}	0.65 (L)^a	Ce^{3+}	1.01
Mg^{2+}	0.72		0.75 (H)^a	Eu^{3+}	0.95
Ca^{2+}	1.00	Ni^{2+}	0.63 (L)^a	Ho^{3+}	0.90
Sr^{2+}	1.18		0.69 (H)^a	Lu^{3+}	0.86

^{a}L = low spin, H = high spin.

Among the alkali metal cations, the log K data in Figure 1 for M^+-18C6 interaction show maximum stability for K^+. In the case of 21C7, the log K data in Table I show the stability order $Cs^+ > Rb^+ > K^+ >> Na^+$. Coronands as large as B_230C10 and B_260C20 form remarkably stable complexes with K^+ and Tl^+.[25,70] These larger polyethers are capable of wrapping around the cation to form a three-dimensional cavity with all oxygen atoms coordinated to the cation. For instance, X-ray crystallographic data indicate that B_230C10 encloses K^+ completely.[196] Evidence for twisted conformations of other large podands in solution in the presence of metal ions has been reported also.[136,197] The stabilities of the complexes formed by these ligands with small cations, such as Na^+, are appreciable, probably as a result of the ligands being capable of reducing the two-dimensional cavity size by twisting to adjust to the size of the smaller cation. A discussion of the macrocycle hole-size cation-diameter relationship is found in ref 20 and 22.

It may be concluded that for the larger alkali and alkaline earth metal ions, cation size is responsible primarily for the complexing characteristics. The smaller cations in these series are solvated strongly and, generally, complexes formed with macrocycles are less stable than those formed by the larger cations of the same family. Depending on the solvent, the energy required for desolvation of the cation may vary and, in some cases, may be too high to be compensated by the complexation step. This effect is operative for Li^+ complexes which, generally do not form in aqueous or methanol solution, but which are quite stable in solvents of low solvating power such as acetonitrile.[17] Larger cations are unable to organize the ligand as well as smaller ones. These two effects cause the ΔH and hence the stability of the 18C6 complexes of cations at the two ends of the size spectrum to be smaller than those of the intermediate size cations. Similarly, complexes formed by large dipositive ions usually have higher stabilities than those formed by monopositive ions of similar size, while the opposite is true for small cations of differing charges. For example, the ligand 18C6 prefers Na^+ over Ca^{2+} (similar ionic radii) while in the large cation range Ba^{2+} is usually preferred over K^+. These cation size effects are reflected, also, in both the enthalpy and entropy changes associated with complexation.[53,198]

2. Number and Stereochemical Arrangement of Ligand Binding Sites

Even the small polyethers, such as 15C5, cannot be considered to be completely rigid molecules. Most of them are quite flexible and are capable of orienting their donor groups in space. The larger macrocycles are free to fold resulting in a smaller three-dimensional cavity which has a closer size correspondence to the cation than does the unfolded ligand. For example, uncomplexed 18C6 exists in an open-cavity conforma-

TABLE III. Cation Selectivity and Extraction Sequences as a Function of Solvent

crown ether		solvent	cation selectivity	ref
B_218C6		water	$K^+ > Na^+ > Rb^+ > Cs^+$	131, 216
		methanol	$K^+ > Na^+ > Rb^+ > Cs^+$	131, 216
		dimethylformamide	$K^+ > Na^+ > Rb^+ > Cs^+$	131, 216
		dimethyl sulfoxide	$K^+ > Na^+ > Rb^+ > Cs^+$	131, 216
		acetonitrile	$Na^+ > K^+ > Rb^+ > Cs^+$	70
None	SCN^-	$H_2O \rightarrow$ organic solvent (56% toluene–44% 1-butanol)	$Cs^+ > Rb^+ > K^+ > Na^+$	217
18C6	picrate ion	$H_2O \rightarrow CH_2Cl_2$	$K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$	218
Cy_218C6	SCN^-		$K^+ > Rb^+ > Cs^+ > Na^+$	217
Cy_218C6	Cl^-	$H_2O \rightarrow CH_2Cl_2$	$K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$	218
	OH^-		$K^+ > Na^+$	219, 220
18C6	picrate ion	$H_2O \rightarrow C_6H_6$	$K^+ > Rb^+ > Cs^+ > Na^+$	221
B_218C6	picrate ion	$H_2O \rightarrow C_6H_6$	$K^+ > Rb^+ > Cs^+ > Na^+$	221
B_218C6	picrate ion	$H_2O \rightarrow C_6H_6$	$K^+ > Tl^+ > Rb^+ > Cs^+ > Na^+ > Li^+$	222, 223

tion with its oxygen atoms alternately above and below their plane.[199] This arrangement of the oxygen donor atoms is maintained in the K^+ complex.[200] However, the structure of the Na^+-18C6 complex is quite different. In this case, the 18C6 is folded with one oxygen atom out of the plane in order to obtain a better fit of the ligand to the smaller Na^+ ion.[201]

Binding constants depend to a great extent on the ion–dipole interaction. Any changes in number, magnitude, and direction of ligand dipoles will affect the binding energy. In a study of four different isomers of Cy_218C6, the following order of alkali cation complexing ability was observed: cis-syn-cis > cis-anti-cis > trans-syn-trans > trans-anti-trans.[114,202] Though the enthalpy of complex formation was found to be more favorable for the cis-anti-cis than for the cis-syn-cis isomer, a less favorable entropy contribution for the latter resulted in the above order of complex stability in the case of these two isomers.[115]

For alkali and alkaline earth metal ions there are no real stereochemical requirements for complexation. However, the donor groups of the ligand should provide an electronically basic environment to replace all or part of the cation's solvation shell. For example, K^+ is 10-coordinated in its bis-B15C5 complex, 6-coordinate planar in its 18C6 complex, 8-coordinate in its B_224C8 complex, presumably 9-coordinate in its B_227C9 complex, and 10-coordinate in its B_230C10 complex.[187]

3. Substitution on the Macrocycle Ring

Addition of benzene groups to 18C6 alters the cation selectivity of the ligand. The K value for the formation of the Ba^{2+}-18C6 complex in methanol solvent is larger than that for formation of the K^+ complex by a factor of 10. On the other hand, B_218C6 displays the opposite preference, binding K^+ better than Ba^{2+} in methanol by approximately the same amount. The change due to aromatic substituents may be attributed to some combination of ligand bulkiness leading to the isolation of the cation from the solvent, and the electron-withdrawing power of the benzo group(s) which weaken the electron-donor ability of the oxygen atoms resulting in a weaker metal–ligand interaction.

The cyclohexano group has a less dramatic effect on the stability of complexes and on cation selectivity. Aliphatic substituents on this ligand do not alter the binding properties to any measurable extent. The variation of the aqueous solution cation binding abilities of the cis-syn-cis and cis-anti-cis isomers of Cy_218C6 is likely due to differences in solvation of their complexes resulting from the different positioning of the bulky cyclohexane substituents.

The dinitro derivative of B_218C6 has more than six times less affinity for Na^+ than has the parent compound (B_218C6) in DMF while the stability of the Na^+ complex of the corresponding amino derivative is nearly identical with that of B_218C6.[125,126,128] This finding is rationalized in terms of the electron-withdrawing and electron-donating properties of the substituents.[126] The stability of Na^+-4′-monosubstituted B15C5 complexes in acetone at 25 °C is altered by a factor of 22 with the substituents NH_2 and NO_2.[69] Similar behavior was noted for disubstituted B15C5 complexes. For those complexes of Na^+ with substituted B15C5 ligands, a good Hammett correlation was obtained by plotting log K values vs. $(\sigma_p^- + \sigma_m)$ with a ρ value of -0.45. The negative ρ value indicates that binding capacity is decreased by electron-withdrawing substituents. The selectivity of K^+ over Na^+ was much less for the nitro-substituted B18C6 than for the methyl-substituted ligand.[69]

The correlation between K and substituent effects is poorer for Li^+ and Na^+ than for K^+, Rb^+, Cs^+, and NH_4^+.[203] For example, changing the substituent from CH_3 to NO_2 resulted in a reduction in the K value by a factor of about 6 for K^+, but only about 3 for Na^+.[69] The greater effect of substituents seen with the larger cations was attributed to the fact that these cations are influenced by all binding sites available in the ligand whereas small cations can minimize substituent effects by selecting the most basic sites.

The effect of a carbonyl group adjacent to an oxygen atom on metal ion binding has been studied for 18C6 and its pyridino derivative.[102,118,204] Introduction of the carbonyl group in 18C6 to form K_218C6 lowers the binding constants in the cases of Na^+, K^+, and Ba^{2+} by 10^2–10^4. The lowered K values are due primarily to decreased ΔH values, the ΔS values becoming even more favorable for complexation. The addition of two carbonyl groups to Py18C6 to form $K_2Py18C6$ lowers the binding capacity for K^+ and Ba^{2+}, but increases that for Na^+. Variation of the ΔH values does not follow any clear trend. The carbonyl groups are not bonded to the cation.[119]

It is known[4,11,134] that the three-dimensional cryptands form considerably more stable metal complexes than do the corresponding two-dimensional coronands. Okahara[76] and Gokel[205] and their co-workers have noted enhancement of stability in cation complexes of three-dimensional N-oligoethylene glycol monoaza crown ethers. An additional factor contributing to complex stability is seen in macrocycles if cation charge neutralization occurs on complexation.[206]

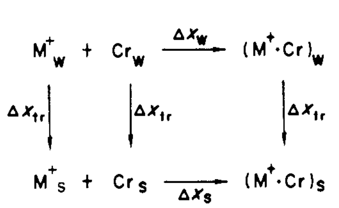
Coronands show pronounced cooperative effects of crown units. Binding constants per crown unit for small cations (Li^+, Na^+) do not vary between polymer and monomer, but with larger cations (K^+, Rb^+, Cs^+) preferential binding by polymers is observed.[207,208] Additional polyether groups in a monomeric macrocycle show no cooperative effect.[209] However, the K value for potassium picrate-L ion-pair formation in tetrahydrofuran is 50 times less if L = monomeric 15C5 than if L = two B15C5 units connected by an ($OCH_2CH_2OCH_2CH_2O$) bridge.[210,211]

Chiral coronands have been synthesized by several workers.[8,212] Arms added to the host provide an additional dimension for the study of host-guest interactions. Such arms may allow manipulation of the hydrophobic-lipophilic balance of the host and may provide counterions for interaction with ionic guests. Resolution of amino acid esters has been reported using binaphthyl host compounds.[213] K values measured in methanol differed nearly twofold for the interaction of the two enantiomers of the protonated methyl ester of alanine with chiral (S,S)-$Me_2K_2Py18C6$.[7] Log K values for the interaction of these guest enantiomers with (S,S)-$Ph_2K_2Py18C6$ showed no difference. Comparison of the log K values for these chiral coronands with the log K values for their interaction with NH_4^+ showed that the NH_4^+ complexes were approximately ten-fold more stable. Thus, steric hindrance was seen in the cases of both of these crowns, but chiral recognition only in the case of the dimethyl crown.

4. Solvent Effects

Frensdorf[25] noted that K values for the reaction of cyclic polyethers with metal cations are 10^3—10^4 larger in methanol than in water. The log K value for the interaction of Na^+ with B15C5 increases regularly with increasing weight percent CH_3OH.[73] The enhancement of stability in methanol over that in water is primarily an enthalpic effect.[73,144] On the other hand, the difference between the reaction entropies found in water and those found in methanol oppose this stability enhancement. The enthalpic stabilization is explained by the expenditure of less energy in the cation desolvation step in the solvent of lower dielectric constant. A compensating effect (enthalpy stabilized, entropy destabilized) has been noted[136] in the variation of the enthalpy and entropy changes of complexation by B_221C7, B_224C8, and B_227C9 with Cs^+ in several solvents of low to medium donicity (nitromethane, acetonitrile, acetone, methanol, and propylene carbonate).

The parameters governing the substitution of a solvent, S, for water W, for M^+-crown (Cr) interaction follow from the following thermodynamic cycle.[14] This



cycle indicates that free energies of transfer ($X = G$) for cation, ligand, and complexed cation need to be considered in order to understand the absolute and relative values of K_W and K_S.

Thermodynamic data for K^+—B_218C6 interaction in aprotic solvents[14] show that values of $\Delta\Delta G + \Delta G_{tr}$ (K^+), change with solvent. These data are interpreted to mean that there is appreciable interaction of the solvent with the crown ether complexes. However, the effect is not large enough to change the order of relative log K values for K^+-B_218C6 interaction: propylene carbonate > acetonitrile > dimethylformamide > dimethyl sulfoxide. Abraham and Ling[214] in a study of free energies and entropies of transfer from water to methanol of 18C6-M^{n+} complexes concluded that 18C6 shields M^{n+} from the solvent more effectively than crystal structure determinations would suggest.

The reactions of the alkali metal ions with Cy_218C6 in methanol, ethanol, and 1-propanol have been studied.[215] As in water, the ligand is consistently selective for K^+ over Na^+ and Cs^+, but selectivity between Na^+ and Cs^+ reverses in going from water to the alcoholic solvents. The equilibrium constant in protic solvents increases regularly for all alkali cations in the order: water < methanol < ethanol < 1-propanol.

