Coordination Chemistry of Alkali and Alkaline Earth Cations

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Contents

I. Introduction

A. Purpose

Coordination chemistry of alkali and alkaline earth cations (M^{z+}) has started developing rapidly only in this decade. The reasons for the delayed interest in this field are the following: (i) the chemistry of M^{z+} had been considered simple and discernible only with the help of the ionic model;[1] (ii) compared to the popularly studied transition metal ions, the complexing ability of M^{z+} is weaker and these cations lack convenient physicochemical properties which can help to detect the weak M^{z+}–ligand interaction; and above all (iii) there had been no obvious necessity for an interest in such studies. Consequently, any observation which evidenced a coordinative interaction of M^{z+} was given little importance.

Na, K, Mg, and Ca play vital roles in biological systems,[2] many of which are not understood as yet. The inorganic chemist (in fact the bioinorganic chemist) undertook this biochemical challenge in the late '60s and realized the importance of understanding the interactive principles of these cations, and of M^{z+} in general. Owing to interdisciplinary nature of the subject, the interest grew fast. Whereas earlier isolated studies were carried out only with conventional ligands, the recent spurt in the field involved the use of macromolecular ligands. The latter is so because in vivo complexation and decomplexation of the concerned cations take place essentially with macromolecular biomolecules, and in the in vitro systems the macromolecular ligands have proved to be more efficient ligands than the conventional ones.

Although hundreds of papers and quite a good number of reviews[3–45] (Table I) have been published on various specialized aspects of the subject, no general review on the subject has appeared which could aid understanding and interrelating coordinative principles of M^{z+} in different systems so as to permit logical interpretations of the known results and to forecast interactive behavior of a cation under a given set of conditions. The present review is an attempt in this direction wherein we endeavor to survey the solution as well as the solid-state results of M^{z+} with the conventional as well as the macromolecular ligands. Therefore, instead of emphasizing the conformation aspect of the complexing ligands and drawing a parallelism between the coordination chemistry of M^{z+} and that of transition cations, we concerned ourselves more in discussing the principles which influence the M^{z+}–solvent, M^{z+}–anion, and M^{z+}–ligand interactions.

The dominating importance of the M^{z+}–anion interaction during the M^{z+}–ligand interaction will be emphasized in particular. Another point which will be emphasized in this article is that the chemistry of M^{z+} does not grade monotonously from Li to Cs (M^+ ions) and from Mg to Ba (M^{2+} ions). The aim of the discussion is to show that the chemistry of a cation is determined both by its size and the charge (charge density) and to show further that the low charge density K, Rb, Cs, and Ba (?) as well as the high charge density Mg and Li (?) show facilitated interaction with electrically neutral ligands while the medium charge density Ca, Sr, and Na behave more anionphilic toward an anionic species.[45,46] The importance to both points is being given in view of the belief that they will ultimately explain the chemical diversities between the seemingly alike pairs of cations in natural systems—between Na and K and between Mg and Ca.[21,22]

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TABLE I. Review Articles on Related Topics

year	author(s)	title	ref
		Preliminary/Short Articles	
1969	H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler	Kinetics and Mechanism of Reactions of Main Group Metal Ions with Biological Carriers	3
1971	J.J. Christensen, J.O. Hill, and R.M. Izatt	Ion Binding by Synthetic Macrocyclic Compounds	4
1971	M.R. Truter and C.J. Pedersen	Cryptates	5
1971	M.R. Truter	Crystal Chemistry of d^0 Cations	6
1972	C.J. Pedersen and H.K. Frensdorff	Macrocyclic Polyethers and Their Complexes	7
1972	J. Smid	Structure of Ion Pair Solvation Complexes	8
1973	S.J. Angyal	Complex Formation Between Sugars and Metal Ions	9
1973	W.E. Morf, D. Ammann, E. Pretsch, and W. Simon	Carrier Antibiotics and Model Compounds as Components of Selective Ion-sensitive Electrodes	10
1975	A.I. Popov	Alkali Metal NMR and Vibrational Spectroscopic Studies on Solvates in Nonaqueous Solvents	11
1976	J. Smid	Solute Binding to Polymers Containing Macroheterocyclic Rings	12
1977	J.-M. Lehn	Cryptates: Macropolycyclic Inclusion Complexes	13
1977	D.E. Fenton	Across the Living Barrier	14
1977	M.R. Truter	Effects of Cations of Groups IA and IIA on Crown Ethers	15
1977	R.M. Izatt, L.D. Hansen, D.J. Eatough, J.S. Bradshaw, and J.J. Christensen	Cation Selectivities Shown by Cyclic Polyethers and Their Thia Derivatives	16
1977	W.J. Cook and C.E. Bugg	Structures of Calcium–Carbohydrate Complexes	17
1977	N.S. Poonia	Probes for Potassium—Comparison of Chemical Behavior and Coordination Chemistry of Potassium, Rubidium, Cesium, Thallous, and Ammonium Ions	18
1978	J.-M. Lehn	Cryptates: The Chemistry of Macropolycyclic Inclusion Complexes	19
		Monographs/Major Reviews	
1966	J.A. Rendleman, Jr.	Complexes of Alkali Metals and Alkaline Earth Metals with Carbohydrates	20
1970	R.J.P. Williams	The Biochemistry of Sodium, Potassium, Magnesium, and Calcium	21
1971	R.J.P. Williams	Biochemistry of Group IA and IIA Cations	22
1972	J. Smid	Spectrophotometric Studies of Ion-Pair Equilibria	22a
1972	R. Winkler	Kinetics and Mechanism of Alkali Ion Complex Formation in Solution	23
1973	J.-M. Lehn	Design of Organic Complexing Agents. Strategies Towards Properties	24
1973	M.R. Truter	Structures of Organic Complexes with Alkali Metal Ions	25
1973	W. Simon, W.E. Morf, and P. Ch. Meier	Specificity for Alkali and Alkaline Earth Cations of Synthetic and Natural Organic Complexing Agents in Membranes	26
1973	R.M. Izatt, D.J. Eatough, and J.J. Christensen	Thermodynamics of Cation–Macrocyclic Compound Interaction	27
1973	P.B. Chock and E.O. Titus	Alkali Metal Ion Transport and Biochemical Activity	28
1973	G. Eisenman, G. Szabo, S. Ciani, S. McLaughlin, and S. Krasne	Ion Binding and Ion Transport Produced by Neutral Lipid-Soluble Molecules	29
1974	J.J. Christensen, D.J. Eatough, and R.M. Izatt	The Synthesis and Ion Binding of Synthetic Multidentate Macrocyclic Compounds	30
1974	P.N. Kapoor and R.C. Mehrotra	Coordination Compounds of Alkali and Alkaline Earth Metals with Covalent Characteristics	31
1974	Yu.A. Ovchinnikov, V.T. Ivanov, and A.M. Shkrob	Membrane-Active Complexones	32
1975	D. Midgley	Alkali-Metal Complexes in Aqueous Solution	33
1975	G. Eisenman and S.J. Krasne	The Ion Selectivity of Carrier Molecules, Membranes, and Enzymes	34
1976	A.I. Popov	The Use of Alkali Metal Nuclear Magnetic Resonance in the Study of Solvation and Complexation of Alkali Metal Ions	35
1976	R.H. Kretsinger and D.J. Nelson	Calcium in Biological Systems	36
1977	W. Burgermeister and R. Winkler-Oswatitsch	Complex Formation of Monovalent Cations with Biofunctional Ligands	37
1978	A.I. Popov	Alkali Metal, Magnesium-25, and Silver-109 NMR Studies of Complex Compounds in Nonaqueous Solvents	38
1978	A.G. Pinkus	Three-Coordinate Magnesium	38a
1978	C.J. Pedersen	Synthetic Multidentate Macrocyclic Compounds	39
1978	N.K. Dalley	Structural Studies of Synthetic Macrocyclic Molecules and Their Cation Complexes	40
1978	G.W. Liesegang and E.M. Eyring	Kinetic Studies of Synthetic Multidentate Macrocyclic Compounds	41
1979	I. M. Kolthoff	Application of Macrocyclic Compounds in Chemical Analysis	42
1979	S. Lindenbaum, J.H. Rytting, and L. Sternson	Ionophores—Biological Transport Mediators	43
1979	R. Bissig, D. Ammann, W.E. Morf, E. Pretsch, and W. Simon	Cation Selectivity of Neutral Macrocyclic and Nonmacrocyclic Complexing Agents in Membranes	44
1979	N.S. Poonia	Multidentate Macromolecules—Principles of Complexation with Alkali and Alkaline Earth Cations	45

B. Scope and Organization

The present article reviews briefly all the aspects of the subject which have been dealt in the previous rather specialized reviews listed in Table I so that a broad and general discussion becomes possible. Information available up to about the middle of 1978 has been included. The results of M^{z+} with conventional ligands (section III) and those with macromolecular ligands (section IV) are discussed separately because the in vivo behavior of M^{z+} cations is controlled by their interactive characteristics with macromolecules while the principles of their in vitro coordination have been understood more through their interaction with low molecular weight conventional ligands. Enough diffraction and solution stability data have been provided to enable a discussion on the interactive principles of M^{z+} in the solid state and in solution.

The solubility process of an inorganic salt in a solvent (M^{z+}–solvent coordination at the solid–solvent interface) is being introduced as a special branch of the subject (section III.A.3). The rather neglected coordinative role of M^{z+} in organic reactions has been highlighted in a separate section (section V).

The chemistry of metal–alkoxides and organometallics[31,277] and the kinetics of M^{z+}-complexation in solution[3,23,37,41] have already been treated extensively so these topics have been treated to a minimum in this review. Beryllium has been excluded from the discussion owing to its unique Lewis acid character which makes it behave differently from its own group cations.[47]

C. Key to Notations

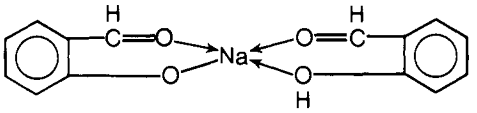
Conventional electrically neutral ligands (including solvents) and anionic ligands have essentially been denoted by the notations usually adopted in the literature. The two classes, however, have been distinguished by using capital and lower-case letters, respectively. Macromolecular multidentate ligands have been represented by Roman numerals except for the crowns for which abbreviations reflecting their structures have been followed. For antibiotics, common names and abbreviations exist which have been used. A comprehensive list is as follows:

acac	acetylacetonate
AEL	1,4-anhydroerythritol
AM	acetamide
anth	anthranilate
Ar	aromatic anion (carbanion)
B15C5	benzo-15-crown-5
B18C6	benzo-18-crown-6
12C4	12-crown-4
14C4	14-crown-4
18C6	18-crown-6
cot	cyclooctatetraene dianion
DA	diacetamide
DB18C6	dibenzo-18-crown-6
DB24C8	dibenzo-24-crown-8
DB27C9	dibenzo-27-crown-9
DB30C10	dibenzo-30-crown-10
dbm	dibenzoylmethane anion
DC18C6	dicyclohexano-18-crown-6
dcta	1,2-diaminocyclohexane-*N*,*N*′-tetraacetate
DDB	*p*,*p*′-diamino-2,3-diphenylbutane
DIEN	diethylenetriamine
DMA	dimethylacetamide
DME	1,2-dimethoxyethane
DMF	dimethylformamide
DMP	dimethyl phthalate
DMPHEN	2,9-dimethyl-1,10-phenanthroline
dnb	3,5-dinitrobenzoate
dnp	2,4-dinitrophenolate
dpa	2,6-pyridinedicarboxylate (dipicolinate)
dpp	1,3-diphenyl-1,3-propanedionate
DX	dioxane
edoda	ethylenedioxydiacetate
edta	ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate
EN	ethylenediamine
fl	fluorenyl anion
GLYCOL-2	ethylene glycol
GLYCOL-3	di(ethylene glycol)
GLYCOL-4	tri(ethylene glycol)
GLYCOL-5	tetra(ethylene glycol)
GLYME-2	1,2-dimethoxyethane (DME)
GLYME-5	tetraglyme
hfac	hexafluoroacetylacetonate
HKH	5-hydroxy-2-hydroxymethyl-γ-pyrone (kojic acid)
HKM	5-hydroxy-2-methoxymethyl-γ-pyrone
HMPA	hexamethylphosphoramide
HMT	hexamethylenetetramine
ida	iminodiacetate
L	a chelating organic anion
M$^+$	an alkali cation
M^{2+}	an alkaline earth cation
M^{n+}	a transition cation
M^{z+}	general abbreviation for M$^+$ and M^{2+}
MBL	*N*-methyl-γ-butyrolactam
MBPO	methylenebis(phosphine oxide)
MDA	*p*,*p*′-methylenedianiline
Me$_2$DB18C6	dimethyldibenzo-18-crown-6
Me$_2$SO	dimethyl sulfoxide
MKH	5-methoxy-2-hydroxymethyl-γ-pyrone
MKM	5-methoxy-2-methoxymethyl-γ-pyrone
MMM	a multidentate macromolecule
N2OC6	2,3-naphtho-20-crown-6
NMA	*N*-methylacetamide
NMF	*N*-methylformamide
NMP	*N*-methyl-2-pyrrolidone
NO$_2$-B18C6	4-nitrobenzo-18-crown-6
NPOE	nonylphenoxypoly(oxyethylene)ethanol
nta	nitrilotriacetate
oda	oxydiacetate
OMPA	octamethylpyrophosphoramide
onp	*o*-nitrophenolate
PC	propylene carbonate
pdc	4*H*-pyran-2,6-dicarboxylate
PDPO	phenacyldiphenylphosphine oxide
PEO	a poly(ethylene oxide)
PHEN	1,10-phenanthroline
pic	picrate (2,4,6-trinitrophenolate)
PKH	phenacylkojate (5-phenacyloxy-2-hydroxymethyl-γ-pyrone)
pnb	*p*-nitrobenzoate
prp	purpurate
sal	salicylate
salen	*N*,*N*′-ethylenebis(salicylideniminato)
TBP	tributyl phosphate
tda	thiodiacetate
TEA	triethanolamine
THF	tetrahydrofuran
THPO	trishydroxymethylphosphine oxide
TMAO	trimethylarsine oxide
tmcot	1,3,5,7-tetramethylcyclooctatetraene dianion
TMDB18C6$\overline{\text{F}}$	tetramethyldibenzo-18-crown-6 (isomer F)
TMDB18C6$\overline{\text{G}}$	tetramethyldibenzo-18-crown-6 (isomer G)
TMED	tetramethylethylenediamine
TMND	1,8-bis(dimethylamino)naphthalene
TMPD	tetramethyl-*o*-phenylenediamine
TMTEA	trimethoxytriethylamine
TOPO	tri-*n*-octylphosphine oxide
TPPO	triphenylphosphine oxide
TU	thiourea
X	an inorganic anion
●	represents the concerned cation in a figure
O	represents an oxygen atom in a figure
>O	represents a water molecule in a figure

II. Historical Background

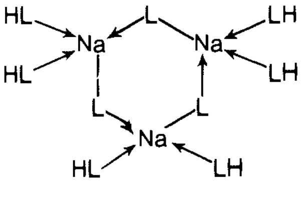
The first derivatives of M^{z+} with electrically neutral ligating molecules to be known were the "metal–ammonias" which were reported in 1830[48] and later.[49] Perhaps under the influence of Alfred Werner in the field of coordination chemistry, the M^{z+}–ammonia products were studied further,[50] understandably with the aim to discover auxiliary valency for M^{z+}. These compounds were synthesized and studied further under the names "ammonates" [51] and "metal-ammines".[52,53] Of these studies, those due to Biltz and co-workers[53] are informative wherein the stoichiometry of the products and the heats of their formation and decomposition have been described. It is these workers who precisely determined stoichiometries of M^{z+}–ammonia products and relative stabilities of the M^{z+}–NH_3 bond for various cations and formally used the term "coordination" for the bonding mode of a neutral ligand.

A parallel work on some organic derivatives of M^{z+} [$ML(HL)_n$ (n = 1 or 2) where HL is an organic acid and L its anion] was first carried out by Ettling[54] in 1840. He reported a rather less defined $Na(salicylaldehydate)(salicylaldehyde)(H_2O)_{1/2}$. In 1906, Hantzsch[55] reported its monohydrated analogue and similar compounds and called them "acid salts". This was followed among others by Bennett's report[56] on K(*p*-hydroxybenzoate)(*p*-hydroxybenzoic acid)(H_2O) in 1915, and by the report of Sidgwick and Plant[57] on M-indoxylspirocyclopentane (M = Li, Na, and K) derivatives, viz., $M(C_{12}H_{12}ON)(C_{12}H_{13}ON)$. Sidgwick and co-workers then carried out intensive work on the synthesis and properties of such compounds[58,59] and arrived at some conclusions on their chemistry and structure. In compounds such as Na(*o*-nitrophenolate)(salicylaldehyde) and Na(salicylaldehydate)(salicylaldehyde) they considered the cation to be quadrivalent and genuinely coordinated by L and HL *independently* in the fashion:

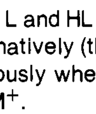


In the $ML(HL)_2$ type of products they considered the cation to be six-coordinated. These conclusions influenced some more contemporary workers. Brady and co-workers,[60,61] e.g., reported the ML(HL) species of M^+ with 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone.[61] Hodgson and Batty[62] reported the ML(HL$'$) type of species of Na or K salts of 2-nitroso-5-methoxyphenol and 3-chloro-2-nitroso-5-methoxyphenol with salicylaldehyde. These workers were also in tune with Sidgwick et al. in calling such products "coordination compounds".

Crawford[63] took a different viewpoint of the $ML(HL)_2$ type of products which, of course, he considered to be covalent compounds. He believed the compound Na(phenylacetate)(phenylacetic acid)$_2$ to be a polynuclear species wherein the anion acts as a charge neutralizer for one cation and a donor for the other cation and in which both the HL molecules coordinate to the cation independently.



Pfeiffer[64] suggested that L and HL could interact with M^+ independently and that, alternatively (though less likely), L could hold M^+ and HL simultaneously wherein, as shown below, HL makes no direct link with M^+.



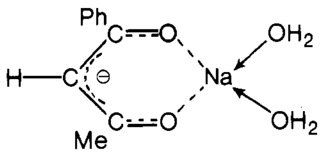
$$\begin{array}{l} L\cdots HL \\ | \\ M \end{array}$$

Detailed discussion on these systems (section III.B.2) will, however, reveal that the formulation of the type shown with some modification is, in fact, correct and that the formation of these compounds is more the chemistry of the L–HL system than of the M^+–HL system.[18]

Parallel information which started becoming available about the same time was on the stable solid solvates of M^{z+} with various organic solvents. Such solvates, of the type M(anion)(solvent)$_n$, were obtained by crystallization of a salt from the concerned solvent. Most such discoveries were accidental observations during solubility studies of the salts. The known solvates of this type include: $M^+(anion)(ROH)_n$[65–69] and $M^{2+}(anion)(ROH)_n$[66–68,70,71] (M^+ = Li, Na, or K; M^{2+} = Mg, Ca, or Sr; ROH is usually MeOH or EtOH or occasionally a higher alcohol), $M^+(anion)(Me_2CO)_n$[72,73] and $M^{2+}(anion)(Me_2CO)_n$[70,73] (M^+ = Li or Na; M^{2+} = Mg, Ca, or Sr), Mg(anion)(PhCHO)$_n$,[70] $Mg(I)_2(RCO_2R')_6$[70] (R = H or Me, and R$'$ = Me or a higher alkyl group), $Mg(halide)_2(Et_2O)_2$,[70,74] $Mg(I)_2(MeCN)_6$,[70] $Li(Cl)(pyridine)_2$,[75] $Mg(halide)_2(aniline)_6$,[70] and $Li(Cl)(quinoline)_2$.[76]

The stable $M(anion)(DX)_n$ (DX = dioxane) products[77,78] could even be obtained from the solutions of the salts in EtOH or Et_2O through solvent exchange with DX (!).

Of all the discoveries made before 1940, those due to Sidgwick and Brewer[58] with respect to the solubility characteristics of the metal β-diketonates carry a historical importance. They noted that the anhydrous Na(1-phenylbutane-1,3-dionato) salt behaved toluene-insoluble whereas its dihydrated form behaved toluene-soluble. The solubility of the dihydrated product in such a nonpolar solvent cannot be explained unless true coordination of the water molecules with Na and covalency in the Na–OH_2 bond are believed to exist. On these grounds the products can be formulated as



wherein the anion and the water molecules act as genuine ligands.

The solubilizing ability of ethereal solvents toward Grignard's reagents and related organometallic compounds was known since the beginning of the century,[79,80] and the synthesis of solvates like $MgBr_2{\cdot}Et_2O$ had also been carried out.[81] However, such observations, too, did not arouse the interest required in the present context.

During the organic reactions involving the use of alkali and alkaline earth hydroxides or salts, the formation of M^{z+}-derivative intermediates with electrically neutral reactants and the reaction intermediates has frequently been postulated (section V). However, such observations have almost been neglected in that neither the organic synthetic chemist attempted deliberate improvements on synthetic procedures through incorporation of appropriate coordinative reactions of M^{z+} nor the coordination chemist was tempted to investigate many more newer organic ligating species to study the coordination chemistry of M^{z+}.

Discrete important observations which illustrate the coordination of a neutral molecule with an s-block cation include: (i) the synthesis of $NaBr(acetamide)_2$ (1901),[82] (ii) synthesis of the crystalline $CaCl_2$(β-D-mannofuranose) (1929),[83] (iii) synthesis of defined M^+–PHEN (PHEN = 1,10-phenanthroline) complexes (1938),[84] (iv) synthesis of stable $MX(EN)_n$ (M^+ = Li or Na; X^- = I, Br, Cl, or ClO_4; and EN = ethylenediamine) and $MCl_2(EN)_n$ (M^{2+} = Ca, Sr, or Ba; and n = 4 or 6) complexes (1945),[85] and (v) change in the mutarotation of D-glucose–$CaCl_2$ mixture on dilution with water (1930).[86] Marullo and Lloyd (1966)[87] made a rather surprising observation in that *p,p'*-diamino-2,3-diphenylbutane (DDB), a seemingly monodentate amine, could precipitate salts like NaCl from water.

The real scientific advancement in the subject took place in 1967 when Pedersen at Du Pont (Delaware) discovered[88] that electrically neutral macrocyclic polyethers act as efficient ligands for M^{z+} (section IV.A). Lehn and co-workers (1969)[89] in France produced bicyclic macromolecules (section IV.C) which possess the ability of dissolving salts like $BaSO_4$ in water. The acyclic multidentates (section IV.D) popularized by Simon and co-workers in Switzerland from the late '60s have added significant information on the interactive behavior of M^{z+} in solution. The observation by Moore and Pressman[90] that valinomycin can act specifically toward alkali cations in mitochondria stimulated studies on M^{z+} using various antibiotics as ligands.

Information on M^{z+}–ligand systems in solution is due mainly to Smid for popularizing the use of spectroscopic and conductance measurements, to Izatt and Christensen for developing calorimetric methods, to Popov and Dye for popularizing M^{z+} nuclear magnetic resonance techniques, and Eigen for incorporating relaxation techniques. For the solid state, earlier X-ray crystallographic work on simple systems of M^{z+} may well be considered oriented to the standardization of the crystallographic techniques; specific work on this subject has been carried out mainly by Truter, Weiss, and Dunitz and Dobler.

III. Conventional Ligands

The ligands which have usually been studied in the coordination chemistry of transition cations are termed as conventional ligands. Since the text has been organized in view of the nature of the ligands, a complex of the type M(anion)(ligand)(solvent) could be treated at three different places. The details of the system have, however, been provided only at one place depending on whether the novelty lies in the discussion of the anion, the ligand, or the solvent.

A. Solvents as Ligands[91]

An interest in understanding the solvation–structural relationship of the solvents toward cationic species has led to the development of a vast field "ion–ion and ion–solvent interactions" on which several comprehensive treatments[92–96] have been published. Evaluation of solvation[97] has, however, more often been carried out for a series of solvents with a cation than for a solvent with a series of cations. This, unfortunately, is less useful in the present context. Despite this we shall endeavor to comment on observations which help to understand ligand action of the solvent where ligand action implies both solvation and coordination.

Several empirical approaches have been put forth to express M^{z+}–solvent interaction. The solvent polarity concept[98] which is based on dielectric constant (ϵ) values is one such approach. Gutmann's donor number concept[92,99] which is related to the thermodynamic observations on solvating abilities of solvents is receiving ever-increasing attention. In the following text we shall follow also a rather simple and expressive classification due to Kay et al.,[100] according to which there are four major classes of the polar solvents, viz., *acidic* solvents, for example, fluorinated alcohols, which do not coordinate with a cation but bond with an anion; *neutral* solvents, for example, acetone, which weakly coordinate with a cation; *basic* solvents, for example, *N,N'*-dimethylformamide (DMF), which strongly coordinate with a cation; and *hydrogen bonding* solvents, for example, water, which strongly coordinate with a cation and also bond with an anion.

In the published works[8,11,22a,35,38,92–96,98,100–105] ion–solvent as well as ion–ion interactions have been discussed extensively; we intend to be concerned also with the solvation of the ion pairs within the lattice and at the solid–solvent interface.

1. M^{z+}-Solvent Coordination in Solution

The solvents, especially in the course of dissolving ionic salts, MX, have to act as ligands, as electron donors for M^{z+}, and possibly as proton donors for X^{z-}. Since the hard[106] M^{z+} exhibit a pronounced affinity for the hard X^{z-}, ion–ion involvements play a more important role during M^{z+}–solvent interactions than is usually realized for transition cations. In solution, therefore, existence of contact ion pairs in addition to solvent-separated ion pairs[94,107] is obviously a more general phenomenon. The importance of ion–ion involvements is, however, greatly determined by the nature of the solvent so that, in general, ion–ion involvements decrease and ion–solvent interactions increase when for a given ion pair a neutral solvent is replaced by a basic one and the latter by a hydrogen bonding one; neutral solvents usually always fail to cause charge separation of an ion pair even at a fairly high solvent/salt ratio,[108] whereas in the case of the hydrogen bonding solvents, formation of the solvent-separated ion pairs is frequently possible even at low solvent/salt ratios.

It is being increasingly realized that M^{z+}–anion and M^{z+}–solvent competitions lead to results which are relatively difficult to predict. This is so because ion solvation is at least a function of charge density of M^{z+}, solvating ability of the solvent, nucleophilicity of the anion, and (in the case of the tight ion-pairs) the solvent/salt ratio. Nevertheless, the following general conclusions are noteworthy.

(a) For a given anion, solvation of a cation with a basic or a hydrogen-bonding solvent is in the order (cf. ref 109):

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$
$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$
$$M^{2+} > \text{similar-sized } M^+$$

At infinite dilution, where the effect of anion is negligible, solvation of even Cs is complete.[110]

(b) For a given anion–solvent system, M^{z+}–anion involvement is counteracted and M^{z+}–solvent interaction is increased as a cation of increasing charge density is involved; in most solvents Li and Na ions are less strongly paired than, for example, Cs with tetraphenylborate.[110]

(c) For a given M^{z+}–solvent system, solvation is hampered as nucleophilicity of the counteranion is increased; ^{133}Cs NMR studies show that in various solvents Cs is less strongly solvated when NCS or a halide is the anion but is more strongly coordinated with the solvent when the rather charge-delocalized NO_3, ClO_4, or Ph_4B is the counterion.[110]

(d) For a given M^{z+}–anion system, solvation is favored as a solvent of increasing donicity and/or ϵ value is involved; ^{133}Cs NMR studies show that solvation of $CsPh_4B$ increases and ion-pair formation constants (given in parentheses) decrease in the order: pyridine (3.7×10^2), acetonitrile (MeCN $\sim$ 40), acetone ($\sim$22), DMF ($\sim$0), and dimethyl sulfoxide (Me_2SO, $\sim$0).[110] The case of pyridine is unique in that it behaves contrary to expectations from Gutmann's donicity scale. It coordinates Cs[110] (and other M^+ [35,108]) most weakly despite the fact that its donicity is highest of all the five solvents.[92] This may in part be due to its low dielectric constant or more likely its moderately "soft" character.[111]

(e) M^{z+}–solvent interaction is favored as chelating ability is incorporated in the solvent through the presence of donor sites on two adjacent carbons and as the number of donor sites of the solvent increases.[112]

(f) The M^{z+}–solvent interaction is practically independent of the salt concentration for a weakly nucleophilic counteranion but is concentration-dependent when the cation–anion involvements dominate; ^{23}Na NMR chemical shifts for SCN, Br, or I (each of which forms a contact ion pair) are markedly concentration-dependent, but those for ClO_4 or Ph_4B (for which the Na^+X^- ion pair exists as a free-solvated or a solvent-separated ion pair) are concentration independent.[113]

(g) M^{z+} NMR studies indicate that of the various cations[110,113–117] the most respectable linear relationship between the chemical shift (and hence the solvent–cation interaction) and the donicity of the solvents is shown by Na.[113–115]

Hydration energies (ΔG) of M^{z+} ions do not bear a linear relationship with the ionic size (M_r^{z+}) as shown in Figure 1. If the value for Na (of the M^+ ions) is considered to conform to the

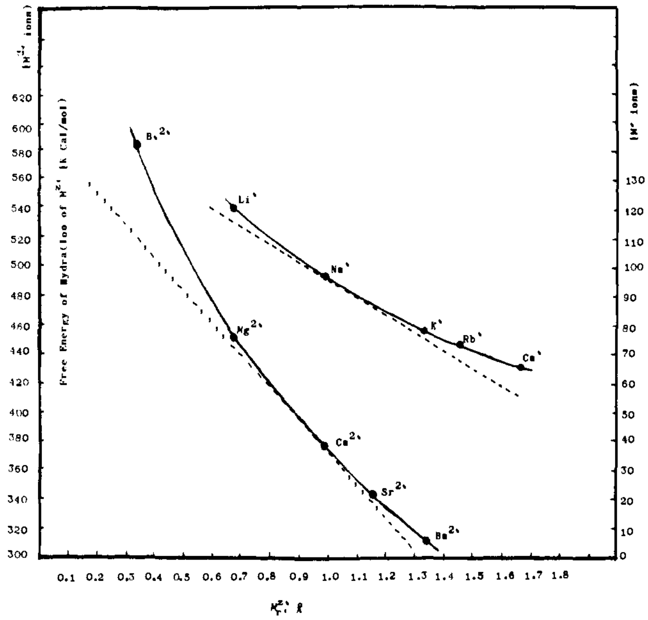


Figure 1. Ionic size vs. hydration energy of the ion plots for M^{z+} ions (data from D. A. Johnson, "Some Thermodynamic Aspects of Inorganic Chemistry", Cambridge University Press, London, 1968, pp 53 and 103).

ΔG–$M_r{}^{z+}$ relationship, then deviations are noted for Li and increasingly for K, Rb, and Cs. Similarly, if the ΔG values for Ca and Sr are considered to conform to this relationship, then deviations are, in particular, noted for Mg and Be in this order. Superimposed results for the two series of cations show that the deviation is particularly strong for the high charge density Li, Mg, and Be, and for the low charge density K, Rb, and Cs in these orders. Such a strong solvation for the high charge density cations is apparently due to the ability of these cations to cause an extensive polarization of the solvent donor atoms, and that for the low charge density cations due to polarization of the cation by the solvent. In the case of the medium charge density Na, Sr, and Ca, hydration is not pronounced in this way because each process is relatively ineffective. During discussion of M^{z+} complexes with other neutral ligands, a similar discrimination will be pointed out.

2. *M^{z+}-Solvent Coordination in Solid State*

Salts of particularly the small cations possess the ability to derive various types of solvents in the crystal lattice to produce what may be called solid solvates.[118] Formation of a solid solvate should basically be determined by the nature of the solvent and to some extent also by the nature of the lattice packing of the salt. The hydrogen-bonding solvents, which can interact with each ion of a crystallizing salt, have chemical reasons to appear in the lattice under most conditions as evidenced by the hydration of various salts, for example. The basic solvents, which also possess a distinct coordinating ability, may be visualized to form solid solvates in a fashion such as the transition cations produce coordination compounds like the metal ammines, although, in the case of M^{z+}-solvent systems the charge neutralizing anion may frequently tend to remain in the first sphere of attraction of the cation. Once "crystallization" of a hydrogen-bonding or a basic solvent becomes possible, it behaves fairly stable in the lattice. Incorporation of a neutral solvent in the lattice is also possible which may not be a simple encagement but, at least in part, because of a definite M^{z+}-solvent interaction. However, such derivatives are usually unstable due to a facilitated solvent/water exchange.

The nature of the counteranion is important in determining the nature of the solid solvate, that is, whether the cation is exclusively within the environment of the solvent molecules (*solvent complex*) or is within that of the counteranion(s) and the solvent molecule(s) (*solvated ion pair*).[119] The counteranion also influences the solvent/M^{z+} ratio in the solid product; the composition of the LiBr and LiI solvates with DX are[120] LiBr(DX) and $LiI(DX)_2$, for example, which may be attributed to the nucleophilicity difference between the halide ions. The basic and especially the neutral solvents form solid solvates usually when the counterion of the solvating cation is charge delocalized (self stabilized), such as ClO_4, or is weakly nucleophilic, such as I, as evidenced by the statistical observations on such compounds in Table II. In the case of hydrogen-bonding (hydroxylic) solvents, a highly nucleophilic anion may also not be deleterious because such an anion can force hydrogen bonding on the solvent proton, and the solvent in turn becomes a stronger ligand for the cation; coordination of the solvent with the cation results in the polarization of its hydroxyl proton, and bonding of the anion with the proton enhances the basicity of the donor site which makes the solvent display a so-called "double action".

a. Solvent Complexes

There are some heavily hydrated salts, especially the inorganic salts of small M^{z+}, which are charge separated and contain the cation coordinated only with the solvent molecules; the anion in the case of protic solvent derivatives is usually held on the polarized hydrogen of the solvent. $Na_2SO_4 \cdot 10H_2O$ is one of the commonly known solvent complexes wherein the cation is within the $Na(OH_2)_6$ octahedron (Na–O, 2.37–2.47 Å).[121] Except for the easily lost molecule of water in $MgSO_4 \cdot 7H_2O$, all the rest of the water molecules surround the cation octahedrally while $SO_4{}^{2-}$ ion is held at the polarized hydrogens of the coordinated water molecules.[122] The $CaX_2 \cdot 6H_2O$ ($X^- =$ Cl or Br) salts[123] contain a nine-coordinated cation (Ca–O, 2.45–2.60 Å) wherein the halide, separated from the cation, is bonded with the water protons. Various other examples of the salts can be found in Table II which can be formulated as $[M(OH_2)_n]^{z+}X^{z-}$. $CaKAsO_4 \cdot 8H_2O$ is a novel system[124] which contains two different spherical cations, each of which is within the exclusive water environment.