Log K values have been reported for the 1:1 interaction in several solvents of various cations with 18C6 and its benzo and dibenzo derivatives. The sequence of the selectivities toward cations is solvent dependent as is illustrated with the M^+-B_218C6 systems in Table III. The cation sequences are the same in water, methanol, dimethylformamide, and dimethyl sulfoxide, but the positions of Na^+ and K^+ are reversed in acetonitrile. A reversal of Na^+/K^+ selectivity in apolar, aprotic solvents was observed for fluorenyl salts also.[224] Sequences for the extraction of alkali metal cations from water into organic solvents[14] are given, also, in Table III. Cation selectivity in these cases depends on differences both in the distribution constants and in the binding constants in the water-saturated organic solvent. DeJong and Reinhoudt[14] point out that, although general patterns in the effect of solvent on extraction sequence are seen, further studies are needed to arrive at a model which would have predictive value.

Arnett and Moriarity[225] report calorimetric results which show large variations in the heat of complexing of DC18C6 with different alkali metal cations. In addition, their results show a considerable solvent effect on ΔH of complexation using H_2O, acetone, tetrahydrofuran, and dimethyl sulfoxide.

5. Cation-Polyamine Complexation

Substitution of sp^3 nitrogen for ether oxygen in the coronand ring reduces the affinity of the ligand for the alkali and alkaline earth metal ions. A large number of cyclic polyamines having three to six functional groups in the ring have been synthesized. However, the majority of these have four functional groups more or less evenly distributed in a ring consisting of 12 to 16 atoms. Unlike coronands and cryptands, these compounds are prepared through one of a number of condensation reactions in which a transition-metal ion functions as a template.

Most monocyclic polyamine macrocycles form metal complexes in which four almost equivalent nitrogen atoms are coordinated in a single plane about the metal ion and two other groups are bound in the axial sites above and below the plane. Relatively few log K values are available for metal ion binding to macrocycles of this type. Kodama and his co-workers[135] report log K values for saturated macrocyclic polyamine ligands with 5 and 6 nitrogen donor atoms and ring sizes of 15 and 18 members. These ligands are particularly effective in complexing bivalent transition-metal ions. Graddon and his co-workers[226] report enthalpy changes for the interaction in acetonitrile of four tetraaza macrocycles with Zn^{2+}. Their results support five-coordinated structures for the complex ions.

Desreux and his co-workers[27] have studied the deuteration in D_2O of two tetraza tetraacetic macrocycles. Two amino groups of each of these macrocycles are deuterated at pD values of ~10. When the acidity is increased, deuterons associate successively with the four carboxylate groups, leaving the remaining two amino groups essentially undeuterated. These macrocycles appear to be the first shown to have nitrogen atoms which are less basic than carboxylate groups.

6. Cation-Polythioether Complexation

Complexes of Ni^{2+} and Co^{2+} with coronands containing three, four, six, and eight ring sulfur atoms have been reported.[227–230] The configuration of the metal ion–coronand complex is a function of the ring size and of the number of sulfur atoms in the ring. For example, a tridentate macrocycle gives a sandwich-type 2:1 ligand:metal complex with Ni^{2+}.[228] Sexadentate ligands with 18—20 ring members have four of the sulfur atoms in a plane with the metal atom and two other sulfur atoms occupying positions above and below the plane.[229] The nickel complex of an octadentate ligand contains two Ni^{2+} ions.[227] Stoichiometry of 4:1 (ligand:metal) for two palladium and platinum complexes is reported indicating bridging by the sulfur donor atoms.[227] Binding constants for the reaction of Cu^{2+} with a number of cyclic polythio ligands in 80% methanol have been determined.[39]

7. Cation–Mixed Donor Atom Macrocycle Complexation

Numerous macrocycles containing mixtures of oxygen, nitrogen, and sulfur donor atoms have been synthesized. Thermodynamic quantities associated with their cation complexation have been determined in a number of cases.

a. **Nitrogen–Oxygen Donor Atoms**. A number of macrocycles containing both nitrogen and oxygen donor atoms have been synthesized.[231–233] Generally, the metal complexes of these macrocycles are 1:1 (metal:ligand) with the metal ion located at the center of the macrocycle. However, recent determinations[80] of log K values in methanol for the reaction of Ag^+, Cd^{2+}, and Pb^{2+} with the coronands 1,7-$A_2$15C5 and 1,10-$A_2$18C6, as well as with the cryptands 2.1.1 and 2.2.2, show that binuclear complexes, M_2L^{2n+}, are present in all these cases, in addition to the expected mononuclear ML^{n+} complexes. Substitution of oxygen by nitrogen in coronands such as 18C6 and $B_2$18C6 results in macrocycles which have less affinity for K^+ than did the parent macrocycle. Log K values in these cases decrease in the order of decreasing electronegativity of the substituted group, O > NR > NH.[25] However, replacing oxygen donor atoms by nitrogen results in increased K values for Ag^+ complexation. The different stability orders in the cases of K^+ and Ag^+ are likely a reflection of different types of bonding in the complexes of these cations; K^+ binding being primarily electrostatic whereas Ag^+ binding may involve both electrostatic and covalent contributions.

An interesting study has been reported of macrocycles in which two additional groups containing OH sites are attached to two nitrogens of diaza crown ethers.[234] The results indicate that K values for complexes of $A_2$15C5 (2.1) with bivalent metal cations such as Ca^{2+}, Sr^{2+}, and Ba^{2+} increase by factors of 85, 89, and 30, respectively. The same trend is observed in the case of the complexes of $A_2$18C6 (2.2) and its derivatives. On the other hand, substituted diaza crowns with equal numbers of binding sites, viz. two CH_2CH_2OH units, have a smaller stabilizing effect than one $CH_2CH_2OCH_2CH_2OCH_2CH_2$ bridge in the cryptands.

Log K values for the interaction of Sr^{2+} and Ba^{2+} with aza crown ethers (R 2.2) decrease markedly as the R substituents become larger.[235] This effect is probably stereochemical in nature.

b. **Sulfur–Oxygen Donor Atoms**. Substitution of sulfur for oxygen in several crown-3, crown-4, crown-5, crown-6, and crown-8 macrocycles produces dramatic effects on K values for metal ion–ligand interaction.[16] In aqueous solution, little or no reaction occurs between the sulfur-containing macrocycles and either alkali or alkaline earth metal ions. Compared to the oxygen-containing macrocycles, the stabilities of metal complexes with Ag^+ and Hg^{2+} are enhanced markedly and those with Tl^+ and Pb^{2+} are reduced by sulfur substitution. For many of the cyclic thioethers, Ag^+ and Hg^{2+} complexes have 1:2 cation:ligand stoichiometries. However, Tl^+ and Pb^{2+} give 1:1 complexes. If the donor sulfur atoms were to point into the ring cavity, the size of the cavity would be decreased considerably. However, X-ray studies indicate that even for crown-4, crown-5, and crown-6 rings, sulfur atoms are directed away from the cavity.[236] Hence, binding of sulfur-containing crowns to Ag^+ and Hg^{2+} may not be of the inclusion type. Formation of 2:1 (metal:ligand) complexes in these systems points to the above possibility.

B. Cation–Cryptand Complexation

An extension of crown-ether chemistry is found in the case of cryptands. These macrobicyclic ligands are capable of ion encapsulation due to their cage-like structures. Generally, their metal complexes have 1:1 metal–ligand ratios.

1. Relative Cation/Anion and Ligand Cavity Sizes

Generally, that metal ion whose ionic crystal radius best matches the radius of the cavity formed by the cryptand on complexation will form the most stable complex. The correspondence between cavity size and complex stability is more pronounced with the cryptands than with the coronands. Figure 2 illustrates how in proceeding through a series of these ligands of increasing size, each of the alkali metal ions is preferen-

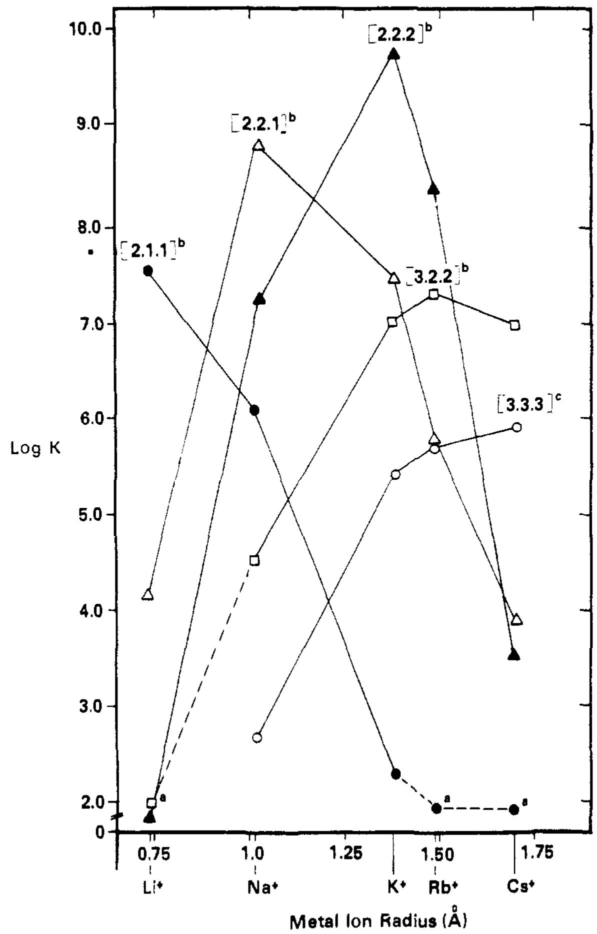


Figure 2. Selectivity of cryptands: log K values for reaction of several cryptands with alkali metal cations at 25 °C vs. cation radius.[134] Data points: (a) value reported <2.0; (b) in 95% CH_3OH; (c) in CH_3OH. Reprinted with permission from ref 134. Copyright 1975, American Chemical Society.

tially bound according to its size.

This correspondence between K values and the match of macrocycle cavity and cation diameters is found for alkaline earth cryptates, also. However, such a correspondence is not found for Cu^{2+}–cryptand complexes.[159]

For smaller macrobicycles, cations near the selectivity peak have ionic diameters close to the ligand cavity diameters calculated using CPK models. Complexation in several nonaqueous solvents of Cs^+ by cryptands 2.2.2, B2.2.2, and 3.2.2 has been studied over the temperature range −100 to 63 °C using a ^{133}Cs NMR technique.[168] It was found that an inclusive complex was formed at all temperatures with cryptand 3.2.2 whose cavity size is commensurate with that of the cation. With B2.2.2, only exclusive complex formation (cation partially enclosed in the ligand cavity) was found, probably due to the smaller cavity size and higher rigidity of this macrocycle. With cryptand 2.2.2, a temperature and solvent-dependent exclusive-inclusive equilibrium was observed. In polar solvents, the equilibrium was essentially completely displaced toward the inclusive complex at ~100 °C, but in tetrahydrofuran solutions the formation of the inclusive complex was hindered by the strong cation–anion interaction.

Binuclear species as well as 1:1 species in propylene carbonate solvent have been reported.[78,81] Although structures of the binuclear species are not known, it is probable that in the 2Pb–2.1.1^{4+} complex both Pb^{2+} cations lie outside the cavity. On the other hand, in the 2Pb-2.2.1^{4+} and 2Pb-2.2.2^{4+} species the larger cavity size may make possible a structure in which either both Pb^{2+} lie outside or one Pb^{2+} lies outside and one Pb^{2+} lies inside the cavity. The pK, ΔH, and ΔS values have been determined[143] for the reaction $H_{i-1}L^{(i-1)+} + H^+ = H_iL^{i+}$ (i = 1, 2) where L = 2.1.1, 2.2.1, 2.2.2. The relative magntidues of the ΔH and ΔS values were used to deduce possible in–out conformations for the protonated forms of the cryptands. When this procedure was used the first proton (highest pK value) in 2.1.1 was postulated to be located inside the cavity while the second proton was postulated to be located outside the cavity both in water and methanol. In the cases of 2.2.1 and 2.2.2, both protons were located inside the cavity in water, but outside the cavity in methanol.

Cylindrical cryptands formed by two rings connected by two bridges have been synthesized. These macrocycles possess two lateral cavities, the macrocyclic units, and one central cavity inside the macrotricycle (e.g., see compound $B_2$2.2/2.2, Chart XII). These ligands are capable of forming mononuclear and binuclear complexes of appreciable stability with alkali and alkaline earth metal cations. The stabilities and selectivities of complexation by these unusual cryptands are such that the ligand may be considered to have two almost independent macrocyclic subunits. These ligands are topologically well suited for the designed positioning of two metal cations in a binuclear inclusion complex.[176]

Comparisons of log K for M^{n+}-cryptand interaction in aqueous solution vs. the ionic radius of M^{n+} show interesting effects.[154] The monovalent alkali metal ions show the lowest complex stability with the cryptands, but exhibit a moderately strong stability dependence on cation size. Complexes formed by the alkaline earth cations are more stable. The bivalent transition- and post-transition-metal cations, which fall in a lower range of ion sizes than the alkaline earth metal ions, form complexes of highest stability and show the greatest dependence of log K on cation size. However, this trend is not sustained in the case of trivalent lanthanide cations which form complexes which are comparable in stability to those of the alkaline earth cations and whose stabilities show almost no dependence on the cation radii. Log K values for the reaction of Eu^{2+} with 2.2.1 and 2.2.2 are larger than those for the corresponding reactions involving Sr^{2+} by 2.5 and 5 log K units, respectively, despite the fact that these cations have nearly identical ionic radii (Table II).

Certain bicyclic alkaneammonium ions exhibit[237] ion pairing with Cl^- and Br^- in which the anion diffuses into the hydrocarbon cavity. Chloride ion appears to form a more stable complex than bromide ion while no encapsulation of I^- was detected.