Some hydrated M^+-nucleotide salts fall in this group and are interesting in the sense that M^+ coordinates to only the water molecules despite the presence of a highly nucleophilic phosphate moiety and the chelating sugar moiety. Such salts are represented by Na(deoxyadenosine 5'-phosphate)$(H_2O)_6$[125] and Na(cyclic guanosine 3',5'-monophosphate)$(H_2O)_4$,[126] each of which contains an octahedrally hydrated cation. Hexaaquomagnesium bis(8-anilino-1-naphthalenesulfonate) hexahydrate, $[Mg(H_2O)_6][C_{10}H_8NSO_3]_2 \cdot 6H_2O$, is such a salt in which each anion is associated with three water molecules and each cation is octahedrally coordinated with six water molecules.[127]

In the complex $Mg_2(edta)(H_2O)_9$[128] one cation is within the anionic environment, $[Mg(edta)H_2O]^{2-}$, in which six of the seven contacts are made by edta but the second cation is within an octahedral environment of only the water molecules. Under most conditions $M(edta)(H_2O)_n$ systems crystallize as solvated ion pairs[129–131] (Table II). From an acidic solution, however, a charge-separated solvent complex, $[Mg(H_2O)_6](H_2edta)$, gets crystallized.[132] This has been attributed[133] to protonation of the edta nitrogens. We, however, believe, that this criterion alone cannot be used, for on acidification the solution equilibrium should also shift toward protonation of carboxylate groups which is a more primary requirement for making the multidentate indifferent to Mg. The system ultimately comes out to be charge separated because (i) Mg is itself strongly hydrating, and (ii) the ligands which can be stabilized by interaction with protonized hydrogen atoms leave Mg octahedrally coordinated with water; the solvent complex $[Mg(H_2O)_6](12\text{-crown-}4)Cl_2$[134] is also formed for these reasons despite the crown ether being a potential ligand.

TABLE II. **Crystallographic Description of Solid M^{z+} Complexes**

compound	bonding features of the cation bond, distance (Å)	coord no. (stereochem)	remarks, if any	ref
		Solvent Complexes		
$Na_2SO_4 \cdot 10H_2O$	Na–OH_2 av 2.43	6 (octahedral)	Octahedra share edges and involve 8 of the water molecules while the other two exist loose	121
$MgSO_4 \cdot 7H_2O$	Mg–OH_2 av 2.06	6 (approx octahedral)	Seventh water molecule exists loose	122
$CaCl_2 \cdot 6H_2O$	Ca–OH_2 2.45–2.59	9		123
$CaBr_2 \cdot 6H_2O$	Ca–OH_2 2.47–2.62	9		123
$LiClO_4 \cdot 3H_2O$	Li–OH_2 av 2.13	6 (octahedral)	Water molecules bridge the cations	*a*
$Mg(NO_3)_2 \cdot 6H_2O$	Mg–OH_2 av 2.06	6 (octahedral)		*b*
$MgSO_3 \cdot 6H_2O$	Mg–OH_2 2.06–2.08	6 (distorted octahedron)		*c*
$MgS_2O_3 \cdot 6H_2O$	Mg–OH_2 2.04–2.12	6 (octahedral)		*d*
$Mg(C_6H_4O_2N)_2 \cdot 6H_2O$	Mg–OH_2 2.02–2.08	6 (octahedral)	$C_6H_4O_2N$ = *p*-nitrosophenolate	*e*
$MgHAsO_4 \cdot 7H_2O$	Mg–OH_2 2.06–2.09	6 (octahedral)	There are two crystallographically different cations	*f*
$Na_2HAsO_4 \cdot 7H_2O$	Na–OH_2 2.35–2.48	6 (octahedral)	There are two crystallographically different cations	*g*
$CaKAsO_4 \cdot 8H_2O$	Ca–OH_2 2.46–2.49 K–OH_2 2.76–2.96	8 (square antiprism) 8 (square antiprism)		124
Na(deoxyadenosine 5′-phosphate)·$6H_2O$	Na–OH_2 2.37–2.45	6 (nearly octahedral)		125
Na(cyclic guanosine 3′,5′-monophosphate)·$4H_2O$	Na–OH_2 2.32–2.68	6 (octahedral)	Adjacent octahedra share edges	126
Mg(8-anilino-1-naphthalenesulfonate)·$6H_2O$	Mg–OH_2 av 2.06	6 (octahedral)		127
Mg_2edta·$9H_2O$	Mg–OH_2 av 2.06	6 (octahedral)	Description refers to only one type of cation	128
$[Mg(OH_2)_6](H_2edta)$	Mg–OH_2 2.05–2.09	6 (octahedral)		132
$[Mg(OH_2)_6](12C4)Cl_2$	Mg–OH_2 2.05–2.08	6 (octahedral)		134
$[Mg(OH_2)_6](Cr_2O_7)(HMT)_2$	Mg–OH_2 av 2.10	6 (octahedral)		135
$[Ca(OH_2)_7](Cr_2O_7)(HMT)_2$	Ca–OH_2 2.33–2.43	7		136
$[Ca(OH_2)_6](HMT)_2 \cdot Br_2 \cdot 4H_2O$	Ca–OH_2 av 2.33	6 (octahedral)		137
NaI·3MeOH	Na–O av 2.47	6 (octahedral)	Columns of Na·3MeOH are bonded through iodide	138
$MgBr_2 \cdot$6MeOH	Mg–O av 2.07	6 (octahedral)	Mg–Br, 6.05 Å	139
$CaBr_2 \cdot$6MeOH	Ca–O av 2.31	6 (semiregular octahedron)	Ca–Br, 5.10 Å	139
NaI·3DMF	Na–O av 2.40	6 (in between trigonal prism and octahedral)	H–I bonds also participate in holding the structure	141
$NaClO_4 \cdot$3DX	Na–O av 2.43	6 (elongated octahedral)	Each DX coordinates two cations while ClO_4 is nonbonding	142
NaI·$3Me_2CO$	Na–O av 2.46	6 (octahedral)	Iodide is exclusively surrounded by methyl hydrogens	143
$[Mg(OH_2)_2(THF)_4]Br_2$	Mg–OH_2 av 2.04 Mg–O(THF) 2.12–2.16	6 (octahedral)	Mg–Br, 4.65 Å	145
		Solvated Ion Pairs		
$MgBr_2 \cdot$2THF	Mg–O av 2.12 Mg–Br av 2.63 Mg–Br av 2.80 (bridge)	6 (distorted octahedron)	Octahedron is formed through two bonds of each type	145
$MgBr_2 \cdot$4THF	Mg–O av 2.16 Mg–Br av 2.62	6 (octahedral)		146
$MgBr_2 \cdot 2Et_2O$	Mg(1)–O 2.09, 2.14 Mg(1)–Br 2.74, 3.02 Mg(2)–O 2.13, 2.16 Mg(2)–Br 3.18, 3.32	4 (irregular tetrahedron)		762
LiCl·DX	Li–O 1.88, 1.95 Li–Cl 2.39, 2.42	4 (irregular tetrahedron)	Each Cl^- and DX is joined to two Li^+ and each Li^+ is coordinated to two DX	147
$MgBr_2 \cdot$6pyridine	Mg–N 2.17–2.28 Mg–Br av 2.77	6 (octahedral)	Two pyridine molecules are nonbonding	148
LiCl·pyridine		4 (tetrahedral)	Tetrahedron is formed through three Cl ions and a pyridine nitrogen	149
LiCl·2pyridine·H_2O	Li–O 1.94 Li–N 2.05, 2.06 Li–Cl 2.33	4 (tetrahedral)		150
$Mg(acac)_2 \cdot 2H_2O$	Mg–OH_2 av 2.15 Mg–O(acac) 2.03–2.04	6 (octahedral)		151
$[Ca(pic)_2(H_2O)_3]$B15C5	Ca–OH_2 2.23–2.42 Ca–O^- 2.28, 2.32 Ca–O(NO_2) 2.46, 2.61	7 (distorted pentagonal bipyramid)	B15C5 is not Ca-coordinated	152

TABLE II (*Continued*)

compound	bonding features of the cation		remarks, if any	ref
	bond, distance (Å)	coord no. (stereochem)		
$Mg(HCOO)_2 \cdot 2H_2O$	Mg(1)–O 2.06–2.11 Mg(2)–O 2.05–2.12	6 (octahedral)	The Mg(1) is coordinated to six oxygens belonging to formate ions only while Mg(2) involves two formate and four water oxygens	*h*
$Sr(HCOO)_2 \cdot 2H_2O$	$Sr-OH_2$ 2.64–2.67 $Sr-O^-$ 2.52–2.67	8	The polyhedron is formed through 3 water and 5 formate oxygens	*i*
$LiHCOO \cdot H_2O$	$Li-OH_2$ 1.97 $Li-O^-$ 1.92–1.95	4 (tetrahedral)	The tetrahedron is formed through one water and 3 formate oxygens	*j*
$NaMeCOO \cdot 3H_2O$	Na–O 2.35–2.56	6 (distorted octahedron)	The octahedron is constituted by 5 water and one acetate oxygens	*k*
$Ca(MeCOO)(MeCOS) \cdot 3H_2O$	$Ca-OH_2$ 2.34–2.41 $Ca-O^-$ 2.30–2.55	7 (distorted pentagonal bipyramid)	Three of the coordinating oxygens are anionic	*l*
$Sr(MeCOO)(MeCOS) \cdot 4H_2O$	$Sr-OH_2$ 2.62–2.75 $Sr-O^-$ 2.50–2.72 $Sr-S^-$ 3.22	9 (very distorted trigonal prism)	Three of the 9 contacts are offered by oxygens of three water molecules	*m*
$Ba(MeCOS)_2 \cdot 3H_2O$	$Ba-OH_2$ 2.71–2.93 $Ba-O^-$ 2.78–2.87 $Ba-S^-$ 3.27, 3.31	9	Four water oxygens, three anionic oxygens, and two anionic sulfurs complete the polyhedron	*n*
$Ca(IO_3)_2 \cdot 6H_2O$	Ca–O 2.44–2.52	8 (distorted Archimedean antiprism)	Each water oxygen coordinates	*o*
$Sr(IO_3)_2 \cdot H_2O$	$Sr-OH_2$ 2.53 $Sr-O^-$ av 2.61	9 (tricapped trigonal prism)	Eight anionic and the water oxygens constitute the polyhedron	*p*
$Li_2SO_4 \cdot H_2O$	Li–O 1.91–2.00	4 (tetrahedral)	Water coordinates with only one type of cation	*q*
$MgSO_4 \cdot 5H_2O$	Mg–O av 2.06	6 (octahedral)	One water molecule is nonbonding	*r*
$BaS_2O_3 \cdot H_2O$	$Ba-OH_2$ 2.81 $Ba-O^-$ 2.77–3.43 Ba–S 3.35, 3.42	11	One water oxygen, 8 anionic oxygens, and two sulfur atoms constitute the polyhedron	s
$CaCl_2 \cdot 4H_2O$	$Ca-OH_2$ 2.35–2.47 Ca–Cl 2.84, 2.85	6 (trigonal prism)		*t*
$CaBr_2 \cdot 4MeOH$	Ca–O av 2.36 Ca–Br av 2.89	6 (distorted octahedron)	The structure of $CaBr_2 \cdot 4EtOH$ is very much similar (Ca–O av 2.365 and Ca–Br av 2.87 Å)	154
$CaCl_2 \cdot 2MeOH$	Ca–O av 2.35 Ca–Cl av 2.75	6 (octahedral)	Four Cl ions and two alcoholic oxygens make the octahedron	*u*
$Ca(NO_3)_2 \cdot 4MeOH$	Ca–O 2.36–2.38 $Ca-O^-$ 2.45–2.59	8 (distorted dodecahedron)	NO_3 ions act as bidentate	*v*
$PhMgBr \cdot 2Et_2O$	Mg–O 2.01, 2.06 Mg–Br 2.44 Mg–C 2.2	4 (tetrahedral)		156
$EtMgBr \cdot 2Et_2O$	Mg–O 2.03, 2.05 Mg–Br 2.48 Mg–C 2.15	4 (tetrahedral)		157
$MeMgBr \cdot 3THF$	Mg–O 2.04–2.28 Mg–Br 2.41, 2.53 (Me)	5 (square pyramid)		158
		Acid Anion Salts—$ML(HL)_n$ Type Compounds		
K(phenylacetate, phenylacetic acid)	K–O 2.72–2.86	6 (octahedral)		*w*
K(*p*-hydroxybenzoate, *p*-hydroxybenzoic acid)$\cdot H_2O$	K–O 2.71–2.85	6 (distorted octahedron)	Water molecule is nonbonding; octahedron is formed with oxygens from six different carboxylate groups	*x*
K(formate, formic acid)	K–O 2.77–3.06	8 (distorted square antiprism)		*y*
K(isonitrosoacetophenonate, isonitrosoacetophenone)	K–O 2.72–2.98 K–N 2.85, 2.91	7 (no recognizable geometry)	Five oxygens and two nitrogens constitute the polyhedron	*z*
K(*o*-nitrophenolate, isonitrosoacetophenone)	K–O 2.73–3.13 K–N 2.84	8 (no recognizable geometry)		*aa*
K(3-hydroxybiuret anion, 3-hydroxybiuret)	K–O 2.67–3.03	8		*bb*
Rb(glycollate, glycollic acid)	Rb–O 2.88–3.07	8		cc
Rb(acetylsalicylate, acetylsalicylic acid)	Rb–O 2.84–2.90	6 (distorted octahedron)		*dd*
Na(acetate, acetic acid)	Na–O 2.40–2.44	6 (trigonal prism)	Lattice carries two types of cations; geometry is less regular for one of them	*ee*
$K(IO_3,HIO_3)$	K–O 2.67–3.04	8 (distorted square antiprism)		180

TABLE II (*Continued*)

compound	bonding features of the cation bond, distance (Å)	coord no. (stereochem)	remarks, if any	ref
		β-Diketonate Complexes		
Li(2,4-pentanedionato)	Li–O av 1.93 Li–O av 1.95	4 (square planar and tetrahedral)	Longer bonds are due to bridging oxygens which form a tetrahedron around Li	172
Na(1-phenylbutane-1,3-dionato)·GLYCOL-2	Na–O$^-$ 2.29, 2.34 Na–O$^-$ (bridge) 2.36 Na–O (glycol) 2.32, 2.33	5 (tetragonal pyramid)		173
Sr(1,3-diphenyl-1,3-propanedionato)$_2$·$\frac{1}{2}$Me$_2$CO	Sr–O$^-$ av 2.44 Sr–O (bridge) av 2.55 Sr–O (Me$_2$CO) 2.60	6 and 7	Unique point about this complex is that it derives acetone even when crystallized from excess EtOH	174
Mg(1,3-diphenyl-1,3-propanedionato)$_2$·2DMF	Mg–O$^-$ av 2.06 Mg–O(DMF) av 2.10	6 (octahedral)	Complex is monomeric	188
Ca(1,3-diphenyl-1,3-propanedionato)$_2$·$\frac{1}{2}$EtOH	Ca–O av 2.37	6 and 7	This complex could be crystallized only from EtOH	189
Rb$_2$[Na(hfac)$_3$]	Na–O$^-$ 2.20–2.47 Rb–O$^-$ 2.86–3.64 Rb–F 2.80–3.35	6 (trigonal prism)		191b
(TMNDH$^+$)[Mg(hfac)$_3^-$]	Mg–O av 2.06	6 (octahedral)		193
		M^{z+}-Purpurate Complexes		
[Li(prp)·H$_2$O]·H$_2$O	Li–O(prp) 1.95–2.14 Li–N(prp) 2.13 Li–OH$_2$ 2.30	5 (square pyramidal)	Structure is constituted of polymeric chains	194
K(prp)·3H$_2$O	K–O 2.79–2.92 K–N 2.99			195
Sr$_2$(prp)$_4$·15H$_2$O	Sr–O(prp) 2.56–3.18 Sr–OH$_2$ 2.61–2.75 Sr–N 2.69, 2.75	9 (no recognizable geometry)		196
[Ca(prp)$_2$(H$_2$O)$_2$]·2H$_2$O	Ca–O(prp) 2.40–2.60 Ca–OH$_2$ 2.31, 2.43 Ca–N 2.56, 2.63	8 (in between square antiprism and hexagonal bipyramid)		197
[Ca(prp)·3H$_2$O](NO$_3$)·2H$_2$O	Ca–O(prp) 2.36–2.57 Ca–OH$_2$ 2.37–2.46 Ca–N 2.60	8 (dodecahedron)		198
		π-Carbanion Complexes		
Li(benzyl)(triethylenediamine)	Li–C$^-$ 2.21 Li–C 2.39, 2.59 Li–N 2.09, 2.11	5 (no recognizable geometry)		203
Li(fl)(quinuclidine)$_2$	Li–C 2.33–2.79 Li–N 2.02, 2.04	5 (no recognizable geometry)		207
Li$_2$(naphthalenide)·2TMED	Li–C 2.26–2.33 Li–N 2.11		Although Li makes 8 contacts it should not be literally taken as coordination number	208
Li$_2$(anthracenide)·2TMED	Li(1)–C 2.33–2.58 Li(1)–N 2.07, 2.10 Li(2)–C 2.27–2.67 Li(2)–N 2.11, 2.12		Each Li makes 8 contacts including 2 with the chelating TMED	209
Li(triphenylmethyl)·TMED	Li–C$^-$ 2.23 Li–C 2.45–2.54 Li–N 2.06, 2.09		The cation makes 6 contacts including 2 with the chelating TMED	210
Li(indenyl)·TMED	Li–C 2.28–2.38 Li–N 2.10, 2.11		The cation makes 7 contacts including 2 with the chelating TMED	211
Mg(indenyl)$_2$	Mg(1)–C(σ) 2.26, 2.32 Mg(1)–C(π) 2.31–2.54 Mg(2)–C(π) 2.26–2.60		Mg(1) makes 7 and Mg(2) 9 contacts	212
Li$_2$(hexatriene dianion)·2TMED	Li–C 2.21–2.40 Li–N av 2.11		Each Li makes 6 contacts including 2 with the chelating TMED	213
Li(7b*H*-indeno[1,2,3-*jk*]fluorenide) (dimeric)	Li–C 2.34–2.45		Each Li makes 12 contacts	215
Na$_2$(tetramethylbis-1,4-dihydro-1,4-naphthylenedialuminate)·2THF	Na–C 2.87–2.96 Na–O av 2.34		Each Na makes 10 contacts including with the 2 monodentate THF	216
		M^{z+}-Multinegative Anion Complexes		
Ca(malonate)·2H$_2$O	Ca–O av 2.39 av 2.53	8 (distorted square antiprism)	Six carboxylate and two water oxygens constitute the polyhedron and the bonds fall in two groups of length	*ff*
	Ca–O 2.38–2.56	8 (bicapped trigonal prism)	This structural redetermination appears more authentic. This publication makes no mention of the preceding one despite a publication gap of 6 months	*gg*

TABLE II (*Continued*)

	bonding features of the cation			
compound	bond, distance (Å)	coord no. (stereochem)	remarks, if any	ref
Sr(malonate)	Sr–O 2.51–2.80	9 (tricapped trigonal prism)		*ff*
Li_2(maleate)·$2H_2O$	Li(1)–O 1.90–2.01 Li(2)–O 1.96–2.02	4 (approx tetrahedron)	One water and three anionic oxygens complete the tetrahedron	*hh*
Na_2(maleate)·H_2O	Na(1)–O^- 2.33–2.48 Na(1)–OH_2 2.35 Na(2)–O^- 2.33–2.46 Na(2)–OH_2 2.44	5 (distorted square pyramid)		*ii*
Ca(fumarate)·$3H_2O$	Ca–O^- 2.29–2.59 Ca–OH_2 2.34–2.61	8 (no recognizable geometry)	Water molecules make 4 contacts	*jj*
Li_2(succinate)	Li–O^- 1.94–1.96	4 (distorted tetrahedron)		*kk*
Ca(hydrogen citrate)·$3H_2O$	Ca–O 2.37–2.49	6 (octahedral)	Water molecules make 2 contacts	*ll*
Ca(dpa)·$3H_2O$	Ca–O 2.37–2.57 Ca–N 2.49	8 (pentagonal bipyramid)	Water molecules make 4 contacts	217
Sr(dpa)·$4H_2O$	Sr–O^- 2.59, 2.64 Sr–N 2.64 Sr–OH_2 2.70, 2.73	9 (monocapped square antiprism)		218
LiHoda	Li–O 2.03–2.12	5 (distorted trigonal bipyramid)		220
NaHoda	Na–O 2.38–2.77	7 (pentagonal bipyramid)		221
KHoda	K–O 2.69–2.93	7 (pentagonal bipyramid)	These are neutron diffraction results; previous X-ray results[221] show K–O range 2.70–2.92 Å	222
RbHoda	Rb–O 2.93–3.09	6 (distorted octahedron)	In all the cation makes 8 contacts; the additional two contacts are with oxygens lying outside two adjacent triangular faces of the octahedron (Rb–O 3.18 Å). Analogous Cs salt is isostructural	222
RbHtda	Rb–O 2.91–2.95	6 (distorted octahedron)	As in KHtda (described next), S atom is noncoordinating (3.63 Å)	224
KHtda	K–O 2.79–2.86	6 (distorted octahedron)		224
Rb(Hida)(H_2ida)	Rb–O 2.99–3.20	8 (no recognizable geometry)	An additional ninth bond (Rb–O 3.53 Å) is rather long while each NH is noncoordinating. Analogous Cs product is isostructural	225
Ca(edoda)·$3H_2O$ (dimeric)	Ca–O 2.38–2.64	8 (approx dodecahedron)	Each water molecule is coordinating; bond lengths for the two Ca–O(ethereal) contacts are markedly different (2.43 and 2.64 Å)	226
Ca(oda)·$6H_2O$	Ca–O 2.38–2.55	8 (no recognizable geometry)	One water molecule is nonbonding and, like one of the Ca–O(ethereal) bonds in the preceding complex, Ca–O(ethereal) bond is shorter (2.43 Å) than either of the carboxylate bonds	227
Na_3(nta)·H_2O	Na(1)–O 2.28–2.67 Na(2)–O 2.33–2.54 Na(3)–O 2.29–2.65 Na(1)–N 2.45 Na(2)–N 2.51	6 (distorted octahedron)	Na(3) is not coordinated with nitrogen	228
Ca(H^+nta)·$2H_2O$	Ca–O 2.32–2.56	7 (pentagonal bipyramid)	The ligand is protonated at the nitrogen atom and a hydrogen of a coordinated water molecule is bonded to a nonbonded carboxylate oxygen	229
Mg[Mg(edta)·H_2O]·$8H_2O$	Mg–O^- 2.03–2.34 Mg–OH_2 2.06 Mg–N av 2.40	7 (distorted pentagonal bipyramid)	The description of coordination about the second type of cation has already been provided in this table under "Solvent Complexes"	128
Na_2[Mg(edta)·H_2O]·$5H_2O$	Mg–O^- 2.08–2.27 Mg–N av 2.38 Mg–OH_2 2.06	7 (in between pentagonal bipyramid and monocapped trigonal prism)		129
	Na–O^- 2.33–2.53 Na–OH_2 2.26–2.73	6 (very irregular octahedron)	Of the six contacts, Na makes three contacts each with water and anionic oxygens	
Rb_2(H_2edta)·$2H_2O$	Rb(1)–O^- 2.69–2.90 Rb(1)–OH_2 2.88, 3.07 Rb(2)–O^- 2.79–3.06	6 (distorted octahedron)	Rb(2) makes no contact with any water oxygen	131
Ca[Fe(dcta)·H_2O]$_2$·$8H_2O$	Ca–O^- av 2.42 Ca–OH_2 2.38–2.42	7 (irregular polyhedron)	Polyhedron is formed by two anionic and five water oxygens	231

TABLE II (*Continued*)

compound	bonding features of the cation		remarks, if any	ref
	bond, distance (Å)	coord no. (stereochem)		
		Sugar Anion and Anionized Sugar Complexes		
Ca(D-arabonate)$_2$·5H$_2$O	Ca–O 2.44–2.52	8 (square antiprism)	Only two water molecules coordinate	247
Sr(D-arabonate)$_2$·5H$_2$O	Sr–O 2.58–2.68	8 (distorted Archimedean antiprism)		247
K(D-gluconate)·H$_2$O: form A	K–O 2.61–3.24	8 (square antiprism)	Neutron diffraction studies	248
form B	K–O 2.68–3.00	8 (irregular polyhedron)	There is a ninth longer (3.34 Å) contact	
Ca(5-keto-D-gluconate)$_2$·2H$_2$O	Ca–O 2.39–2.47	8 (square antiprism)		249
Ca(2-keto-D-gluconate)$_2$·3H$_2$O	Ca–O 2.34–2.73	9 (irregular polyhedron)	The polyhedron is constituted by three carboxylic, one ethereal, four hydroxylic, and one water oxygens	250
Ca(Br)(α-D-glucuronate)·3H$_2$O	Ca–O 2.38–2.57	8 (square antiprism)	Only two water molecules coordinate	251
CaNa(α-D-galacturonate)$_3$·6H$_2$O	Ca–O 2.41–2.82	9 (tricapped trigonal prism)	The polyhedron is constituted by oxygens from three sugar anions, and three water molecules	252
	Na–O 2.39–2.48	6 (distorted octahedron)		
	Ca–O 2.40–2.83	9 (tricapped trigonal prism)	Ca-O distances fall in three groups: av 2.40, 2.42, and 2.83 Å for each group. Although, this redetermination was published after the preceding one, preliminary communication of the structure appeared earlier (ref *mm*)	253
	Na–O 2.36–2.50	6 (distorted octahedron)		
SrNa(α-D-galacturonate)$_3$·6H$_2$O	Sr–O 2.52–2.87	9 (tricapped trigonal prism)	The bonding modes of the two cations are fairly similar to those in the preceding complex	252
	Na–O 2.37–2.53	6 (distorted octahedron)		
Sr[(4-*o*-4-deoxy-β-L-*threo*-hex-4-enosyl)α-D-galacturonate]·4.5H$_2$O	Sr–O 2.48–2.79	8 (distorted square antiprism)	The polyhedron is formed through three water and five carbohydrate oxygens	254
K(D-glucarate)	K–O 2.43–3.32	8 (distorted cubic prism)	The polyhedron is formed through four carboxylic and four hydroxyl oxygens	241
Ca(ascorbate)$_2$·2H$_2$O	Ca–O 2.41–2.53	8 (slightly distorted square antiprism)		256
	Ca–O 2.41–2.52	8 (distorted square antiprism)	This and the preceding determinations were published simultaneously	257
Na(ascorbate)	Na–O 2.42–2.72	6 (distorted octahedron)		258
Na(D-isoascorbate)·H$_2$O	Na–O 2.30–2.39	6 (distorted octahedron)		259
Ba(2-*o*-sulfonato-L-ascorbate)·2H$_2$O	Ba–O 2.76–3.06	10 (irregular)	Three water molecules and three sulfonatoascorbate anions participate in coordination	260
Ca(α-D-glucoisosaccharate)$_2$	Ca–O 2.38–2.51	8 (square antiprism)		261
Ca(Br)(lactobionate)·4H$_2$O	Ca–O 2.37–2.52	8 (distorted square antiprism)	The cation is coordinated to three water molecules and to the gluconate moieties of the carbohydrate	262
Na$_3$(6-phospho-D-gluconate)·2H$_2$O	Na–O 2.28–2.49	4 (distorted tetrahedron) 5 (distorted tetragonal pyramid) 6 (distorted octahedron)	There are three crystallographically different cations and, interestingly, each displays a unique bonding mode while maintaining a rather limited bond length range	*nn*
Ba(α-ribose 5-phosphate)·5H$_2$O	Ba–O 2.67–3.80	12 (distorted icosahedron)		264
Ca(thymidylate)·6H$_2$O	Ca–O 2.29–2.69	7 (undefined geometry)	Three water and four phosphate oxygens complete the polyhedron	266
Ba(uridine 5′-phosphate)(H$_2$O)$_n$	Ba–O 2.70–3.00	8 (distorted square Archimedean antiprism)	Two more rather long Ba–O (3.3 Å) bonds exist which extend out from the triangular faces	267
Li(NAD$^+$)(dimer)	Li–O 1.86–1.92 Li–N 2.13	4 (tetrahedral)		268
		Complexes with Electrically Neutral Ligands		
K$_2$(cot)(GLYME-3)	K(1)–C av 2.98 K(2)–C av 3.05 K(2)–O 2.82–3.25		K(1) coordinates to only cot rings. K(2) is on one side coordinated by four oxygens while shielded on the other side by cot	285
Rb$_2$(cot)(GLYME-3)	Rb(2)–O 2.90–3.20		Crystal structure is isomorphous with that of the preceding complex	286
K(biphenyl)(GLYME-5)$_2$	K–O 2.82–3.05	10 (irregular geometry)		287
Rb(biphenyl)(GLYME-5)$_2$	Rb–O 2.93–3.15	10 (irregular geometry)		288
K$_2$(tmcot)(GLYME-3)$_2$	K–O av 2.83 K–C av 3.00		Compound exists as a trimer	289

TABLE II (*Continued*)

compound	bonding features of the cation		remarks, if any	ref
	bond, distance (Å)	coord no. (stereochem)		
K[Ce(cot)$_2$](GLYME-3)$_2$	K-O 2.74–2.79 K-C av 3.16		Potassium on one side is complexed with GLYME-3 and on the other by one of the two cot rings	290
Li(dimesitylborohydride)-(GLYME-2)$_2$	Li-O 2.00–2.35 Li-H av 2.06	6 (undefined)		291
Mg(antipyrine)$_6$(ClO$_4$)$_2$	Mg-O av 2.06	6 (octahedral)		299
[Li(TPPO)$_4$]I·TPPO	Li-O av 1.97	4 (tetrahedral)	Li$^+$-I$^-$ distance not less than 8.5 Å	321
[Mg(Me$_3$PO)$_5$·H$_2$O](ClO$_4$)$_2$	Mg-O 2.05–2.11 Mg-OH$_2$ 2.19	6 (octahedral)	Compared to the anhydrous analog, described next, the axial Mg-O bond is longer (2.05 Å) due to water coordination from the other axial side	768
[Mg(Me$_3$PO)$_5$](ClO$_4$)$_2$	Mg-O 1.94–2.06	5 (square pyramid)	The axial Mg-O bond is 1.94 Å. Whereas in the preceding complex ClO$_4$ is bound to the coordinated water hydrogens, it is isolated herein	768
[Mg(OMPA)$_3$](ClO$_4$)$_2$	Mg-O av 2.06	6 (octahedral)		302
[Na(MBPO)$_3$]Br·3H$_2$O	Na-O av 2.45	6 (trigonal prism)		331
[Mg(TMAO)$_5$](ClO$_4$)$_2$	Mg-O 1.92–2.05	5 (square pyramid)		334
[Ca$_2$(TMAO)$_9$](ClO$_4$)$_4$	Ca-O av 2.28 av 2.42	6 (approx octahedral)		335
NaBr(sucrose)·2H$_2$O	Na-O 2.40 Na-Br 2.94	6 (octahedral)		358
CaBr$_2$(D-lactose)·7H$_2$O	Ca-O 2.38–2.54	8 (square antiprism)	Four water molecules participate in coordination	361
CaBr$_2$(α-D-galactose)·3H$_2$O	Ca-O 2.35–2.55	8 (distorted square antiprism)	Closest Ca-Br contact is 4.5 Å	362
CaBr$_2$(*myo*-inositol)·5H$_2$O	Ca-O 2.37–2.52	8 (distorted square antiprism)	Four water molecules coordinate; Ca-OH$_2$ bonds (av 2.41 Å) are shorter	363
CaBr$_2$(α-D-fucose)·3H$_2$O	Ca-O 2.32–2.44	7 (pentagonal bipyramid)		365
CaBr$_2$(α,α-trehalose)·H$_2$O	Ca-O 2.32–2.47	7 (pentagonal bipyramid)	Closest Ca-Br contact is 4.59 Å	366
CaCl$_2$(β-D-fructose)·2H$_2$O	Ca-O 2.33–2.46	7 (pentagonal bipyramid)		367
CaBr$_2$(β-D-fructose)·2H$_2$O	Ca-O 2.32–2.47	7 (pentagonal bipyramid)		368
CaCl$_2$(α-D-xylose)·3H$_2$O	Ca-O 2.32–2.51	7 (distorted pentagonal bipyramid)		369
CaCl$_2$(β-L-arabinose)·4H$_2$O	Ca-O 2.33–2.70	8 (square antiprism)		370
CaCl$_2$(β-D-fructose)$_2$·3H$_2$O	Ca-O 2.45–2.50	8 (square pyramid)	Only two water molecules coordinate	371
SrCl$_2$(*epi*-inositol)·5H$_2$O	Sr-O 2.55–2.68	9 (irregular polyhedron)	Only four water molecules coordinate	374
MgCl$_2$(*myo*-inositol)·4H$_2$O	Mg-O 2.03–2.14	6 (octahedral)		375
NaClO$_4$·AEL	Na-O(AEL) 2.29–2.36 Na-O(ClO$_4$) 2.37–2.59	6 (distorted octahedron)		376
KI(PKH)$_2$	K-O 2.74–2.92	8 (irregular coordination)		381
CsNCS(PKH)	Cs-O 3.01–3.32 Cs-S 3.60, 3.80 Cs-N 3.45	8 (irregular coordination)		382
NaI(PKH)$_2$·2H$_2$O	Na-O 2.30–2.58	6 (approx octahedron)	The shortest and the longest bonds are formed with water molecules	383
NaBr(AM)$_2$	Na-O 2.32–2.37 Na-Br 2.99, 3.12	6 (distorted octahedron)	The longer Na-Br distance is due to bridging of Br from adjacent molecule	387
Ca(NO$_3$)$_2$(urea)$_4$	Ca-O 2.30–2.36	6 (octahedral)		388
Ca(NO$_3$)$_2$(urea)·3H$_2$O	Ca-O 2.35–2.68	8 (irregular coordination)		389
CaBr$_2$(urea)$_6$	Ca-O 2.32–2.33	6 (slightly distorted octahedron)		390
LiI(urea)$_2$		4 (distorted tetrahedron)		393
Sr(ClO$_4$)$_2$(biuret)$_4$	Sr-O 2.49–2.69	8 (distorted square antiprism)		394
NaBr(DA)$_2$	Na-O av 2.32 Na-Br 2.78	5 (square pyramid)		398
KI(DA)$_2$	K-O 2.64–2.73 K-O(bridge) 2.82, 2.97	7 (irregular)		399
CaBr$_2$(DA)$_4$	Ca-O av 2.42	8 (square antiprism)		400
Ca(ClO$_3$)$_2$(DA)$_4$·H$_2$O	Ca-O 2.41–2.44	8 (square antiprism)	The water molecule is nonbonded and one of the amide nitrogens is hydrogen bonded to a ClO$_3$ oxygen	770
Ca(ClO$_4$)$_2$(DA)$_5$	Ca-O 2.38–2.45	8 (square antiprism)	The closest approach of the noncoordinated DA oxygen is 4.93 Å	401
Ba(ClO$_4$)$_2$(DA)$_5$	Ba-O 2.73–2.91	10 (symmetrical bicapped square antiprism)		402

TABLE II (*Continued*)

compound	bonding features of the cation bond, distance (Å)	 coord no. (stereochem)	remarks, if any	ref
$Sr(ClO_4)_2(DA)_4\cdot H_2O$	Sr–O 2.54–2.69	9 (monocapped square antiprism)	The lower energy tricapped trigonal (D_{3h}) prism is not formed but the higher energy monocapped sq antiprism (C_{4v}) results	403
$Mg(ClO_4)_2(DA)_4\cdot 2H_2O$	Mg–O 2.03–2.05	6 (octahedral)	Two DA molecules are nonbonded and axial positions are occupied by the water molecules	404
$NaCl(urea)\cdot H_2O$	Na–O 2.26–2.42	6 (distorted octahedron)	The octahedron is formed by two Cl ions, two water oxygens, and two urea oxygens	*oo*
$NaI(glycine)_2\cdot H_2O$	Na–O 2.32–2.64	6 (octahedral)	The octahedron is completed by two oxygens from each of monodentate COO^-, the bridged water molecule, and the bridged COO^-	410
$CaI_2(glycine)_3\cdot H_2O$	Ca–O 2.31–2.54	7 (irregular)		411
$CaCl_2(sarcosine)_3$	Ca–O 2.29–2.36	6 (octahedral)		412
$LiBr(alanylglycine)\cdot 2H_2O$	Li–O 1.88–1.94	4 (tetrahedral)		413
NaI(cysteiylglycine)	Na–O 2.16–2.23	4 (tetrahedral)		414
$CaCl_2(glycylglycylglycine)\cdot 3H_2O$	Ca–O 2.30–2.50	7 (approx pentagonal bipyramid)	Only two water molecules coordinate	415
$Na(onp)(PHEN)_2$	Na–N 2.44–2.56 Na–O^- 2.28 Na–O 2.42	6 (undefined)		421
$Rb(onp)(PHEN)_2$ (dimeric)	Rb–N 3.05–3.08 Rb–O^- 2.84 Rb–O 2.95, 3.19	7 (undefined)	The complex dimerizes through the longer Rb–O bond	421
$[Sr(PHEN)_2\cdot 4H_2O](ClO_4)_2\text{-}(PHEN)_2$	Sr–N 2.78–2.81 Sr–O av 2.60	8 (distorted cubic)		423
$[Ba(PHEN)_2\cdot 4H_2O](ClO_4)_2\text{-}(PHEN)_2$	Ba–N av 2.95 Ba–O 2.74–2.78	8 (distorted cubic)		423
$LiCl(EN)_2$	Li–N 2.06–2.08	4 (tetrahedral)	Bond distances and bonding modes for $LiBr(EN)_2$ are fairly comparable	433
$LiI(EN)_3$	Li–N av 2.26	6 (distorted octahedron)	Li^+–I^- distance is at least 4.8 Å	434
$NaCl(DDB)_3$	Na–N av 2.61	6 (distorted octahedron)	Analogous complexes of $NaNO_3$ and NaCN have also been investigated crystallographically (Na–N distances, av 2.66 and 2.64 Å, respectively)	439
NaI(TEA)	Na–O 2.45–2.62 Na–N 2.61 Na–I 3.29	7 (irregular geometry)	The longest and the shortest Na–O contacts are due to bridging hydroxyl oxygens	443
NaI(TMTEA)	Na–O 2.34–2.37 Na–N 2.46 Na–I 2.97	5 (approx trigonal bipyramid)		444
$Sr(NO_3)_2(TEA)_2$	Sr–O 2.53–2.59 Sr–N av 2.83	8 (approx cubic)		445
$Ba(OAc)_2(TEA)_2$	Ba–O 2.74–2.80 Ba–N 3.02, 3.11 Ba–O^- 2.73	9 (irregular geometry)		446
		Complexes with Coordinated Ligands		
$[(Co\text{-}salen)_2Na(THF)_2]BPh_4$	Na–O(salen) 2.39–2.48 Na–O(THF) 2.35, 2.37	6 (distorted octahedron)		457
$[(Ni\text{-}salen)_2Na(MeCN)_2]BPh_4\cdot 2MeCN$	Na–O 2.39–2.42	6 (approx octahedral)		458
$[(Cu\text{-}salen)_2Na(ClO_4)]$-*p*-xylene	Na–O(salen) av 2.36 Na–O(ClO_4) av 2.55	6 (approx octahedral)		459
$[(Ni\text{-}N,N'\text{-}ethylenebis(acetylacetonimi-nato)_2Na(ClO_4)]$	Na–O 2.35–2.64	6 (very irregular geometry)		460
K-bis(tri-*p*-tolylphosphine)-Cu(I)bis(dithiooxalato-*o*,*o*′)-stannate$\cdot 2Me_2CO$	K–O 2.63–3.14	7 (irregular geometry)	Acetone oxygens form the shortest contacts	461
Ba-neptunyl(V)triacetate$\cdot 2H_2O$	Ba–O(OAc) av 2.72 Ba–OH_2 av 2.93	8 (in between dodecahedron and square antiprism)		462
Li-ethylenediamine-*N*,*N*′-di-acetato-*N*,*N*′-di-3-propionatochromate$\cdot 5H_2O$	Li–O 1.95–1.98	4 (tetrahedral)	The tetrahedron is formed by an acetate oxygen and three water oxygens	463
$Na_2[Fe(CN)_5(NH_3)]2H_2O$	Na(1)–O av 2.50 Na(1)–N 2.47–2.49 Na(2)–O av 2.50 Na(2)–N 2.44–2.51	6 (distorted octahedron)	Two water oxygens and four cyanide nitrogens complete the octahedron	465

TABLE II (*Continued*)

compound	bonding features of the cation		remarks, if any	ref
	bond, distance (Å)	coord no. (stereochem)		
$Na_2[Pt(CN)_4Br_2]\cdot 2H_2O$	Na–O 2.41, 2.43 Na–N 2.50–2.70	6 (distorted octahedron)		466a
$Ba[Pt(CN)_4]\cdot 4H_2O$	Ba–O 2.86–2.93 Ba–N 2.92–3.04	10 (undefined geometry)	Six water oxygens and the four cyanide nitrogens make the contacts	466b
$Rb_2[Pt(CN)_4Br_2]$	Rb–N 3.00–3.30 Rb–Br 3.66, 3.68	8 (distorted bicapped trigonal prism)		466c
$Cs_2[Pt(CN)_4]\cdot H_2O$	Cs(1)–O 3.16 Cs(1)–N 3.24–3.41	8 (irregular geometry)		466d
	Cs(2)–O 3.13 Cs(2)–N 3.29–3.51	7 (irregular geometry)		
$Na_2[Pt(CN)_4]\cdot 3H_2O$	Na(1)–O 2.41–2.49 Na(1)–N 2.52–2.60	6 (approx octahedral)	There are five crystallographically different Na ions each in an octahedral environment; the contacts of the cyanide nitrogens are 3, 2, 2, 4, and 4 with Na(1), Na(2), Na(3), Na(4), and Na(5), respectively	466e
$KNa[Pt(CN)_4]\cdot 3H_2O$	Na–O 2.40–2.83 Na–N 2.41, 2.54	6 (nearly regular octahedron)		466f
	K–O 2.77, 3.08 K–N 2.86–2.91	6 (distorted octahedron)		
$K_2[Pt(CN)_4](F,HF)_{0.3}\cdot 3H_2O$	K–O 2.76–2.88 K–N 2.99–3.02 K–F 3.00–3.32	9 (irregular geometry)		466g
		Complexes with Crowns		
K(ethyl acetoacetato)(18C6)	K–O(18C6) 2.83–3.02 K–O(enolate) 2.65, 2.73	8 (undefined geometry)		474
$[Na(12C4)_2](Cl,5H_2O)$	Na–O 2.47–2.52	8 (square antiprism)	Cl ions are completely embedded in chains of the water molecules	475
$[Na(12C4)_2](OH,8H_2O)$	Na–O av 2.48	8 (square antiprism)		477
$[RbSCN(18C6)]_2$	Rb–O 2.93–3.15 Rb–N 3.23, 3.31	8 (undefined)		481
$[CsNCS(18C6)]_2$	Cs–O 3.03–3.27 Cs–N 3.30, 3.32	8 (undefined)		482
$[CsNCS(TMDB18C6\bar{F})]_2$	Cs–O 3.07–3.34 Cs–N 3.19, 3.25	8 (undefined)		483
$[RbNCS(B18C6)]_2$	Rb–O 2.91–3.13 Rb–N 3.04, 3.05	8 (undefined)		484
$[(Rb_{0.55}Na_{0.45})NCS(DB18C6)]$	Rb–O 2.86–2.94 Rb–N 2.94	7 (hexagonal pyramid)	NCS is nonbonding for Na (3.32 Å)	487
	Na–O 2.74–2.89	6 (hexagonal)		
[K(18C6)]NCS	K–O 2.77–2.83	6 ("very flat" octahedron)	NCS is disordered (K–S,N 3.19 Å)	488
[K(N20C6)]NCS	K–O av 2.80	6 (hexagonal)	Original publication shows K to be 8-coordinated (approximately hexagonal bipyramid) despite a disordered NCS (K–S,N 3.26 Å)	489
$RbNCS(NO_2\text{-}B18C6)$	Rb–O 2.95–3.08 $Rb–O(NO_2)$ 3.09, 3.81 Rb–NCS not mentioned	7 (irregular hexagonal pyramid)	"Rb is bonded in the molecule by ionic interaction with the SCN"	490, *pp*
$CsNCS(NO_2\text{-}B18C6)$	Cs–O 3.04–3.25 $Cs–O(NO_2)$ 3.30, 3.57	7 (undefined)	The longer $Cs–O(NO_2)$ bond is rather too long for a contact and NCS is disordered (Cs–N 3.44, and Cs–S 3.68 Å)	491
$[Cs(TMDB18C6\bar{G})_2]NCS$	Cs–O 3.12–3.36	12 (hexagonal antiprism)	These distances are shorter than those reported (3.17–3.43 Å) in the preliminary communication (ref 480)	483
$(Naonp)_2(DB24C8)$	Na–O 2.47–2.62 $Na–O(NO_2)$ 2.40 $Na–O^-$ 2.30, 2.32	6 (irregular)	For each cation only three ring oxygens coordinate while the middle two are rather nonbonding (av 2.96 Å)	492
[Na(DC18C6 *cis-anti-cis*)-$(H_2O)_2$]Br	Na–O 2.68–2.97 $Na–OH_2$ av 2.35	8 (hexagonal bipyramid)		493
$[Na(B15C5)(H_2O)]I$	Na–O 2.35–2.43 $Na–OH_2$ 2.29	6 (pentagonal pyramid)	Iodide is bonded with hydrogens of two water molecules coordinated to the respective cations in adjacent complex molecules	494
$[Na(18C6)(H_2O)]NCS$ (dimeric)	Na–O 2.45–2.62 $Na–OH_2$ 2.32	7 (distorted pentagonal bipyramid)	The system dimerizes through bonding of water molecules with N of NCS ions	495
$NaBr(DB18C6)\cdot 2H_2O$				
A: $[Na(DB18C6)(H_2O)_2]Br$	Na–O 2.63–2.82 $Na–OH_2$ 2.27, 2.31	8 (hexagonal bipyramid)	Molecules A and B are linked by a bromide ion through bonding hydrogens of coordinated water molecules	496
B: $[NaBr(DB18C6)(H_2O)]$	Na–O 2.54–2.89 $Na–OH_2$ 2.35 Na–Br 2.82	8 (hexagonal bipyramid)		

TABLE II (*Continued*)

	bonding features of the cation			
compound	bond, distance (Å)	coord no. (stereochem)	remarks, if any	ref
$[K(B15C5)_2]I$	K–O 2.78–2.96	10 (irregular pentagonal antiprism)	This was the first charge separated sandwich of an alkali cation to be known	498
$[K(DB30C10)]I$	K–O 2.85–2.93	10 (undefined)		499
$KI(DB18C6)(H_2O)_{1/2}$				
A: $[K(DB18C6)(H_2O)]^+$	K–O 2.73–2.79 K–OH_2 2.72	7 (hexagonal pyramid)	Unlike the counterpart molecule B, this molecule contains an iodide-separated cation (K–I, 6.16 Å)	500
B: KI(DB18C6)	K–O 2.73–2.79 K–I 3.52	7 (hexagonal pyramid)		
$(KNCS)_2(DB24C8)$	K–O 2.73–2.82 K–O(bridge) 2.90, 2.98 K–N 2.87, 2.88	7 (undefined)	For each cation only three ring oxygens coordinate exclusively while the middle two bridge the cations; the NCS ion bridges the cations from each axial side	501
$[Mg(H_2O)_6](12C4)Cl_2$			Described under "Solvent Complexes" (ref 134)	
$Mg(NCS)_2(B15C5)$	Mg–O 2.17–2.20 Mg–N av 2.06	7 (pentagonal bipyramid)		505b
$[Ca(12C4)\cdot 4H_2O](2Cl, 4H_2O)$	Ca–O 2.51–2.54 Ca–OH_2 2.38–2.40	8 (distorted square antiprism)		514
$[Ca(pic)_2\cdot 3H_2O](B15C5)$			Described under "Solvated Ion Pairs" (ref 152)	
$[Ca(dnb)_2(B15C5)](B15C5, 3H_2O)$	Ca–O 2.52–2.78 Ca–O^- 2.46–2.47	9 (undefined)	The nonchelating B15C5 bonds with the available hydrogens of the water chain	512
$Ca(NCS)_2(B15C5)\cdot H_2O$	Ca–O 2.46–2.61 Ca–OH_2 2.40 Ca–N 2.42, 2.43	8 (very irregular geometry)		505b
$Ca(NCS)_2(B15C5)\cdot MeOH$	Ca–O 2.51–2.55 Ca–O(MeOH) 2.38 Ca–N 2.40, 2.49	8 (very irregular geometry)		505b
$Ca(NCS)_2(18C6)$	Ca–O 2.56–2.74 Ca–N av 2.35	8 (hexagonal bipyramid)		504
$[Sr(B18C6)\cdot 3H_2O](ClO_4)_2$	Sr–O 2.66–2.72 Sr–OH_2 2.55–2.58	9 (undefined)	Two water molecules coordinate the cation from one axial side while the third from the other	508
$Ba(ClO_4)_2(B18C6)\cdot 2H_2O$	Ba–O 2.80–2.85 Ba–OH_2 2.78, 2.84 Ba–O(ClO_4) 2.79, 2.93	10 (undefined)		508
$Ba(NCS)_2$(DC18C6 *cis-syn-cis*)$\cdot H_2O$	Ba–O 2.80–2.91 Ba–OH_2 2.80 Ba–N av 2.88	9 (undefined)		503
$Ba(ClO_4)_2(DB24C8)$	Ba–O 2.76–3.04 Ba–O(ClO_4) 2.72, 2.79	10 (undefined)	There is an additional 11th contact with ClO_4 (3.33 Å)	507
$Ba(pic)_2(DB24C8)\cdot 2H_2O$	Ba–O 2.86–3.00 Ba–OH_2 2.73, 2.77 Ba–O^- 2.67, 2.71 Ba–O(NO_2) 3.09	10 (undefined)	Only five crown oxygens participate and one of the coordinated water molecules offers its protons for bonding with two of the crown oxygens; eighth crown oxygen is idle	513
		Complexes with Crown-Related Macrocycles		
KNCS(I)	K–O 2.82–2.84 K–N av 2.86 K–N(NCS) 3.33	7 (hexagonal pyramid)	NCS ions link the complex molecules	550
$Mg(IV)Cl_2\cdot 6H_2O$	Mg–N 2.24–2.31 Mg–OH_2 av 2.10	7 (pentagonal bipyramid)	Four water molecules are nonbonding	558
$SrCl_2(IVA)\cdot 2H_2O$	Sr–N 2.71–2.74 Sr–Cl 2.92, 2.93	8 (hexagonal bipyramid)	Both the water molecules are nonbonding	*qq*
$Ca(NCS)_2(V)$	Ca–O,N av 2.64	8 (hexagonal bipyramid)	Ca–NCS distances not mentioned	560
$Sr(NCS)_2(V)\cdot H_2O$	Sr–O,N av 2.78 Sr–OH_2 2.59	9 (undefined)	Sr–NCS distances not mentioned	560
$Sr(NCS)_2(VI)\cdot H_2O$	Sr–O,N 2.69–2.80 Sr–OH_2 2.58 Sr–N(NCS) av 2.63	9 (undefined)		555
		Complexes with Cryptands		
[Li-2.1.1]I	Li–O 2.08–2.17 Li–N av 2.29	6		598
[Na-2.2.1]NCS	Na–O 2.45–2.52 Na–N 2.59, 2.70	7		599
[Na-2.2.2]I	Na–O 2.57–2.58 Na–N 2.72, 2.78	8		601

TABLE II (*Continued*)

compound	bonding features of the cation		remarks, if any	ref
	bond, distance (Å)	coord no. (stereochem)		
[Na-2.2.2]$_2$[Fe(CO)$_4$]	Na–O av 2.53 Na–N av 2.80	8	The system was investigated to know the stereochemistry of the anionic moiety while concealing Na	602
[K-2.2.2]I	K–O 2.78–2.79 K–N av 2.87	8		603
[Rb-2.2.2]NCS·H$_2$O	Rb–O 2.88–2.93 Rb–N 2.99, 3.01	8		605
[Cs-2.2.2]NCS·H$_2$O	Cs–O 2.96–2.97 Cs–N 3.02, 3.05	8		605
[Ca-2.2.2(H$_2$O)]Br$_2$·2H$_2$O	Ca–O 2.49–2.55 Ca–OH$_2$ 2.42 Ca–N av 2.72	9		606
[Ba-2.2.2(NCS)(H$_2$O)]NCS	Ba(1)-O 2.75–2.82 Ba(1)–N 2.94, 3.00 Ba(1)–OH$_2$ 2.88 Ba(1)–N(NCS) 2.91 Ba(2)–O 2.74–2.89 Ba(2)–N 2.99, 3.00 Ba(2)–OH$_2$ 2.84 Ba(2)–N(NCS) 2.88	10		608
[Ba-3.2.2(H$_2$O)$_2$](NCS)$_2$	Ba–O 2.80–3.09 Ba–N 3.08, 3.18 Ba–OH$_2$ 2.81, 2.87	11		609
[2Na-XXIII]I$_2$	Na–O 2.39–2.48 Na–N 2.70, 2.73	7		613
		Complexes with Acyclic Multidentates		
NaNCS[MeO(C$_6$H$_4$)O-(CH$_2$CH$_2$O)$_3$(C$_6$H$_4$)OMe]	Na–O 2.35–2.54 Na–N 2.33	7		637b
[Rb(XXXIII)]I	Rb–O 2.88–3.09 Rb–N 2.91, 2.96	7		642
[Ca(XL)$_2$]Cl$_2$	Ca–O(carbonyl) av 2.36 Ca–O(ether) av 2.46	8		651
		Complexes with Antibiotics		
[K(valinomycin)]I$_3$/I$_5$	K–O 2.69–2.83	6 (octahedral)		661
[K(enniatin B)]I	K–O 2.6–2.8	6 (octahedral)		668
[Na(nonactin)]NCS	Na–O(carbonyl) av 2.42 Na–O(ether) av 2.77	8 (deformed cubic)		652
[K(nonactin)]NCS	K–O(carbonyl) av 2.77 K–O(ether) av 2.84	8 (approx cubic)		675
[Cs(nonactin)]NCS	Cs–O(carbonyl) av 3.16 Cs–O(ether) av 3.12	8 (distorted cubic)		676
[Na(tetranactin)]NCS	Na–O(carbonyl) av 2.44 Na–O(ether) av 2.82	8 (distorted cubic)		677
[K(tetranactin)]NCS				
A:	K–O(carbonyl) av 2.77 K–O(ether) av 2.87	8 (approx cubic)	Isomorphous with the analogous Na complex	677
B:	K–O(carbonyl) av 2.78 K–O(ether) av 2.88	8 (approx cubic)	Isomorphous with the analogous Rb complex	
[Rb(tetranactin)]NCS	Rb–O(carbonyl) av 2.91 Rb–O(ether) av 2.94	8 (approx cubic)		677
[Cs(tetranactin)]NCS	Cs–O(carbonyl) av 3.10 Cs–O(ether) av 3.06	8 (distorted cubic)	Isomorphous with the analogous Rb complex	676
Li(antamanide)Br·MeCN	Li–O 2.04–2.24 Li–N(MeCN) 2.07	5 (square pyramidal)		160
Na(antamanide analog-Phe^4,Val^6)Br·EtOH	Na–O 2.25–2.36 Na–O(EtOH) 2.28	5 (square pyramidal)		161
Na$_2$$^+$(X-537 A)$_2$$^-$	Na–O 2.28–2.77	6 (monocapped pentagon)	The dimer exists in two forms; the pentagonal coordination with one anion is monocapped by oxygen from the other anion	686
Na$_2$$^+$(X-537 A)$_2$$^-$·2H$_2$O	Na(1)–O 2.42–2.67 Na(1)–OH$_2$ 2.45	7	The system is a head-to-tail dimer	686
	Na(2)–O 2.40–2.72 Na(2)–OH$_2$ 2.37, 2.40	6		
Ba$_2$$^{2+}$ (X-537 A)$_4$$^-$·2H$_2$O	Ba–O 2.71–3.08	9	Six oxygens from one antibiotic anion, two from the other and a water oxygen participate in coordination	687
Ca^{2+}(A23187)$_2$$^-$	Ca–O 1.92–2.10 Ca–N 2.21, 2.22	6 (octahedral)		688

TABLE II (*Continued*)

compound	bonding features of the cation		remarks, if any	ref
	bond, distance (Å)	coord no. (stereochem)		
$Ca^{2+}(A23187)_2^{-}\cdot H_2O$	Ca-O 2.27-2.38 Ca-N 2.58, 2.69 $Ca-OH_2$ 2.38	7 (undefined)		689
$Na^{+}(monensin)Br^{-}$	Na-O 2.35-2.50	6 (distorted octahedron)	Bromide is hydrogen bonded to a carboxyl and a hydroxyl oxygen of a monensin molecule	691
		Complexes with Other Macromultidentates		
$[Li(cyclodisarcosyl)_2]ClO_4$	Li-O 1.89-1.95	4 (tetrahedral)	The structure involves infinite two dimensional network wherein each cation binds four different ligand molecules	707
$Mg(phthalocyanine)(pyridine)_2\cdot H_2O$	Mg-N av 2.04 $Mg-OH_2$ 2.02	5		722

[a] A. Sequeira, J. Bernal, I. D. Brown, and R. Faggiani, *Acta Crystallogr., Sect. B*, **31**, 1735 (1975). [b] A. Braibanti, A. Tiripicchio, A. M. Manotti-Lanfredi, and F. Bigoli, *ibid.*, **25**, 354 (1969). [c] H. Flack, *ibid.*, **29**, 656 (1973). [d] S. Baggio, L. M. Amzel, and L. N. Becka, *ibid.*, **25**, 2650 (1969). [e] H. J. Talberg, *Acta Chem. Scand., Ser. A*, **31**, 37 (1977). [f] G. Ferraris and M. Franchini-Angela, *Acta Crystallogr., Sect. B*, **29**, 286 (1973). [g] G. Ferraris and G. Chiari, *ibid.*, **26**, 1574 (1970). [h] G. de With, S. Harkema, and G. J. van Hummel, *Acta Crystallogr., Sect. B*, **32**, 1980 (1976). [i] J. L. Galigne, *ibid.*, **27**, 2429 (1971). [j] A. Enders-Beumer and S. Harkema, *ibid.*, **29**, 682 (1973). [k] K.-T. Wei and D. L. Ward, *ibid.*, **33**, 522 (1977). [l] M. M. Borel and M. Ledesert, *J. Inorg. Nucl. Chem.*, 37, 2324 (1975). [m] M. M. Borel and M. Ledesert, *Acta Crystallogr., Sect. B*, 31, 725 (1975). [n] M. M. Borel and M. Ledesert, *ibid.*, 32, 2388 (1976). [o] B. Morosin, J. G. Bergman, and G. R. Crane, *ibid.*, **29**, 1067 (1973). [p] A. M. Manotti-Lanfredi, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio-Camellini, *ibid.*, **28**, 679 (1972). [q] A. C. Larson, *Acta Crystallogr.*, **18**, 717 (1965). [r] W. H. Baur and J. L. Rolin, *Acta Crystallogr., Sect. B*, **28**, 1448 (1972). [s] L. Manojlovic-Muir, *ibid.*, 31, 135 (1975). [t] U. Thewalt and C. E. Bugg, *ibid.*, **29**, 615 (1973). [u] H. Gillier-Pandraud and M. Philoche-Levisalles, *C. R. Acad. Sci., Ser. C*, **273**, 949 (1971). [v] A. Leclaire, *Acta Crystallogr., Sect. B*, **30**, 2259 (1974). [w] Lj. Manojlovic and J. C. Speakman, *ibid.*, **24**, 323 (1968). [x] Lj. Manojlovic, *ibid.*, **24**, 326 (1968). [y] G. Larson and I. Nahringbauer, *ibid.*, **24**, 666 (1968). [z] M. A. Bush, H. Luth, and M. R. Truter, *J. Chem. Soc. A*, 740 (1971). [aa] M. A. Bush and M. R. Truter, *J. Chem. Soc. A*, 745 (1971). [bb] I. K. Larsen, *Acta Chem. Scand., Ser. A*, **28**, 787 (1974). [cc] L. Golic and J. C. Speakman, *J. Chem. Soc.*, 2521 (1965). [dd] S. Grimvall and R. F. Wengelin, *J. Chem. Soc. A*, 968 (1967). [ee] J. C. Speakman and H. H. Mills, *J. Chem. Soc.*, 1164 (1961). [ff] B. Briggman and A. Oskarsson, *Acta Crystallogr., Sect. B*, 33, 1900 (1977). [gg] A. Karipides, J. Ault, and A. T. Reed, *Inorg. Chem.*, 16, 3299 (1977). [hh] W. G. Town and R. W. H. Small, *Acta Crystallogr., Sect. B*, **29**, 1950 (1973). [ii] M. N. G. James and G. J. B. Williams, *ibid.*, 30, 1257 (1974). [jj] M. P. Gupta, S. M. Prasad, R. G. Sahu, and B. N. Sahu, *ibid.*, 28, 135 (1972). [kk] H. Klapper and H. Kiippers, *ibid.*, **29**, 21 (1973). [ll] B. Sheldrick, *ibid.*, **30**, 2056 (1974). [mm] J. A. Hjortas, B. Larsen, and S. Thanomkul, *Acta Chem. Scand., Ser. B*, **28**, 689 (1974). [nn] G. D. Smith, A. Fitzgerald, C. N. Caughlan, K. A. Kerr, and J. P. Ashmore, *Acta Crystallogr., Sect. B*, 30, 1760 (1974). [oo] J. H. Palm and C. H. MacGillavry, *Acta Crystallogr.*, 16, 963 (1963). [pp] Here and hereinafter the first line description of the bond lengths, whether specified or not, applies to the M^{z+}-O,N(macromolecule) bonds. [qq] J. de O. Cabral, M. F. Cabral, W. J. Cummins, M. G. B. Drew, A. Rodgers, and S. M. Nelson, *Inorg. Chim. Acta*, 30, L313 (1978).

The complexes $[Mg(H_2O)_6](Cr_2O_7)(HMT)_2$,[135] $[Ca(H_2O)_7](Cr_2O_7)(HMT)_2$,[136] and $[Ca(H_2O)_6](Br)_2(HMT)_2(H_2O)_4$[137] (HMT = hexamethylenetetramine) are solvent complexes for the reasons that the cation in each is strongly hydrated, the anion is highly nucleophilic (see above), and HMT is too weak to desolvate the cation.

The solid solvates such as $[Na(MeOH)_3]I$,[138] $[M(MeOH)_6]Br_2$[139] (M^{2+} = Mg or Ca), and possibly $[Mg(EtOH)_6](ClO_4)_2$[140] are also charge separated and it is expected because these solvents can also display double action which is favorable to charge separation.

Formation of solvent complexes through the use of hydrogen-bonding solvents is understandable and is, in fact, common. With basic solvents like DMF, charge separation is also not difficult to understand. Indeed, $[Na(DMF)_3]I$[141] has been revealed to be a charge-separated ($Na^{+}-I^{-}$, 6.98 Å) complex. However, charge separation of a cation such as Na with neutral solvents has also been noted which is surprising. The solvate $[Na(DX)_3]ClO_4$[142] is one such example wherein the cation is hexacoordinated with only DX molecules. The solvate $[Na(Me_2CO)_3]I$[143] is another solvent complex of this category wherein, Na is six-coordinated with Me_2CO molecules and the $C-H^{+\delta}$ protons take care of iodide ions as in $[Na(DMF)_3]I$.[141] In these complexes[141,143] the $C-H^{\delta+}\cdots I^{-}$ interaction is obviously a consequence of CO→Na coordination so that the driving force for the salt-solvent interaction is nothing other than the genuine coordination of the cation.

The solvent complex $[Mg(THF)_4(H_2O)_2]Br_2$[144,145] is a rare example of an ion-separated mixed solvate which can be prepared[144] by the reaction of the required amount of water with either $MgBr_2(THF)_2$, $MgBr_2(THF)_3$, or $MgBr_2(THF)_4$. This solid phase is an ion-separated (Mg-Br, 4.65 Å) octahedral system in which the $Mg-OH_2$ bonds (2.04 Å) are shorter than the Mg-THF bonds (2.12 and 2.16 Å).[145]

b. Solvated Ion Pairs

The weakly coordinating solvents, which are usually aprotic neutral solvents, can ligate with a cation but fail to stabilize the anion. For this reason, their solid solvates are expected to be ion-paired under most conditions. The solid solvates $MgBr_2(THF)_2$[145] (Mg-Br, 2.63 and 2.8 Å), $MgBr_2(THF)_4$[146] (Mg-Br, 2.62 Å), $MgBr_2(Et_2O)_2$[762] (Mg-Br, 2.74-3.32 Å), LiCl(DX)[147] (Li-Cl, 2.39 and 2.42 Å), $MgBr_2(pyridine)_6$[148] (Mg-Br, 2.77 Å), and LiCl(pyridine)[149] and $LiCl(pyridine)_2(H_2O)$[150] (Li-Cl, 2.33 Å), for example, are solvated ion pairs.

When the charge-neutralizing anion is a chelating organic anion, the electrostatic as well as spatial requirements of the cation are both greatly fulfilled so that solvation takes place to a limited degree and the product is ion-paired even when the solvent is water. In $Mg(acac)(H_2O)_2$[151] and $Ca(pic)_2(H_2O)_3$,[152] for example, X-ray analysis has revealed water to be metal-coordinated but the systems are ion paired. When a particular system involves a solvent like water or methanol, a change in the degree of solvation can lead to a remarkable structural difference and the more highly solvated species, as expected, has chances to be charge separated. The solvates $MgSO_4\cdot 7H_2O$[122] and $CaBr_2(MeOH)_6$[139] in contrast to $MgSO_4\cdot 4H_2O$[153] and $CaBr_2(MeOH)_4$,[154] respectively, are charge-separated solvent complexes.