2. Number and Stereochemical Arrangement of Ligand Binding Sites

Cryptands can assume any of three conformations according to the configuration of the two nitrogen bridgeheads—namely, in–in, in–out, or out–out. Free 2.2.2 cryptand exists in the in–in conformation in the crystalline state. In complexes, the same configuration persists with the metal ion being included in the cavity. These cryptand ligands are more rigid than podands over a broader range of cavity sizes and show a wide range of selectivity. However, cryptands having sizes greater than that of 2.2.2 show signs of flexibility in ion encapsulation. Lehn and Sauvage[134] concluded that rigid ligands display "peak selectivity", while flexible ligands exhibit "plateau selectivity." Rigid ligands which are too small to accommodate the metal ion may form 2:1 complexes.

NMR spectral studies indicate that the out-out isomer of 1,11-diazabicyclo[9.9.9]nonacosane bis(deuteriochloride) was slowly converted into the in-in isomer when dissolved in 50% deuteriotrifluoroacetic acid until an equilibrium condition was reached. Chloride ion reacted with the in-in form to produce a new anion consistent with the encapsulation of the halide ions in the molecular cavity of the bicyclic amine.[237] It was postulated that, in part, the stability of the complexes must be due to the high positive potential of the hole with respect to anions and from hydrogen bonding within the cavity. However, the encapsulated and external chloride ions exchanged rapidly.

Numerous polyoxamacrobicyclic diamines have been synthesized.[134,172,176] These ligands form metal ion complexes by encapsulating the ion in the central cavity of the macrocycle. X-ray structural determinations confirm the position of the metal ion and indicate that the two nitrogen atoms participate in bond formation along with the oxygen donors. These ligands are capable of forming very stable complexes and can selectively encapsulate ions. Since these macrocycles have a three-dimensional arrangement of binding sites, the stability constants are usually higher than those of the similar two-dimensional ligands. For example, log K for the reaction in methanol:water (95%/5% v/v) solutions of K^+ with the 2.2.2 cryptand is larger than that with 2.2. This "macrobicyclic effect" is of enthalpic origin.[99,144]

3. Substitution on the Macrocycle Ring

Addition of benzene rings to either one or two bridges of the 2.2.2 cryptand alters the selectivity of this ligand toward metal ions.[172] With one benzo substituent, the stability in 95% methanol of the Na^+ complex increases compared to the corresponding 2.2.2 complex while the stabilities of the K^+ and Ba^{2+} complexes decrease. Addition of another benzene substituent (to the second bridge) causes a further decrease in the stabilities of the K^+ and Ba^{2+} complexes with the stability of the K^+ complex being slightly greater than that of the Ba^{2+} complex. The stability decrease in the case of the Ba^{2+} complexes as ligand bulkiness increased was attributed to decreased interaction of the complexed cation with the polar solvent.

Cox and his co-workers[174] studied the effect of substituents on the thermodynamic and kinetic stability of alkali metal cryptates in methanol. They found that alkyl ($C_{10}H_{21}$) and benzo substitution caused a reduction in the cryptate stabilities which was attributable to a cooperative action of reducing the complex formation rates and increasing the complex dissociation rates.

4. Solvent Effects

The stability constants for the 1:1 reaction of cryptands with cations in methanol are larger than those for the same reaction in water. The degree to which stability is enhanced for methanol over water is dependent on the cation and cryptand under consideration.[134]

Spiess et al.[81] report that log K values for formation of complexes of Pb^{2+} with 2.2.1 and 2.2.2 in various solvents increase in the order water, methanol, propylene carbonate. This stability order parallels the order of decreasing solvating ability of these solvents. On the other hand, these authors find that the Pb—$2.1.1^{2+}$ stability in these solvents increases in the order propylene carbonate, methanol, water. This reversal in stability order with respect to solvent is ascribed to the noninclusive nature of the 2.1.1 complex.

Cation selectivity by macrobicyclic ligands is affected by the nature of the solvent. For example, the selectivity curve for the alkali metal ions is steeper in methanol than in water especially on the side corresponding to larger cations.

In determining selectivity, the solvation of the cation has been considered to be more important than the solvation of the complex. However, for ligands which are large enough to encapsulate the entire cation, the solvent can act only on the entire complex species and has no direct interaction with the cation.[164] On the other hand, a study of the volumes of complexation of cryptands with mono- and divalent cations in water and methanol showed that 2.2.2 did not totally shield the complexed cation from the environment.[238] With the organic ethylene groups on the outside of the complex, the cation may be considered to be embedded in a hydrophobic environment. This isosteric effect is more pronounced in the cryptands and, presumably, contributes to the higher selectivity of the cryptands for metal ions. The importance of ligand solvation has been shown by Abraham et al.[239] in their work on the overall transfer of Na^+ complexes from water to methanol where a large contribution of the ligand solvation effect must be considered in elucidating thermodynamic properties of the reaction. It has been suggested that cryptates might be useful in providing extra thermodynamic assumptions for the estimation of the thermodynamics of transfer of single ions. Two possible extreme cases (L = cryptand, tr = transfer): (a) $\Delta G_{tr}(ML^+) = \Delta G_{tr}(L)$, $\Delta H_{tr}(ML^+) = \Delta H_{tr}(L)$; (b) $\Delta G_{tr}(ML^+) = 0$, $\Delta H_{tr}(ML^+) = 0$ were pointed out by Gutknecht et al.[151] for aprotic polar solvents. However, Abraham et al.[240] indicated from their work on water–methanol systems that neither (a) nor (b) is valid in terms of enthalpy and free energy changes.

Popov[140] used multinuclear NMR to study alkali metal ion–macrocycle complexation in nonaqueous solvents. He reports a solvent dependency of K, ΔH, and ΔS for the interaction of Cs^+ with $B_2$30C10 and 2.2.2. In the case of Cs^+–2.2.2 interaction, ΔH and ΔS were essentially invariant with solvent during formation of the "inclusive" complex (Cs^+ shielded from the solvent), but during formation of the "exclusive" complex (Cs^+ partially exposed to the solvent) ΔH and ΔS varied significantly with solvent. It was concluded that the cation is largely desolvated in the formation of exclusive complexes.

C. Cation–Spherand Complexation

Spherands are a new class of macrocycles synthesized by Cram and his co-workers[241–245] in which the ligating sites are fully organized during synthesis rather than during complexation. These macrocycles show remarkable selectivity toward cations. For example, when the ionic diameter for cations becomes too large for the preformed cavity, no complexation occurs. This behavior is in contrast to that of coronand and cryptand macrocycles (Figures 1 and 2) in which size related peak selectivity is found. The order of relative binding strengths as measured by extraction of Li^+ and Na^+ picrates in $CDCl_3$ saturated with D_2O at 25 °C is spherands > cryptands > hemispherands > coronands > open-chain polyethers.[241]

D. Anion Effect

The main emphasis in the work on ion encapsulation by coronands and cryptands has been on the interaction of solvated cations with these ligands. Some authors have given consideration to the reaction of ion pairs with macrocycles in computing K values valid in solvents of medium to low dielectric constant. However, the effect of the anion on the reactivity of the cation with these ligands has usually been suppressed deliberately either through the choice of noncoordinating anions such as tetraphenylborate ion or, more often, by using high dilution conditions during experiments. Work with K^+-picrate and NH_4^+-picrate ion pairs and with K^+ and NH_4^+ indicates preference for the free cations over the ion pair in the case of complexation with bis(crown ethers) in tetrahydrofuran.[211] However, Shchori et al.[124] found that $B_2$18C6 forms stronger complexes in water with $[BaCl]^+$ than with Ba^{2+}. This result was attributed to partial charge neutralization. NMR spectral studies of K^+–2.2.2 cryptand complex in acetonitrile indicated formation of hydrogen bonds between the NH group of this ligand and the accompanying acetate anion.[246]

E. Macrocyclic Effect

Increased stability is observed for the complexes of cyclic ligands over those with an open chain of similar composition. Cabbiness and Margerum[51] term this extra stability the "macrocyclic effect". In work on cyclic tetraamine ligands, they note that the macrocyclic effect is about ten times larger than the chelate effect observed for Cu^{2+} with multidentate amine complexes. Cyclic polyethers form much more stable complexes than do their corresponding open-chain analogues. Attempts to assign either an enthalpic or entropic origin to the macrocyclic effect have been unsuccessful. Depending on the system investigated, either or both origins have been identified for this effect.

1. Tetraamines

Margerum and his co-workers found the enthalpy term to predominate when the formation of Ni^{2+} complexes of $A_4 12C_4$ (cyclam) and its noncyclic analogue are compared.[48,247] Dei and Gori reached a similar conclusion from their work on the Cu^+ complexes of these ligands.[248] However, both Paoletti and his coworkers[30,249,250] and Kodama and Kimura[28,31,32] found that the entropy term was responsible primarily for the macrocyclic effect using Cu^{2+} complexes of cyclen and its noncyclic analogue. Paoletti and his co-workers concluded that the relative magnitude of the enthalpy contribution is critically dependent on the match between cation and ligand cavity sizes for transition metals.[251]

2. Polythia Ethers

Lucia, et al.[252] report log K, ΔH, and ΔS values for the reaction in aqueous solution of Cu^{2+} with a series of open-chain and cyclic polythioethers. These ethers are not solvated extensively and the tetrathioether complex shows a much smaller macrocyclic effect than does the corresponding tetraamine complex. These authors found ΔH for the reaction of Cu^{2+} with the open-chain thia ligands to be virtually identical to that with the optimally fitting cyclic ligand $T_4$14C4. Log K values for formation of the two complexes were significantly different leading to the conclusion that in this case the macrocyclic effect is entirely attributable to the more favorable entropy change associated with the formation of the less flexible cyclic ligand.

3. Cyclic Polyethers

Frensdorff[25] noted a remarkable increase in the stability of metal complexes of cyclic polyethers over those of their linear counterparts by comparing the complexes of Na^+ and K^+ with pentaglyme and 18C6 in methanol. Comparison of the stability of Pb—18C6^{2+} to those of Pb—tetraglyme(2+) and Pb:tetraglyme$_2$(2+) led Kodama and Kimura[103] to conclude that the macrocyclic effect, in this case, could be attributed entirely to the favorable entropy contribution. In a recent study,[92] log K, ΔH, and ΔS values for the interaction in methanol of Na^+, K^+, and Ba^{2+} with five podands and their noncyclic analogues indicated that the effect, generally, is the result of more favorable enthalpy factors. For example, stabilization of K^+ by 18C6 compared to either pentaethylene glycol or pentaglyme is due totally to the enthalpy contribution, while the Ba^{2+} complex is stabilized by both enthalpy and entropy, though the enthalpy term predominates. However, it is pointed out that the results do not conclusively point to any single microscopic source for the macrocyclic effect in polyethers, but they do indicate that unfavorable conformational enthalpy changes of the linear polyethers are important factors. It may be concluded that the macrocyclic effect is not yet simply defined and that different systems may respond to different stabilizing factors.

4. Mixed Donor Atom Macrocycles

Izatt et al.[16] compared the stabilities of a number of linear ligands containing five heteroatoms (S, O) to their cyclic analogues. The stabilities of 2:1 (metal:ligand) Ag^+ and Hg^{2+} complexes of the linear ligands differ only slightly from those of the corresponding cyclic ligands. The ΔH values for 1:1 reactions were also similar. In the case of sulfur-substituted crown ethers, it is doubtful if the metal ion is situated in the ring cavity in the complex. If only outwardly turned sulfur atoms are involved in complexation, no "macrocyclic effect" is to be expected.

Enhanced stabilities due to the macrocyclic effect have been attributed to the slow decomposition rates of complexes of metal ions with macrocycles compared to those with their open-chain analogues. Busch and his co-workers termed this effect "multiple juxtapositional fixedness."[253] This effect is also apparent in the decomposition rate of the cyclic tetraamine complex of Cu^{2+}, which is much lower than that of its linear counterpart.[254] The straight chain ligand can undergo successive S_N1 replacement steps, and, in acid medium, the dissociated groups can be quickly protonated. However, dissociation of a complex involving a macrocyclic ligand requires the distortion of the ligand so as to weaken a coordination bond for final rupture. Invariably, this will impart higher stability to complexes with cyclic ligands. This result has been substantiated through the work of Jones et al.[255] using a cyclic tetrathia complex. In this case, the ligands are free from protonation processes. The authors conclude that configurational effects in the dissociation step are mainly responsible for the extra stability of the complex formed by the macrocycle over that formed by the linear analogue.

F. Cryptate Effect

The increase in the stability of complexes formed by the macrobicyclic ligands over those formed by macrocycles has been noted by Lehn and his co-workers.[134] This stability increase is more pronounced than that described as the macrocyclic effect and has been designated either as a "cryptate effect" or as a "macrobicyclic cryptate effect." By comparing the thermodynamic quantities associated with formation of the K^+-2.2.2 complex to those for the K^+–$Cy_2$18C6 complex, Kauffmann et al. concluded that the cryptate effect is of enthalpic origin.[144] Similar comparisons between the stability data for Ba^{2+} and Ca^{2+} complexes of monocyclic and bicyclic ligands indicate, also, that the cryptate effect is a result of enthalpic stabilization.[99]

III. Kinetics of Cation–Macrocycle Interaction

Kinetic studies of metal cation–macrocycle interactions began with the investigations of biological macrocycles. These ligands are similar to the synthetic crown ethers and cryptands in their complexation properties. Reaction of monovalent cations with valinomycin in methanol may be represented by where M^+,

$$M^+_{solv} + V'_{solv} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M^+_{solv}\ V' \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} MV^+$$

solv, and V represent the cation, solvent, and valinomycin, respectively. The final step is a diffusion-controlled bimolecular collision reaction with an open form of valinomycin followed by replacement of solvent molecules around the cation by ester carbonyl oxygen atoms of the ligand. The second step involves encapsulation of the cation by valinomycin. The latter step is the rate-determining one.[12,178]

Kinetic and activation parameters for cation–macrocycle interactions are given in Table IV, together with the method, temperature, and solvent (medium) used in their determination, and appropriate literature references. Excluded from Table IV are data relating to reactions in which the ligand deprotonates as a result of complex formation as well as ligand exchange reactions such as those in which the cation is complexed by other than the solvent species.

A. Crown Ethers

Shchori et al.[269] from an ^{23}Na NMR spectral study of Na^+-$B_2$18C6 complexation in DMF concluded that the primary reaction involved is a complexation process:

$$Na^+,nDMF + B_218C6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Na^+,B_218C6 + nDMF$$

Through the use of LiSCN to maintain constant ionic strength (LiSCN did not react with $B_2$18C6), it was concluded that changes in solvent activity were responsible for the observed change in the rate.

The interaction of monovalent cations with $B_2$30C10 in methanol was studied by Chock[139] using a Joule heating temperature jump (T-jump) relaxation procedure at 280 and 258.7 nm. He postulated that $B_2$30C10 exists in solution in at least two, and more probably three, conformations and that a fast crown ether conformational transition occurs before complex formation. The three conformations postulated are (a) an unreactive species, (b) an open configuration, which is the predominant species in the absence of cations, and (c) a closed configuration, which is stabilized by a monovalent cation.[265] This description has since been borne out by H^1 and C^{13} NMR studies of 18C6, B18C6, $B_2$18C6, and $B_2$30C10 in their complexed and uncomplexed states in various solvents.[265a] The scheme can be represented as shown below where CR_1 and CR_2 represent, respectively, two different conformations of the macrocycle polyether. This sequence of steps is just the opposite of those chosen for cation complexation by valinomycin.

$$CR_1 \xrightarrow{fast} CR_2$$

$$CR_2 + M^+ \underset{k_d}{\overset{k_f}{\rightleftharpoons}} MCR^+$$

Shchori et al.[128] report extensive studies of the effect of solvents and ring substituents on the kinetics of complexation of Na^+ by $B_2$18C6. Appreciable effects of both parameters are found. For example, compared to $B_2$18C6, the presence of electron-withdrawing nitro groups on the benzene rings of *cis*-4,4′-dinitro-$B_2$18C6 causes a simultaneous increase in the decomplexation rate and decrease in the complexation rate in dimethylformamide solvent at 25 °C resulting in a fivefold decrease in the K value. On the other hand, substitution of amino groups in the same positions of these benzene rings does not alter the decomplexation rate, but increases the complexation rate resulting in little change in the K value. The activation energy for decomplexation of Na^+ by $B_2$18C6 and its derivatives is constant at 53 ± 4 kJ in all solvents studied but is substantially less (34 kJ/mol) for decomplexation of the Na^+-$Cy_2$18C6 complex in methanol. The flexibilities of the dicyclohexano derivative over the dibenzo one is considered responsible for the lower activation energy for complexation.[128]

The rate constant for the decomplexation of sodium ion by valinomycin in methanol at 25 °C has been determined by a ^{23}Na NMR procedure.[97] A similar study of M^+-$B_2$18C6 complexation in methanol at −34 °C

TABLE IV. Kinetic Parameters for the Formation of Cation-Macrocycle Complexes[a]

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(K mol)	method	T, °C	medium[c]	ref
$(CbMA)_4$12C4	Mg^{2+}	1.3×10^2				Spec	15	H_2O (pH 8.5), 0.25 M NaCl	29
	Mg^{2+}	4.9×10^2				Spec	25	H_2O (pH 8.5), 0.1 M NaCl	29
	Mg^{2+}	9.6×10^2				Spec	25	H_2O (pH 9.4), 0.25 M NaCl	29
	Mg^{2+}	8.0×10^2				Spec	25	H_2O (pH 9.0), 0.25 M NaCl	29
	Mg^{2+}	6.8×10^2				Spec	25	H_2O (pH 8.8), 0.25 M NaCl	29
	Mg^{2+}	3.3×10^2				Spec	25	H_2O (pH 8.5), 0.25 M NaCl	29
	Mg^{2+}	42				Spec	25	H_2O (pH 7.6), 0.25 M NaCl	29
	Mg^{2+}	12				Spec	25	H_2O (pH 6.8), 0.25 M NaCl	29
	Mg^{2+}	2.6				Spec	25	H_2O (pH 5.8), 0.25 M NaCl	29
	Mg^{2+}	0.26				Spec	25	H_2O (pH 5.0), 0.25 M NaCl	29
	Mg^{2+}	2.3×10^2				Spec	25	H_2O (pH 8.5), 0.4 M NaCl	29
	Mg^{2+}	9.2×10^2				Spec	34.2	H_2O (pH 8.5), 0.25 M NaCl	29
	Ca^2	6.7×10^5				Spec	25	H_2O (pH 9.4), 0.25 M NaCl	29
	Ca^{2+}	2.4×10^5				Spec	25	H_2O (pH 8.5), 0.25 M NaCl	29
	Ca^{2+}	1.1×10^4				Spec	25	H_2O (pH 7.6), 0.25 M NaCl	29
	Sr^{2+}	8.2×10^4				Spec	25	H_2O (pH 9.5), 0.25 M NaCl	29
	Sr^{2+}	1.1×10^4				Spec	25	H_2O (pH 8.5), 0.25 M NaCl	29
	Sr^{2+}	9.5×10^2				Spec	25	H_2O (pH 7.6), 0.25 M NaCl	29
	Ba^{2+}	6.8×10^3				Spec	25	H_2O (pH 9.5), 0.25 M NaCl	29
	Ba^{2+}	1.2×10^3				Spec	25	H_2O (pH 8.5), 0.25 M NaCl	29
	Ba^{2+}	1.4×10^2				Spec	25	H_2O (pH 7.6), 0.25 M NaCl	29
	Ni^{2+}	2.9×10^2				Spec	25	H_2O (pH 7.4), 0.25 M NaCl	29
	Ni^{2+}	1.4×10^2				Spec	25	H_2O (pH 7.0), 0.25 M NaCl	29
	Ni^{2+}	56				Spec	25	H_2O (pH 6.2), 0.25 M NaCl	29
	Ni^{2+}	25				Spec	25	H_2O (pH 5.5), 0.25 M NaCl	29
	Ni^{2+}	8.0				Spec	25	H_2O (pH 4.9), 0.25 M NaCl	29
	Ni^{2+}	7.5				Spec	25	H_2O (pH 4.8), 0.25 M NaCl	29
	Ni^{2+}	2.6				Spec	25	H_2O (pH 4.3), 0.25 M NaCl	29
	Ni^{2+}	2.0				Spec	25	H_2O (pH 4.0), 0.25 M NaCl	29
	Cu^{2+}	2.6×10^4				Spec	25	H_2O (pH 4.9), 0.25 M NaCl	29
	Cu^{2+}	1.9×10^4				Spec	25	H_2O (pH 4.6), 0.25 M NaCl	29
	Cu^{2+}	6.0×10^3				Spec	25	H_2O (pH 4.3), 0.25 M NaCl	29
	Cu^{2+}	2.3×10^3				Spec	25	H_2O (pH 4.0), 0.25 M NaCl	29
	Zn^{2+}	6.1×10^3				Spec	25	H_2O (pH 5.8), 0.25 M NaCl	29
	Zn^{2+}	5.5×10^2				Spec	25	H_2O (pH 5.0), 0.25 M NaCl	29
	Zn^{2+}	1.5×10^2				Spec	25	H_2O (pH 4.6), 0.25 M NaCl	29
$T_4$12C4	Cu^{2+}	0.408×10^4	2.9			Spec	25	30% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.379×10^4	3.0			Spec	25	40% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.375×10^4	3.4			Spec	25	40% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.268×10^4	3.6			Spec	25	50% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.183×10^4	4.5			Spec	25	60% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.232×10^4	4.1			Spec	25	60% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.154×10^4	4.3			Spec	25	70% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.196×10^4	4.4			Spec	25	70% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.122×10^4	4.4			Spec	25	80% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	1.2×10^3	4.4			Cal	25	80% MeOH, 0.1 M $HClO_4$	255
	Cu^{2+}	0.788×10^4	3.01			Spec	25	90% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.053×10^4	1.5			Spec	25	95% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
$T_4$13C4	Cu^{2+}	5.6×10^4	22			Spec	25	25% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	4.3×10^4	27			Spec	25	35% MeOH, 0.10 M ClO^{4-} ($HClO_4$)	38
	Cu^{2+}	3.1×10^4	35			Spec	25	50% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	2.1×10^4	46			Spec	25	65% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	1.38×10^4	51			Spec	25	80% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	1.4×10^4	51			Cal	25	80% MeOH, 0.1 M $HClO_4$	255
	Cu^{2+}	0.96×10^4	28			Spec	25	90% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	0.58×10^4	12.2			Spec	25	95% MeOH, 0.10 M ClO_4^- ($HClO_4$)	38
$A_2$14C4	Ni^{2+}		8.8×10^{-1}	45	−95	Spec	25	H_2O, 1 M HCl	256
$B_2A_2$14C4	Ni^{2+}		8.8×10^{-1}	45 (d)	−95 (d)	Spec	25	H_2O, 1.0 M HCl	257
	Ni^{2+}		8.7×10^{-1}			Spec	25	H_2O, 0.2 M HCl, $\mu = 1$ (KCl)	257
	Ni^{2+}		6.1×10^{-1}			Spec	25	90% D_2O, 1.0 M, HCl	257
	Ni^{2+}		6.9			Spec	25	95% MeOH, 0.1 M HCl	42
	Ni^{2+}		6.6			Spec	25	95% MeOH, 0.05 M HCl, $\mu = 0.1$, Me_4NCl	42
	Cu^{2+}		15			Spec	25	95% MeOH, 0.05 M HCl, 0.1 M Me_4NCl	44
	Cu^{2+}		16			Spec	25	95% MeOH, 0.1 M HCl	44
$MeB_2A_2$14C4	Ni^{2+}		1.2×10^{-1}			Spec	25	H_2O, 0.2 M HCl, $\mu = 1.0$, KCl	257
	Ni^{2+}		1.4×10^{-1}			Spec	25	H_2O, 1.0 M HCl	42, 257
	Ni^{2+}		1.1×10^{-1}			Spec	25	90% D_2O, 1.0 M HCl	257
	Ni^{2+}		5.2×10^{-1}			Spec	25	95% MeOH, 0.1 M HCl	42
	Ni^{2+}		4.8×10^{-1}			Spec	25	95% MeOH, 0.05 M HCl, $\mu = 0.1$, Me_4NCl	42
$(CbMA)_4$14C4	Ca^{2+}	5.1×10^5				Spec	25	H_2O (pH 10.4)	29
	Ca^{2+}	4.2×10^4				Spec	25	H_2O (pH 9.4)	29
	Ca^{2+}	9.5×10^2				Spec	25	H_2O (pH 8.5)	29
	Ca^{2+}	35				Spec	25	H_2O (pH 7.5)	29
	Ni^{2+}	6.5×10^2				Spec	25	H_2O (pH 7.5)	29
	Ni^{2+}	3.8×10^2				Spec	25	H_2O (pH 7.3)	29
	Ni^{2+}	3.0×10^2				Spec	25	H_2O (pH 7.0)	29

TABLE IV (Continued)