Solvated organometallic compounds and the metal alkoxides can be treated as solvated ion pairs because the M-C or the M-O bond gets polarized owing to coordination of the solvent with cation.[155] In such compounds, however, ion association (and covalency) in the $(R)C^{\delta-}-M^{\delta+}$ or the $RO^{\delta-}-M^{\delta+}$ bond is ex-

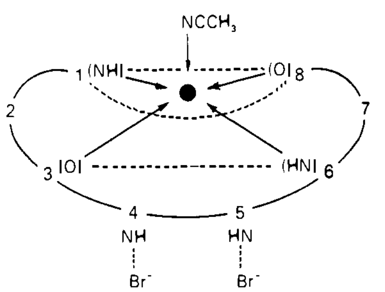


Figure 2. Li(antamanide)Br·MeCN complex (schematic); 1, 2, 3, . . . denote constituting amino acids as described in Figure 34 (x).

tremely high and the same may be treated as solvated intimate ion pairs. Such solvates, wherein a genuine coordination of the solvent is revealed by X-ray analysis, among others, include: $PhMgBr(Et_2O)_2$,[156] $EtMgBr(Et_2O)_2$,[157] $MeMgBr(THF)_3$,[158] and t-$BuOMgBr_2(Et_2O)$.[159]

c. Solvated Complexes

There are numerous compounds of the type M(anion)(ligand)(solvent) where "ligand" is the main ligand and "solvent" acts as a coligand. At instances, the solvent molecule may get into the composition just to fill up the unoccupied regions of the complexed cation, as MeCN in Li(antamanide)Br·MeCN[160] (Figure 2) or EtOH in Na(antamanide)Br·EtOH.[161] In some cases, however, the role of solvent is all important in causing charge separation/ion-pair loosening of the salt which is followed by complexation with the main ligand. This is expected for the complexes NaX(benzo-15-crown-5)(H_2O) (X^- = Br or I) which cannot be crystallized in the anhydrous state from a dehydrated reaction mixture, but are obtained in a hydrated form only from reaction mixtures containing some water.[46] Many other solvated complexes will be encountered in sections III.C and IV depending upon the nature of the main ligand and at the respective places in Table II.

3. M^{z+}-Solvent Coordination at Solid-Solvent Interface

Herein we comment on solvation of an ion pair at the surface of the solid lattice with an external solvent as encountered during solubilization of a crystal in a solvent. In an attempt[162] to explain the solubilization process of alkali and alkaline earth halides in water, it was argued that lattice energy of the salt and dielectric constant of the solvent are not of the basic importance and among other factors only influence the rate and magnitude of solubilization. This is because, for example, (i) the rather low lattice energy salts such as CsI and $KClO_4$ are relatively insoluble in water, and (ii) for the series CsI to CsF solubility in water as well as lattice energy of the salt both increase toward fluoride. Since salts like $BaSO_4$ and $KClO_4$, which are predominantly ionic, are practically insoluble in water, it was also argued[162] that the ion-solvation process is not initiated by the ions owing to their formal (or partial) charge.

The solubility vs. charge density difference plots for M^{z+} halides are shown in Figure 3 which reveals that (i) in the case of higher charge density M^{z+} (compartment A plots) solubility increases toward iodide, i.e., as the anion becomes increasingly polarizable (Fajans' rule[163]), and (ii) for lower charge density M^{z+} (compartment B plots) solubility increases as the cation behaves increasingly polarizable, i.e., either toward the large cation (KF to CsF) or toward the small anion (CsI to CsF). This leads to the conclusion[162] that for each cation solubility of the salts increases

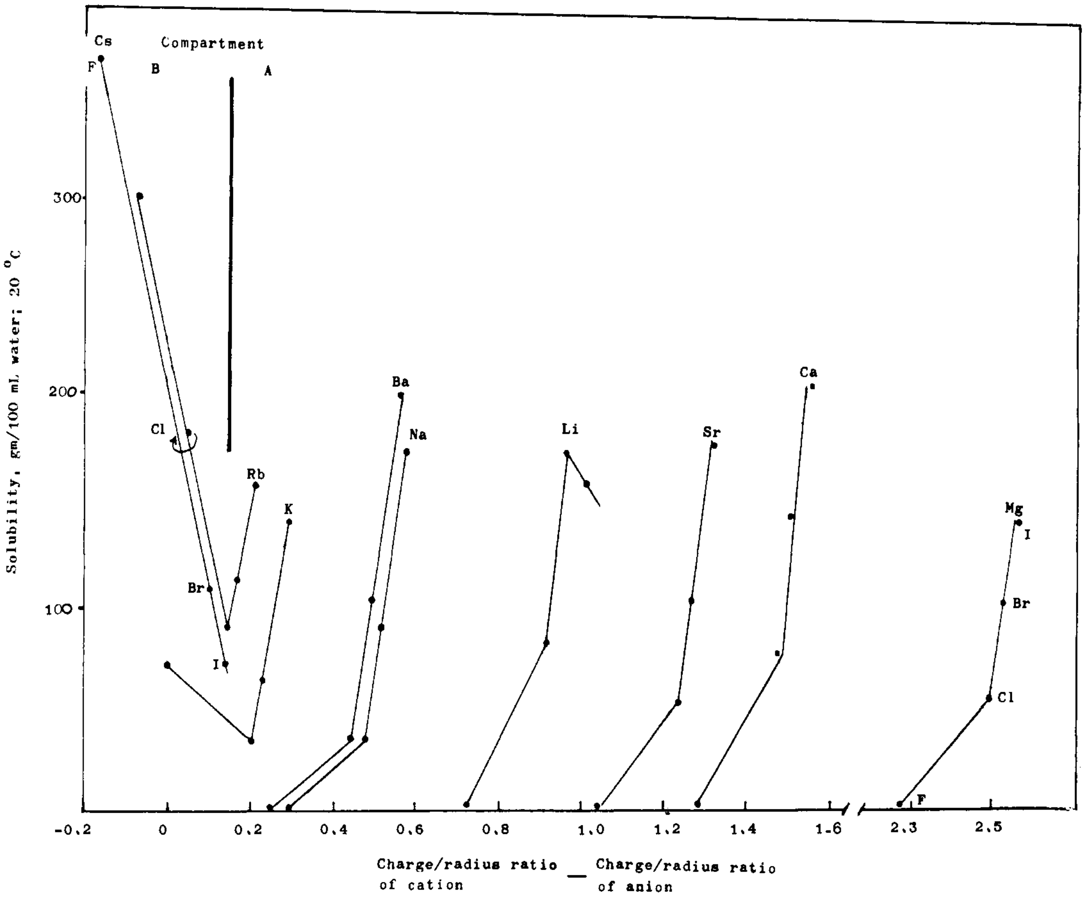


Figure 3. Solubility (g/100 mL at 20 °C) vs. charge/radius ratio difference of the ions constituting the metal halide (data from (i) W. F. Linke, "Solubilities", Vol. 1 and 2, 4th ed, American Chemical Society, Washington D.C., 1958, 1965; (ii) "Handbook of Chemistry and Physics", 46th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1965.

as the charge density difference of the constituting ions increases. As the difference increases, the larger ion (M^{z+} or X^-) on the crystal surface gets increasingly polarized and accordingly becomes the site of attack by the solvent molecules from appropriate poles. After this has happened, the polarizing ion also starts solvating and, consequently, the salt dissolves; adsorption studies of MeOH on solid metal halides also indicate[164] that M^{z+}–MeOH interaction is unrelated to the lattice energy of the salt but is governed by the nature of the ions constituting the salt.

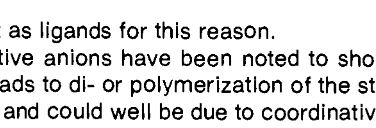
B. Anions as Ligands

1. General Considerations

The involvement of the charge neutralizing anion as one of the ligands in the complexes of M^{z+} is much more usual than that in the coordination compounds of transition cations. To cite, the solution of metallic Na in liquid ammonia ($[Na(NH_3)_n]^+ + e^0_{-1}$) on treatment with NO gas results in $[Na(NH_3)_n]^+NO^-$ from which only Na^+NO^- is crystallized.[165] This behavior of the alkali cation is unlike the general behavior of the transition cations which yield ammine complexes from ammonia. This situation is in line with the HSAB concept.[106] In some recent publications[166-169] we have been attempting to demonstrate that the key to the synthesis of M^{z+} complexes with electrically neutral ligands is the nature of the charge neutralizing anion; the role of the anion becomes increasingly important as donicity of the solvent medium falls.[110] The cation–anion interaction increases also with increase in charge density of M^{z+} and increases in the orders Cs to Li, Ba to Mg, and M^+ to similar-sized M^{2+}.

The ligation of M^{z+} with an anion depends essentially on electrostatic attractions, but there can be a degree of covalency in the bond depending on whether one of the ions polarizes the counterion. This is implied when we term an anion as a ligand in the following discussion. When an anion participates in coordination, the polarizing ability of the cation for the neutral coligand (if any) is diminished; that various salts are insoluble even in donor organic solvents indicates that the anion has bound the cation to the extent that the latter fails to solvate. Under conditions inhibiting solvation of the cation, anion can in general be expected to exercise a strong control on the cation and in the sense of this description may be considered a ligand of main importance.

In case the anion carries additional neutral donor sites, then as a ligand it becomes more so powerful and acts as a charge neutralizer as well as serves to satisfy the coordinative requirements of M^{z+}. The edta anions, for example, belong to this group and it explains why they act as effective sequestering agents. It is for these reasons that sugar anions such as gluconate and "anionized sugars" such as sugar phosphates are efficient ligands (vide infra). If the anion is devoid of the additional donor site but can act as a bi- or a tridentate anion because of its charge delocalization, even then its status as a ligand is important. Purpurate, β-diketonates, chelating organic anions such as o-nitrophenolate (onp), or chelating organic acid anions such as [(8-hydroxyquinolinate)(8-hydroxyquinoline)]$^-$



are important as ligands for this reason.

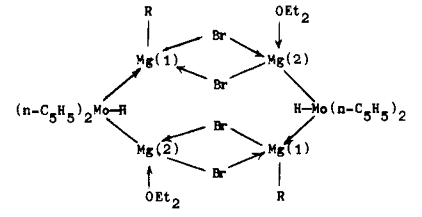


Figure 4. Bis-μ-[bis(η-cyclopentadienyl)hydridomolybdenum]-bis-[di-μ-bromo-[alkylmagnesium][(diethyl ether)magnesium]].

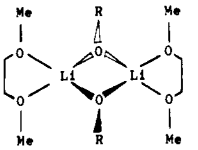


Figure 5. Postulated dimeric structure of lithium alkoxide in DME.

Mononegative anions have been noted to show a bridging action that leads to di- or polymerization of the structure. This is interesting and could well be due to coordinative interaction of the anion, the negative charge of which has been neutralized by one of the interacting cations. In the compound bis-μ-[bis(η-cyclopentadienyl)hydridomolybdenum]-bis[di-μ-bromo-[alkylmagnesium][(diethyl ether)magnesium]][170] (Figure 4), for example, the basic role of bromide in holding the two molecular halves should be of significance. Also, lithium alkoxide dimerizes (Figure 5) in 1,2-dimethoxyethane (DME).[98,171] There is no reason why this should happen unless the bridging action of the oxide oxygen is not favorable over chelation of the cation with DME. $MgBr_2(THF)_2$[145] (Mg–Br$^-$, 2.8 Å), 2,4-pentanedionatolithium[172] (Li–O$^-$, 1.95 Å), (1-phenylbutane-1,3-dionato)(ethylene glycol)sodium[173] (Na–O$^-$, 2.36 Å), and bis(1,3-diphenyl-1,3-propanedionato)strontium hemiacetonate[174] (Sr–O$^-$, 2.55 Å) are some more systems which involve bridging through the anionic atom shown in parentheses. It is not clear from the available results whether the bridging bond is in the direction of the available p orbital of the anionic site, but each such bond is longer than the other bond the anionic site establishes.

The anion can fail to contact the cation in the lattice as, for example, in the compound sodium 2-methyl-6-*endo*-hydroxybicyclo[2.2.1]heptane-2-*endo*-carboxylate trihydrate.[175] Herein the cation is coordinated with five water molecules and the alcoholic oxygen, while the water protons block the carboxylate. All this happens owing to double action of water as described during discussion on solid solvates (section III.A.2).

Ion pairs involving simple anions and common solvents have been discussed in the preceding subsection while the ion-paired complexes of electrically neutral conventional ligands will be discussed in the next subsection with a view to give importance to the coordination that an s-block cation undergoes with a conventional ligand. The cation–anion interactions in solution have been touched during discussion on solvation in solution (section III.A) and will be again taken up especially during discussion on selectivity of M^{z+}–crown complexation (section IV). In this subsection some classified systems of the chelating anions are being taken up for which interesting cation–anion bondings have been revealed, particularly by the diffraction techniques.

2. Delocalized Mononegative Anions Which Act Multianionic

The charge of a mononegative organic anion can be delocalized either through the formation of an acid anion as that of L^- by the formation of $[L.HL]^-$ (where L^- is an organic anion such as onp), or due to delocalization of its bond(s) as known for β-diketonates, purpurate, or aromatic π carbanions. Such anions bind M^{z+} through more than one site and we discuss below such bonding modes.

a. Acid Anions

Organic salts (ML) of particularly the large M^+ ions when dissolved in polar media interact with the parent acid of L^-, HL, or with another organic acid, HL′, to produce $ML(HL)_n$ or $ML(HL')_n$

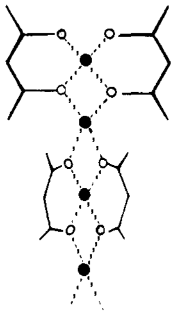


Figure 6. 2,4-Pentanedionatolithium (schematic).

type of product. In some cases, such as KOH–8-hydroxyquinoline,[176,177] the 1:1 reaction produces, instead of ML, ML(HL) species because of disproportionation of ML in solution. As also mentioned in section II, ML(HL)$_n$ species are of the first compounds to be called coordination compounds of alkali cations. The solubility of various such products in nonpolar media led to the conclusion[57–62] that HL (or HL$^{\prime}$) is covalently bonded to the cation in a state independent from L$^-$. By now a number of such compounds are known.[25,176–179] X-ray (in some cases neutron) diffraction studies have been carried out and the subject has been reviewed[179] (see also Table II). Principles controlling their formation have been discussed recently.[18]

Available information leads to the conclusion that the compounds in question are not the coordination compounds of the type believed by Sidgwick and co-workers.[57–59] In fact, their formation is basically not due to coordinative properties of M$^+$ but due to conjugative interaction of L$^-$ with HL (or HL$^{\prime}$). The strong Lewis acids Li and M^{2+} keep L$^-$ tightly paired and do not permit the latter to undergo conjugation. As the charge density of M$^+$ decreases, the conjugation is favored. For Na, a 1:1 conjugation is usual whereas for K, Rb, or Cs a 1:2 conjugation is frequent especially when L$^-$ is a strong proton acceptor such as 8-hydroxyquinolinate, and HL (or HL$^{\prime}$) is a high pK_a acid which retains its bonded proton. The [L(HL)$_n$]$^-$ or [L(HL$^{\prime}$)$_n$]$^-$ anion acts as a unified hydrophobic charge neutralizer for M$^+$, extensively coordinates the latter (Table II), and consequently renders it soluble in nonpolar media—an observation which misled earlier workers[57–62] about the structural aspects of the ML(HL)$_n$ and ML(HL$^{\prime}$)$_n$ type products.

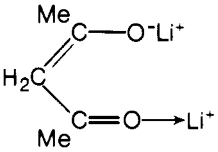
The [L,HL]$^-$ formation involves an equal sharing of the proton by the two L moieties whereas in the case of [L,HL$^{\prime}$]$^-$, a L + HL$^{\prime}$ $\rightarrow$ L$^{\prime}$ + HL type of proton transfer takes place in accordance with the difference in pK_a between HL and HL$^{\prime}$ so that the synthesis of ML(HL$^{\prime}$)$_n$ products is often impaired by the separation of the less soluble salt, ML or ML$^{\prime}$. The difficulty arising from the separation of a salt is pronounced when the reaction involves a low charge density M$^+$ (K, Rb, or Cs) in the presence of a delocalized anion like pic or a high charge density M$^+$ (Li) in the presence of an anion with a localized charge such as onp.[162]

$KIO_3 \cdot HIO_3$ is a unique example of an inorganic acid salt of the type [MX,HX] of which the structural features are known.[180] It involves a packing of $[IO_3 \cdots HIO_3 \cdots HIO_3]^-$, $[IO_3 \cdots IO_3]^{2-}$, and K ions through electrostatic forces wherein the cation is eight-coordinated in a distorted square antiprism.

b. β-Diketonates

The status of β-diketonates as anionic ligands for M^{z+} is respectable and is, in fact, one of the earliest to be recognized[763] as mentioned in section II. An account of structure and reactivity of the M$^+$-β-diketone enolates has appeared in a *Tetrahedron* report.[98]

Acetylacetonate (acac) chelates M$^+$ strongly even in a polar medium like MeOH; the strength of the M$^+$acac$^-$ ion pair (^{1}H NMR studies[181]) increases with increase in the charge density of M$^+$,[181–185] so much so that Li is almost completely chelated and acac experiences a Na/Li exchange when, for example, LiClO$_4$ is added to Na(acac). At a low concentration of Li with respect to acac, obtained by adding a little of LiClO$_4$ to Na(acac), an anionic species [Li(acac)$_2$]$^-$ containing four-coordinated Li exists in solution.[181] This anionic soluble complex may even exist in the form [Li(acac)$_2$(MeOH)$_n$]$^-$ where the anionic ligands may either constitute a D_{2h} square plane or a D_{2d} distorted tetrahedron.[172,186] Solutions containing excess cation, such as Li(acac) + LiClO$_4$, contain [Li$_2$(acac)]$^+$ ($K = 1.1 \times 10^3$ M^{-1})[187] in which acac probably acts as a monodentate charge localized anion in the fashion:



The study of metal-β-diketonates[98,181] has revealed an interesting relationship between ion-pair formation and stereochemistry of the anion; small cations which force chelation on the anion arrest carbonyl functions in the cis form (*Z,Z* form) whereas larger cations which form weak ion pairs allow the coulombic repulsions between the carbonyls to rotate one (*E,Z* form) or both (*E,E* form) carbonyls along C–C bond(s).

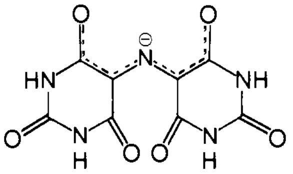
For M$^+$ ions, X-ray diffraction solid-state studies have been carried out on 2,4-pentanedionatolithium[172] and (1-phenylbutane-1,3-dionato)(ethylene glycol)sodium.[173] The former complex consists of endless chains of [Li(acac)$_2$]$^-$ anions which are connected by Li ions (Figure 6) wherein the anion constitutes a square plane (Li–O$^-$, 1.93 Å) while each bridging Li ion is within an approximately tetrahedral environment (Li–O$^-$, 1.95 Å) of two pairs of oxygens belonging to neighboring [Li(acac)$_2$]$^-$ ions. In the Na complex only one β-diketonate chelates the cation whereas ethylene glycol, acting as a monodentate, connects the adjacent Na ions to generate a polymeric structure.[173] The lattice contains five-coordinated cation in a square-pyramidal environment formed by a chelating β-diketonate ion (Na–O$^-$, 2.29 and 2.34 Å), two connecting glycol molecules (Na–O, 2.32 and 2.33 Å), and a shared oxygen of the neighboring chelated anion (Na–O$^-$, 2.36 Å). The classical analogous complex (1-phenylbutane-1,3-dionato)sodium dihydrate[58] is stable in the solid state and being toluene-soluble appears to carry water molecules bound covalently with the cation.

The β-diketonate complexes of M^{2+} ions, of which structures are known, are: Mg(acac)$_2$(H$_2$O)$_2$,[151] Mg(dpp)$_2$(DMF)$_2$,[188] Ca(dpp)$_2$(EtOH)$_{1/2}$,[189] and the dimeric Sr(dpp)$_2$(Me$_2$CO)$_{1/2}$[174] where dpp is 1,3-diphenyl-1,3-propanedionato anion. The structural information on the systems is provided in Table II. A complex of two different spherical cations, which was rather unique at the time it was reported,[190] is Na[Mg(acac)$_3$] wherein the higher charge density cation is within anionic environment while the lower charge density cation acts as a charge neutralizer for the entire anionic entity.

Conditions for the formation of the anionic complexes become more favorable when the nucleophilicity of the anionic ligand is diminished, as of hexafluoroacetylacetonate (hfac) due to the highly electronegative fluorine atoms. The complexes obtained from this anion are of the types[191,192] (M$^+$)$_m$[M$^+$(hfac)$_n$$^-$] ($m$ = 1 or 2, and n = 2 or 3) and [TMNDH$^+$][M^{z+}(hfac)$_n$$^-$] wherein, too, the higher charge density cation gets into the anionic complex; TMND = 1,8-bis(dimethylamino)naphthalene. The former group complexes are:[191] M$^{\prime}$[M(hfac)$_2$] (M$^{\prime}$ = Cs when M is K or Rb, or is Rb when M is K), M$^{\prime}_2$[M(hfac)$_3$] (M$^{\prime}$ = Rb or Cs, and M = Na), and M$^{\prime}$[M(hfac)$_2$(H$_2$O)] (M$^{\prime}$ = K, Rb, or Cs when M = Li, or is K when M = Na). The latter group complexes are:[191,192] [TMNDH$^+$][Li(hfac)$_2$]$^-$, [TMNDH$^+$][Na(hfac)$_2$(H$_2$O)]$^-$, [TMNDH$^+$][Mg(hfac)$_3$]$^-$, [TMNDH$^+$]$_2$[Ca(hfac)$_4$]$^{2-}$, and [TMNDH$^+$][Ca(hfac)$_3$(H$_2$O)$_2$]$^-$. Of the first group complexes, the crystal structure of Rb$_2$[Na(hfac)$_3$], which is isomorphous with $Cs_2[Na(hfac)_3]$, is known.[191] The lattice carries $Na(hfac)_3{}^{2-}$ anionic entities wherein Na is six-coordinated by all the three hfac anions with $Na-O^-$ bonds ranging from 2.20 to 2.47 Å. The Rb ions contact the oxygen and fluorine atoms on the top and bottom of the trigonal prism so obtained, and it may be emphasized that interaction of a halogen *atom* with an alkali cation is one of the rare instances. Of the second group complexes, the crystal structure of $[TMNDH^+][Mg(hfac)_3]^-$ is known.[193] The lattice carries $Mg(hfac)_3{}^-$ entities wherein Mg is octahedrally coordinated involving all the three hfac anions. This property of formation of the anionic complexes appears to be bestowed mainly to the high charge density cations.

c. Purpurate

Purpurate (prp) is another anion the mononegative charge of which is delocalized and gets distributed on more than one donor atom. In the complexes $[Li(prp)(H_2O)]\cdot H_2O$,[194] $K(prp)\cdot 3H_2O$,[195]



$Sr_2(prp)_4\cdot 15H_2O$,[196] $[Ca(prp)_2(H_2O)_2]\cdot 2H_2O$,[197] and $[Ca(prp)(H_2O)_3](NO_3)\cdot 2H_2O$,[198] prp constantly acts as a tridentate ligand but displays a variety in the bonding modes with the cations in question (Table II). All these complexes have been obtained by the reaction of an appropriate salt with $NH_4(prp)$. The complex $[Ca(prp)_2(H_2O)_2]\cdot 2H_2O$ gets crystallized from water whereas the other calcium complex is obtained from EtOH. The latter complex is interesting in the sense that Ca chooses to have two different charge neutralizing anions, prp and NO_3, of which only prp gets into the coordination sphere.

d. π-Carbanions

Formation of the mono- and dinegative anions of hydrocarbons with alkali metals has been known for a long while,[199] and the subject has been under a number of investigations.[200-216] The aromatic carbanions so obtained serve as π-donor ligands and the M^{z+}-carbanion derivatives behave as ion pairs wherein covalency in the $M^{z+}-C$ bond is implied. In such ion pairs the cation possesses more low-energy orbitals than the valence electrons, whereas the combining atom or group is without any unshared electron pair so that the bonds are delocalized and the cation employs all its low-energy orbitals[201,202] to produce a multicenter π-bonded organometallic species. Such species may be of the types M^+Ar^-, $M_2{}^+Ar^{2-}$, or $M^{2+}Ar_2{}^-$ where Ar stands for an aromatic carbanion. Such a multicenter π-bonding is exhibited particularly for the small cations, usually when the latter are "solvated" [203] with a sterically bulky ligand such as tetramethylethylenediamine (TMED), triethylenediamine, or 1,2-dimethoxyethane (DME); the M^{z+}-carbanion bonding is feasible because complete solvation of the cation with bulky ligand(s) is not possible on steric grounds. Interest in M^{z+}-carbanion systems led to their detailed studies in solution, and to their synthesis and crystallography in the solid state.

Solution work has particularly been carried out on the $M^{z+}-fl^-$ (fl^- = fluorenyl anion) ion pairs employing spectrometric techniques and the subject has been reviewed by Smid.[8,22a] The cation in such systems is expected[204,205] to be on the five-membered ring which in the case of the Li^+fl^- ion pair has been confirmed with the help of ^7Li NMR spectroscopy.[206]

Solid M^{z+}-carbanion ion pairs, of which molecular structures have been solved, include Li(benzyl)(triethylenediamine),[203] $Li(fl)(quinuclidine)_2$,[207] K(fl)(TMED),[764] $Li_2(naphthalenide)(TMED)_2$,[208] $Li_2(anthracenide)(TMED)_2$,[209] Li(triphenylmethyl)(TMED),[210] Li(indenyl)(TMED),[211] $Mg(indenyl)_2$,[212] Li_2(hexatriene dianion),[213] $Li_2(acenaphthyne)(TMED)_2$,[214] Li(7b*H*-indeno[1,2,3-*jk*]fluorenide)[215], and $Na_2(tetramethylbis(1,4\text{-}dihydro\text{-}1,4\text{-}naphthylene)dialuminate)(THF)_2$.[216] The structural features of the ion pairs derived from mononegative carbanions are outlined below.

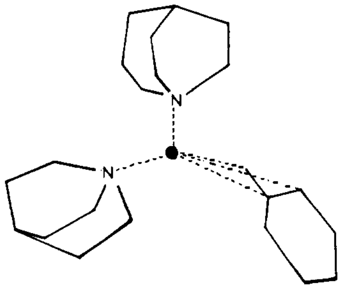


Figure 7. Li(benzyl)(triethylenediamine) (schematic).

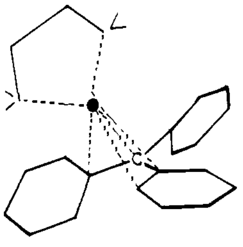


Figure 8. Li(triphenylmethyl)(TMED) (schematic).

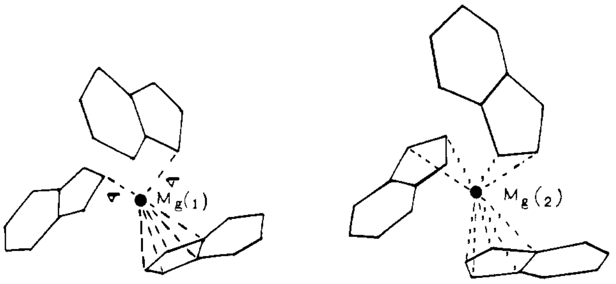


Figure 9. $Mg(indenyl)_2$ (schematic); unlabeled bonds are π bonds.

In Li(benzyl)(triethylenediamine)[203] the cation is formally sp^2 hybridized. In addition to the three σ bonds, two with the diamine nitrogens (Li–N, 2.09 and 2.11 Å) and one with the nonaromatic carbon ($Li-C^-$ = 2.21 Å), the cation interacts also with two phenyl carbons of the carbanion (Li–C, 2.39 and 2.59 Å) (Figure 7). In Li(fl)(quinuclidine)[207] three-center Li–C bonds are established through two carbon p orbitals of the highest occupied molecular orbitals and one low energy molecular orbital of the carbanion (Li–C, 2.33, 2.47, and 2.79 Å). In Li(triphenylmethyl)(TMED),[210] the cation makes three shorter (Li–N, 2.06 and 2.09 Å; $Li-C^-$, 2.23 Å) and three longer bonds with three different phenyl carbons (Li–C, 2.45, 2.51, and 2.54 Å), as shown in Figure 8. In Li(indenyl)(TMED),[211] the TMED-chelated cation (Li–N, 2.10 Å) depicts a five-centered interaction with the five-membered ring of the carbanion (Li–C, 2.28 to 2.38 Å). Unlike this complex, the Mg $(indenyl)_2$ ion pair[212] is unsolvated and contains the cation in two different types of environments; each cation interacts with three indenyl moieties through the five-membered ring, but multicenter bonds with all the three indenyls are formed only by Mg(2) as shown in Figure 9. The rather unique Li(7b*H*-indeno[1,2,3-*jk*]fluorenide)[215] (Figure 10) ion pair exists as a 2:2 sandwich of Li ions with the carbanions of a highly delocalized nature. Such a solid phase, which is formed without the aid of an additional chelating (solvating) agent, owes its formation largely to the covalent interaction between the unoccupied orbitals of the cation and the occupied molecular orbitals of the

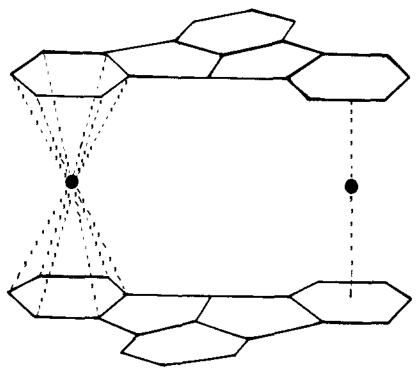


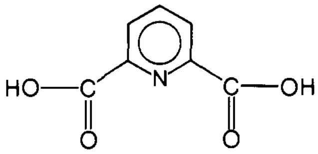
Figure 10. Li(7b*H*-indeno[1,2,3-*jk*]fluorenide) (schematic).

carbanion and to a lesser extent by electrostatic interaction or other factors such as lattice packing.

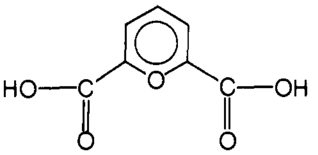
3. Multinegative Anions

The structural information for the rather simple multinegative anion derivatives is provided in Table II. In the following text we limit our discussion on the derivatives of those anions which either carry a biological relevance or present some interesting bonding modes. A hydrated system of edta wherein the cation is exclusively within the solvent environment has been described under solvent complexes (section III.A.2).

To know whether Ca in conjunction with 2,6-pyridinedicarboxylic acid (dipicolinic acid, H_2dpa) could be involved to lock and strengthen the structure of the bacterial spores, molecular structure studies on the compounds $Ca(dpa)(H_2O)_3$[217] and $Sr(dpa)(H_2O)_4$[218] have drawn attention. The former complex has been found to contain the cation in an eight-coordinated state wherein the anion acts as a tridentate through the nitrogen and one oxygen from each carboxylate. Of the extensive bonding that the cation undergoes there is a strong dimerizing linkage which may be related to the structure strengthening of the spores in the presence of Ca and H_2dpa in biological systems. In the $Sr(dpa)(H_2O)_4$ complex (Figure 11), dpa acts as a tridentate but the cation is nine-coordinated. The discrete dimers that occur in $Ca(dpa)(H_2O)_3$ are also not present in the Sr complex. $Ca(pdc)(H_2O)_3$[219] (pdc = 4*H*-pyran-2,6-dicarboxylate) is found to be isostructural with $Ca(dpa)(H_2O)_3$, and, interestingly, pdc can substitute dpa in metabolic properties the latter imparts to the bacterial spores.

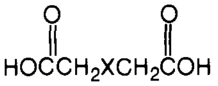


(H_2dpa)



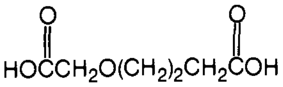
(H_2pdc)

Various metal derivatives of oxydi-, thiodi-, and iminodiacetic acids, and ethylenedioxydiacetic acid (H_2edoda) have been synthesized and subjected to crystallography. The derivatives include MHoda (M = Li to Cs),[220-223] MHtda (M = K or Rb),[224] $M(Hida)(H_2ida)$ (M = Rb or Cs),[225] $Ca(edoda)(H_2O)_3$,[226] and $Ca(oda)(H_2O)_6$.[227] These compounds have been examined to determine, in particular, the coordination, conformation, and hydrogen-bonding features of the anionic ligands. The Ca derivatives can be synthesized by the reaction of the concerned acid, H_2oda or H_2edoda, even with a neutral salt like $Ca(NO_3)_2$;[226,227] for the synthesis of M^+ derivatives a 1:1 reaction of the acid with an alkali hydroxide is required.



$\mathrm{HO\overset{O}{\overset{\|}{C}}CH_2XCH_2\overset{O}{\overset{\|}{C}}OH}$

X = O, oxydiacetic acid (H_2oda)
X = S, thiodiacetic acid (H_2tda)
X = NH, iminodiacetic acid (H_2ida)



$\mathrm{HO\overset{O}{\overset{\|}{C}}CH_2O(CH_2)_2CH_2\overset{O}{\overset{\|}{C}}OH}$

H_2edoda

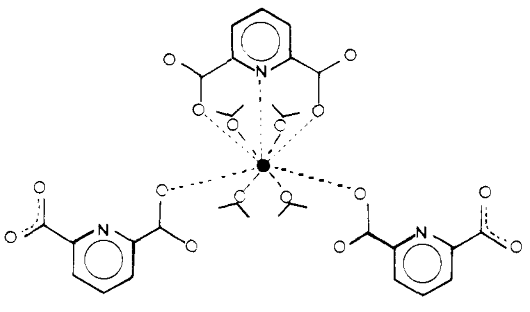


Figure 11. $Sr(dpa)\cdot 4H_2O$.

The M^+–O contacts in the MHoda species are Li(5),[220] Na(7),[221] K(7),[221,222] Rb(8),[222,223] and Cs(8) (isostructural with the analogous Rb derivative).[223] The $M(Hida)(H_2ida)$ (M = Rb or Cs)[225] derivatives are structurally dissimilar to the ML,HL type of products discussed in section III.B.2. The difference lies in that the monoprotonated and the diprotonated anions coordinate the cation independently. The cation lacks bonding contacts with nitrogen atoms and is surrounded by oxygens only (Table II). In the KHtda and RbHtda compounds the M^+–S distances are almost the same but are rather long (3.64 Å).[224] In the complex $Ca(oda)(H_2O)_6$[227] the cation is eight-coordinated and the anion is triply chelating through the ethereal oxygen and two anionic oxygens, one each from a carboxylate function; only five water molecules coordinate the cation to complete a distorted dodecahedron while the sixth water molecule exists loose in the lattice. The complex $Ca(edoda)(H_2O)_3$[226] is dimeric wherein the cation is again eight-coordinated and the anion acts as a tetradentate ligand through two ethereal and two terminal carboxylate oxygens. It is noteworthy that edoda is as Ca-philic as oda and that there is no increase in the Ca-sequestering capacity in going from oda to edoda.[226]

Other important carboxylates are the aminopolycarboxylates for which, in addition to the solution studies (e.g., ref 33), diffraction studies have been carried out. The molecular structures of two derivatives of the powerfully ligating nitrilotriacetate (nta), viz., $Na_3(nta)\cdot H_2O$[228] and $Ca(H^+nta)\cdot 2H_2O$,[229] have been solved. The cation in each system is extensively coordinated. The main difference is that the seven-coordinated Ca involves no Ca–N contacts whereas in the Na complex two of the three crystallographically different environments for the cation provide Na–N contacts (2.45 and 2.51 Å, respectively).