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^‡$,[b] kJ/mol	$\Delta S^‡$,[b] J/(K mol)	method	T, °C	medium[c]	ref
	Ni^{2+}	1.5×10^2				Spec	25	H_2O (pH 6.1)	29
	Ni^{2+}	1.4×10^2				Spec	25	H_2O (pH 5.5)	29
	Zn^{2+}	1.3×10^4				Spec	25	H_2O (pH 5.9)	29
	Zn^{2+}	3.5×10^3				Spec	25	H_2O (pH 5.0)	29
	Zn^{2+}	2.3×10^3				Spec	25	H_2O (pH 4.6)	29
T_414C4	Cu^{2+}	9.3×10^4	7			Spec	25	25% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	7.6×10^4	7.9			Spec	25	35% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	5.5×10^4	10.2			Spec	25	50% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	3.8×10^4	12			Spec	25	65% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	2.6×10^4	8.6			Spec	25	80% MeOH, 0.1 M ClO_4^- ($HClO_4$	38
	Cu^{2+}	2.8×10^4	9			Cal	25	80% MeOH, 0.1 M $HClO_4$	38, 255
	Cu^{2+}	1.77×10^4	4.5			Spec	25	90% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	1.20×10^4	1.1			Spec	25	95% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
B_2A_215C4	Ni^{2+}		2.7×10^{-3}			Spec	25	H_2O, pH 4.5	257
	Ni^{2+}		3.6×10^{-3}			Spec	25	H_2O, 0.5 M HCl	257
	Ni^{2+}		3.5×10^{-3}			Spec	25	H_2O, 1.0 M HCl	42, 257
	Ni^{2+}		3.5×10^{-3}	68	−63	Spec	25	H_2O, 1 M HCl	256
	Ni^{2+}		3.1×10^{-3}			Spec	25	H_2O, 0.05 M HCl, μ = 1.0, KCl	257
	Ni^{2+}		3.1×10^{-3}			Spec	25	H_2O, 0.1 M HCl, μ = 1.0, KCl	257
	Ni^{2+}		3.1×10^{-3}			Spec	25	H_2O, 0.2 M HCl, μ = 1.0, KCl	257
	Ni^{2+}		2.5×10^{-3}			Spec	25	90% D_2O, 1 M HCl	257
	Ni^{2+}		6.5×10^{-3}			Spec	25	90% MeOH, 1.0 M HCl	257
	Ni^{2+}		1.1×10^{-2}			Spec	25	95% MeOH, 0.1 M HCl	42
	Ni^{2+}		1.2×10^{-2}			Spec	25	95% MeOH, 0.05 M HCl, μ = 0.1, Me_4NCl	42
	Ni^{2+}	0.42×10^{-3}				Spec	10.5	MeOH	258
	Ni^{2+}	0.61×10^{-3}				Spec	14.0	MeOH	258
	Ni^{2+}	0.95×10^{-3}				Spec	17.9	MeOH	258
	Ni^{2+}	1.31×10^{-3}				Spec	22.4	MeOH	258
	Ni^{2+}	1.77×10^{-3}				Spec	26.0	MeOH	258
	Ni^{2+}	2.36×10^{-3}				Spec	30.0	MeOH	258
	Cu^{2+}		$>10^2$			Spec	25	95% MeOH, 0.1 M HCl	44
HOB_2A_215C4	Ni^{2+}		1.7×10^{-2}			Spec	25	H_2O, 1 M HCl	257
	Ni^{2+}		1.7×10^{-2}			Spec	25	H_2O, 0.1 M HCl, μ = 1.0, KCl	257
	Ni^{2+}		1.1×10^{-2}			Spec	25	90% D_2O, 1 M HCl	257
	Ni^{2+}		2.3×10^{-1}			Spec	25	95% MeOH, 0.1 M HCl	42
	Ni^{2+}		2.2×10^{-1}			Spec	25	95% MeOH, 0.05 M HCl, μ = 0.1 ($N(CH_3)_4Cl$)	42
$Me_2B_2A_215C4$	Ni^{2+}		3.8×10^{-4}			Spec	25	H_2O, 1.0 M HCl	42, 257
	Ni^{2+}		3.6×10^{-4}			Spec	25	H_2O, 0.1 M HCl, μ = 1.0, KCl	257
	Ni^{2+}		3.2×10^{-4}			Spec	25	90% D_2O, 1.0 M HCl	257
T_415C4	Cu^{2+}	23.5×10^4	95			Spec	25	H_2O, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	4.3×10^4	20			Spec	25	80% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	4.3×10^4	1.9×10^2			Cal	25	80% MeOH, 0.1 M $HClO_4$	255
A_216C4	Ni^{2+}		6.4×10^{-4}	97	52	Spec	25	H_2O, 1 M HCl	256
B_2A_216C4	Ni^{2+}		5.4×10^{-3}			Spec	25	95% MeOH, 0.1 M HCl	42
	Ni^{2+}		5.7×10^{-3}			Spec	25	95% MeOH, 0.05 M HCl, μ = 0.1, Me_4NCl	42
	Ni^{2+}	0.46×10^{-3}				Spec	14.3	MeOH	258
	Ni^{2+}	0.70×10^{-3}				Spec	18.3	MeOH	258
	Ni^{2+}	0.94×10^{-3}				Spec	22.1	MeOH	258
	Ni^{2+}	1.02×10^{-3}				Spec	26.0	MeOH	258
	Ni^{2+}	1.51×10^{-3}				Spec	29.4	MeOH	258
	Ni^{2+}	1.66×10^{-3}				Spec	32.6	MeOH	258
	Ni^{2+}		6.4×10^{-4}			Spec	25	H_2O, 1.0 M HCl	257
	Ni^{2+}		4.7×10^{-4}			Spec	25	90% D_2O, 1.0 M HCl	257
	Ni^{2+}		6.5×10^{-4}			Spec	25	H_2O, 0.1 M HCl, μ = 1.0, KCl	257
	Ni^{2+}		3.6×10^{-3}			Spec	25	90% MeOH, 1 M HCl	257
	Cu^{2+}		$>10^2$			Spec	25	95% MeOH, 0.1 M HCl	44
T_416C4	Cu^{2+}	15.8×10^4	1.44×10^3			Spec	25	25% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	10.1×10^4	1.72×10^3			Spec	25	35% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	6.8×10^4	1.80×10^3			Spec	25	50% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	2.1×10^4	3.52×10^3			Spec	25	65% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	2.9×10^4	3.2×10^3			Cal	25	80% MeOH, 0.1 M $HClO_4$	38, 255
	Cu^{2+}	1.7×10^4	1.03×10^3			Spec	25	95% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
A_217C4	Ni^{2+}		>0.5			Spec	25	H_2O, 1 M HCl	256
B_2A_217C4	Ni^{2+}		>0.5			Spec	25	95% MeOH, 0.1 M HCl	42
	Ni^{2+}		>0.5			Spec	25	90% MeOH, 1.0 M HCl	257
	Cu^{2+}		85			Spec	25	95% MeOH, 0.1 M HCl	44
cis-Me_6A_4-18C4-diene	Cu^{2+}		1.40×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (0.5 × 10^{-2} M HOAc)	259
	Cu^{2+}		2.59×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (1.0 × 10^{-2} M HOAc)	259
	Cu^{2+}		4.50×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (2.0 × 10^{-2} M HOAc)	259
	Cu^{2+}		6.51×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$, (3.0 × 10^{-2} M HOAc)	259
	Cu^{2+}		9.19×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (4.0 × 10^{-2} M HOAc)	259
	Cu^{2+}		0.54×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$, (pOH 2.02)	259
	Cu^{2+}		14.48×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$, (pOH 1.84)	259
	Cu^{2+}		2.13×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$, (pOH 1.71)	259
	Cu^{2+}		5.85×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (pOH 1.54)	259

TABLE IV (Continued)

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(K mol)	method	T, °C	medium[c]	ref
	Cu^{2+}		7.60×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$, (pOH 1.41)	259
trans-Me_8A_4-18C4-diene	Ni^{2+}		1.5×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 1.4)	259
	Ni^{2+}		1.6×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 1.2)	259
	Ni^{2+}		1.8×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 1.0)	259
	Ni^{2+}		2.4×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 0.71)	259
	Ni^{2+}		2.8×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 0.54)	259
	Ni^{2+}		3.3×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 0.41)	259
	Ni^{2+}		3.5×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 0.32)	259
	Ni^{2+}		3.6×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 0.24)	259
	Ni^{2+}		3.6×10^{-4}			Spec	25	H_2O, μ = 1.0 (HNO_3, $NaNO_3$) (pH 0.0)	259
	Ni^{2+}		3.6×10^{-4}			Spec	25	H_2O, μ = 0.97, pH 0.013 (HNO_3)	259
	Ni^{2+}		5.8×10^{-4}			Spec	29	H_2O, μ = 0.97, pH 0.013 (HNO_3)	259
	Ni^{2+}		8.2×10^{-4}			Spec	32	H_2O, μ = 0.97, pH 0.013 (HNO_3)	259
	Ni^{2+}		1.10×10^{-3}			Spec	36	H_2O, μ = 0.97, pH 0.013 (HNO_3)	259
	Ni^{2+}		2.00×10^{-3}			Spec	42	H_2O, μ = 0.97, pH 0.013 (HNO_3)	259
	Cu^{2+}		2.98×10^{-3}			Spec	25	H_2O, HCl (pH 1.71)	259
	Cu^{2+}		3.73×10^{-3}			Spec	25	H_2O, HCl (pH 1.41)	259
	Cu^{2+}		4.42×10^{-3}			Spec	25	H_2O, HCl (pH 1.24)	259
	Cu^{2+}		2.28×10^{-3}			Spec	20	H_2O, μ = 0.97, pH 0.013 ($HClO_4$)	259
	Cu^{2+}		3.20×10^{-3}			Spec	22.5	H_2O, μ = 0.97, pH 0.013 ($HClO_4$)	259
	Cu^{2+}		4.80×10^{-3}			Spec	25	H_2O, μ = 0.97, pH 0.013 ($HClO_4$)	259
	Cu^{2+}		5.96×10^{-3}			Spec	28	H_2O, μ = 0.97, pH 0.013 ($HClO_4$)	259
	Cu^{2+}		10.56×10^{-3}			Spec	34	H_iO, μ = 0.97, pH 0.013 ($HClO_4$)	259
	Cu^{2+}		1.20×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 2.0)	259
	Cu^{2+}		1.57×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 1.7)	259
	Cu^{2+}		1.84×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 1.5)	259
	Cu^{2+}		2.25×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 1.4)	259
	Cu^{2+}		2.60×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 1.3)	259
	Cu^{2+}		2.74×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 1.2)	259
	Cu^{2+}		3.10×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 1.0)	259
	Cu^{2+}		3.88×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 0.71)	259
	Cu^{2+}		4.38×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 0.54)	259
	Cu^{2+}		4.41×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 0.41)	259
	Cu^{2+}		4.58×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 0.32)	259
	Cu^{2+}		5.00×10^{-3}			Spec	25	H_2O, μ = 1.0 ($HClO_4$, $NaClO_4$) (pH 0.01)	259
	Cu^{2+}		0.14×10^{-3}			Spec	25	H_2O, μ = 0.1 ($NaClO_4$) (pOH 2.02)	259
	Cu^{2+}		0.73×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (pOH 1.71)	259
	Cu^{2+}		1.75×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (pOH 1.54)	259
	Cu^{2+}		2.63×10^{-3}			Spec	25	H_iO, μ = 0.1, $NaClO_4$ (pOH 1.41)	259
	Cu^{2+}		4.27×10^{-3}			Spec	25	H_2O, μ = 0.1, $NaClO_4$ (pOH 1.84)	259
	Cu^{2+}		1.21			Spec	25	H_2O, μ = 0.5, $NaClO_4$ (NaOH 0.2 M)	259
	Cu^{2+}		2.05			Spec	25	H_2O, μ = 0.5, $NaClO_4$ (NaOH 0.3 M)	259
	Cu^{2+}		2.91			Spec	25	H_2O, μ = 0.5 $NaClO_4$ (NaOH 0.4)	259
	Cu^{2+}		2.14×10^{-3}			Spec	25	D_2O/DCl (pD 1.71)	259
	Cu^{2+}		2.58×10^{-3}			Spec	25	D_2O/DCl (pD 1.41)	259
	Cu^{2+}		3.0×10^{-3}			Spec	25	D_2O/DCl (pD 1.24)	259
15C5	Na^+	2.6×10^8	5.1×10^7			US	25	H_2O	260
	K^+	4.3×10^8	7.8×10^7			US	25	H_2O	260
	Rb^+	4.4×10^8	1.4×10^8			US	25	H_2O	260
	Sr^{2+}	6.5×10^7	7.3×10^5			US	25	H_2O	261
	Ba^{2+}	1.2×10^8	2.3×10^6			US	25	H_2O	261
	Ag^+	6.7×10^8	8.2×10^7			US	25	H_2O	260
	Hg^{2+}	1.6×10^8	3.3×10^6			US	25	H_2O	261
	Tl^+	8.0×10^8	5.0×10^7			US	25	H_2O	260
	Pb^{2+}	3.2×10^8	4.6×10^6			US	25	H_2O	261
	Gly^+	5.6×10^7	$<2 \times 10^7$			US	25	H_2O	262
$T_5$15C5	Cu^{2+}	44×10^4	17			Spec	25	35% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	36×10^4	30			Spec	25	50% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	21.5×10^4	50			Spec	25	65% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	14.6×10^4	150			Spec	25	80% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	7.9×10^4	103			Spec	25	90% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
	Cu^{2+}	6.2×10^4	45			Spec	25	95% MeOH, 0.1 M ClO_4^- ($HClO_4$)	38
18C6	Li^+	$\sim 8 \times 10^7$	$\sim 6 \times 10^7$			US	25	H_2O	263
	Na^+	2.2×10^8	3.4×10^7			US	25	H_2O	263
	K^+	1.0×10^{10}	3.7×10^6			US	25	H_2O	264
	K^+	4.3×10^8	3.7×10^6	16.7	−33.5	US	25	H_2O	265
				42.7 (d)	13.0 (d)				
	K^+	5.9×10^8	7.9×10^6			US	35.7	H_2O	265
	K^+	5.8×10^8	9.1×10^6			US	40.3	H_2O	265
	K^+	6.3×10^8	1.2×10^7			US	45.8	H_2O	265
	K^+	1.65×10^4		67.7	63	NMR	25	1,3-dioxolane	266
	K^+	1.74×10^4		62.3	46	NMR	25	1,3-dioxolane	266
	K^+	4.1×10^5		36	−17	NMR	25	Me_2CO	266
	K^+	5.7×10^5		55.2	50	NMR	25	Me_2CO–1,4-Diox (80:20 v/v)	266
	K^+	6.8×10^5		36	−13	NMR	25	MeOH	266

TABLE IV (Continued)