Diffraction results for the edta derivatives are available for $Mg[Mg(H_2O)edta]\cdot 8H_2O$,[128] $Na_2[Mg(H_2O)edta]\cdot 5H_2O$,[129] $[Mg(H_2O)_6](H_2edta)$,[132] $Ca_2(edta)(H_2O)_7$,[230] and $M_2^+(H_2edta)(H_2O)_2$ ($M^+ = K$[130] or Rb[131]). When M^+ and M^{2+} are both involved in such a complex, it is M^{2+} which gets into the anionic complex (compare hfac complexes discussed in section III.B.2) as noted for $Na_2[Mg(H_2O)edta]\cdot 5H_2O$ but in competition with a transition cation it serves only as a charge neutralizer for the anionic complex as noted for $Ca[Fe(H_2O)dcta]_2\cdot 8H_2O$[231] (dcta = 1,2-diaminocyclohexane-*N*,*N'*-tetraacetate).

4. Sugar Anions and Anionized Sugars

Here we term a species such as gluconate as a sugar anion and a sugar phosphate (or a sugar phosphate in a nucleotide) as an anionized sugar. The main difference of these anions from those discussed above is that they carry rather a series of neutral donor sites. The study of the M^{z+}–sugar anion systems is important because anionic sugars located on the cell membrane are believed to modify the surface charge of the membrane,[232] to regulate the mobility of M^{z+} around and across the cell membrane,[233,234] and, in general, to influence the recognition

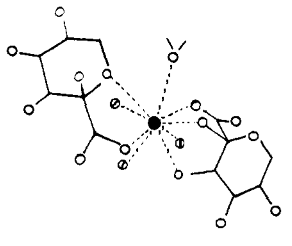


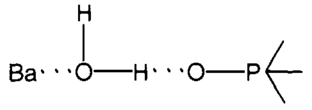
Figure 12. $Ca(2\text{-keto-D-gluconate})_2 \cdot 3H_2O$. (⊖ oxygen is from adjacent anion).

and interactivity of the region.[235] Further interest is involved because such anions located in the intracellular regions modify some physicochemical properties of the tissues through interaction with M^{z+}.[236] Because of its biological implications[237] and understandably its pronounced interactions, the anionphilic Ca has more frequently been investigated with these ligands compared to the other cations. Such studies in solution include those on calcium ascorbate,[238-240] calcium and potassium glucarate,[241] calcium uronate oligomers,[242] and calcium uronic acid.[243] Alginate, a copolymer of 1,4-linked D-mannuronic and L-guluronic acids, which can precipitate M^{2+} ions from water,[244,245] has been subjected to Na/M^{2+} exchange studies.[246] The selectivity order shown by this anion is Ba > Ca ~ Sr ≫ Mg which, of course, is influenced by the ratio of the constituting acids in the polysaccharide anion.

The solid phases which have been the subject of X-ray crystallography are: M(D-arabonate)$_2$(H_2O)$_5$,[247] (M = Ca or Sr), K(D-gluconate)(H_2O),[248] Ca(5-keto-D-gluconate)$_2$(H_2O)$_2$,[249] Ca(2-keto-D-gluconate)$_2$(H_2O)$_3$,[250] Ca(Br)(α-D-glucuronate)(H_2O)$_3$,[251] MNa(α-D-galacturonate)$_3$(H_2O)$_6$, (M^{2+} = Ca[252,253] or Sr[252]), Sr[(4-*o*-4-deoxy-β-L-*threo*-hex-4-enosyl)-α-D-galacturonate](H_2O)$_{4.5}$,[254] Ca(D-glucarate)(H_2O)$_4$,[255] K(D-glucarate),[241] Ca(ascorbate)$_2$(H_2O)$_2$,[256,257] Na(ascorbate),[258] Na(D-isoascorbate)(H_2O),[259] Ba(2-*o*-sulfonato-L-ascorbate)(H_2O)$_2$,[260] Ca(α-D-glucoisosaccharate)$_2$,[261] and Ca(Br)(lactobionate)(H_2O)$_4$.[262] The Ca derivatives which were worked out by 1975 have been reviewed by Cook and Bugg.[17] A brief discussion on the other Ca systems and of other cations is provided below.

K(D-gluconate)(H_2O)[248] is an interesting case in that in one crystalline form the cation is eight-coordinated only with the hydroxyl and water oxygens and *not* with carboxylate whereas in the other crystalline form, K–O^- (COO^-) is the shortest (2.68 Å) bond in a nine-coordinated system. The rather more anionphilic Ca in Ca(2-keto-D-gluconate)$_2$(H_2O)$_3$[250] is sandwiched by the two anionic ligands in conjunction with coordination of a water molecule (Figure 12). The polyhedron around the nine-coordinated cation differs significantly from the standard seven- or eight-coordination polyhedra generalized for the hydrated or the coordinated calcium by Cook and Bugg.[17] In the complexes MNa(α-D-galacturonate)$_3$(H_2O)$_6$ (M^{2+} = Ca or Sr)[252,253] the divalent cation is nine-coordinated and involves the anionic sites whereas Na is octahedrally coordinated only with the hydroxyl oxygens. Such a preference of the higher charge density cation for the anionic environment has also been highlighted for hfac and edta complexes (vide supra). The cation in each of K(D-glucarate)[241] and Ca(D-glucarate)(H_2O)$_4$[255] is eight-coordinated; K employs six different monoanionic ligands whereas Ca, perhaps owing to an extensive participation of the water molecules, involves only two dianionic ligands. In Na(ascorbate)[258] and Na(isoascorbate)(H_2O)[259] the cation is six-coordinated, but the octahedron is significantly more distorted in the anhydrous system; that Na(ascorbate) and K(D-glucarate) crystallize in an anhydrous state is unlike most other sugar anion systems.

Regarding sugar phosphates and sugar phosphate moieties belonging to nucleosides and nucleotides, i.e., anionized sugars, we do not intend an extensive survey. The following information on these systems may, however, be noted. Two metal derivatives of the sugar phosphates have been characterized crystallographically, viz., K_2(glucose-1-phosphate)(H_2O)$_2$,[263] which is isomorphous with the analogous diammonium derivative, and Ba(α-ribose-5-phosphate)(H_2O)$_5$[264] in which the cation maintains seven short (2.67–2.88 Å) as well as five long (3.14–3.80 Å) contacts constituting a distorted icosahedron; all the three interactions of α-ribose hydroxyls belong to the shorter group. A rather interesting feature of the lattice is that barium ion is not linked directly to the phosphate oxygens but is connected through bonding water molecules in the fashion



$$\mathrm{Ba\cdots \overset{\displaystyle H}{\overset{|}{O}}{-}H\cdots O{-}P\!\!<}$$

The hexaphosphate of *myo*-inositol, a sugar-related species, forms sodium derivatives in three different states of hydration, viz., $Na_{12}(C_6H_6P_6O_{24})(H_2O)_x$ where x = 33, 35, or 38.[265] Regarding nucleotide–sugar phosphate derivatives, a few have been mentioned under solvent complexes (section III.A.2). The structural features of Ca(thymidylate)(H_2O)$_6$[266] and Ba(uridine 5′-phosphate)(H_2O)$_n$[267] contrast with each other in the sense that the anionphilic Ca makes direct contacts with the phosphate oxygens whereas Ba–PO_4 interactions are intercepted by the neutral water molecules as illustrated for Ba(α-ribose 5-phosphate)(H_2O)$_5$ above. The Li(NAD^+)[268] complex (NAD^+ = oxidized form of nicotinamide adenine dinucleotides) presents an interesting feature in that Li coordinates to N(7) of adenine (Li–N, 2.13 Å)—an interaction which is in general absent for the various M^{z+}-nucleotide systems in solution;[269] detailed solution work on M^{z+}-nucleotide systems has led to the conclusion that only phosphate oxygens serve as interaction sites for the cation[270] and that stability of the metal derivative is basically (roughly) determined by interaction ability of the phosphate moiety(ies).

Further details on M^{z+}-nucleotide systems may be traced back to the earlier treatments.[270-275]

C. Electrically Neutral Ligands as Ligands

Whether O-donor or N-donor, ligands of this group can be divided in two categories:

(i) Ligands which are devoid of a polar or a polarizable hydrogen such as a glyme or 1,10-phenanthroline. Such ligands stabilize only the cation and not its counteranion and usually produce ion-paired complexes. The ligand/M^{z+} ratio in the product is usually low and is a function of the nucleophilicity of the anion; the ligand/M^{z+} ratio decreases as the nucleophilicity of the anion increases.[167] Although these ligands do not complex a cation via its charge separation, yet charge separation of the complexing salt may become a consequence of complexation. Ligands of this group complex M^{z+} effectively when electron density of the donor atom is supplemented (a) by a delocalized electronic system of the molecule bearing the donor atom as in 1,10-phenanthroline,[276] (b) by incorporation of electronic effects, e.g., by substitution of +I group(s) on the donor atom as Me in a glyme or in TMED, or (c) by supporting the donor atom through direct linkage with an electronegative atom such as oxygen in pyridine oxides, arsine oxides, and phosphine oxides. Ligands conforming to condition (c) may be termed "reinforced ligands". With the small cations in particular, which exhibit a self-complexing[45] property due to their high charge density, these ligands can force a charge separation of the complexing salt on steric as well as electronic grounds, and usually yield charge-separated products of a high ligand/M^{z+} ratio.

(ii) Ligands, such as hydroxyl compounds or amines that carry a polar proton or polarizable hydrogen atom. Such ligands can stabilize also the counteranion of the complexing cation by bonding it at the polar hydrogen and act as "double action li-

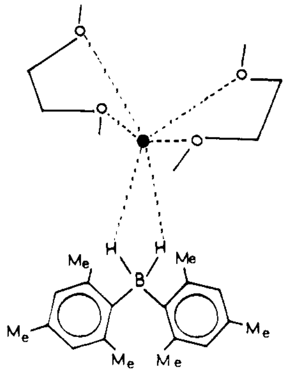


Figure 13. Li(dimesitylborohydride)(GLYME-2)$_2$.

gands" which are exemplified by sugars and amides. During complexation with these ligands, complexation of the cation and bonding of the anion aid each other and hence charge separation of the complexing salt.[18] The charge-separated products so obtained are usually marked by a high coordination number for the complexed cation. With the ligands of this group, complexation is facilitated when the complexing salt, in addition to a highly acidic M^{z+}, is composed of a highly basic anion; only under these conditions are M^{z+} complexation and anion stabilization both facilitated.[18] This is in contrast with the behavior of the group (i) ligands, the efficiency of which for a given cation enhances with decrease in the nucleophilicity of the counteranion. In complexes of these group ligands the ultimate behavior of the counteranion can be any of: pairing with the complexed cation, bonding with polar protons of the ligand, and inclusion in the system as a disordered ion depending on availability of the space around the cation and compactness of the resulting lattice. In the following discussion classification of the ligands has been done both in view of the nature of the donor atom and of these principles involved during their complexation.

1. Simple O-Donor Ligands

In addition to the O-donor solvents (section III.A), there are some neutral molecules such as glymes, esters, and individual compounds like antipyrine and tropone which interact with M^{z+} through ethereal or carbonyl oxygens.

Glymes, i.e., the dimethyl ethers of the diols, can be represented by the general formula $MeO(CH_2CH_2O)_nMe$ and denoted by GLYME-2 (n = 1, also called 1,2-dimethoxyethane), GLYME-3 (n = 2, also called diglyme), and so on. Compared to the parent diols they are more well known ligands, essentially because of their frequent use as solvents for diverse reactions involving M^{z+} and to the consequent formation of M^{z+}-glyme derivatives. In GLYME-2, for example, solid MgX_2(GLYME-2)[277] separated out during synthesis of the Grignards reagents which makes glymes unsuitable for this synthesis. The product $NaBH_4$(GLYME-3) crystallizes during the use of $NaBH_4$ in GLYME-3.[278] The formation of K(*tert*-butoxide)(GLYME-2)$_n$ has been postulated[279] during the use of potassium *tert*-butoxide in the glyme for the synthesis of 18-crown-6. A chelate of lithium alkoxide[98,171] in GLYME-2 has been formulated as shown in Figure 5. The recent synthesis of $LiPH_2$(GLYME-2) by metalation of PH_3 with n-BuLi in the glyme[280] is seemingly planned in view of the chelating character of the glyme. The glyme complexes of M^+ for some bulky anions, such as [M(GLYME-3)$_2$][Ta(CO)$_6$] and [M(GLYME-3)$_3$][Mo(CO)$_5$I], have been known for some time.[281]

Since the glymes are relatively poor ligands, deliberate synthesis of M^{z+}-glyme complexes demands the maintenance of some particular conditions: that the effect of the external solvent and that of the counteranion be minimal. Recently, Heijer and Driessen[282] devised experimental conditions conforming to these requisites and complexed highly ion-paired salts such as $MgCl_2$ and $CaCl_2$ to obtain [M(GLYME-2)$_3$](SbCl$_6$)$_2$ using the glyme as medium as well as the ligand and $SbCl_5$ as a sponge to consume Cl. These complexes, undoubtedly, contain an octahedrally complexed cation but, like the most other solid complexes of the glymes, undergo glyme/water exchange and decompose in moisture. The reaction is possible in $MeNO_2$ wherein the intermediate [M(MeNO$_2$)$_6$](SbCl$_6$)$_2$ yields[283] the desired complex by interaction with the glyme.

Of the metal(II) organometallic derivatives, Me_2Mg(GLYME-2) is the relevant complex which has been characterized[284] wherein the glyme chelates with a zerovalent cation. Chelation of glymes has been revealed crystallographically in M_2(cot)(GLYME-3) (M^+ = K[285] or Rb,[286] and cot = cyclooctatetraene dianion), M(biphenyl)(GLYME-5)$_2$ (M^+ = K[287] or Rb[288]), K_2(tmcot)(GLYME-3)$_2$[289] (tmcot = 1,3,5,7-tetramethylcyclooctatetraene dianion), K[Ce(cot)$_2$](GLYME-3)$_2$,[290] and Li(dimesitylborohydride)(GLYME-2)$_2$.[291] The K_2(cot) and Rb_2(cot) complexes are isomorphous and are both ion-paired[286] with the rather nucleophilic cot, whereas the K(biphenyl) and Rb(biphenyl) complexes are nonisomorphous and are both charge separated.[287] The Li(dimesitylborohydride)(GLYME-2)$_2$ complex is rather unique in that the chelated cation bonds with hydridic hydrogens as shown in Figure 13.

M^{z+}-glyme complexation in solution has been followed calorimetrically,[112] conductometrically,[292] and, using fluorenyl salts, spectrophotometrically,[8,22a] which lead to a general conclusion that complexation enhances with increase in chain length of the glymes. This, of course, holds up to a certain chain length beyond which there is a little effect as noted for Li^+fl^- beyond GLYME-4 and for Na^+fl^- beyond GLYME-5;[22a] the 1:1 K^+fl^--glyme ion pairs undergo charge separation with the second molecule of the glyme and the process is in accordance with its chain length but the efficiency is at a maximum when it is GLYME-4 beyond which steric factors make the glyme less efficient.[22a] Superimposed on the chain length factor is also the effect of the counteranion which has been discussed in a rather informatory review.[22a] For a discussion on the interactive behavior of a glyme with respect to some common solvents recent publications may be consulted.[108,293] The K-glyme interactions under a competitive effect of MeOH have also been studied.[294] Discussion on complexation with GLYME-5 and higher glymes will be provided in section IV.D.

Although esters are poorly coordinating species especially for the larger (low charge density) M^+, yet M^{z+}-ester coordination is evidenced by the observations: (i) $LiClO_4$ and $Ba(ClO_4)_2$ salts are highly soluble in methyl acetate, propionate, and isobutyrate,[295] (ii) the complex $Ba(ClO_4)_2$(methyl pivalate)$_4$ can be crystallized[295] from a saturated solution of the salt in the ester, and (iii) various esters afford solid Mg complexes of the composition $MgI_2(RCO_2R')_6$[70] (R = H or Me and R' = Me or a higher alkyl group). Solid complexes of the bidentate dimethyl phthalate (DMP) have been synthesized for $MgCl_2$ and $CaCl_2$ under a minimized effect of chloride[296] as maintained during the synthesis of M^{2+}(GLYME-2)$_3$ complexes.[282] This involved the use of MCl_2-DMP-$InCl_3$ reaction mixtures in anhydrous $MeNO_2$ so as to obtain $M^{2+}(DMP)_3(InCl_4)_2^-$.

For acetic anhydride, 1:1 complexes of MOAc salts (M = Li to Cs) and 1:2 complexes with $Mg(OAc)_2$ and $Ca(OAc)_2$ have been claimed[297] to be synthesized through a direct reaction of the reactants. We, however, have found[765] that under the recommended conditions of the reaction the products obtained for Li, Na, and K (that we studied) were, in fact, of the composition M(OAc,HOAc), i.e., of the ML,HL type (section III.B.2). This is, obviously, because of the hydrolysis of acetic anhydride during the reaction.

Coordination of the monocarbonyl tropone (2,4,6-cycloheptatrien-1-one) with the rather high lattice energy salts LiBr and $CaBr_2$ and production of the complexes[298] LiBr(tropone) and

$CaBr_2(tropone)_2$ is itself interesting. Antipyrine, which is also a monodentate carbonyl compound,[299] is capable of dissolving the salts, and solid complexes of the composition $[M^{2+}(antipyrine)_6]X_2^-$ (X^- = ClO_4 for Mg, Ca, and Sr, or BF_4 for Mg and Ca) can be crystallized.[300,301] X-ray analysis[299] of $Mg(antipyrine)_6(ClO_4)_2$ shows that only the oxygen, which is favorable sterically as well as electronically, coordinates with the cation.

2. Reinforced O-Donor Ligands

Herein is discussed the ligating ability of the oxides of some compounds of the electronegative elements such as phosphine oxides, pyridine oxides, arsine oxides, phosphoramides, alkyl phosphates, and alkyl sulfoxides—the ligands in which the donor ability of oxygen is reinforced by the electronegative atom to which it is bound. Ligation of oxides such as dimethyl sulfoxide (Me_2SO) and hexamethylphosphoramide (HMPA) had been discovered during their use as solvents whereas that of phosphine oxides and alkyl phosphates has been established through their use as extractants. In the case of alkyl phosphates, in particular, the interest lies in the need to understand the interaction behavior of high-energy molecules such as adenosine triphosphate (ATP) with M^{z+} in natural systems.[302] The ligand/M^{z+} ratio in the complex can be as high as 5 to 6 and charge separation of the complexed cation is possible under most conditions.

In solution, complexation of tributyl phosphate (TBP) with M^{z+} has been investigated for various counteranions employing phase-transfer studies;[303-308,766] the ligand/M^{z+} ratio for $NaClO_4$–TBP and $Sr(ClO_4)_2$–TBP systems in *n*-hexane is 5[308] and for $Sr(ClO_4)_2$–TBP in benzene is 4.[303] Complexation of triphenylphosphine oxide (TPPO) with ML (M^+ = Li to Rb, and L^- = an organic anion such as 2,4-dinitrophenolate) in THF has been followed conductometrically.[292] The interaction enhances in the order Rb to Li and the ligand has been noted to act independently even when THF contains water. Chelation of MX (M^+ = Li to Cs and X^- = Cl, Br, and I) with $Ph_2P(O)CH_2P(O)Ph_2$ and of NaI with $R_2P(O)CH_2P(O)R_2$ (R = Bu, BuO, and *p*-$MeOC_6H_4$) and $Ph_2P(O)CH_2P(O)(OEt)CH_2P(O)Ph_2$ has been followed conductometrically in MeCN medium.[309] Phosphoramides such as HMPA and OMPA (octamethylpyrophosphoramide) in solution render the ion pairs loose,[206,310] but the counteranion deters the M^{z+}-ligand interaction in accordance with its nucleophilicity; enhancement in molar conductance of MX_z in $MeNO_2$ on the addition of OMPA is counteracted by X^- in the order Cl > NO_3 > ClO_4.[310] For Na as a standard cation in $MeNO_2$, Me_2SO has been found to be roughly as[311] coordinating as HMPA, as expected from Gutmann's donicity scale;[92] in the presence of pyridine it undergoes structure breaking and its donicity is enhanced.[311] The M^+–Me_2SO coordination in solution has been followed for diverse systems employing NMR,[116,311,312] solution IR,[313,314] conductometry,[315] and calorimetry.[316] Ion-pair loosening ability of Me_2SO has been illustrated[116] and, in the case of Na, coordination number 6 has been established.[108,317] For some alkali salts, coordination with related sulfoxides such as dipropyl sulfoxide and dibutyl sulfoxide has also been monitored employing solution IR.[313]

Some solution work has led to the formation of solid complexes; during the study of synergetic effect of various organophosphates, and aryl- and alkylphosphines on the extraction of Li and Na with dibenzoylmethane anion (dbm), water-insoluble complexes such as $Li(dbm)(TBP)_2$ (oily) and $Li(dbm)(TOPO)_2$ (white solid) (where TOPO = tri-*n*-octylphosphine oxide) have been characterized.[318] Employing TOPO as extractant in the water/*p*-xylene system, Li has been separated from other M^+ ions in the form of $Li(dbm)(TOPO)_2$ complex.[319]

The solid complexes of some phosphine oxides which have been characterized include $MX(TPPO)_5$ (M^+ = Li[320,321] or Na,[320] and X^- = Br, I, etc.[320]), $LiI(TPPO)_4$,[322] $MX_2(TPPO)_4$ (M^{2+} = Mg or Ca, and X^- = ClO_4[323] or BF_4[324]), $LiX(PDPO)$[325] (X^- = Br or I), $Mg(ClO_4)_2(PDPO)_3$ (PDPO = phenacyldiphenylphosphine oxide),[325] and $Mg(ClO_4)_2(THPO)_6$[326] (THPO = trishydroxymethylphosphine oxide). In most systems, especially where the anion is weakly nucleophilic, a high ligand/M^{z+} ratio is found and the phosphine oxide fulfils both electrostatic and spatial requirements of the cation. X-ray analysis of $LiI(TPPO)_5$[321] supports the conclusion and reveals a tetrahedral coordination of the cation with four TPPO molecules while both I and the fifth TPPO molecule exist disordered in the lattice. In $Mg(ClO_4)_2(THPO)_6$,[326] a high THPO/Mg ratio perhaps compensates the low basicity of the ligand. For Bu_3PO[767] and Me_3PO[768] as ligands see as cited.

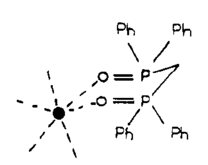
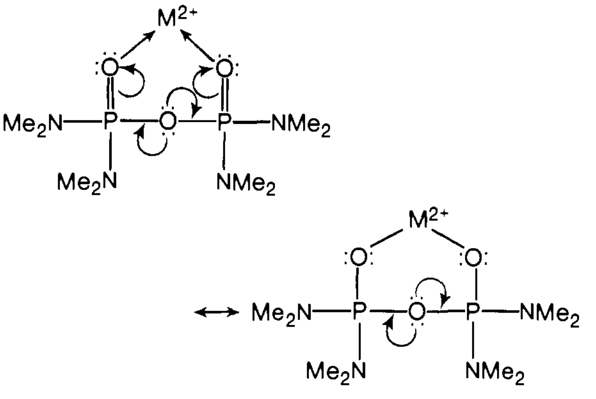


Figure 14. $Na(MBPO)_3Br{\cdot}3H_2O$ (ligation of one molecule is shown).

Solid complexes of HMPA with M^+, viz., $MX(HMPA)_n$ (where M^+ = Li with X^- = Cl, Br, SCN, ClO_4, NO_3, and BF_4, or Na with X^- = I, SCN, and ClO_4; and n = 1 to 4) are known[327-329] wherein IR spectral studies indicate P=O→M^+ coordination. It may be noted that with HMPA the self-complexing Li can complex even in the presence of anions like Cl and Br. More work, however, is needed to settle some conflicting results.[329] The complex $MgBr_2(HMPA)_2$ has been obtained following a rather interesting method of synthesis which involves interaction of HMPA with EtMgBr in Et_2O to produce rather labile crystals of the product.[330] The monoclinic crystals, which can be protected under a layer of ligroin, change phase on storage.[330] Various solid complexes of OMPA have been characterized for M^+ as well as M^{2+}.[310] The complexes for ClO_4 carry only OMPA molecules (1 to 3) whereas those for Cl derive also two or four molecules of water. In such products P=O stretching frequency is lowered and P–O–P and P–NMe stretching[310] frequencies are raised indicating P=O coordination and charge delocalization of the ligand molecule as shown in eq 1. X-ray crystallography on the complex $[Mg(OMPA)_3](ClO_4)_2$[302] indicates that the cation is chelated only through the P=O sites of the bidentate and that the pyrophosphate ring adopts planarity around the cation, not due to any d_π–d_π type of delocalization but due to packing forces involved in the lattice.



(1)

Another bidentate phosphine oxide, methylenebis(phosphine oxide) (MBPO), reacts with NaBr to produce charge-separated $[Na(MBPO)_3]Br{\cdot}3H_2O$ (Figure 14).[331] The six-coordinated cation in a chair-shaped trigonal prism is near to the donor oxygens (2.45 Å) but is nonbonded to Br (>5 Å) and the water (~3.8 Å) molecules. Infrared characteristics of P=O around 1200 cm^{-1} are almost the same as for the uncomplexed ligand indicating that P=O→Na bonding is essentially electrostatic due to directional unsuitability of the 12 lone pairs. This probably also

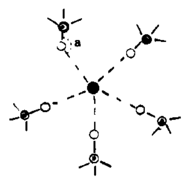


Figure 15. $Mg(TMAO)_5(ClO_4)_2$ (cationic part; ⊙ denotes As).

explains why a chair-shaped geometry is preferred over octahedral.[331]

Complexes of the composition $MX_z(ligand)_n$ (M^{z+} = Li, Na, Mg, or Ca, and n = 2, 4, or 6) have been synthesized from a weakly solvating medium like Et_2O where ligand is a pyridine oxide such as pyridine 1-oxide, 4-methylpyridine 1-oxide, 4-methoxypyridine 1-oxide, or 4-cyanopyridine 1-oxide.[332] The $O \rightarrow M^{z+}$ coordination in the pyridine 1-oxide complexes is indicated by lowering of the 1265 and 840 cm^{-1} absorption peaks of the ligand and by the difference in the exothermic decomposition temperature of the complexes (305–320 °C) and the ligand (273 °C).[332]

Arsine oxides, with $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$, yield solid complexes of the types $[M(R_3AsO)_4ClO_4](ClO_4)$ and $[M(R_3AsO)_5](ClO_4)_2$[333–335] in which M^{2+} was originally[333] postulated to be five-coordinated. X-ray analysis of $[Mg(TMAO)_5](ClO_4)_2$[334] reveals the cation to be five-coordinated in a square pyramid (Figure 15). The appropriate electronic and spatial characteristics of the five molecules of TMAO (trimethylarsine oxide) render the system charge separated and confer to the cation an unusual stereochemistry which, of course, is common for this cation in biomolecules such as chlorophylls (section IV.F). The Mg–O distances range between 1.92 and 2.05 Å; for the shorter (axial) Mg–O bond a strong π-bonding has been argued in view of a rather wider angle a.[334] X-ray analysis of the complex $[Ca_2(TMAO)_9](ClO_4)_4$[335] shows the system to be binuclear (Figure 16). The cation which is octahedrally bound to the six ligand molecules is charge separated and the two ClO_4 ions are disordered. The three ligands which bridge the cations make longer (2.42 Å) contacts than the other three ligands (2.28 Å) each of which is bound to one cation. The large-sized Ca does not force a π-bonding ("trans effect") on any of the Ca–O bonds and a higher coordination number is depicted unlike that of Mg in $[Mg(TMAO)_5](ClO_4)_2$.

Solid M^+–Me_2SO complexes have been obtained[336] from salt solutions in Me_2SO, either by evaporation of the solvent or by insolubilization of the product with benzene. Such solid complexes, which include $KSCN(Me_2SO)_2$, $KI(Me_2SO)_{1.5}$, $NaX(Me_2SO)_n$ (n = 1.5 to 4), and $LiX(Me_2SO)_n$ (n = 1 to 3.5), show lowering of infrared absorption frequencies due to S–O wherein all the Me_2SO molecules in the product are not equivalent. The diversity should be attributed to the nature of X which can be known precisely by the diffraction techniques alone. The conditions under which $Ba(pnb)_2$–Me_2SO (pnb = *p*-nitrobenzoate) has been synthesized are interesting in that the complex is separated from Me_2SO which contained water.[337] The success of this synthesis may be attributed to a sort of immobilization of water molecules through bonding with strong proton accepting Me_2SO molecules.[338]

3. Double Action O-Donor Ligands

The term "double action" has been introduced during discussion on M^{z+}-solvent coordination in the solid state (section III.A.2) and applies to a ligand which is capable of stabilizing a cation and an anion simultaneously. In addition to the hydroxylic solvents discussed in that section, other ligands which display this ability include diols, carbohydrates, amides, and related molecules.

The diols (glycols) of the general formula $HO(CH_2CH_2O)_nH$ are the simple hydroxylic multidentates known for M^{z+}, although systematic studies on the lower members ($n < 5$) had not been carried out until recently.[339,769] We arbitrarily separate the lower members from the rather more studied higher homologues which have been treated as acyclic macromolecules (section IV.D). A reason for this bifurcation is that during complexation with the lower glycols there *can be* a contribution of the polarizable hydroxyl hydrogens whereas in the case of the higher homologues these hydrogens may be deactivated through a possible intramolecular bonding. In the following text the diol ligands, like the glymes, are abbreviated as GLYCOL-2 (n = 1), GLYCOL-3 (n = 2), and so on.

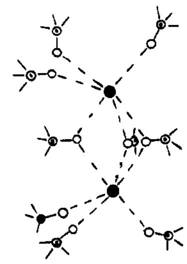


Figure 16. $Ca_2(TMAO)_9(ClO_4)_4$ (cationic part; ⊙ denotes As).

There is unfortunately no evidence in the literature that the lower glycols have ever been systematically studied as ligands for M^{z+}. Of the casual observations which reveal M^{z+}–glycol interaction are (i) the effect of glycols on $E_{1/2}$ values of M^+ in aqueous medium,[340] (ii) the effect of some alkali halides on the structure of GLYCOL-2,[341] (iii) the effect of GLYCOL-2 on viscosity of CsCl,[342] (iv) solubilization of the metal-β-diketonates in GLYCOL-2 and the consequent crystallization of Na(1-phenylbutane-1,3-dionato)(GLYCOL-2)[173] (diffraction studies on which show GLYCOL-2 to be bridging the diketonate-complexed cations), and (v) speculative chelation of glycols with M^+ during template synthesis of crown ethers.[279]

Solution stabilities of M^{z+}–glycol (glycol = GLYCOL-3 to GLYCOL-5) complexes have recently been determined in our laboratory[339] employing $M(pic)_z$ in water as well as in 2-propanol where M^{z+} is Li, Na, K, Cs, or Mg to Ba. In water, only Na and K (log K values <2) undergo complexation whereas in 2-propanol Li and Ca (log K values >2) do so, although, in each medium stabilities and selectivities are rather low. The $Ca(pic)_2$–GLYCOL-5 reaction mixtures in 2-propanol instantly yielded a crystalline complex $Ca(pic)_2(GLYCOL\text{-}5)(H_2O)$ which insolubilized almost quantitatively leaving no yellow color in the medium; complexes of the other $M(pic)_z$ salts do not even crystallize under these conditions. IR spectral studies indicate pic ions to be paired with the anionphilic Ca despite the presence of polar hydroxyl hydrogens in the lattice, the point for the confirmation of which we have undertaken X-ray diffraction studies on the system. Although in the known complex Na(1-phenylbutane-1,3-dionato)(GLYCOL-2)[173] there is also no charge separation carried out by the hydroxyl hydrogens, yet it is significant to note that these two complexes of glycols are air-stable unlike the most known complexes of the analogous glymes (e.g. ref 287) which though carry electron-supplying Me groups on the terminal oxygens.

Complexation of M^{z+} with carbohydrates is by now well known. The subject has been reviewed in 1966 by Rendleman,[20] in 1973 by Angyal,[9] and for the 1976 Jerusalem symposium by Cook and Bugg.[17] Conditions that influence M^{z+}–carbohydrate complexation have been discussed at length by Rendleman, although, at that time enough information on the subject was not available which could lead to unshakable conclusions. A little was known by that time particularly about the conformational requirements of these ligands for complexation and about the stability values of the complexes in solution. Angyal discussed complexation in solution particularly with respect to NMR techniques whereas Cook and Bugg restricted themselves to the X-ray diffraction results on the Ca systems.

The study of M^{z+}–carbohydrate systems has in part been stimulated by the information[17,343,344] that sugars and related compounds around the cell membrane contribute toward cation transport across the cell membrane. Indeed, the work has been oriented to establish the conformational aspects of a complexing carbohydrate under the electrophilic influence of a cation and to discover the conformation–complexation relationship for the carbohydrate rather than to discover the coordinative characteristics of M^{z+}. Partly because of its biological implications[2,21,22,36,345] and partly because of its ability to complex strongly with these ligands,[9,346,347] Ca has essentially been used for the former type of work.