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(K mol)	method	T, °C	medium[c]	ref
	Rb^+	4.4×10^8	1.2×10^7			US	25	H_2O	263
	Cs^+	7.8×10^9	4.4×10^7			US	25	H_2O	264
	Cs^+	9.5×10^3		33	−59	NMR	25	Py	94
	Ca^+	$<1.0 \times 10^6$	$>3.2 \times 10^7$			US	25	H_2O	263
	Sr^{2+}	7.7×10^7	1.5×10^5			US	25	H_2O	261
	Ba^{2+}	1.3×10^6	1.7×10^4			US	25	H_2O	261
	Ag^+	11.2×10^6	3.5×10^7			US	25	H_2O	263
	Hg^{2+}	4.0×10^8	1.5×10^6			US	25	H_2O	261
	Tl^+	9.0×10^6	4.8×10^6			US	25	H_2O	263
	Pb^{2+}	3.3×10^6	1.8×10^4			US	25	H_2O	261
	NH_4^+	5.6×10^6	4.4×10^7			US	25	H_2O	263
	PhN_2^+		24			NMR	−75	$CHCl_2F$ (anion = PF_6^-)	268
	4-$FPhN_2^+$		19			NMR	−80	$CHCl_2F$ (anion = BF_4^-)	268
	4-$CH_3PhN_2^+$		20			NMR	−79	$CHCl_2F$ (anion = BF_4^-)	268
	4-CH_3PhN_2		24			NMR	−75	$CHCl_2F$ (anion = BF_4^-)	268
	3-$NO_2Ph^+N_2$		18			NMR	−82	$CHCl_2F$ (anion = BF_4^-)	268
	4-$NO_2Ph^+N_2$		16			NMR	−80	$CHCl_2F$ (anion = BF^{4-})	268
	α-Ala^+	6.1×10^7	5.4×10^7			US	25	H_2O	262
	β-Ala^+	6.6×10^7	7.2×10^7			US	25	H_2O	262
	γ-aminobutric acid (1+)	5.1×10^7	8.3×10^7			US	25	H_2O	262
	Gly^+	8.4×10^7	12.2×10^7			US	25	H_2O	262
	Thr^+	3.8×10^7	6.0×10^7			US	25	H_2O	262
cis-syn-cis-$Cy_2$18C6	Cs^+	11×10^3		33	−58	NMR	25	PC	94
cis-anti-cis-$Cy_2$18C6	Na^+	2.6×10^6	5.2×10^4			NMR	25	MeOH	128
$B_2$18C6	Na^+		4.8×10^{-3}			NMR	−13	DMF	269
	Na^+	$\sim 6 \times 10^7$	$\sim 10^5$			NMR	25	DMF	269
	Na^+	3.2×10^6	1.4×10^4			NMR	25	MeOH	128
	K^+		610			NMR	−34	MeOH	270
	Sr^{2+}	9.6×10^4	2.7×10^1			Spec	−15	MeOH, μ = 0.05 ($LiClO_4$)	130
syn-Nit_2B_2-18C6	Na^+	2.3×10^7	2.0×10^5			NMR	25	DMF	128
syn-Am_2B_2-18C6	Na^+	1.2×10^6	1.9×10^5			NMR	25	DMF	128
21C7	*p*-$CH_3PhN_2^+$		43			NMR	−52	$CHCl_2F$ (anion = BF_4^-)	268
24C8	*p*-$CH_3PhN_2^+$		19			NMR	−92	$CHCl_2F$ (anion = BF_4^-)	268
$B_2$30C10	Na^+	$>1.6 \times 10^7$	$>1.3 \times 10^5$			Spec	25	MeOH, μ = 0.15 (LiCl)	139
	K^+	6×10^6	1.6×10^4			Spec	25	MeOH, μ = 0.15 (LiCl)	139
	Rb^+	8×10^6	1.8×10^4			Spec	25	MeOH, μ = 0.15 (LiCl)	139
	Cs^+	8×10^6	4.7×10^4			Spec	25	MeOH, μ = 0.15 (LiCl)	139
	Tl^+	8×10^6	2.5×10^4			Spec	25	MeOH, μ = 0.15 (LiCl)	139
	NH_4^+	$>3 \times 10^7$	$>1.1 \times 10^5$			Spec	25	MeOH, μ = 0.15 (LiCl)	139
1.1.1	H^+ (in^+in) to (in in)		$<7 \times 10^{-10}$			NMR	25	D_2O	283
	H^+ (in out^+) to (in^+in)	2.3×10^{-4}				NMR	25	D_2O	283
	H^+ (2) (out^+out^+) to (in^+in)	3.8×10^{-3}				NMR	25	D_2O	283
	H^+ (2) (in^+in) to (in^+in^+)	3.1×10^{-7}	1.4×10^{-6}			NMR	25	D_2O	283
2.1.1	H^+	0.359	3.70×10^2			PJ	5.15	H_2O	142
	H^+	0.512	4.74×10^2			PJ	10	H_2O	142
	H^+	0.756	6.30×10^2			PJ	15	H_2O	142
	H^+	1.11	8.34×10^2			PJ	20	H_2O	142
	H^+	1.59	1.08×10^3	49.3 35.1 (d)	−76.1 −69.0 (d)	PJ	25	H_2O (extrapolated)	142
	H^+ (2)	$\sim 4 \times 10^5$				Cal	25	MeOH (extrapolated)	276
	Li^+	8×10^3	0.025			Cond	25	H_2O	272
	Li^+	0.98×10^3	4.9×10^{-3}	86.9 (d)	1.7 (d)	NMR	25	H_2O (anion = I^-)	273
	Li^+		1.3×10^{-2}	64 (d)	−65 (d)	NMR	25	DMF (anion = ClO_4^-)	273
	Li^+	1.4×10^5	1.4×10^{-2}			Cond	25	DMF (anion = ClO_4^-)	274
	Li^+		2.32×10^{-2}	65 (d)	58 (d)	NMR	25	Me_2SO (anion = ClO_4^-)	273
	Li^+	1.5×10^4	2.12×10^{-2}			Cond	25	Me_2SO (anion = ClO_4)	274
	Li^+	1.8×10^5	6.0×10^{-4}			Cond	25	EtOH (anion = Cl^-)	274
	Li^+		7.4×10^{-3}	56 (d)	−95 (d)	NMR	25	Form (anion = ClO_4^-)	273
	Li^+	4.8×10^5	4.4×10^{-3}			Cond	25	MeOH	146
	Li^+	1.3×10^4	4.81×10^{-3}			Cond	25	NMP (anion = ClO_4^-)	274
	Li^+	$<3 \times 10^7$	$\leq 10^{-5}$			Cond	25	PC	147
	Li^+		0.12×10^{-3}	79 (d)	−52 (d)	NMR	25	Py (anion = ClO_4^-)	273
	Na^+	9×10^4	1.4×10^2			TJ	?	H_2O	275
	Na^+	$\sim 2 \times 10^5$	~ 5			Cond	25	Me_2SO (anion = ClO_4^-)	274
	Na^+	8.8×10^6	7.1×10^{-1}			Cond	25	EtOH (anion = ClO_4^-)	274
	Na^+	3.1×10^6	2.50			Cond	25	MeOH	146
	Na^+	5.4×10^4	4.7×10^{-1}			Cond	25	NMP (anion = ClO_4^-)	274
	Na^+	2.1×10^7	3.6×10^{-2}			Cond	25	PC	147
	Ca^{2+}	2.6×10^2	0.82			Cond	25	H_2O	272
	Ca^{2+}	1.1×10^2	0.69	57.3, 56.0 (d)	−13, −59 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl)	150

TABLE IV (Continued)

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(K mol)	method	T, °C	medium[c]	ref
	Ca^{2+}	1.1×10^2	0.69	57	−13	Spec	25	H_2O	150
				56 (d)	−59 (d)				
	Ca^{2+}	1.6×10^2	0.10	33	−92	Spec	25	H_2O (anion = Cl)	157
				11 (d)	−226 (d)				
	Ca^{2+}	9.04×10^3	3.6×10^{-2}			Cond	25	MeOH	152
	Ca^{2+}	$\sim 2.4 \times 10^2$	$\sim 2 \times 10^{-1}$			Cond	25	DMF	274
	Tl^+		31			Cond	25	90% MeOH	160
	Tl^+		4×10^4			Cond	25	90% MeOH (acid catalzyed)	160
2.2.1	H^+	$4 \times 10^5(2)$	$5 \times 10^{-3}(2)$			Spec	25	MeOH	276
	Li^+	$\sim 3 \times 10^6$	~ 13			Cond	25	EtOH	274
	Li^+		12.0			Cond	−20	MeOH	156
	Li^+		15.2			Cond	−15	MeOH	156
	Li^+		19.2			Cond	−10	MeOH	156
	Li^+		24.0			Cond	−5	MeOH	156
	Li^+	1.88×10^7	78.4	13.3	−61	Cond	25	MeOH	156
	Li^+			23.8 (d)	−129 (d)	Cond	25	MeOH	156
	Li^+	1.8×10^7	75			Cond	25	MeOH	146
	Li^+		1.23	54 (d)	−62 (d)	NMR	25	Py (anion = ClO_4^-)	273
	Na^+	3.6×10^6	14.5			Cond	25	H_2O	272
	Na^+	6×10^6	18			TJ	?	H_2O (pH 12.5)	275
	Na^+	1.8×10^7	2.5×10^{-1}			Cond	25	DMF (anion = ClO_4^-)	274
	Na^+	7.2×10^6	7.5×10^{-1}			Cond	25	Me_2SO (anion = ClO_4^-)	274
	Na^+	4.2×10^7	2.62×10^{-3}			Cond	25	EtOH (anion = ClO_4)	274
	Na^+	1.7×10^8	2.35×10^{-2}			Cond	25	MeOH	146
	Na^+	8.74×10^7	1.96×10^{-2}	15.3	−42	Cond	25	MeOH	156
	Na^+			64.6 (d)	−61 (d)	Cond	25	MeOH	156
	Na^+		3.07×10^{-2}			Cond	30	MeOH	156
	Na^+		4.73×10^{-2}			Cond	35	MeOH	156
	Na^+		7.19×10^{-2}			Cond	40	MeOH	156
	Na^+		10.7×10^{-2}			Cond	45	MeOH	156
	Na^+	5.9×10^5	1.67×10^{-1}			Cond	25	NMP (anion = ClO_4^-)	274
	Na^+	$<10^{10}$	$<10^{-2}$			Cond	25	PC	147
	K^+	3×10^7	2×10^3			TJ	?	H_2O	275
	K^+	$\sim 1.3 \times 10^7$	~ 2.6			Cond	25	DMF (anion = ClO_4^-)	274
	K^+	4.9×10^7	1.35×10^{-1}			Cond	25	EtOH (anion = I^-)	274
	K^+	3.36×10^8	0.969	10.0	−48	Cond	25	MeOH	156
	K^+			70.0 (d)	10 (d)	Cond	25	MeOH	156
	K^+		1.57			Cond	30	MeOH	156
	K^+		2.51			Cond	35	MeOH	156
	K^+		3.95			Cond	40	MeOH	156
	K^+		6.10			Cond	45	MeOH	156
	K^+	3.8×10^8	1.09			Cond	25	MeOH	146
	K^+	1.7×10^6	1.35			Cond	25	NMP (anion = ClO_4^-)	274
	K^+	2.8×10^8	3.7×10^{-2}			Pot	25	PC	147
	Rb^+	8.3×10^7	11			Cond	25	EtOH (anion = Cl^-)	274
	Rb^+	4.1×10^8	75			Cond	25	MeOH	146
	Rb^+		2.57			Cond	−10	MeOH	156
	Rb^+		4.25			Cond	−5	MeOH	156
	Rb^+		6.86			Cond	0	MeOH	156
	Rb^+		10.9			Cond	5	MeOH	156
	Rb^+		17.1			Cond	10	MeOH	156
	Rb^+		26.5			Cond	15	MeOH	156
	Rb^+	3.02×10^8	60	−0.1	−83	Cond	25	MeOH	156
	Rb^+			56.3 (d)	−22 (d)	Cond	25	MeOH	156
	Rb^+	8.0×10^7	7.5			Cond	25	PC	147
	Cs^+	1×10^8	$\sim 2 \times 10^3$			Cond	25	EtOH (anion = NO_3^-)	274
	Cs^+	$\sim 5 \times 10^8$	$\sim 2.3 \times 10^4$			Cond	25	MeOH	146
	Cs^+	$\sim 3.3 \times 10^7$	$\sim 4 \times 10^2$			Cond	25	PC	147
	Ca^{2+}	1.6×10^4	2.2×10^{-3}	58, 63 (d)	29, −84 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl)	150
	Ca^{2+}	5.9×10^3	6.6×10^{-4}			Cond	25	H_2O	272
	Ca^{2+}	1.2×10^4	1.9×10^{-3}	44.4	−17, −46 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl) (anion = Cl^-)	157
				74.4 (d)					
	Ca^{2+}	3.7×10^3	8.0×10^{-4}			Cond	25	DMF	274
	Ca^{2+}	1.9×10^4	2.3×10^{-6}			Cond	25	MeOH	152
	Sr^{2+}	5.7×10^4	2.6×10^{-3}	53.3, 79 (d)	21, −33 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl)	150
	Sr^{2+}	3.3×10^4	1.47×10^{-3}			Cond	25	H_2O	272
	Sr^{2+}	9.2×10^4	8.2×10^{-7}			Cond	25	MeOH	152
	Ba^{2+}	1.22×10^5	6.1×10^{-2}			Cond	25	H_2O	272
	Ba^{2+}	1.92×10^6	4.6×10^{-5}			Cond	25	MeOH	152
	Eu^{2+}		2×10^{-4}	63.1 (d)	−105 (d)	Volt	25	H_2O, 0.1 M Et_4NClO_4 (pH 2.5)	158
	Eu^{2+}		1×10^{-4}			Volt	25	H_2O, 1 M $LiClO_4/HClO_4$	158
	Eu^{3+}		3.0×10^{-7}	79.1 (d)	−107 (d)	Volt	25	H_2O, 0.5 M $NaClO_4$ (pH 2.5)	158
	Eu^{3+}		4.0×10^{-7}	80.3 (d)	−98 (d)	Volt	25	H_2O, 0.1 M Et_4NClO_4 (pH 2.5)	158
	Eu^{3+}		4.1×10^{-7}			Volt	25	H_2O, 0.5 M $NaClO_4$ (pH $\sim$7)	158

TABLE IV (Continued)