As ligands, carbohydrates offer a major advantage in that they can display double action, but the associated disadvantage during their use in aqueous medium is that they may undergo hydration in preference to complexation with a cation—a feature attributed to their hydrophilicity. Such a difficulty is pronounced for the highly solvating cations such as Li and Mg (for which complexation is scarce) or in general when the cation is chelated by the counteranion. The relatively anionphilic cations such as Ca and Sr, for which competitive solvation may be less acute (Figure 1), are more efficiently complexed; for the mononegative anions such as Cl or NO_3 stability values with the α-pyranose form of D-allose are distinctly higher for Ca (5.1–6.4) and Sr (5.1–5.9) compared to Ba (2.9) or Mg (0.19).[346] With sugar anions and anionized sugars (section III.B.4), which act as anions as well as multidentates, Ca by far leads the other cations in producing complexes.

At early stages, the M^{z+}–carbohydrate interaction in solution had been followed with the help of paper electrophoresis, polarimetry, conductivity, and viscosity measurements.[20,348] Recently, ^1H NMR[9,346,349–352] and ^{23}Na NMR[353–355] spectroscopy, EMF measurements[347,352] including those using ion-selective electrodes,[352] and calorimetric measurements[356] have been used to obtain the solution information with regard to complexation and conformation of carbohydrates. The essential bonding mode of the sugars is through hydroxyl groups.[9,17] The most suited state of the sequential three hydroxyl groups of the ligating sugar is cis-cis for a five-membered molecule and an axial-equatorial-axial (ax–eq–ax) for a six-membered one.[9,340,346,347,349,352] Such a sequence of hydroxyl groups is favorable for solution complexation because[252] they can constitute the required equilateral triangle on the cation and give rise to favorable entropy factors. For complexation in the solid state, where not the entropy factors but those related to lattice packing are important, just the pairs of the adjacent hydroxyl groups are usually involved with the cation.[252]

The importance of ax–eq–ax arrangement for solution complexation has been revealed by ^1H NMR studies on, for example, an equilibrium mixture of α- and β-pyranose forms of D-allose, where the α-anomer possesses the required sequence of OH groups, undergoes effective complexation.[346] Sugars such as D-glucose, D-arabinose, and D-mannose (except β-D-mannofuranose), which lack such a sequence, do not complex (with $CaCl_2$, ^1H NMR studies[346]). Recent EMF studies[347] have revealed that L-arabinose and D-xylose, which exist essentially in the pyranose form and lack the ax–eq–ax sequence, complex weakly as expected. On the other hand, β-D-lyxose does complex (^1H NMR studies[346,350]) because in this molecule the ax–eq–ax arrangement is possible.

Complexation of sugars in solution is due basically to the presence of three sequential hydroxyl groups of the types mentioned, but in the course of crystallization the problems related to lattice packing usually reduce the number of M^{z+}–sugar contacts and create conditions favorable for water molecules to act as coligands. When the stated structural requirements are not met (as in D-glucose), the sugar behaves generally noncomplexing in the solid phase also. Even Ca fails[357] to yield a complex with D-glucose under all common conditions; $Ca(pic)_2$–glucose reaction mixtures from EtOH–water media, for example, reproducibly yielded only a pentahydrate, $Ca(pic)_2{\cdot}5H_2O$.[357] When such a sugar is present as a moiety in a higher carbohydrate, it may interact in collaboration with the countermoiety, glucose in the complex $NaBr(sucrose)(H_2O)_2$,[358] for instance.

Considerable X-ray structural analysis on crystalline complexes has been carried out to determine the binding sites and the complexation characteristics of the carbohydrates. The most highly studied, no doubt, are the Ca complexes,[17] but the first to be undertaken was $NaBr(sucrose)(H_2O)_2$.[358] In this complex Na is six-coordinated through the water molecules and hydroxyl groups of three different sugar molecules and is paired with the Br ion. The Na–Br distance (~2.94 Å), interestingly, is shorter than the one in uncomplexed NaBr (~2.98 Å). This is apparently because in the uncomplexed salt, Na^+ polarizes the electronic system of Br^- toward itself (Fajans' rule[163]). To restore the electrostatic equilibrium between the two ions, an increase in the internuclear distance takes place.[162] Consequently, the observed internuclear distance becomes longer than the one calculated using ionic radii in the gaseous phase.[359] When Na^+ is stabilized through complexation with sucrose, polarization of Br^- is diminished or vanished and the internuclear distance decreases.

X-ray analysis of Ca–carbohydrate complexes has revealed the cation to be seven- or eight-coordinated, which according to Cook and Bugg[17] is reminiscent of the hydration characteristics of Ca in the solid phase. The complexes $CaBr_2$(D-lactose)$(H_2O)_7$,[360,361] $CaBr_2(\alpha$-D-galactose$)(H_2O)_3$,[360,362] and $CaBr_2$(*myo*-inositol)$(H_2O)_5$[360,363] all contain an eight-coordinated cation forming a square antiprism through coordination with water molecules and hydroxyl groups of the carbohydrate; $CaBr_2$(D-lactose)$(H_2O)_7$,[360,361] which is isostructural with $CaCl_2$(D-lactose)$(H_2O)_7$,[364] is charge separated (Ca–Br, ~4.9 Å) enabling Br to bond with water and sugar protons.

In the complex $CaBr_2(\alpha$-D-fucose$)(H_2O)_3$[365] the coordination number of Ca is reduced to 7 and, consequently, Ca–O bonds become shorter (2.32 to 2.44 Å) compared to, for example, the well-known $CaBr_2$(D-lactose)$(H_2O)_7$ (2.38 to 2.54 Å).[361] Of the other seven-coordinated Ca complexes $CaBr_2(\alpha,\alpha$-trehalose$)(H_2O)$,[366] $CaCl_2(\beta$-D-fructose$)(H_2O)_2$,[367] $CaBr_2(\beta$-D-fructose$)(H_2O)_2$,[368] and $CaCl_2(\alpha$-D-xylose$)(H_2O)_3$,[369] the fructose complexes are isostructural with each other.[368] The complex $CaBr_2(\beta$-D-fructose$)(H_2O)_2$ is of interest in that it was crystallized from (probably a neglected) an aqueous solution of $CaBr_2$–sucrose which was made in an attempt to crystallize a $CaBr_2$–sucrose complex.[368] The complex $CaCl_2(\alpha$-D-xylose$)(H_2O)_3$[369] is of interest in that each oxygen of the sugar except the ring oxygen interacts with the cation in the lattice. Unlike this complex, the ring oxygen in the complex $CaCl_2(\beta$-L-arabinose$)(H_2O)_4$[370] coordinates (where Ca is eight-coordinated). This is a rare mode of bonding.

The two unique complexes which contain eight-coordinated Ca are: (i) $CaCl_2(\beta$-D-fructose$)_2(H_2O)_3$[371] in which sugar/Ca ratio is 2, and (ii) $CaCl_2(\beta$-D-mannofuranose$)(H_2O)_4$[372] wherein the sugar is chelating triply through sequential hydroxyl groups which are rare features for solid sugar complexes. The latest addition to the Ca complexes is $CaCl_2(\alpha$-D-allopyranosyl-α-D-allopyranoside$)(H_2O)_5$[373] which X-ray studies reveal to be a pentadentate complex.

In conclusion, common features of the Ca complexes are: (i) at least one water molecule participates in coordination; (ii) Ca–O contacts are either 7 (shorter) or 8 (longer); (iii) Ca–O distances, except in $CaCl_2(\beta$-L-arabinose$)(H_2O)_4$[370] (2.33–2.70 Å), range between 2.32 and 2.55 Å; and (iv) calcium is separated from the counteranion (halide).

Unequivocal coordination of Sr in sugar systems has been

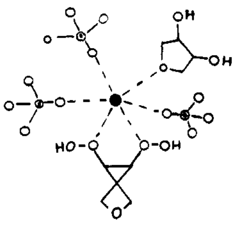
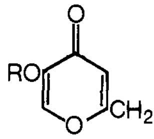


Figure 17. $NaClO_4(AEL)$ (© denotes Cl).

known through structural analysis of only $SrCl_2$(*epi*-inositol)-$(H_2O)_5$.[374] The cation in this complex is nine-coordinated (Sr–O_{av}, 2.63 Å). In addition to four water molecules, one ligand molecule interacts as a bidentate and the other as a tridentate, the latter through three vicinal hydroxyl groups in the ax–eq–ax position. For Mg, also only one system, viz., $MgCl_2$(*myo*-inositol)$(H_2O)_4$,[375] has been investigated crystallographically. The cation is coordinated to all the four water molecules and two cis-vicinal hydroxyl groups of inositol in an octahedral arrangement. Another sugar-related molecule, which has been studied as a ligand, is 1,4-anhydroerythritol (AEL).[376] Crystalline complexes $NaI(AEL)_2$, NaSCN(AEL), and $NaClO_4$(AEL) have been synthesized from EtOH and molecular structure of the last is known.[376] The cation is within a distorted octahedron constituted by three monodentate ClO_4 ions, one molecule of AEL which acts as a bidentate through a pair of hydroxyl oxygens, and another molecule of AEL which interacts only through the ethereal oxygen (Figure 17). The Na–O(AEL) distances (2.29–2.36 Å) are distinctly smaller than the Na–O distances (2.32–2.62 Å) found in the classical complex NaBr(sucrose)$(H_2O)_2$[358] whereas the Na–O(ClO_4) distances (2.37–2.59 Å) are comparatively longer.

The crystal lattice bonding behavior for a neutral and an anionic sugar appears to differ in that the neutral sugar experiences a greater conformation effect on complexation with the cation. This is understandable because the interaction of a cation with an anionic ligand is essentially through the anionic sites, whereas for a neutral sugar the electrostatic effects of the cation are operative exclusively on the hydroxyl groups which are forced into conformational changes.[262]

Kojic acid (5-hydroxy-2-hydroxymethyl-γ-pyrone) and its derivatives constitute an interesting family of sugar-related ligands:



R = R′ = H, kojic acid (**HKH**)
R = Me; R′ = H, 5-methoxy ether (**MKH**)
R = H; R′ = Me, 2-methoxymethyl ether (**HKM**)
R = R′ = Me, 5-methoxy-2-methoxymethyl ether (**MKM**)
R = $PhCOCH_2$; R′ = H, phenacylkojate (**PKH**)
K = γ-pyrone skeleton

In an attempt to methylate HKH with dimethyl sulfate and KOH in different proportions under different conditions, it was observed[377,378] that one of the methylation products, MKH, underwent in situ complexation in the aqueous reaction medium with the byproduct salts, $KHSO_4$ and K_2SO_4, to produce defined colorless crystalline complexes K_2SO_4(MKH), $KHSO_4(MKH)_2$ (mp 180 °C), and $KHSO_4(MKH)_2$ (mp 205 °C), the final authentification of which is in progress. Attempted synthesis employing K_2SO_4–MKH and $KHSO_4$–MKH reaction mixtures failed under all conditions which indicates that in the paired state the polarizing ability of K^+ for MKH is effectively diminished by the highly nucleophilic SO_4^{2-} whereas during a methylation reaction K^+ and SO_4^{2-} are generated as independent ions so that K^+–MKH complexation takes place before SO_4^{2-} pairs with K^+. Of the three complexes, the aqueous solutions of K_2SO_4(MKH) and $KHSO_4(MKH)_2$ (mp 205 °C) do not test for SO_4^{2-} with $BaCl_2$, but aqueous solutions of the melts in each case do. This indicates that in these complexes a strong $-CH_2OH\cdots SO_4^{2-}$ bonding is operative and SO_4^{2-} is not tested unless the bonds are thermally ruptured. In fact, bonding of the anion with $-CH_2OH$ contributes strongly toward making MKH a successful ligand; MKM, which does not contain any such anion-stabilizing proton, proved to be a poor ligand. HKH and HKM, which carry a rather acidic proton, undergo a metathetical reaction instead of complexation in the undissociated form.

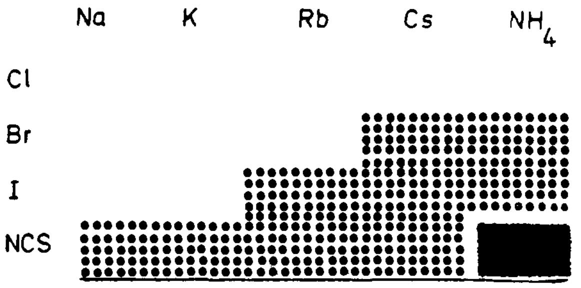


Figure 18. Stoichiometries of $MX(PKH)_n$ complexes: black (synthesis not possible), dotted (1:1 complexes), and blank (1:2 complexes).

Phenacylation studies on HKH with phenacyl bromide in EtOH employing NaOH as alkali established that the reaction product is invariably $NaBr(PKH)_2$ instead of PKH.[379] This led to an interest in studies on PKH as a ligand for M^+ ions[380] and to syntheses of various solid complexes depicted in Figure 18.[18] Molecular structures of $KI(PKH)_2$,[381] CsSCN(PKH),[382] and $NaI(PKH)_2$-$(H_2O)_2$[383] are known. Potassium in its complex is eight-coordinated through two tridentate molecules of PKH and two other molecules of PKH which act monodentate through $-CH_2OH$, while I^-, unconnected to K^+, bonds with the hydroxyl proton of a coordinated $-CH_2OH$. In the complex $NaI(PKH)_2(H_2O)_2$ one PKH molecule interacts as a tridentate and one as a monodentate while the cation continues to be hydrated with two molecules of water (Na–O, 2.30 and 2.58 Å). Iodide bonds with $-CH_2OH$ as in the **K** complex. The cation in CsSCN(PKH) is eight-coordinated despite a low PKH/Cs ratio which is due to an extensive bridging of the cation with PKH molecules and SCN^- ions.

Poonia generalized that 1:2 MX–PKH (Figure 18) complexes, which are obtained only if M^+ is of a higher charge density and/or X^- is of a higher basicity, should be charge separated.[18] This is so because during their formation simultaneous polarization of two PKH molecules by M^+ and a forced bonding of $-CH_2OH$ with X^- should aid each other and hence cause charge separation of the complexing salt. In other cases, where complexes obtained are 1:1, the system should be ion-paired. X-ray results[381–383] obtained on MX–PKH complexes obtained so far are in line with this generalization.

As ligands, amides and related compounds have drawn attraction largely because their mode of interaction with M^{z+} is believed to have a bearing on biomolecules such as peptides which are involved during diverse biological functions of Na, K, Mg, and Ca, e.g., biological mineralization or cell membrane transportation.

Solution (spectroscopic) and theoretical (MO calculations) studies on M^{z+}–amide systems have been carried out[295,384,385] where amide is a simple molecule such as DMF, NMA (*N*-methylacetamide), or DMA (*N*,*N*-dimethylacetamide). A general conclusion is that interaction of M^{z+} takes place through the carbonyl function. Since this interaction leads to delocalization of the amide nitrogen electron pair, these studies derive information on complexation through evaluation of a decrease in C–O and increase in C–N bond orders. Rao and co-workers[385] used M^{z+} more to study the structural features of the complexed amides whereas Baron and co-workers[295] used these cations as coordinating tools to differentiate between the ligating abilities of amides and other carbonyl compounds. In the present context, the studies by Rode[384] are more relevant and conclusive; the coordinating behavior of M^{z+} with DMF (Figure 19) is of particular interest from two viewpoints: (i) M^+–DMF bond strength trends are comparable to those of ΔG (hydration) shown in Figure 1, and (ii) the coordinative effects exercised by M^{2+} ions are comparable to those by similar-sized M^+ ions, presumably because the polarizing ability of the M^{2+} ions toward DMF is partly counteracted owing to their greater involvement with the counteranions. Information on M^{2+}–DMA complexation has also been obtained polarographically.[386]

Solid-state studies on M^{z+}–amide systems have been carried out for primary amides such as acetamide (AM)[82,387] and urea,[388–393] primary-cum-secondary amides such as biuret,[394] secondary amides such as *N*-methylformamide (NMF),[395] NMA,[396] and diacetamide (DA),[397–404,770] and tertiary amides such as DMF,[141,395,397,405] DMA,[295] *N,N,N',N'*-tetramethylurea (TMU),[395] *N*-methyl-2-pyrrolidone (NMP),[397,406] and *N*-methyl-γ-butyrolactam (MBL).[407] Information of interest is provided below.

The only complex of AM which has been the subject of crystallography is $NaBr(AM)_2$[387] which carries an octahedrally coordinated cation involving four molecules of AM and two Br ions; Br behaves nucleophilic enough to pair with the cation as well as to bond with the $-NH_2$ proton. Complexation with urea is rather susceptible to the environment. In $Ca(NO_3)_2(urea)_4$[388] and $Ca(NO_3)_2(urea)(H_2O)_3$[389] there is a distinct difference in coordinative preferences in that the cation in the anhydrous product involves four Ca–O(urea) bonds while each NO_3 simply acts as a monodentate, whereas in the hydrated product there is only one Ca–O(urea) bond while each NO_3 acts as a bidentate. In the heavily coordinated $CaBr_2(urea)_6$,[390] the cation is exclusively in the octahedral environment of the urea molecules. The complex $LiI(urea)_2$[393] is also charge separated, but the unique feature is that each urea molecule binds two cations simultaneously; that a small cation like Li does not coordinate with nitrogen may be because the latter gets cationized (positively polarized) owing to $(H_2N)_2CO \rightarrow Li$ coordination. With the chelating biuret, $Sr(ClO_4)_2$ produces charge-separated $Sr(ClO_4)_2(biuret)_4$[394] wherein the eight-coordinated cation lies exclusively in the oxygen environment.

Of the secondary amides, DA has been studied most,[397-404] and a number of M^+- and M^{2+}–DA complexes have been characterized.[397] The stoichiometry of the solid phases is interesting in that for M^+ the DA/M^+ ratio is constantly 2 whereas for M^{2+} the ratio varies from 2 to 5.

Neither $KI(DA)_2$[399] nor $NaBr(DA)_2$[398] is charge separated (K^+–I^-, 3.56 Å; Na^+–Br^-, 2.8 Å), and DA molecules in each system chelate in a plane. While one axial position in each complex is filled by the anion, the other in the case of the Na complex is filled by a nonbonding nitrogen (Na–N, 3.86 Å) and in the case of the K complex by the bridging oxygens (K–O, 2.82 and 2.97 Å) belonging to two different DA molecules. In the K complex the K^+I^- ion pair is not quite tight, and iodide appears to make a bonding approach to nitrogens (N–I, 3.67 and 3.68 Å). This perhaps indicates that (i) compared to sodium, potassium is vulnerable to the chelating neutral ligands as shall also be emphasized in section IV, and (ii) the amide nitrogen gets cationized so as to attract the iodide.

In the case of M^{2+}–DA complexes, an intriguing variation of stoichiometry has aroused interest in their structural analysis which has revealed that the coordination number of M^{2+} in these complexes increases from Mg to Ba. Magnesium in the apparently highly coordinated $Mg(DA)_4(ClO_4)_2(H_2O)_2$[404] is only six-coordinated; two of the DA molecules "complex" only the protons of the metal-coordinated water molecules which the cation prefers over the ClO_4 ions (solventphilicity of Mg). (See also Figure 1.) The cation in $Ca(ClO_3)_2(DA)_4 \cdot H_2O$,[770] $CaBr_2(DA)_4$,[400] and $Ca(ClO_4)_2(DA)_5$[401] is eight-coordinated and each system is charge separated; the fifth DA molecule in the last complex is nonbonding. In the complex $Sr(ClO_4)_2(DA)_4(H_2O)$[403] the cation enhances its coordination number to 9 due to coordination with a molecule of water. The cation in $Ba(ClO_4)_2(DA)_5$[402] is ten-coordinated and like Sr in the preceding complex is charge separated. It is worth mentioning that all described M^{2+}–DA complexes are charge separated in contrast to the M^+ complexes.

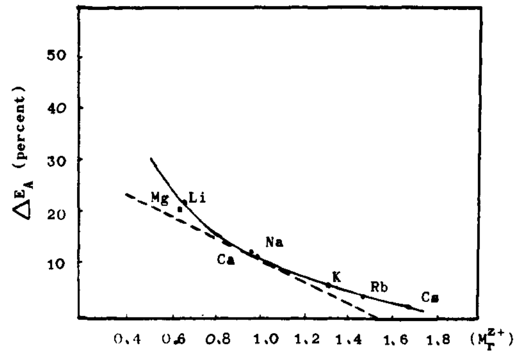


Figure 19. Showing interacting ability of M^{z+} ions with DMF (through percentual change of rotational barrier for DMF) as a function of ionic size (modified from ref 384).

Of the tertiary amide complexes,[141,395,397,405–407] $NaI(DMF)_3$[141] is of interest. Surprisingly, three monodentate molecules of DMF can successfully effect charge separation of the salt while the CH proton behaves electrophilic enough to bond with iodide.

In conclusion, complexation of M^{z+} with amides is consistently through the carbonyl function whereas NH and NH_2 functions usually participate toward the stabilization of counteranion. The latter could be either due to a forced bonding with a proton in the case of a nucleophilic anion like Cl, or due to dipolar interaction[408] of the anion like SCN with nitrogen which is cationized due to $CO \rightarrow M^{z+}$ coordination; IR spectral studies on MX–urea (MX = an alkali halide) systems indicate that the interactions primarily involve hydrogen rather than oxygen atoms.[409] Despite an active state of NH and NH_2 functions some systems can continue to be ion-paired as noted for $NaBr(AM)_2$,[387] $Ca(NO_3)_2(urea)_4$,[388] $Ca(NO_3)_2(urea)(H_2O)_3$,[389] $NaBr(DA)_2$,[398] and $KI(DA)_2$.[399]

The other amides and related compounds, which are even more potential double action species, are amino acids and peptides, for despite their molecular nature they operate as zwitterions. The NH_3^+ function of these ligands can compete successfully with M^{z+} for the anion while M^{z+} enjoys the anionic carboxylate site on the ligand. Such a situation has been revealed by diffraction studies on the complexes $NaI(glycine)_2(H_2O)$,[410] $CaI_2(glycine)_3(H_2O)$,[411] $CaCl_2(sarcosine)_3$,[412] $LiBr(alanylglycine)(H_2O)_2$,[413] $NaI(cysteiylglycine)$,[414] and $CaCl_2(glycylglycylglycine)(H_2O)_3$.[415]

4. Simple N-Donor Ligands

1,10-Phenanthroline (PHEN) is an important ligand of this category which has been found successful for complexation of M^{z+}.[84,167,177,192,416–426] In view of the negative charge (0.377) carried by the donor nitrogens,[276] we[167] consider PHEN to be a sort of "anionic ligand" despite its molecular nature, a feature which makes it behave M^{z+}-philic. As a ligand, PHEN was first used for M^+ ions[84] though later it has also been studied with M^{2+} ions.[416,417]

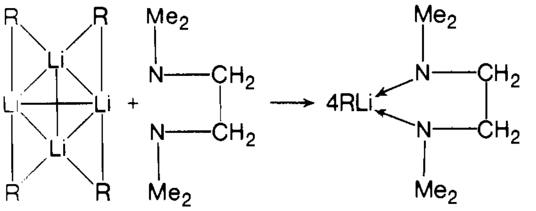
Of the M^+ ions, 1:2 (M^+:PHEN) solid complexes can in general be synthesized for the larger cations (Rb and Cs).[419] The relatively smaller Na forms 1:2 complexes only when the reaction mixture contains foreign proton donor species which can stabilize the counteranion.[167] All types of M^+–PHEN complexes, however, decompose in *N*-methylpyrrolidone and show conductance of the parent salt.[176,177] X-ray analysis of Na(onp)-$(PHEN)_2$ and $Rb(onp)(PHEN)_2$ (which is isostructural with the analogous K complex) shows that in each complex both PHEN molecules are M^+-coordinated[421] (Table II); the Na complex is monomeric but the Rb complex dimerizes through a nitro oxygen.

In the case of ML-PHEN systems, where L is an organic anion such as onp, chelation of M^+ by L (ortho-substituted) was considered to be a prerequisite for M^+-PHEN complexation.[419] Later[167] it was concluded that the ortho group on L aids complexation merely because it delocalizes the charge of L; this causes M^+ to become accordingly indifferent to L and polarizes PHEN more effectively. The M^+-PHEN interaction is favored also when HL is used in the ML-PHEN reaction mixture.[167] Employing such reaction mixtures, complexes containing acid anions, viz., $M(PHEN)_n(L,HL)$ (n = 1 or 2), also have been synthesized.

Stoichiometric $M(ClO_4)_2(PHEN)_4(H_4O)_4$ complexes have been characterized wherein all PHEN molecules had been believed to undergo coordination.[417] However, spectroscopic studies[422] and recent X-ray analysis[423] have revealed that even for the larger cations the complexes are, in fact, of the type $[M(PHEN)_2(H_2O)_4](ClO_4)_2(PHEN)_2$ (M^{2+} = Sr or Ba) where the tetraaquated cation is complexed with two PHEN molecules and gets into an eight-coordinated distorted cubic environment.

Despite two electron-supplying Me groups on carbon atoms adjacent to the donor nitrogens, 2,9-dimethyl-1,10-phenanthroline (DMPHEN) proved to be a poor ligand (for K), although, KL(DMPHEN) (L = anth or sal) complexes have been characterized,[177] which is perhaps due to steric effects of the substituents. Synthesis of Na and K complexes also failed[167,177] with 4,7-diphenyl-1,10-phenanthroline (perhaps owing to depolarization of the donor nitrogens with the phenyl substituents) and 2,2'-bipyridyl and 2,2'-biquinoline (owing to the preferred configuration of these ligands being trans[427,428]). The cis configuration, required for the formation of complexes, cannot be forced by M^+ because of the dominant ionic and hence weak nature of the M^+-N bonds; the higher charge density Li, Mg, and Ca, for which the M^{z+}-N bond can be comparatively covalent, undergo 1:1 complexation with 2,2'-bipyridyl as with PHEN.[192]

Diamines which are devoid of any polarizable hydrogen also function as successful ligands. TMED is the most popular ligand of this category and has been used for some time[155] to monomerize alkylmetals and to make them reactive in general. Lithium of Li_4R_4 (R = Me or Ph), for example, can be chelated with TMED to facilitate the conversion (eq 2). Defined complexes of TMED with organometallic compounds are not uncommon.



(2)

Starting from Li(n-Bu)(TMED), for example, Li_2(naphthalenide)-$(TMED)_2$[208] and $Li_2(anthracenide)(TMED)_2$[209] have been synthesized employing a typical nonpolar medium. X-ray analysis of these complexes and of Li(benzyl)(triethylenediamine),[203] K(fl)(TMED),[764] Li(triphenylmethyl)(TMED),[210] Li(indenyl)-(TMED),[211] and $Li_2(acenaphthyne)(TMED)_2$[214] has revealed the cation to be chelated with the diamine as also with the carbanion. The $Mg(R)_2(TMED)$ (R = Me or Ph) complexes are known to exist in benzene wherein they are monomeric.[284b] $Mg(Me)_2(TMED)$ can be sublimed without decomposition. An analogous complex, $Mg(Me)_2(TMPD)_2$ (TMPD = tetramethyl-*o*-phenylenediamine), is stable, although it loses the ligand on heating.[284b] Recently, solid complexes of the type $Mg(R)_2(TMED)$ have been characterized where R is Me_3CCH_2, Me_3SiCH_2, or $PhMe_2CCH_2$.[429]

$M(hfac)_z$ salts, wherein the coordination ability of M^{z+} is pronounced owing to fluorination of the anion, readily interact with TMED, PHEN, and 2,2'-bipyridyl to produce solid complexes such as $Li(hfac)(TMED)(H_2O)_n$ (n = 1 or 2), $Ca(hfac)_2$-(TMED), Li(hfac)(PHEN), $Na(hfac)(PHEN)(H_2O)$, $Ca(hfac)_2$-$(PHEN)(H_2O)$, and $Ca(hfac)_2$(2,2'-bipyridyl).[192] For TMED, the tendency of M^{z+} for such a coordinative saturation increases with the charge density of the cation. In principle, this behavior should be general. The chelate $Mg(hfac)_2(TMED)$ is also known;[430] its solid-state NMR characteristics are similar to those in $CDCl_3$ or C_6H_6,[192] and to those of Li(hfac)(TMED) in C_6H_6.[431] The M^{z+}-TMED chelation in each is indicated by a downfield shift of the Me-N singlet.

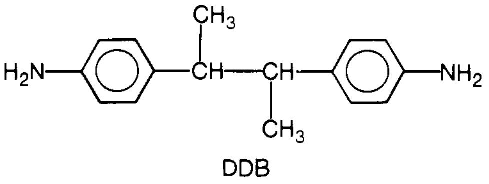
5. Double Action N-Donor Ligands

The simplest ligand of the group is ethylenediamine (EN) which is capable of dissolving various inorganic salts[85] and of producing solid solvates such as $LiCl(EN)_2$, $LiBr(EN)_2$, $LiI(EN)_3$, $NaI(EN)_3$, $NaClO_4(EN)_3$, $CaCl_2(EN)_6$, $SrCl_2(EN)_6$, and $BaCl_2(EN)_4$. In such systems the behavior of EN is parallel to that of water; repeated crystallization of $LiI(H_2O)_3$ from anhydrous EN ultimately affords $LiI(EN)_3$.[85] We noted[432] that $M(pic)_2(EN)_n$ (M^{2+} = Mg or Ca and n = 1 or 2) complexes can be readily synthesized by the interaction of the reactants in EtOH, the IR spectra of which show broad bands around 1900 and 2500 cm^{-1} and hence $-NH_2\cdots$pic type of bonding. The $-NH_2\cdots$anion bonding and hence charge separation of the complexing salt is general and has been noted for $LiX(EN)_n$ (n = 2 when X^- = Cl or Br[433] and is 3 when X^- = I[434]) wherein Li-X distances range from 4.20 to 4.80 Å. Conformational studies of EN in $LiX(EN)_2$ (X^- = Cl to I) and $LiI(EN)_3$ solid complexes, employing Raman spectroscopy, reveal that in the former EN is in the gauche as well as the trans forms, whereas in the latter it is only in the gauche form.[435]

Physicochemical studies on complexation of salts with EN have been carried out in the absence[105,108] and presence[436] of a competing ligand. These studies include ^{23}Na NMR studies on M^+-cryptates (discussed in section IV.C) and mixed solvent studies in benzene medium using $NaAlF_4$ as a standard species.

Solid complexes of diethylenetriamine (DIEN) with M^{2+} ions have been characterized[437] which include $[M(DIEN)_3]X_2$ (M^{2+} = Ca, Sr, and Ba; X^- = ClO_4, Br, and I) and $[Ca(DIEN)_3](ClO_3)_2$. Each complex is postulated to contain a nine-coordinated cation. Complexation of trimethylethylenediamine with $MgMe_2$ has also been reported.[284b]

A rather surprising observation was made by Marullo and Lloyd[87] in that a seemingly monodentate amine, p,p'-diamino-2,3-diphenylbutane (DDB), is capable of precipitating MX salts as $MX(DDB)_3$ from purely aqueous medium. Later, chemical[438] and X-ray diffraction[439] studies confirmed the speculation of these workers in that the cation is octahedrally coordinated with the DDB molecules wherein the latter works as a bidentate. The earlier[87] observation on DDB induced the use of p,p'-methylenedianiline (MDA).[440-442] X-ray analysis[442] of $NaCl(MDA)_3$ revealed that, like $NaCl(DDB)_3$, the cation is six-coordinated by the chelating MDA molecules and that Cl is held by the amino protons.



DDB

6. Miscellaneous Ligands

Under this heading we discuss ethanolamines, which offer both N and O for chelation, thiourea wherein S is the donor site, and other species such as nitrous oxide and hydrogen cyanide.

Solution (conductance) studies on M^+ ions with triethanolamine (TEA) have indicated that stability values in THF are in the order Li > Na > K > Rb.[292] Crystalline complexes NaI(TEA),[443] NaI(TMTEA) (TMTEA = trimethoxytriethylamine),[444] $Sr(NO_3)_2(TEA)_2$,[445] and $Ba(OAc)_2(TEA)_2$[446] have been subjected to structural analysis. Sodium ion, five-coordinated in NaI(TMTEA) and seven-coordinated in NaI(TEA), is paired with iodide. The Na–N distances are in general longer than the Na–O distances presumably because of preferred pairing of Na with iodide located opposite to the nitrogen atom. The eight-coordinated Sr in $Sr(NO_3)_2(TEA)_2$ is charge separated while NO_3 ions are held strongly by the hydroxyl groups of TEA. The nine-coordinated Ba in $Ba(OAc)_2(TEA)_2$ is "almost" charge separated showing only one $Ba–O^-$(OAc) contact of about 2.73 Å.

Thiourea (TU) has been studied extensively.[447-449] Earlier workers reported various complexes of the types $MX(TU)_4$ (M^+ = Li to Cs)[447] and $CaX_2(TU)_6$ (X^- = Cl or I).[448] Recent detailed work[449] has, however, indicated that complexation takes place only for the larger cations K, Rb, and Cs especially when Br or I is the counteranion. The products have been classed as ionic in which the polarizable TU molecules separate the cation from the counteranion. Further work[450] has also shown that the complexes are stabilized by electrostatic interactions alone. MX–TU complexation has been considered to be controlled by the lattice energy of MX; salts of lattice energy $\gtrsim 160$ kcal/mol are believed to be noncomplexing.[449] That NaI (164 kcal/mol) does not produce a solid complex also suggests, however, that problems of lattice packing arising from S/M^+ size ratio may also contribute to the process. Stabilization of X through bonding with NH_2 groups of TU should be a process favorable to M^+–S interaction, but it should have not been verified[451] through a comparative complexation study with thioacetamide which is a compound chemically different from TU.

The complex $[Mg(HCN)_6](InCl_4)_2$ has been synthesized from a solution of $MgCl_2$ and $InCl_3$ in liquid HCN wherein the cation is believed to be six-coordinated through N ends.[452] For some observations with ligands such as nitrous oxide,[453] 1,8-naphthyridine,[454] 1,2,7-trihydroxyanthraquinone,[455] 5,6-dibromo-2,3,4-trihydroxyacetophenone,[456] and thiobendazole,[140] see as cited.

D. Coordinated Ligands as Ligands

Structural studies have revealed that in complexes which contain a transition cation (M^{n+}) as well as M^{z+}, the latter occupies a respectable coordination position with respect to those ligands which are coordinated also with the former. Such ligands may be considered as "coordinated ligands" or "metal complexes as ligands".

Complexes of the types $[(M^{n+}\text{–Schiff base})_2M^+(\text{solvent})_x]X$[457,458] and $[(M^{n+}\text{–Schiff base})_2M^+(\text{solvent})_xX]$,[459,460] which can be crystallized employing a reaction mixture of MX and the concerned M^{n+}(Schiff base) complex (M^{n+} = Cu^{2+}, Co^{2+}, or Ni^{2+}) in the "solvent", have been the subject of structural analysis. The charge-separated complexes of the former group are obtained for $MBPh_4$ salts and the ion-paired ones of the latter group for $MClO_4$ salts. In each of $[(\text{Co-salen})_2Na(THF)_2]BPh_4$[457] and $[(\text{Ni-salen})_2Na(MeCN)_2]BPh_4$[458] (salen = *N,N'*-ethylenebis(salicylideniminato)) the sodium ion is six-coordinated with two molecules of the solvent and both bidentate M^{n+}–salen species; in the latter complex there are two more MeCN molecules but these are not coordinating. In each of $[(\text{Cu-salen})_2Na(ClO_4)]$-*p*-xylene[459] and $[(\text{Ni-}N,N'\text{-ethylenebis(acetylacetoniminato)})_2Na(ClO_4)]$[460] Na is again chelated with the M^{n+}–Schiff base complex and the cation completes the distorted octahedron through pairing with ClO_4 ions.

Recent work on compounds like K-bis(tri-*p*-tolylphosphine)-Cu^+-bis(dithiooxalato-*O,O'*)stannate·$2Me_2CO$,[461] Ba-neptunyl(V)triacetate·$2H_2O$,[462] and Li-ethylenediamine-*N,N'*-diacetato-*N,N'*-di-3-propionatochromate(III)·$5H_2O$[463] has also revealed coordination of M^{z+} through the metal complex moieties.

In the cyano complexes of M^{n+} such as $Na_4[Mn(CN)_6]\cdot 10H_2O$,[464] $Na_4[Fe(CN)_4]\cdot 10H_2O$,[464] and $Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$,[465] the sodium ion is six-coordinated wherein CN participates. The same type of interaction has been noted by Williams and co-workers[466] for a number of complexes derived from $Pt(CN)_2$.

IV. *Macromolecular Ligands*

The multidentate macromolecules (MMM), which have been studied as ligands for M^{z+}, include natural antibiotics and synthetic compounds such as crowns and cryptands. The antibiotics can be cyclic or acyclic whereas the synthetic ligands can be acyclic, monocyclic, or polycyclic. The macromolecular ligands have recently become more important to the chemistry of M^{z+} than the conventional ligands; this is primarily because they bind M^{z+} effectively and render the latter soluble in nonpolar solvents[467] and secondly because they are more relevant to the chemistry of M^{z+} in biological systems which therein involve essentially the macrobiomolecules. The strong M^{z+}–MMM interaction is due basically to the multichelate effect (for acyclic MMM) or to the superchelate effect[45]—multichelate effect plus macrocyclic effect[468-471] (for closed-chain MMM). Solution as well as solid-state studies on M^{z+}–MMM systems have been carried out extensively and the interest is continued (refs 4–7, 10, 12–16, 19, 22a–30, 32, 34, 35, 37, 39–45). To a significant extent, however, M^{z+} have been used as tools to study conformational aspects of MMM. The following discussion is concerned with only those results which allow simulation of comparative binding strengths of M^{z+} in solution and of their interactive characteristics in the solid state.

A. Crowns[472]

Crown ethers (Figure 20) are the first potential MMM to be synthesized and used as ligands for M^{z+};[7,39,88,473] in fact, the synthesis and study of the other MMM have been triggered by the results the crown ethers have shown.[88] Although crowns have been found to be versatile ligands for M^{z+}, until recently complexation studies have been restricted mainly to M^+. Reviews on various aspects of M^{z+}–crown chemistry have appeared either exclusively (refs 7, 27, 39) or where this topic forms a part (refs 14, 18, 22a, 25, 28, 30, 37, 40–42, 45). They include those on general aspects,[7,14,30] the thermodynamics of M^{z+}–crown interaction in solution,[27] the selectivity of M^{z+}–crown interaction in membranes,[26] the comparative reaction behavior of crowns toward M^+,[18] on crystal chemistry (X-ray analysis) of M^{z+}–crown complexes,[6,15,25,40] and the principles controlling the M^{z+}–crown interaction.[45]

Regarding M^+ ions, recent attention has not been directed, as before,[39] to increasing the list of M^+–crown complexes. It has been focussed either on structural analysis of selected M^+–crown systems or on the selectivity studies of the systems in solution especially as a function of the structural features of crowns. Structural analysis has been aimed at determining the conformation and bonding modes of a given crown in complexes with different M^+, making comparisons of changes that arise from the attachment of substituents on the donor ring, or just ascertaining structural features of the charge neutralizing anion[474] of the cation being complexed. Lately, information on M^{2+}–crown systems has started becoming available.

1. *Coordinative Characteristics of M^+ in Solid Crown Complexes*

The M^+–crown complexes are broadly of the types:[45] 1:1 ion-paired encapsulates, 1:1 incomplete encapsulates, 2:1

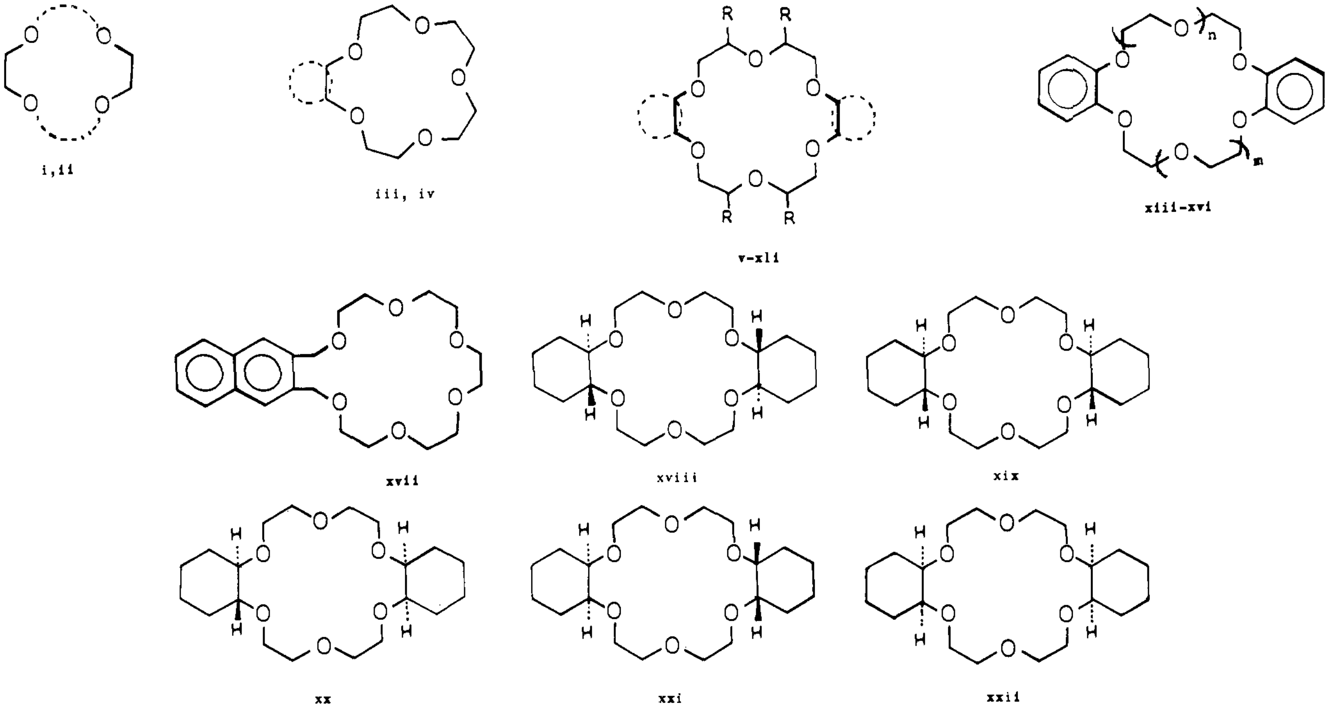
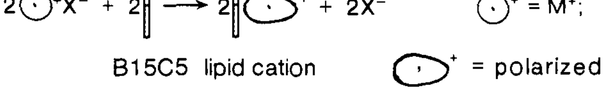


Figure 20. Crowns: (i) 12C4: broken arc = $-CH_2-CH_2-$; (ii) 14C4: broken arc = $-CH_2-CH_2-CH_2-$; (iii) 15C5: broken circle representing no attached nucleus; (iv) B15C5: broken circle representing benzo nucleus; (v) 18C6: R = H, broken circle representing no attached nucleus; (vi) B18C6: R = H, only one broken circle representing benzo nucleus; (vii) NO_2-B18C6: R = H, only one broken circle representing nitrobenzo nucleus; (viii) DB18C6: R = H, each broken circle representing benzo nucleus; (ix) Me_2DB18C6: R = H, each broken circle representing methylbenzo nucleus; (x) TMDB18C6**F**: R = Me, each broken circle representing benzo nucleus (**F** isomer); (xi) TMDB18C6G: R = Me, each broken circle representing benzo nucleus (G isomer); (xii) DC18C6: R = H, each broken circle representing cyclohexano nucleus (isomers xviii–xxii); (xiii) DB21C7: *n* = 1, *m* = 2; (xiv) DB24C8: *n* = *m* = 2; (xv) DB27C9: *n* = 2, *m* = 3; (xvi) DB30C10: *n* = *m* = 3; (xvii) N20C6; (xviii) DC18C6 *trans-anti-trans*; (xix) DC18C6 *trans-syn-trans*; (xx) DC18C6 *trans-cis*; (xxi) DC18C6 *cis-anti-cis*; (xxii) DC18C6 *cis-syn-cis*.

ion-paired bimetallic encapsulates, complete encapsulates (1:2 charge separated sandwich encapsulates and 1:1 charge separated wrap-around encapsulates), and 2:2 ion-paired bimetallic sandwich encapsulates. Whereas the principles governing the formation of nonsandwich encapsulates have been discussed earlier,[45] those controlling the formation of the sandwiches are discussed below.

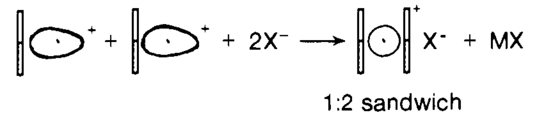
a. 1:2 Charge-Separated Sandwich Encapsulates

These complexes are obtained by complexation of a crown with a comparatively larger M^+ (according to common concepts)—B15C5 with K, Rb, or Cs[45] and 12C4 with Na,[475] for example. The stoichiometry is invariant irrespective of the proportion of the reactants employed for the synthesis. In the case of the KX-B15C5 system,[46] for instance, 1:1 reaction mixtures for which 1:1 complexes exist in solution[476] yield nothing other than 1:2 sandwiches. We believe that in the 1:1 solution complex the rather large cation is effectively polarized and stabilized owing to a close approach of the small donor ring to produce a "lipid cation" of the type (schematic):



(3)

Such a lipid cation exists practically bare because anionic species from one axial direction are prevented by the electrophobic crown ring and on the other axial direction by the accumulated electronic system of the cation. Lacking solvation and/or charge neutralization, the 1:1 lipid–cation fails to crystallize but disproportionates as follows:



(4)

The phenomenon of cation polarization appears to derive its justification because synthesis of 1:2 charge-separated sandwiches is possible for each low charge density M^+ irrespective of whether the anion is Br, I, or NCS.[88,478-480] The charge-separated state of the complexes $[Na(12C4)_2](Cl, 5H_2O)$[475] and $[Na(12C4)_2](OH, 8H_2O)$[477] may be because during their synthesis excess crown was used while the counteranion of Na was extensively bonded by using water as a synthesis medium, but the concept of cation polarization can be applicable for this cation too if these 1:2 complexes can be synthesized from 1:1 reaction mixtures in nonaqueous polar media.

b. 2:2 Ion-Paired Sandwich Encapsulates

The encapsulates $[RbNCS(18C6)]_2$,[481] $[CsNCS(18C6)]_2$,[482] $[CsNCS(TMDB18C6F)]_2$,[483] and $[RbNCS(B18C6)]_2$[484] have been characterized to be 2:2 ion-paired sandwiches. These complexes are formed by the MNCS salts of low charge density M^+ (Rb or Cs) with the 18C6-cavity crowns, although, in view of the ion-cavity radius concept,[7,88] 1:2 charge-separated complexes should have been formed. The ion-paired nature of these sandwiches appears to be due to the following characteristics of the cation, the anion, and the crown. (i) The basicity of a six-oxygen ring is at its maximum for the unsubstituted 18C6 but it decreases as 18C6 is changed to DB18C6 through attachment of the acidic benzo nuclei. (ii) Electrostatic stabilization that a crown ring can provide to a cation should decrease in the order K, Rb, and Cs (cf. ref 485) not only because the M^+ ion tends to be located at a distance from the ring in accordance with its size[486] but also because the self-encapsulating ability decreases in this order.[45] (iii) The bonding modes of NCS with a crown-complexed M^+ can change from bonding as a monodentate[487] (Figure 21) to bonding as a bridging anion[481-484] (Figure 22) to a nonbonded disordered state (Figure 23)[488,489] as anionphilicity of the cation in M^+-crown decreases from its highest in the complexes of the less basic DB18C6, e.g.,

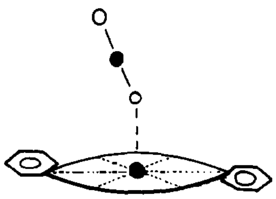


Figure 21. RbNCS(DB18C6) molecule in the complex $[(Rb_{0.55}Na_{0.45})NCS\ (DB18C6)]$ wherein NCS acts as a monodentate.

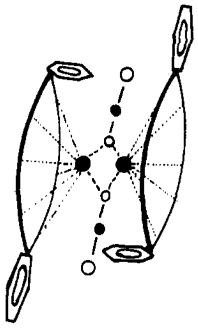


Figure 22. $[CsNCS\ (TMDB18C6\bar{F})]_2$ wherein NCS acts as a bridging anion (schematic).

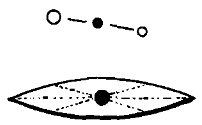


Figure 23. [K(18C6)]NCS wherein NCS is disordered (schematic).

NaNCS(DB18C6)[487] and KNCS(DB18C6) to that in the complexes of a stronger crown, e.g., $[RbNCS(18C6)]_2$[481] and $[CsNCS(18C6)]_2$[482] to that in complexes of strong crowns and strongly complexing M^+, e.g., [K(18C6)]NCS[488] and [K(N20C6)]NCS[489]. It can, therefore, be due to a medium-order anionphilicity shown by the rather distantly located and weakly complexed Rb and Cs in $[MNCS(18C6)]_2$, $[RbNCS(B18C6)]_2$, and $[CsNCS(TMDB18C6\bar{F})]_2$ complexes in which bridging is allowed to NCS. Since in each 2:2 complex one of the M^+–N bonds with the bridging NCS is shorter than the other, it appears that the shorter bond is of the electrostatic nature while the longer is formed through overlap of a stereochemically suited filled p orbital of the nitrogen.

The cation in the 1:1 ion-paired complexes RbNCS(NO_2-B18C6) (Rb–O, ~3.00 Å)[490] and CsNCS(NO_2-B18C6) (Cs–O, ~3.15 Å)[491] is almost at the same distance from the ring oxygens as in the analogous 2:2 ion-paired sandwiches $[RbNCS(18C6)]_2$ (Rb–O, ~3.02 Å)[481] and $[CsNCS(18C6)]_2$ (Cs–O, ~3.15 Å).[482] The cation in the NO_2-B18C6 complexes so interacts with the nitro oxygen(s) of the adjacent symmetry-related complex molecule (Figures 24 and 25) that these systems may also be treated as 2:2 ion-paired sandwiches. The only difference is that in the Rb complex the NCS interacts only with its own cation while the molecule dimerizes through $(NO_2)O^- \cdots M^+$ contacts whereas in the Cs complex the chelating NO_2 groups make SCN almost disordered and serve alone to dimerize the complex.

Two of the isomers obtained on grafting four Me groups on the ring carbons of DB18C6, namely, TMDB18C6$\bar{F}$ (Me groups cis, anti, cis, cis with respect to benzene ring) and TMDB18C6$\bar{G}$ (Me groups trans, anti, trans, trans) undergo complexation with CsNCS in methanol. The $\bar{F}$ isomer produces a 2:2 sandwich of the ion-paired nature, $[CsNCS(TMDB18C6\bar{F})]_2$[483] whereas the $\bar{G}$ isomer yields a 1:2 charge-separated sandwich, $[Cs(TMDB18C6\bar{G})_2]SCN$.[480,483] The 1:2 complexation and charge separation of CsNCS in the latter case may be attributed to the prevention of NCS ions from interaction with Cs by the four benzo nuclei which form a sort of blockade (Figure 26) which is not the case for $[CsNCS(TMDB18C6\bar{F})]_2$ shown in Figure 22.

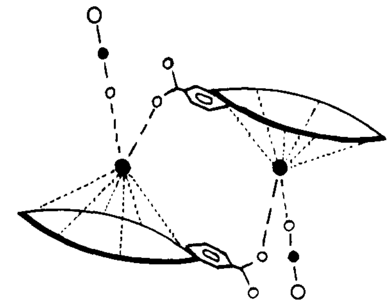


Figure 24. RbNCS(NO_2-B18C6) which is 2:2 because of bonding through nitro oxygens (schematic).

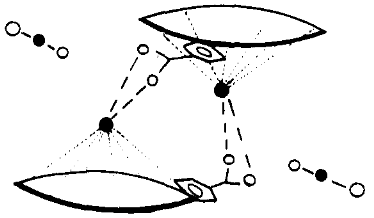


Figure 25. CsNCS(NO_2-B18C6) which is 2:2 due to chelating nitro functions (schematic).

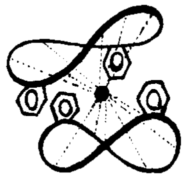


Figure 26. $[Cs(TMDB18C6\bar{G})_2]NCS$ (schematic).

c. Stoichiometry and Composition of Na- and K-Crown Complexes

The coordinative characteristics of Li and Na are roughly represented by Na and those of K, Rb, and Cs by K. The coordinative characteristics of M^+ with crowns, therefore, can be brought out through a discussion on complexation on the representative crowns (B15C5, 18C6, DB18C6, DB24C8, and DB30C10) with Na and K only.

DB30C10 is exactly double B15C5 and, interestingly, the results shown by a molecule of DB30C10 are comparable to those with two molecules of B15C5. Salts of the medium charge density Li and Na, which usually produce ion-paired complexes with macrocycles (refs 39, 88, 160, 161, 478, 487, 492–497) (wherein a coordinated molecule of a polar solvent like water is considered[45] to be an anionic species), undergo 1:1 complexation with B15C5 and 2:1 with DB30C10 (Figure 27) involving contacts of the anionic species with M^+ from the axial sides of the crown ring. Salts of the low charge density K, Rb, and Cs, on the contrary, undergo 1:2 complexation (sandwich encapsulation) with B15C5 and 1:1 complexation (wrap-around encapsulation) with DB30C10 to produce charge-separated complexes (Figure 27). Complete encapsulation of the low charge density M^+ has been attributed to the successful incorporation of the macrocyclic effect[468,469] of the macrocycle on thermodynamic grounds (ligand encapsulation—a special case of ligand complexation) which is unlike that of a high charge density cation like Mg exhibiting a "sacrificial" encapsulation within the macrocycle on electrostatic grounds so as to avail itself of the macrocyclic effect (self-encapsulation).[45]

With B15C5 and 18C6, Na consistently produces 1:1 ion-paired complexes such as $[Na(18C6)(H_2O)]NCS$[495] and NaX(B15C5) (X^- = Br, I, and NCS).[478] In the former complex,

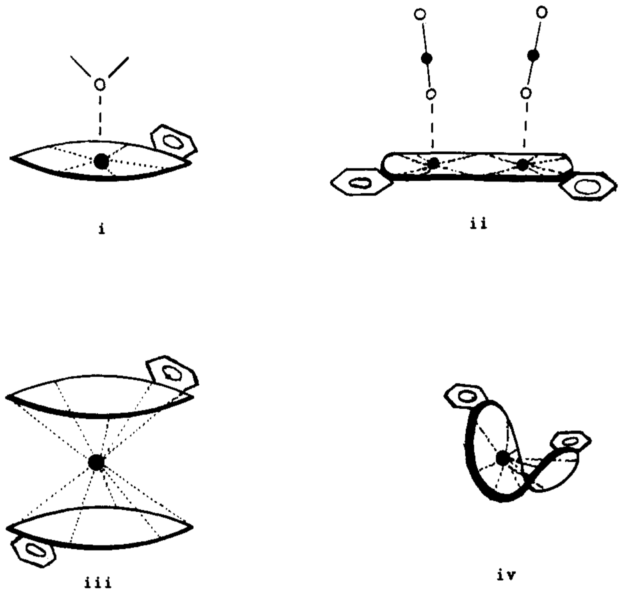


Figure 27. (a) Ion-paired complexes of Na: (i) $[Na(B15C5)(H_2O)]I$ and (ii) $(NaNCS)_2(DB30C10)$ (M. R. Truter, personal communication to N.S.P.). (b) Charge-separated complexes of K: (iii) $[K(B15C5)_2]I$ and (iv) $[K(DB30C10)]I$ (all schematic).

where the cavity of the crown is larger than the cation, the donor ring is distorted by the cation to suit its size. Though the cation is bound on one of the axial sides by the out-of-the-plane ring oxygen, the electrostatic requirements of the cation are not met and an additional coordination with a water molecule takes place from the other axial side (Figure 28). This is indicative of a distinct anionphilicity of Na. The conformation of a 6-oxygen flexible donor ring can be dictated by Na which behaves rather electrophilically for a donor ring so as to make tight contacts as in $[Na(DC18C6\textit{cis-anti-cis})(H_2O)_2]Br$[493] and $[Na(18C6)(H_2O)]NCS$[495] while the dictation is not possible on rigid rings in the complexes of which the Na-anionic species affinity is shown up and the cation establishes rather longer contacts with the ring as noted[487] for the Na-DB18C6 moiety in the complex $[(Rb_{0.55}Na_{0.45})NCS(DB18C6)]$.

In contrast to the behavior of sodium, potassium frequently undergoes charge separation with each of B15C5, DB18C6, 18C6, and DB30C10. Unlike the Li and Na salts, the K salts irrespective of the nature of the anion and of the reaction medium, and of the proportion of the reactants, yield 1:2 charge-separated sandwiches with B15C5 and 1:1 charge-separated wrap-around complexes with DB30C10, a feature which has been ascertained by X-ray analysis of $[K(B15C5)_2]I$[498] and $[K(DB30C10)]I$.[494a,499] This behavior of K has to be attributed to its own Lewis acid character rather than to any spatial or steric features of the crown, for X-ray analysis has revealed that even in the planar complex $[K(18C6)]NCS$[488] the cation due to an effective stabilization with 18C6 undergoes charge separation and the counteranion exists disordered in the lattice; in the complex $KI(DB18C6)(H_2O)_{1/2}$,[500] where the crown is relatively less basic than 18C6, the cation is though paired with iodide in the anhydrous molecule but undergoes separation from iodide in the other molecule wherein the required stabilization is achieved from a coordinating molecule of water from an axial side. This is a distinct difference of K from Na in that it can be separated from the counteranion through encapsulation with electrically neutral chelating nucleophiles under a rather wide range of conditions.

When the stabilization provided by the crown does not meet a minimum requirement, K tends to behave like Na as noted under most conditions during the use of DB24C8[501] and DB18C6.[46,478] Especially when the counteranion is a chelating organic anion, L, DB24C8 consistently produces 2:1 bimetallic complexes with Na as well as K;[478] in the complex $(Naonp)_2(DB24C8)$[492] both Na ions are complexed with the crown oxygens while one onp anion chelates one Na ion from each axial side and also serves to bridge between two molecules in the lattice. Under anhydrous conditions, both KNCS and NaNCS yield 2:1 bimetallic products which because of the close resemblance of their IR characteristics are expected to be structurally similar.[46] Single crystal analysis[501] has revealed that in the complex $(KNCS)_2(DB24C8)$ both the cations are complexed within the cavity of the crown while each NCS ion bridges the two cations (Figure 29); NCS ion, like the organic anions, pairs strongly with M^+ [502] even when the latter is in a complexed state and it may be emphasized that formation of the bimetallic products is due essentially to this feature.[45]

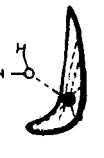


Figure 28. $[Na(18C6)(H_2O)]NCS$ (schematic form of a monomer).

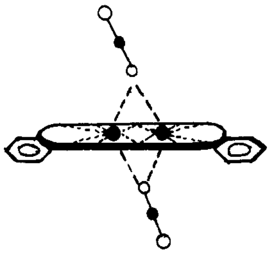


Figure 29. $(KNCS)_2(DB24C8)$ (schematic).

2. *Coordinative Characteristics of M^{2+} in Solid Crown Complexes*

Information on M^{2+}–crown complexes is relatively much less available. The synthesis of complexes has become possible only when the crown is potentially nucleophilic such as 12C4, B15C5, B18C6, or 18C6 and the counteranion is such as favoring solubilization of the salt particularly in an organic reaction medium. The anions which have been found useful in this regard are NCS,[88,473,503–506] ClO_4,[506–509] BPh_4,[506,510] and aromatic anions,[152,168,169,509,511–513] (and Cl, when water is used as medium[134,514]). The complexes for which structural information is available include $[Mg(H_2O)_6](12C4)(Cl)_2$,[134] $Mg(NCS)_2(B15C5)$,[505b] $[Ca(12C4)(H_2O)_4](2Cl,4H_2O)$,[514] $[Ca(pic)_2(H_2O)_3](B15C5)$,[152] $[Ca(dnb)_2(B15C5)](B15C5,3H_2O)$,[512] $Ca(NCS)_2(B15C5)(H_2O$ or $MeOH)$,[505] $Ca(NCS)_2(18C6)$,[504] $[Sr(B18C6)(H_2O)_3](ClO_4)_2$,[508] $Ba(ClO_4)_2(B18C6)(H_2O)_2$,[508] $Ba(NCS)_2(DC18C6\textit{cis-syn-cis})(H_2O)$,[503] $Ba(ClO_4)_2(DB24C8)$,[507] and $Ba(pic)_2(DB24C8)(H_2O)_2$[513] (Table II).

A common structural feature of the M^{2+}–crown complexes is that the lattice system is ion-paired. In the heavily hydrated $[Mg(H_2O)_6](12C4)Cl_2$[134] and $[Ca(12C4)(H_2O)_4](2Cl,4H_2O)$[514] the coordinated water molecules display a double action and serve to keep off the chloride ions and, in the case of the Mg complex, also the crown molecule. The nonchelation[152] or a restricted[512] chelation of the crown molecule appears to be a profound feature of the CaL_2 complexes which may be attributed to (i) anionphilicity of Ca, (ii) chelating nature of L, and (iii) complexing ability of the crown with water protons;[134,152,512] for B15C5, even a novel proton complex, $(B15C5,H^+)(pic)$, has been synthesized in the hydrated state.[515]

In view of the stronger polarizing ability, the M^{2+} ions should have been complexed with the crowns more favorably than the M^+ ions. The situation, however, is opposite. This observation can be attributed[45] to a higher degree of involvement of the cation with the counteranion as shall be briefly discussed below; for a given anion and a solvent medium, for example, Ba is much less transported across a liquid membrane with DB18C6 compared to K.[516]

3. *Effect of Anion on M^{z+}-Crown Complexation*

As expected for an electrically neutral ligand devoid of polarizable hydrogen atoms, an adverse effect of the charge neutralizer on the M^{z+}-crown interaction is in general operative; for M^{2+} ions, the effect is pronounced in particular. Thus, whereas complexes of the MBr and MI salts with B15C5 can be synthesized for Li through Cs,[478] it is not possible for Mg and Ca under any condition;[45,479a] MgI_6(DB18C6) and BaI_6(DB18C6) complexes have been reported[88] synthesized by the interaction of the crown with MI_2 in the presence of iodine (where iodine appears to stabilize iodide during M^{2+}-DB18C6 interaction), but the complexes are not well defined. The case of Mg with a small cavity crown like B15C5 is apparently special in that compared to Ca, for instance, Mg exhibits a greater affinity for the donor ring in a similar manner that it exhibits a general solvent-philicity, although, involvement of this cation with the counteranion is expected to be higher than Ca.

Solubilization of a salt by a neutral ligand in a nonpolar medium is an index of M^{z+}-ligand complexation; solubility of KX in various nonpolar media, as induced by DC18C6, increases[7] as X is changed from Cl to Br to I, i.e., as an anion of a decreased nucleophilicity is employed. Cation transport studies across a hydrophobic layer ($CHCl_3$) indicate that complexation of a cation (Li, Na, K, or Ba) with DB18C6 increases in general from Cl to I, and as a "small" [516] anion like Cl or OH is replaced by a "large" anion like pic, H_2PO_4, or NO_3, and as a multiply charged anion (HPO_4^{2-}) is replaced with a monovalent anion ($H_2PO_4^-$). This collectively indicates that M^{z+} complexation is a function of the counteranion and is facilitated as the nucleophilicity of the latter decreases.

In the solid state, the charge neutralizing anion exercises a pulling effect on the cation from the complexing crown ring as noted for the Br-paired molecule (molecule B) in the complex NaBr(DB18C6)$\cdot 2H_2O$[496] and in $(Naonp)_2$(DB24C8).[492] In the complexes $Ca(dnb)_2(B15C5)_2 \cdot 3H_2O$[512] and $Ca(pic)_2$(B15C5)$\cdot$ $3H_2O$[152] the chelating organic anion deters Ca-crown interaction so that a/the nonchelating molecule of B15C5 is found in each lattice.

The anion not only pulls the cation out of the donor ring but establishes bonds shorter than the M^{z+}-ring bonds. In the complex K(ethylacetoacetato)(18C6)[474] the $K-O^-$ bonds are 2.65 and 2.73 Å while the K-O(crown) bonds range from 2.8 to 3.0 Å as against the usual length (~2.8 Å) for K-crown systems.[25] Further, whereas K lies roughly in the plane of the ring in the complex [K(18C6)]NCS,[488] ethyl acetoacetate anion in the concerned complex pulls K out of the 18C6 ring by about 0.9 Å. In the complex $Ca(dnb)_2(B15C5)_2(H_2O)_3$[512] the $Ca-O^-$ bonds (2.47 Å) are significantly shorter than the Ca-O(crown) distances (2.57 and 2.72 Å) and the cation is out of the ring plane by as much as 1.38 Å.

When the anion is chelating as well as bulky, it dictates the very M^{z+}-crown complexation so that both bonding behavior and conformation of the crown are affected. The pic anions in the complex $Ba(pic)_2(DB24C8)(H_2O)_2$[513] neither permit the formation of a 2:1 bimetallic product as possible for similar-sized K with this crown (Figure 29) nor do they allow wrap-around of the crown as possible around the same cation with the same crown in the complex $Ba(ClO_4)_2$(DB24C8)[507] which contains the self-stabilized perchlorate. The bonding behavior is unique in the sense three of the eight crown oxygens fail to coordinate with the cation (Figure 30) to make possible the insertion of a water molecule between the ring and the cation. The effect of the anion on bonding behavior and conformation of a crown may be recorded permanently even if the anion is ultimately separated from the complexed cation as in the B15C5 sandwiches. Such effects which the anion exercises during the process of complexation have been noted for NaX-B15C5 sandwiches when ClO_4 is replaced with BPh_4;[517] unlike considered earlier,[517] it is less probable that the anion effect is exercised in the lattice after complexation.

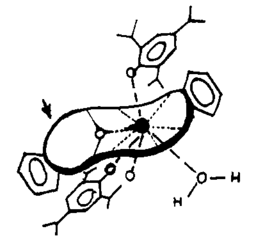


Figure 30. $Ba(pic)_2(DB24C8)\cdot 2H_2O$ (schematic).

Some highly nucleophilic anions such as Cl do not permit the very synthesis of M^{z+}-crown complexes. If, however, such an anion is effectively stabilized by an appropriate proton donor present in the reaction, it can be prevented from being deleterious and synthesis can be carried out. Water used as a reaction medium for NaCl- or NaOH-12C4 reactions not only helps the complexation but also makes possible the formation of complete encapsulates, $[Na(12C4)_2](Cl,5H_2O)$[475] and $[Na(12C4)_2]$-$(OH,8H_2O)$.[477] Complexes of KCl have been synthesized in the form $[K(B15C5)_2]$(Cl,HL)[518] where HL is onpH or dnpH, and binds Cl during K-B15C5 complexation.

4. *M^{z+}-Crown Complexation in Solution*

Solution studies with crowns are being carried out (i) to learn the role of crowns in phase transfer of M^{z+} from aqueous to the nonpolar organic media,[7,39,88,510,519–527] (ii) to determine the binding constants of M^{z+}-crown systems under different conditions employing UV spectroscopy,[528–530] NMR spectroscopy,[531] CD measurements,[532] potentiometry[533] and potentiometry with ion selective electrodes,[476,534] conductometry,[535] polarography,[536] and calorimetry,[16,27,485,537–540] and (iii) to study the rate constants for the purpose of understanding the interactive mechanisms employing relaxation techniques.[37,41,529a,541,542]

Whereas the earlier work[7,88,476,519a] led to a simple conclusion in that the stability values are understandable essentially from cation-cavity size considerations (ion-cavity radius concept), later work[485,535–540,542] has made it appear that the problem is much less simple. While the ion-cavity radius concept is becoming undervalued,[30,45,540] the importance of structural features of the crown[485,523,539,543] and of interactive preferences of M^{z+} between the crown and anion[45,516] or solvent[485,528,535,544] is being increasingly realized.