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(K mol)	method	T, °C	medium[c]	ref
	Eu^{3+}		3×10^{-7}			Volt	25	H_2O, 1 M $LiClO_4/HClO_4$	158
	Yb^{3+}		1.3×10^{-6}	93.3 (d)	−43.9 (d)	Volt	25	H_2O, 0.5 M $NaClO_4$	158
	Cu^{2+}	37.0	0.11	209 (d)	−414 (d)	Spec	25	Me_2SO	159
	Ag^+		4.5×10^{-4}			Cond	25	H_2O	272
	Tl^+	6.7×10^7	10.5			Spec	25	H_2O	160
	Tl^+		250			Spec	25	90% MeOH (acid catalyzed)	160
	Tl^+		0.1			Spec	25	90% MeOH	160
	Tl^+		60			Spec	25	90% MeOH (acid catalyzed)	160
K_2Py2.2.1	Na^+	3×10^6	1.5×10^4			TJ	25	H_2O	277
	K^+	5×10^6	3×10^3			TJ	25	H_2O	277
Py2.2.1	K^+	3×10^6	7×10^3			TJ	25	H_2O	277
2.2.2	H^+	1.93×10^2	3.15×10^6			TJ	5.15	H_2O	142
	H^+	2.62×10^2	4.10×10^6			TJ	10	H_2O	142
	H^+	3.83×10^2	5.72×10^6			TJ	15	H_2O	142
	H^+	5.15×10^2	7.35×10^6			TJ	20	H_2O	142
	H^+	7.31×10^2	9.98×10^6	44.3, 38 (d)	−40.6, 17 (d)	TJ	25	H_2O (extrapolated)	142
	Li^+		$>3 \times 10^2$			Cond	25	MeOH	146
	Na^+	2×10^5	27			NMR	3	H_2O (anion = Cl^-)	278
	Na^+		147.4	−67.4 (d)	22.2 (d)	NMR	25	H_2O	279
	Na^+	1.1×10^6	3.0×10^{-1}			Cond	25	EtOH (anion = ClO_4^-)	274
	Na^+		165	51.5 (d)	−31.8 (d)	NMR	25	EDA	279
	Na^+		3×10^2			NMR	34	EDA (anion = Br^-)	280
	Na^+		5.1×10^2			NMR	44	EDA (anion = Br^-)	280
	Na^+		8.5×10^2			NMR	51	EDA (anion = Br^-)	280
	Na^+		1.3×10^3			NMR	56	EDA (anion = Br^-)	280
	Na^+		2.5×10^3			NMR	65	EDA (anion = Br^-)	280
	Na^+		2.5×10^3			NMR	75	EDA (anion = Br^-)	280
	Na^+	2.7×10^6	2.87			Cond	25	MeOH	146
	Na^+	3.8×10^6	5.68			Cond	25	NMP (anion = ClO_4^-)	274
	Na^+		1.14	56.9 (d)	−52.7 (d)	NMR	25	Py	279
	Na^+		8.03	57.7 (d)	−34 (d)	NMR	25	THF	279
	K^+	2.0×10^6	7.5			Cond	25	H_2O	272
	K^+		5.5			Spec	25	H_2O	160
	K^+		590			Spec	25	H_2O (acid catalyzed)	160
	K^+	2×10^6	9			TJ	?	H_2O, pH 12.5	275
	K^+	8×10^6	42			NMR	35	H_2O (anion = Br^-)	278
	K^+	7.5×10^6	38			NMR	36	H_2O (anion = F^-)	278
	K^+	7.5×10^6	38			NMR	36	H_2O (anion = Cl^-)	278
	K^+	3.8×10^7	4.0×10^{-1}			Cond	25	DMF (anion = ClO_4^-)	274
	K^+	3.5×10^7	2.68			Cond	25	Me_2SO (anion = NO_3^-)	274
	K^+	1.3×10^6	4.08×10^{-3}			Cond	25	EtOH (anion = I^-)	274
	K^+	4.7×10^6	1.8×10^{-2}			Cond	25	MeOH	146
	K^+	$\sim 1 \times 10^7$	1.33×10^{-1}			Cond	25	NMP (anion = ClO_4^-)	274
	K^+	4.5×10^6	3×10^{-3}			Cond	25	PC	147
	Rb^+	7.5×10^5	38			NMR	9	H_2O (anion = Cl^-)	278
	Rb^+	1.7×10^8	9.17×10^{-2}			Cond	25	EtOH (anion = Cl^-)	274
	Rb^+	7.6×10^6	8.0×10^{-1}			Cond	25	MeOH	146
	Rb^+	9.5×10^6	5.0×10^{-1}			Cond	25	NMP (anion = NO_3^-)	274
	Rb^+	1.8×10^6	1.7×10^{-1}			Cond	25	PC	147
	Cs^+		9.0×10^6	54 (d)	69 (d)	NMR	25	DMF	94
	Cs^+		≥355			NMR	−79	MeOH	168
	Cs^+	$\sim 9 \times 10^6$	$\sim 4 \times 10^4$			Cond	25	MeOH	146
	Cs^+	$\sim 5 \times 10^6$	$\sim 3 \times 10^2$			Cond	25	PC	147
	Ca^{2+}	7.3×10^3	0.26	33, 34 (d)	−59, −138 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl)	150
	Ca^{2+}	$>10^3$	~ 0.1			Pot	25	H_2O (anion = Cl^-)	278
	Ca^{2+}	6.6×10^3	0.26	31, 34 (d)	−63, −140 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl) (anion = Cl^-)	157
	Ca^{2+}	1.4×10^3		70.7	54	Spec	25	H_2O, pH 9.2, μ = 0.1 (piperidine HCl)	150
	Ca^{2+}	5.5×10^3	0.21			Cond	25	H_2O	272
	Ca^{2+}	3.1×10^2	4.4×10^{-2}			Cond	25	DMF	274
	Ca^{2+}	3.6×10^4	2.2×10^{-4}			Cond	25	MeOH	152
	Sr^{2+}	1.0×10^4	1.0×10^{-4}	31, 74 (d)	−63, −71 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl)	150
	Sr^{2+}	6×10^3	10^{-4}			Pot	25	H_2O (anion = Br^-)	278
	Sr^{2+}	7.5×10^3	7.5×10^{-5}			Cond	25	H_2O	272
	Sr^{2+}	2.2×10^3		68	46	Spec	25	H_2O, pH 9.2, μ = 0.1 (piperidine HCl)	150
	Sr^{2+}	5.4×10^4	6.8×10^{-9}			Spec	−15	MeOH, μ = 0.05 ($LiClO_4$)	130
	Sr^{2+}	3.1×10^5	5.5×10^{-7}			Cond	25	MeOH	152
	Ba^{2+}	7.0×10^4	2.2×10^{-5}	28, 87 (d)	−54, −38 (d)	Spec	25	H_2O, pH 11.5, μ = 0.1 (piperidine HCl)	150
	Ba^{2+}	3×10^4	10^{-5}			Pot	25	H_2O (anion = Cl^-)	278

TABLE IV (Continued)

ligand	ion	k_f, M^{-1} s^{-1}	k_d, s^{-1}	$\Delta H^{\ddagger}$,[b] kJ/mol	$\Delta S^{\ddagger}$,[b] J/(K mol)	method	T, °C	medium[c]	ref
	Ba^{2+}	1.3×10^4		82	109	Spec	25	H_2O, pH 9.2, μ = 0.1 (piperidine HCl)	150
	Ba^{2+}	5.5×10^4	1.75×10^{-5}			Cond	25	H_2O	272
	Ba^{2+}	$\sim 5 \times 10^6$	$\sim 6.3 \times 10^{-7}$			Cond	25	MeOH	152
	Eu^{2+}		3×10^{-5}	78.6 (d)	−66.9 (d)	Volt	25	H_2O, 0.5 M Et_4NClO_4 + 0.033 M $Ba(NO_3)_2$	158
	Eu^{2+}		$\sim 5 \times 10^{-5}$			Volt	25	H_2O, 0.1 M $LiClO_4/HClO_4$	158
	Eu^{3+}		1.1×10^{-3}	57.7 (d)	−109 (d)	Volt	25	H_2O, 0.1 M Et_4NClO_4 (pH ~ 7)	158
	Eu^{3+}		1×10^{-3}			Volt	25	H_2O, 0.1 M $LiClO_4/HClO_4$	158
	Tl^+	1.4×10^5	5.5			Spec	25	H_2O	160
	Tl^+		2200			Spec	25	H_2O (acid catalyzed)	160
	Tl^+		0.12			Spec	25	90% MeOH	160
	Tl^+		92			Spec	25	90% MeOH (acid catalyzed)	160
	Tl^+	2.5×10^8	60			NMR	40	H_2O (anion = Cl^-)	278
	Tl^+	2×10^8	51			NMR	−6	H_2O (anion = NO_3^-)	278
	H^+	0.59×10^2	1.42×10^6			PJ	0	H_2O	142
	H^+	0.88×10^2	2.06×10^6			PJ	5	H_2O	142
	H^+	1.18×10^2	2.66×10^6			PJ	10	H_2O	142
	H^+	1.71×10^2	3.75×10^6			PJ	15	H_2O	142
	H^+	2.39×10^2	5.06×10^6			PJ	20	H_2O	142
	H^+	3.29×10^2	6.76×10^6	44.3, 40 (d)	−47, 20 (d)	PJ	25	H_2O (extrapolated)	142
	Li^+	3.3×10^7	2.1×10^5			Cond	25	MeOH (extrapolated)	173
	Na^+	8.78×10^7	2.78	55.1 (d)	−52 (d)	Cond	25	MeOH	173
	K^+	2.57×10^8	0.158	76.8 (d)	3 (d)	Cond	25	MeOH	173
	K^+	5.8×10^7	5.7×10^{-2}			Cond	25	PC	281
	Rb^+	3.15×10^8	20.4	70.1 (d)	7 (d)	Cond	25	MeOH	173
	Rb^+	1.3×10^8	3.32			Cond	25	PC	281
	Cs^+	4.17×10^8	4.3×10^5			Cond	25	MeOH	173
	Ca^{2+}	7.4×10^3	0.38			Spec	25	H_2O	282
	Sr^{2+}	7.3×10^3	3.3×10^{-4}			Spec	25	H_2O	282
	Ba^{2+}	7.0×10^4	7.5×10^{-4}			Spec	25	H_2O	282
	Ba^{2+}	4.1×10^5	3.5×10^{-6}			Cond	25	MeOH	152
	Ba^{2+}	4×10^5				Spec	25	MeOH	152
	Ca^{2+}	6.4×10^3	5×10^{-4}			Cond	25	MeOH	152
	Ca^{2+}	5×10^3	3.2×10^{-4}			Spec	25	MeOH	152
	Sr^{2+}	4.6×10^4	1.4×10^{-6}			Pot	25	MeOH	152
$B_2$2.2.2	Na^+	4.9×10^7	1.23			Cond	25	MeOH	174
	Na^+	$\geq 10^9$	<0.2			Cond	25	PC	281
	K^+	1.5×10^8	2.7×10^{-1}			Cond	25	MeOH	174
	K^+	2.9×10^7	2.03×10^{-2}			Cond	25	PC	281
	Rb^+	1.1×10^8	1.3×10^2			Cond	25	MeOH	174
	Rb^+	8.0×10^7	18.8			Cond	25	PC	281
	Cs^+		3.44×10^5	60 (d)	63 (d)	NMR	25	PC	94
	Ca^{2+}	5×10^2	4.7×10^{-4}			Cond	25	MeOH	152
	Ca^{2+}	3×10^2	3.4×10^{-4}			Spec	25	MeOH	152
	Ca^{2+}	1.1×10^2	0.24			Spec	25	H_2O	282
	Sr^{2+}	4.8×10^3	4.3×10^{-6}			Cond	25	MeOH	152
	Sr^{2+}	5×10^3				Spec	25	MeOH	152
	Sr^{2+}	2.9×10^2	6.3×10^{-4}			Spec	25	H_2O	282
	Ba^{2+}	5.6×10^4	1.7×10^{-4} (pot)			Cond	25	MeOH	152
	Ba^{2+}	8×10^4	2.9×10^{-4}			Spec	25	MeOH	152
	Ba^{2+}	4.6×10^3	1.73×10^{-2}			Spec	25	H_2O	282
Dec2.2.2	Na^+	4.2×10^7	3.7			Cond	25	MeOH	174
	K^+	1.2×10^8	4.7×10^{-2}			Cond	25	MeOH	174
	Rb^+	7.4×10^7	5.4×10^{-1}			Cond	25	MeOH	174
py2.2.1	K^+	3×10^8	7×10^3			TJ	25	H_2O	277
K_2py2.2.1	Na^+	3×10^8	1.5×10^4			TJ	25	H_2O	277
	K^+	5×10^8	3×10^3			TJ	25	H_2O	277
3.2.2	Cs^+		1090			NMR	25	MeOH	168
valinomycin	Na^+	1.2×10^7	2×10^6			US	25	MeOH	12
	K^+	4×10^7	1.3×10^3			US, TJ	25	MeOH	12
	Rb^+		7.5×10^2			TJ	25	MeOH	12
	Cs^+		2.2×10^3			TJ	25	MeOH	12
	NH_4^+	1.3×10^7	2.5×10^5			US	25	MeOH	12
monactin	Na^+	3×10^8	6×10^5			Spec	20	MeOH	271
antamanide	Na^+	7.7×10^5	2.6×10^1			Spec	20	MeCN	271
(cyclic decapeptide of Pro, Phe, Val, Ala)	Na^+	1.1×10^5	2.1×10^2			Spec	20	MeOH	271
	Ca^{2+}	4.9×10^3	1.9×10^2			Spec	20	MeOH	271
perhydroantamanide	Na^+	4.1×10^5	4.1×10^2			Spec	20	MeOH	271

[a] Methods: Cal = calorimetry, Cond = conductivity, NMR = nuclear magnetic spectroscopy, PJ = pressure jump, Spec = spectrophotometer, TJ = temperature jump, US = ultrasound, Volt = voltammetry. [b] Generally, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are calculated from k_f data. In those cases where these values are based on k_d values, a d is placed in parentheses following the value. [c] Solvents: Diox = 1,4-dioxane, DMF = dimethylformamide, Me_2SO = dimethyl sulfoxide, EDA = ethylenediamine, EtOH = ethanol, Form = formamide, MeCN = acetonitrile, Me_2CO = acetone, MeOH = methanol, NMP = N-methylpropionamide, PC = propylene carbonate, Py = pyridine, THF = tetrahydrofuran, μ = ionic strength.

using ^{39}K and ^{87}Rb NMR spectroscopy has been reported.[270] However, extrapolation by Liesegang et al.[264] of these data to 25 °C gave a dissociation rate for K^+–$B_2$18C6 which was larger by a power of 10 than the value determined previously at this temperature. The k_f value computed by using this k_d value is the same as the theoretical value for a diffusion-controlled reaction.[264] The discrepancy may be due to extrapolation of data over such a wide temperature range (–34 °C to 25 °C).

The kinetics of cation complexation by 15C5 and 18C6 in water have been studied extensively by Eyring and his co-workers.[263] Concentration-independent relaxation data in aqueous solution of 18C6 without any alkali or alkaline earth metal salt have been determined, also.[264] Relaxation times for 15C5 are found to be slower than those for 18C6. The smaller macrocycle is less flexible and hence a longer relaxation time is envisaged for 15C5.[260] However, preliminary data with aqueous solutions of 15C5 and potassium chloride indicate that the concentration-dependent complexation reaction is as fast as that between K^+ and 18C6. The probable explanation of this apparent contradiction may be that the conformations involved in complexation are not the ones in the equilibrium process.[12]

The rate constants for complex formation are similar for the reaction of either alkali or alkaline earth metal cations with 18C6 and 15C5 suggesting that loss of cation solvation is the dominant factor in complex formation, cavity size being unimportant. For Tl^+, Ag^+, and Hg^{2+}, a small decrease in k_{23} was observed for the ligand 15C5 compared to 18C6.[261] Eyring et al.,[265] after considering the above results and taking into consideration the hypothesis that activation enthalpies for decomplexation are due mainly to a conformational rearrangement of the ligand, suggested that the selectivity of a crown ether is due to variations in $\Delta S_d^{\ddagger}$.

Conformational transitions of the cyclodecapeptide antamanide were measured ultrasonically. The complexation rate constants for Na^+ and Ca^{2+} complexes in methanol are both substantially smaller than those for $B_2$30C10, monactin, and valinomycin. This has been attributed to the fact that the antamanide ring is less flexible resulting in substantial desolvation of the cation which becomes in turn the rate-determining step.[271]

Petrucci and his co-workers[329–331] reported ultrasonic kinetic studies of 15C5 and 18C6 complexation of Na^+ and K^+ in nonaqueous solvents such as dimethylformamide, ethanol, and 1,2-dimethoxyethane. They prefer to describe their kinetic data in terms of a sequence of successive steps involving both ion desolvation and ligand rearrangement analogous to the mechanism noted above for valinomycin rather than the less general Chock mechanism. This is true because, in solvents that do not bind as tightly to the cation as does water, a rearrangement of the macrocyclic ligand rather than cation desolvation can become the slowest reaction step in the overall complexation mechanism.

B. Cryptands

Macrobicyclic ligands of the cryptand type have at least two basic bridgehead nitrogen atoms. The pK values of these NH groups are about 7 and 9. Proton-transfer reactions of cryptands occur in two distinct steps, corresponding to formation of mono- and diprotonated species. Rates for these reactions depend on the particular cryptand investigated. For example, rates for 2.1.1 are much faster than those for 1.1.1, but are still several orders of magnitude lower than those expected for a diffusion-controlled reaction in the direction which is favored from a thermodynamic standpoint.[276,283] Interconversions among various in and out conformations have been suggested as reasons for the slow rates observed.[276]

Lehn et al.[284] observed temperature-dependent changes in the H^1 NMR spectra of cryptand 2.2.2 on addition of either potassium, sodium, rubidium, or thallium salts. These changes were attributed to variations in the exchange rates of the metal cryptates with temperature. The following complexation–decomplexation process was indicated by the experimental data:

$$M^{n+},mH_2O + 2.2.2_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{n+},2.2.2_{aq} + mH_2O$$

The decomplexation of K–2.2.2^+ was unaffected by changing anions (Cl^-, Br^-) which indicates that ion pairing does not affect the rate of decomplexation of the cryptate.[284] In the cryptates, complexation rates are approximately 10^6 M^{-1} s^{-1} for the alkali metal cations. Differences in the equilibrium constants for formation of these complexes are reflected in variations both in the decomplexation rate and in the complexation rate. For example, the dissociation rate in CH_3OH of Sr–2.2.2^{2+} is approximately 10^9 times slower than that of Sr–$B_2$18C6^{2+}.[130]

Ceraso and Dye[280] noted that the exchange rates of sodium cryptate in ethylenediamine and water are the same. They concluded that the rate-limiting step is the dissociation of the complex. The free energy of activation for the complexation of Tl^+ with 2.2.2 is 4.5 kcal/mol while the corresponding value for the alkali metal cation is 8.6 kcal/mol. The specific rate of association for Tl^+ with 2.2.2 is 100 times larger than for the corresponding alkali metal cation.[12] This difference was explained by assuming that the orbitals of the metal ion may play a decisive role in complexation. Conformational change in the ligand may occur after association of the ligand to Tl^+ without any loss of the solvent molecule.[12]

Cahen et al.[273] deduced a similar decomplexation process from the exchange rates and thermodynamic parameters for the interaction of Li^+ with 2.1.1 using a ^7Li NMR spectral method. Their study in pyridine solution indicated that the decomplexation rate for Li^+–2.2.1 is 10^4 times as rapid as that for Li^+–2.1.1. The greater decomplexation rate in the former case was attributed to the greater flexibility of 2.2.1. Also, far-infrared and Raman spectroscopic studies of Li^+ and Na^+ cryptates show that the alkali metal cations are completely enclosed in the cryptand cavity and that the cation–cryptand interaction is electrostatic in nature.[285]

Loyola et al.[157] studied the kinetics of Ca^{2+} interaction with 2.2.2, 2.2.1, and 2.1.1 by using a stopped-flow apparatus. These investigators propose a mechanism in which the cryptand undergoes a conformational rearrangement prior to complexation. Activation energy values for these systems suggest that the formation of the transition state involves little loss of water molecules attached to the metal ion.

Cox et al.[146] studied the dissociation rates for a variety of alkali metal cryptates in methanol. The pronounced selectivity of the cryptands for alkali metal cations is reflected entirely in the dissociation rates, with the formation rates increasing monotonically with increasing cation size. For larger cryptands, interactions between the cryptand and the incoming cation compensate effectively for the loss of cation solvation. Cox and his co-workers[274] extended this study to the solvents ethanol, *N*-methylpropionamide, dimethyl sulfoxide, and dimethylformamide. Again, a good correspondence was found in the cases of 2.1.1, 2.2.1, and 2.2.2 between dissociation rates and K, formation rates being nearly the same. Alkali metal ion complexes with B2.2.2 in methanol have been studied by potentiometric, calorimetric, and stopped-flow experiments.[173] The entropies of complexation and activation, and the increase of the decomplexation rate through acid catalysis indicate that much of the conformational flexibility of the ligand is retained in its Na^+ complex. Absence of an acid catalytic effect for K^+ and Rb^+ cryptates is attributed to the reduction in the mobility of the cryptands by steric strain.

The higher stability constants observed for cryptate formation in propylene carbonate relative to water are a result of both smaller dissociation rates and, to a lesser extent, larger formation rates.[147] Similar results were found for alkali metal–cryptand interaction in methanol.[174] From a study of the dissociation rates of complexes between alkali metal ions and 2.2.1 in methanol by a stopped flow technique, it was learned that the dependence of decomplexation rate and stability on ionic raius was found, also, for the corresponding enthalpies of activation and complexation, respectively, but the preference of Na^+ over K^+ is reversed. This fact and the observation that Na–$2.2.1^+$ dissociation is enhanced by proton catalysis, led to the suggestion that the cavity radius of 2.2.1 lies between the ionic radii of Na^+ and K^+.[156]

A kinetic study of Li^+ and Ca^{2+} complexation by cryptand 2.1.1 using stopped-flow calorimetry indicated that the complexation occurs first to one face of the bicyclic ligand with the ion partially complexed by the ligand and the solvent followed by a rearrangement of the complex to a more stable conformation (total ion encapsulation). The slowness of the complexation rate suggests the presence of some ligand rate-limiting step rather than the usual rapid stepwise water loss or diffusion-controlled encounter.[155]

C. Macrocycles Containing Nitrogen Donor Atoms

Compounds of this type have been used as models to explain metal ion-macrocycle reactions in biological systems. Margerum and his co-workers[48,51,254,286] have reported extensive investigations on the interaction of Cu^{2+} and Ni^{2+} with macrocycles containing nitrogen donor atoms. Lin et al.[287] made kinetic measurements on the complexation of cyclic and noncyclic polyamines with Cu(II) in basic aqueous media to ensure the absence of ligand protonation. These workers conclude[287] that for the complexation of $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ with open-chain tetraamine ligands first-bond formation was the rate-determining step, while for the cyclic ligands the rate-determining step changes from first- to second-bond formation as the reactant changes from $Cu(OH)_3^-$ to $Cu(OH)_4^{2-}$. From a study of Co^{3+} complexes with a series of saturated tetraaza macrocyclic ligands of varying ring sizes, Hung and Busch[288] concluded that for the trans isomers the sequence of rates for replacement of chloride ion by water correlates well with the strain energies calculated from the macrocycles in the starting complexes. The strain energy is presumed to be largely relieved in the transition state. The corresponding cis isomers show a modest range of rates and a clear isokinetic effect.

Hertli and Kaden[289] and Hay and Norman[290] found no difference in reactivity toward Ni^{2+} between the cyclic and the open-chain tetraaza ligands in either CH_3CN, dimethyl sulfoxide, or dimethylformamide. On the other hand, in water the monoprotonated species are the reactive forms and the cyclic and open-chain ligands differ significantly in their complexation rates.[291]

D. Macrocycles Containing Oxygen and Nitrogen Donor Atoms

The kinetics of dissociation in acid medium of a range of Ni(III) complexes with coronands containing oxygen and nitrogen donor atoms have been measured. A decrease in the dissociation rate as the macrocycle ring size increases from 14 to 16 members is followed by a sharp increase in the rate for the complex with the 17-membered ring ligand. The occurrence of a minimum rate at 16-membered ring size is a clear indication of macrocyclic ring size control of kinetic stability.[256] A similar study with copper(II) complexes with O–N donor macrocycles in 95% methanol did not show any break in either the kinetic or thermodynamic stabilities for the 16-membered ring ligand, contrary to the findings with the Ni^{2+} complexes, indicating no ring-size discrimination effects for copper complexes. Cu(II) forms a five-coordinated complex with an anion and four donor groups from the macrocycle.[44]

E. Kinetic Data for Reactions Involving Metal–Macrocycle Complexes

The kinetic data compiled in Table IV are for the reaction of cations with macrocycles to form cation–macrocycle complexes. Kinetic data are also available for the subsequent reaction of these complexes with various species. These data include the following reaction types: substitution reactions involving coordinated anions and NH_3 for a large number of cobalt- and copper–tetraaza macrocycle complexes,[288,292–324] ligand exchange in Cu^{2+}-macrocycle[325] and in Tl^+-, Ca^{2+}-, and Pb^{2+}-cryptand[326] complexes, and reduction potentials for M^{3+}-cryptands (M = Eu, Yb)[158,327] and Co^{3+}-tetraaza[328] macrocycle systems. The reader is referred to the indicated references for further information on these systems.

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Nomenclature

A	aza (nitrogen heteroatom)
Adr	adrenalin
Acet	acetamido
Aceto	methylcarbonyl
Al	allyl
Ald	aldehydo
Am	amino
Arg	arginine
B	benzo
Br	bromo
Bu	*n*-butyl
Bz	benzyl
Cb	carboxylate
Cba	carboxamide
Cl	chloro
9C3	9-crown-3
12C4	12-crown-4
Cy	cyclohexano
Cyl	cyclohexyl
Dec	*n*-decyl
DMD	2,2-dimethyl-1,3-dioxolan-4-yl
Dodec	*n*-dodecyl
E	ethylene
en	ethylenediamine
Et	ethyl
Glu	glutamyl
Hex	*n*-hexyl
K	keto
M	methylene
Me	methyl
Nap	naphthalene
nic	nicotinamide
Nit	nitro
Non	nonyl
Oct	*n*-octyl
Octadec	octadecyl
Pent	pentamethylene
Ph	phenyl
Phe	phenylalanyl
Phos	P=O
Pr	propyl
Pro	proline
Py	pyridine
Quin	quinoline
Sul	sulfonate
T	thia (sulfur heteroatom)
t-Bu	tertiary butyl
Tetradec	tetradecyl
THF	tetrahydrofuran
Trit	triphenylmethyl
Try	tryptophanyl

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