When cation-cavity size is the only consideration, M^{z+}-crown interaction is most favored for a cation of the size nearest to the cavity. For example, 12C4 is most selective for Li, B15C5 is for Na, DC18C6 is for K, and DB24C8 is for Cs.[476,536,545] The next preference of a crown is for a cation which is larger than its cavity because M^{z+}-crown contacts become possible without causing any folding of the cavity and because the cation tends to be polarized (ligand encapsulation); complexes of Rb and Cs with B15C5 in water, for example, are more stable than that with K.[538] Complexation with a crown is least favored when cation is of the size smaller than the cavity, for conformational changes of the crown during complexation are major, and the cation is strongly bound with the anionic species; all crowns of the cavity size greater than that of 4-oxygen ring (12C4 or 14C4) reject Li under most conditions.[529a,535]

Coordinative characteristics of a cation during interaction with a crown become increasingly detectable as the cavity size of the ring exceeds the cation size. This is so because under these conditions M^{z+}-crown complexation becomes increasingly dependent on the flexibility of the macrocycle and competing

TABLE III. Stability Constants of M^{z+}–Ligand Complexes[a]

		exptl conditions[c]		stability value	
ligand	method[b]	medium, temp, counteranion	cation	(in terms of)	ref
GLYCOL-3	CON	i-PrOH, 30, pic	Li	3.21×10^2 (K_2)	339
			Ca	6.99×10^2 (K_2)	
GLYCOL-4	CON	i-PrOH, 30, pic	Li	2.88×10^2 (K_2)	339
			Ca	5.65×10^2 (K_2)	
		H_2O, 30, pic	K	0.25×10^2 (K_2)	
GLYCOL-5	CON	i-PrOH, 30, pic	Li	2.37×10^2 (K_2)	339
		H_2O, 30, pic	Na	0.36×10^2 (K_1)	
			K	0.27×10^2 (K_1)	
			Ca	0.38×10^2 (K_1)[d]	
15C5	CAL	H_2O, 25, Cl	Na	0.70 ± 0.10 (log K_1)	538
			K	0.74 ± 0.08 (log K_1)	
			Rb	0.62 ± 0.10 (log K_1)	
			Cs	0.8 ± 0.2 (log K_1)	
			Sr	1.95 ± 0.08 (log K_1)	
			Ba	1.71 ± 0.06 (log K_1)	
B15C5	CAL	H_2O, 25, Cl	Na	0.4 (est.) (log β_1)	485
			K	0.38 ± 0.10 (log β_1)	
		20/80 wt % $MeOH/H_2O$, 25, Cl	Na	0.72 ± 0.03 (log β_1)	
			K	1.20 ± 0.10 (log β_1)	
		40/60 wt % $MeOH/H_2O$, 25, Cl	Na	1.17 ± 0.12 (log β_1)	
			K	1.92 ± 0.04 (log β_1)	
		60/40 wt % $MeOH/H_2O$, 25, Cl	Na	1.64 ± 0.04 (log β_1)	
		70/30 wt % $MeOH/H_2O$, 25, Cl	Na	1.99 ± 0.10 (log β_1)	
			K	1.5 ± 0.3 (log β_1)	
				4.15 ± 0.02 (log β_2)	
			Rb	1.8 ± 0.2 (log β_1)	
				3.77 ± 0.05 (log β_2)	
			Cs	1.70 ± 0.01 (log β_1)	
		80/20 wt % $MeOH/H_2O$, 25, Cl	Na	2.26 ± 0.02 (log β_1)	
			K	2.2 ± 0.2 (log β_1)	
				4.80 ± 0.05 (log β_2)	
	POL	MeCN, 22, ClO_4	Na	4.55 (log K_1)	536
		SCN	K	3.40 (log K_1)	
		ClO_4	Rb	2.90 (log K_1)	
		ClO_4	Cs	3.10 (log K_1)	
18C6	CAL	H_2O, 25, Cl	Na	0.80 ± 0.10 (log K_1)	538
			K	2.03 ± 0.10 (log K_1)	
			Rb	1.56 ± 0.02 (log K_1)	
			Cs	0.99 ± 0.07 (log K_1)	
			Ca	<0.5 (log K_1)	
			Sr	2.72 ± 0.02 (log K_1)	
			Ba	3.87 ± 0.02 (log K_1)	
		70/30 wt % $MeOH/H_2O$, 25, Cl	Na	2.76 ± 0.02 (log β_1)	485
			K	4.33 ± 0.05 (log β_1)	
			Rb	3.46 ± 0.10 (log β_1)	
			Cs	2.84 ± 0.01 (log β_1)	
			Ca	2.51 ± 0.02 (log β_1)	
			Sr	5.0 ± 0.1 (log β_1)	
			Ba	6.0 (est) (log β_1)	
	SPEC	H_2O, 25	Na	<2 (K_1)	529b
			K	112 (K_1)	
			Cs	6.3 (K_1)	
B18C6	POL	MeCN, 22, ClO_4	Na	4.90 (log K_1)	536
		SCN	K	5.30 (log K_1)	
		ClO_4	Rb	4.40 (log K_1)	
		ClO_4	Cs	4.05 (log K_1)	
		MeOH, 22, SCN	K	5.20 (log K_1)	
cyclohexano-18C6	SPEC	H_2O, 25	Li	<5 (K_1)	529b
			Na	6.3 (K_1)	
			K	80 (K_1)	
			Cs	6.3 (K_1)	
DB18C6	SPEC	H_2O, 25	Li	<1 (K_1)	529b
			Na	14.6 ± 1.0 (K_1)	
			K	46.5 ± 0.8 (K_1)	
			Rb	12.0 ± 1.1 (K_1)	
			Cs	6.8 ± 0.8 (K_1)	
			Ca	<1 (K_1)	
			Sr	10 ± 1.5 (K_1)	
			Ba	~90 (K_1)	

TABLE III (*Continued*)

ligand	method[b]	exptl conditions[c] medium, temp, counteranion	cation	stability value (in terms of)	ref
	CON[e]	Me$_2$SO, 25, ClO$_4$	Li	~0 (K_1)	535
			Na	2.03×10^3 (K_1)	
			K	2.47×10^3 (K_1)	
			Rb	2.32×10^3 (K_1)	
			Cs	2.03×10^3 (K_1)	
		DMF, 25, ClO$_4$	Li	0.98×10^3 (K_1)	
			Na	2.26×10^3 (K_1)	
			K	3.59×10^3 (K_1)	
			Rb	3.30×10^3 (K_1)	
			Cs	3.03×10^3 (K_1)	
		PC, 25, ClO$_4$	Li	1.68×10^3 (K_1)	
			Na	7.20×10^3 (K_1)	
			K	125×10^3 (K_1)	
			Rb	5.55×10^3 (K_1)	
			Cs	3.49×10^3 (K_1)	
	POL	MeCN, 22, ClO$_4$	Na	5.00 (log K_1)	536
		SCN	K	4.70 (log K_1)	
		ClO$_4$	Rb	3.70 (log K_1)	
		ClO$_4$	Cs	3.50 (log K_1)	
		MeOH, 22, SCN	K	4.60 (log K_1)	
	^{133}Cs NMR	MeCN, 25, Ph$_4$B	Cs	35 ± (K_1)	486
		Me$_2$CO		$>10^3$(K_1)	
		PC		~10^3 (K_1)	
		pyridine		(7 ± 2)10^3 (K_1)	
				230 ± 20 (K_2)	
		DMF		30 ± 3 (K_1)	
		Me$_2$SO		22 ± 3 (K_1)	
DC18C6 *cis-syn-cis*[f]	SPEC	H$_2$O, 25	Li	4 (K_1)	529b
			Na	30–70 (K_1)	
			K	150 (K_1)	
			Rb	33 (K_1)	
			Cs	18 (K_1)	
			Ca	1 (K_1)	
			Sr	1750 (K_1)	
			Ba	3700 (K_1)	
	CAL	H$_2$O, 25, Cl	Na	1.21 ± 0.09 (log K_1)	538
DC18C6 *cis-anti-cis*	SPEC	H$_2$O, 25	Na	15–40 (K_1)	529b
			K	60 (K_1)	
			Rb	7.6 (K_1)	
			Cs	8 (K_1)	
			Ca	~1 (K_1)	
			Sr	430 (K_1)	
			Ba	1900 (K_1)	
	CAL	H$_2$O, 25, Cl	Na	0.69 ± 0.12 (log K_1)	538
DC18C6 *trans-anti-trans*	POT	MeOH, 24.5, Cl	Na	2.52 ± 0.1 (log K_1)	543
		19	K	3.26 ± 0.1 (log K_1)	
		22	Rb	2.73 ± 0.1 (log K_1)	
		19.5	Cs	2.27 ± 0.1 (log K_1)	
DC18C6 *trans-syn-trans*	POT	MeOH, 21, Cl	Na	2.99 ± 0.1 (log K_1)	543
		22.5	K	4.14 ± 0.1 (log K_1)	
		23	Rb	3.42 ± 0.1 (log K_1)	
		19	Cs	3.00 ± 0.1 (log K_1)	
DMDB18C6	POL	MeCN, 22, ClO$_4$	Na	5.10 (log K_1)	536
		SCN	K	4.80 (log K_1)	
		ClO$_4$	Rb	4.00 (log K_1)	
		ClO$_4$	Cs	3.40 (log K_1)	
		MeOH, 22, SCN	K	5.00 (log K_1)[g]	
DB24C8	CAL	70/30 wt % MeOH/H$_2$O, 25, Cl	Na	1.54 ± 0.01 (log β_1)	485
			K	2.42 ± 0.01 (log β_1)	
			Rb	2.55 ± 0.01 (log β_1)	
			Cs	2.48 ± 0.01 (log β_1)	
	POL	MeCN, 22, ClO$_4$	Na	4.00 (log K_1)	536
		SCN	K	3.70 (log K_1)	
		ClO$_4$	Rb	3.40 (log K_1)	
		ClO$_4$	Cs	3.80 (log K_1)	
		MeOH, 22, SCN	K	3.20 (log K_1)	
DMDB24C8	POL	MeCN, 22, ClO$_4$	Na	4.10 (log K_1)	536
		SCN	K	3.90 (log K_1)	
		ClO$_4$	Rb	3.90 (log K_1)	
		ClO$_4$	Cs	3.90 (log K_1)	
		MeOH, 22, SCN	K	3.50 (log K_1)	

TABLE III (*Continued*)

		exptl conditions[c]		stability value	
ligand	method[b]	medium, temp, counteranion	cation	(in terms of)	ref
DB27C9	CAL	70/30 wt % MeOH/H_2O, 25, Cl	Na	1.50 ± 0.01 (log β_1)	485
			K	2.86 ± 0.01 (log β_1)	
			Cs	1.42 ± 0.02 (log β_1)	
DB30C10	POL	MeCN, 22, ClO_4	Na	3.60 (log K_1)	536
		SCN	K	4.70 (log K_1)	
		ClO_4	Rb	4.70 (log K_1)	
		ClO_4	Cs	3.50 (log K_1)	
		MeOH, 22, SCN	K	3.90 (log K_1)	
DMDB30C10	POL	MeCN, 22, ClO_4	Na	3.60 (log K_1)	536
		SCN	K	4.80 (log K_1)	
		ClO_4	Rb	4.90 (log K_1)	
		ClO_4	Cs	3.80 (log K_1)	
		MeOH, 22, SCN	K	4.70 (log K_1)	
		ClO_4	Rb	4.65 (log K_1)	
III	CAL	MeOH, 25, Cl	Na	4.09 ± 0.02 (log K_1)	563
			K	5.35 ± 0.06 (log K_1)	
			Ba	7.6 (log K_1)	
VIII	CAL	MeOH, 25, Cl	Na	2.5 ± 0.1 (log K_1)	539
			K	2.79 ± 0.02 (log K_1)	
			Ba	3.1 ± 0.2 (log K_1)	
IX	CAL	MeOH, 25, Cl	Na	1.8 ± 0.18 (log K_1)	539
			K	2.55 ± 0.03 (log K_1)	
			Ba	1.41 ± 0.11 (log K_1)	
X	CAL	MeOH, 25, Cl	Na	4.29 ± 0.06 (log K_1)	563
			K	4.66 ± 0.02 (log K_1)	
			Ba	4.34 ± 0.02 (log K_1)	
XII[h]	SPEC	THF, 25, pic	K	650 × 10^5 (K_1)	579b
XIII	POT[i]	H_2O, temp not mentioned, Cl	Na	5.4 (log K_1)	575
			K	5.7 (log K_1)	
			Rb	3.8 (log K_1)	
XIV	POT	H_2O, temp not mentioned, Cl	Na	3.5 (log K_1)	575
			K	4.3 (log K_1)	
			Rb	4.4 (log K_1)	
XVIII: form [2.2.2]	^{7}Li NMR	H_2O, 30, I	Li	0.99 ± 0.15 (log K_1)	*j*
		pyridine, 30, ClO_4		2.94 ± 0.10 (log K_1)	
	^{133}Cs NMR	PC, 46, Ph_4B	Cs	4.0 ± 0.9 × 10^3 (K_1)	594
		Me_2CO		3.8 ± 0.3 × 10^3 (K_1)	
		DMF		7.0 ± 0.6 × 10^1 (K_1)	
		PC, 25, Br		3.97 (log K_1)	588
		Me_2CO		4.03 (log K_1)	
		DMF		2.16 (log K_1)	
		Me_2SO		1.45 (log K_1)	
		pyridine		>5 (log K_1)	
		MeCN		4.57 (log K_1)	
XIX	^{133}Cs NMR	PC, 25, Br	Cs	3.17 (log K_1)	588
		Me_2CO		3.54 (log K_1)	
		DMF		1.70 (log K_1)	
		pyridine		3.76 (log K_1)	
		MeCN		3.55 (log K_1)	
XXII[k]	POT	95/5 vol % MeOH/H_2O, 25, Cl	Na	3.2 (log K_1)	611
			K	4.0 (log K_1)	
			Rb	3.5 (log K_1)	
			Cs	3.5 (log K_1)	
XXIII[k]	POT	95/5 vol % MeOH/H_2O, 25, Cl	Na	3.6 (log K_1)	611
			K	4.8 (log K_1)	
			Rb	3.7 (log K_1)	
			Cs	4.4 (log K_1)	
		90/10 vol % MeOH/H_2O, 25, Cl	Ca	4.0 (log K_1)	
			Sr	5.5 (log K_1)	
			Ba	6.7 (log K_1)	
XXIV[k]	POT	95/5 vol % MeOH/H_2O, 25, Cl	Na	3.0 (log K_1)	611
			K	3.6 (log K_1)	
			Rb	3.0 (log K_1)	
		90/10 vol % MeOH/H_2O, 25, Cl	Ca	3.6 (log K_1)	
			Sr	4.9 (log K_1)	
			Ba	5.9 (log K_1)	
XXVI	SPEC	MeOH, 25, SCN	Na	4.58 ± 0.03 (log K_1)	530
			K	5.25 ± 0.02 (log K_1)	
XXVII	SPEC	MeOH, 25, SCN	Na	4.89 ± 0.03 (log K_1)	530
			K	4.78 ± 0.03 (log K_1)	

TABLE III (*Continued*)

ligand	method[b]	exptl conditions[c]	cation	stability value	ref
		medium, temp, counteranion		(in terms of)	
XXVIII	^{7}Li NMR	$MeNO_2$, 33, ClO_4	Li	>4 (log K_1)	615
		MeCN, 33, ClO_4		3.23 ± 0.07 (log K_1)	
		MeCN, 33, Br		3.13 ± 0.12 (log K_1)	
		THF, 33, ClO_4		3.12 ± 0.09 (log K_1)	
		pyridine, 33, ClO_4		2.64 ± 0.10 (log K_1)	
	^{23}Na NMR	$MeNO_2$, 25, Ph_4B	Na	>4 (log K_1)	
		MeCN, 25, ClO_4		>4 (log K_1)	
		pyridine, 25, ClO_4		>4 (log K_1)	
		DMF, 33, Ph_4B		>4 (log K_1)	
	^{133}Cs NMR	$MeNO_2$, 25, SCN	Cs	1.67 ± 0.02 (log K_1)	
		pyridine, 25, Ph_4B		1.96 ± 0.01 (log K_1)	
XXXIII	SPEC	MeOH, 25, SCN	Na	3.22 ± 0.01 (log K_1)	530
				2.49 ± 0.01 (log K_2)	
			K	3.51 ± 0.02 (log K_1)	
				2.14 ± 0.02 (log K_2)	
			Mg	4.99 ± 0.01 (log K_1)	
				4.83 ± 0.01 (log K_2)	
				4.63 ± 0.01 (log K_3)	
				4.40 ± 0.04 (log K_4)	
XXXIV	SPEC	MeOH, 25, SCN	Na	3.92 ± 0.02 (log K_1)	530
				3.80 ± 0.02 (log K_2)	
			K	2.75 ± 0.06 (log K_1)	
				2.00 ± 0.01 (log K_2)	
XXXV	POT	EtOH	Li	6.1 × 10^1 (K_1)	645b
			Na	3.0 × 10^1 (K_1)	
			K	<10 (K_1)	
			Rb	<10 (K_1)	
			Ca	6.1 ± 1.3 × 10^2 (K_1)	
			Ba	1.4 × 10^3 (K_1)	
				2.3 × 10^1 (K_2)	
XXXVII	POT	EtOH, 30, NO_3	Li	60 ± 10 (K_1)	649
		SCN	Na	130 ± 20 (K_1)	
		SCN	K	70 ± 10 (K_1)	
		SCN	Rb	80 ± 13 (K_1)	
		NO_3	Mg	990 ± 140 (K_1)	
		NO_3	Ca	1790 ± 440 (K_1)	
				65 ± 21 (K_2)	
		ClO_4	Sr	4150 ± 600 (K_1)	
				2600 ± 390 (K_2)	
		ClO_4	Ba	2700 ± 300 (K_1)	
				690 ± 85 (K_2)	

[a] Stability data on M^{z+}-anion[33,644], M^{z+}-MMM (synthetic),[30,37] and M^{z+}-antibiotic[37] systems, which have been compiled extensively, are not included. [b] CON, conductometric; CAL, calorimetric; POL, polarographic; SPEC, spectrophotometric; POT, potentiometric employing cation-selective electrodes. The stability values obtained employing M^+ NMR techniques are apparent values. [c] As also evident from some data in this table, the stability value under a given set of conditions is a function of the charge neutralizing anion. We, therefore, feel that anion should also be specified while describing stability values. [d] The complex crystallized from *i*-PrOH was dissolved in H_2O for stability determination. [e] The stability values refer to 1.52 × 10^{-3} M concentration; values at ohter concentrations follow the same order. [f] The data obtained with mixtures of isomers[486,536] are excluded because compositions of ligand mixtures have not been mentioned despite the fact that different isomers show different stability values for a given cation.[529b,538,543] [g] In view of the stability trends of the M^{z+}-crown systems in general and those reported in ref 536, a higher stability of KNCS-DMDB18C6 complex in MeOH compared to that in MeCN is rather surprising. [h] Other related ligands, which differ in the nature of the bridging chain, form less stable complexes. [i] These values were determined employing 20-mmol salt. [j] Y. M. Cahen, J. L. Dye, and A. I. Popov, *J. Phys. Chem.*, **79**, 1289 (1975). [k] Stability values for the analogous bimetallic 2:1 complexes are constantly lower.

effects of the anionic species for M^{z+} are shown which can be assessed. Thus, binding constants for M^+ ions are generally in the order K > Rb > Cs > Na > Li irrespective of whether the macrocycle is the 30-atom-ring DB30C10,[529a] the 32-atom-ring nonactin,[26] or the 36-atom-ring valinomycin,[26] although, in view of the solvation terms for the M^+ ions and conformation energy terms for the large cavity ligands, the sequence should have been Cs > Rb > K > Na > Li. The observed order can be explained by considering the Lewis acid status of each concerned cation. The stability values are higher for the low charge density K, Rb, and Cs because of the operation of ligand encapsulation[45] as against the higher charge density Na and Li which are more involved with the anionic species and for which the conformation energy problems of the macrocycle are acute; the sequence for the former group cations is K > Rb > Cs instead of Cs > Rb > K because contribution from their self-encapsulating ability decreases from K to Cs.[45] That there is a contribution of self-encapsulation for the large cations and a counteracting effect due to involvement with the anionic species for the small cations is also evidenced by the observation that in water the 18C6-cavity crowns show[529b,537,538] a general selectivity order Ba > Sr > K > Rb > Cs ~ Na > Li > Ca > Mg wherein the stability values are higher for Ba and Sr than the comparable sized M^+ ions (K and Rb) and lower for Ca and Mg than the comparable sized M^+ ions (Na and Li).

The effect of solvent medium on the stability of a given M^{z+}-crown system has generally been recognized (refs 16, 485, 486, 528, 535, 544, 546), so much so that the M^+/M^{2+} selectivity patterns for a crown toward similar-sized cations can be reversed just by the change of the solvent medium.[544b] Observations on M^+-DB18C6 complexes in Me_2SO, DMF, and PC (PC = propylene carbonate)[535] are of interest which not only demonstrate a strong solvent effect but also strengthen the arguments provided above. In the most strongly solvating Me_2SO (Table III), the stability sequence is K > Rb > Cs ~ Na ≫ Li. In the solvent of the next donicity (DMF) the stability values are raised and so also the selectivity for large M^+ (K, Rb, and Cs) over the small M^+ (Na and Li). In the solvent of the lowest donicity (PC) three observations are distinct: (i) stability values are raised further, (ii) the value for K is raised, in particular, and (iii) the Na value becomes higher (!) than that for Rb and Cs. Collective observations in all the three solvents indicate that selectivity of the crown for a larger over a smaller cation (for K over Na in particular) is enhanced as donicity of the medium decreases so that solvent competition toward M^+-crown interaction is reduced and, in the case of smaller M^+, the counteracting interaction effects of the cation with the anionic species become pronounced. In most cases such as with DC18C6 in water or MeOH,[16,88] with DB18C6 in Me_2SO, DMF, or PC,[535] or with $Me_2DB18C6$ in oxetane[528] there is a general K over Na selectivity. However, in THF, $Me_2DB18C6$ shows a selectivity for Na over K,[528] although the same anion (fluorenyl) was used as in oxetane. This appears to be so because for the delocalized fluorenyl the anion effect is diminished and crown/solvent competition determines the selectivity so that for the more highly solvating oxetane Na experiences a stronger solvation whereas in THF it exhibits a stronger complexation with the crown and hence the rather uncommon Na over K selectivity.

The relatively ignored crown–solvent interaction, which should contribute strongly toward destabilization of M^{z+}-crown complexation, is also an important factor especially in the protic medium. Such an interaction appears pronounced when the donor ring is small or, if large, is flexible so as to undergo (crown)$O-^{\delta+}H$(solvent) contacts and is basic enough to ensure the required charge transfer. Thus, of B15C5, 18C6, and DB24C8 (in MeOH–water, 7:3), and 15C5, 18C6, and DC24C8 (in water) the M^+-crown stabilities and selectivities are consistently pronounced for 18C6, and of the latter group crowns the most highly flexible DC24C8 is the least complexing (practically noncomplexing).[16] These observations may be explained in view of the crown–solvent interactions which are expected to be pronounced either for the small cavity 15C5–crowns or for the flexible DC24C8 so that the 15C5–crowns (despite the possibility of effective M^{z+}-O contacts) and DC24C8 (despite flexibility and a more basic nature of the donor ring compared to DB24C8) prove less strongly complexing; X-ray analysis of $Ca(pic)_2(B15C5)(H_2O)_3$[152] and $Ca(dnb)_2(B15C5)_2(H_2O)_3$[512] complexes has indeed revealed a molecule of B15C5 to be complexed exclusively with the water protons, B15C5 can be crystallized in a monohydrated state (ν_{OH}, around 3400 cm^{-1}),[479] NMR studies in MeCN indicate strong conformation changes for B15C5 in the presence of D_2O,[479a] and pH titrations show $(B15C5H^+)ClO_4$ complex to be stable up to pH 5[479b] (see also ref 547).

The ring frame remaining the same, M^+-crown interaction is strongly a function of the number and nature of the substituents on the ring which control the basicity as well as the flexibility of the donor ring. In principle, the complexing ability should decrease in the order unsubstituted ring > alicyclic-fused ring > aromatic-fused ring as is well known for the series 18C6, DC18C6, and DB18C6.[476] Whereas 18C6-cavity crowns and 21C7-cavity crowns are appreciably complexing[16,476] hexabenzo-18-crown-6 and heptabenzo-21-crown-7 are noncomplexing.[548] Different isomers obtained in the case of alicyclic-fused ring show different complexing ability; of the five DC18C6 isomers the M^+-crown stabilities in methanol are higher for trans-syn-trans and cis-syn-cis than for trans-anti-trans and cis-anti-cis, respectively, and for cis-anti-cis and cis-syn-cis compared to trans-anti-trans and trans-syn-trans, respectively.[543]

Complexation principles of M^{2+} ions are comparatively less rationalized. The interaction of these cations with a crown vs. anionic species overweigh each other so abruptly that either these cations (Ca and especially Mg) do not complex with crowns or they (Sr and especially Ba) complex more strongly than similar-sized M^+ ions in water (e.g., ref 538). This behavior arises from their charge density which makes them behave either strongly anionphilic or strongly complexing depending upon the nucleophilicity of the counteranion, donicity of the solvent medium, and those structural features of the crown which are related to its complexing property. With various crowns, the stability values decrease rapidly in the order Ba, Sr, Ca, and Mg, and with B15C5, for example, are drastically lowered by the use of less polar MeOH (in water medium)[16] (Table III) which indicates that the cation is made to prefer the counteranion through an increase in the charge density of M^{2+} and a decrease in the polarity of the medium.

From the foregoing discussion it may be concluded that the cation selectivity of a crown within and between M^+ and M^{2+} ions is strongly influenced by the size of the cation with respect to that of the donor ring. It is dependent even more on the nature of the anionic species including the solvent medium, and on the structural features of the crown such as donor number and the ring substituents. However, the electrostatic and thermodynamic parameters, sometimes, so modify the operative M^{z+}-crown, M^{z+}-anion, M^{z+}-solvent, and crown–solvent interactions that the results become difficult to understand. It is difficult, for example, to explain (i) why B15C5 should fail to complex Mg, Ca, and Sr in MeOH–water (7:3) while in the same medium these cations can be complexed by 18C6,[485] and (ii) why for DB27C9 the stability sequence of M^+ in a medium (MeOH–water, 7:3) is K > Na > Cs while, in conformity with the ion-cavity radius concept, the sequence with DB24C8 in the same medium is Cs > K > Na.[485]

B. Crown-Related Macrocycles

The M^{z+}-complexing macrocycles of this class (compounds I to XVII, Figure 31) are related to Pedersen's original crown ethers but differ from the latter in one or more of the following ways: (i) One or more donor sites of the ring are nonoxygens (refs 7, 16, 30, 37, 39, 476, 519a, 549–553) as are, for example, Pedersen's crown sulfides.[549] (ii) One or more oxygen or nonoxygen heterocycle nuclei form a part of the ring while remaining donor sites may be oxygens or nonoxygens[554–568] as are, for example, the Cram group's furan-based macrocycles.[564] (iii) The ring carbons are replaced by functions such as carbonyl with or without conforming to feature (ii)[539,557,563,569–572] as are the crown esters of the Christensen–Izatt group[539] or the crown lactones of the Vogtle group.[557] (iv) The aromatic moiety, which is fused on the ring, carries a substituent[12,573] such as the Smid group's pendant crowns[12] or the Vogtle group's papaverine crown ethers.[573] (v) Two crowns are bridged together[12,574,575] as are the Smid group's intermolecularly bridged macrocycles[12] or Parsons' intramolecularly bridged crowns.[575] (vi) The very ring carbons of the crown are replaced by electronegative atoms such as nitrogen[576] or phosphorus[577] as are, for example, the acetonitrile oxide oligomers.[576]

To obtain category (i) macrocycles replacement of O with NH, NR, or S has been carried out, but the resulting macrocycles have in general been found to be less strongly binding with M^{z+} (in the order O, NR, NH, and S);[7,16,37] in the case of NH-macrocycles the selectivity for K over Na, however, is enhanced.[519a] Structural analysis of the KNCS(I) complex reveals[550] that the K–N distances (2.86 Å) are detectably longer than the K–O distances (av, 2.83 Å) and unlike in the complex [K(18C6)]NCS[488] the NCS anion behaves bonding and is not disordered. Both the features indicate that the N atoms are weaker donors and K is less stabilized than with 18C6.

The binding ability of some category (i) to (iii) type macrocy-

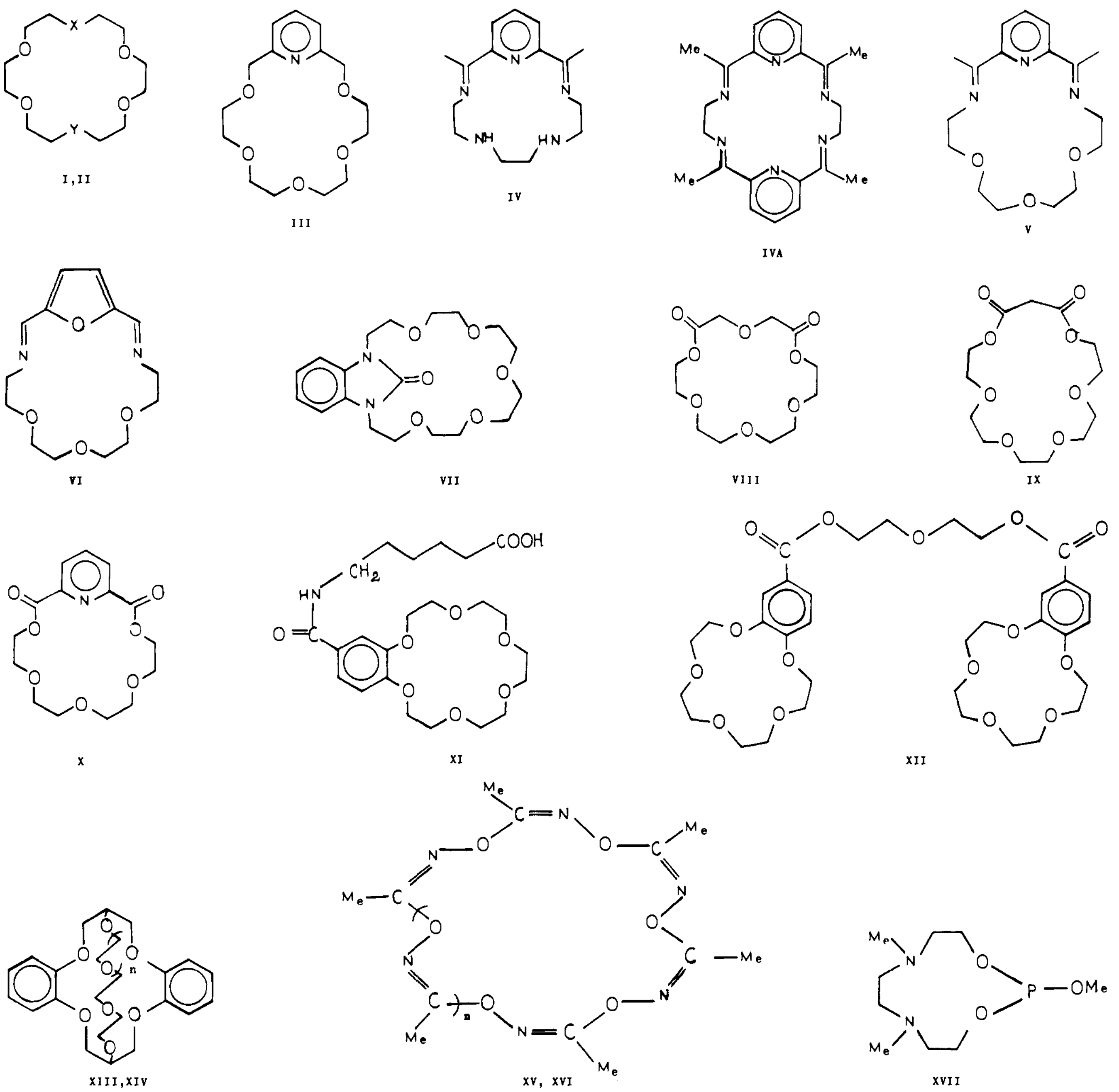


Figure 31. Crown-related macrocycles (I to XVII). I: X = Y = N; II: X = N, Y = O; XIII: *n* = 1; XIV: *n* = 2; XV: *n* = 1; XVI: *n* = 2.

cles has been compared employing Na, K, and Ba in MeOH.[563] With K, for instance, the complexing ability of III is comparable to that of 18C6 but II binds poorly. In MeOH, stability sequences with VIII and IX are Ba > K > Na and K > Na > Ba, respectively.[539] Ligand VIII is distinctly weaker than 18C6 but the binding power is significantly improved in ligand X which is rather surprising.[563]

Some specific observations on a few category (ii) macrocycles are as follows. Compound IV has been synthesized employing Mg as a template.[558] Structural analysis of its complex $Mg(IV)Cl_2 \cdot 6H_2O$ reveals Mg to be separated from Cl while coordinated with all the five ring nitrogens and from the axial sides with two water molecules.[558] Compound V has been synthesized employing Ca, Sr, or Ba as a template.[560] The complexes $Ca(NCS)_2(V)$, $Sr(NCS)_2(V) \cdot H_2O$, and $Ba(NCS)_2(V) \cdot H_2O$ have been characterized and structures of the former two complexes have been solved. Calcium in $Ca(NCS)_2(V)$[560] interacts with all the six donor atoms and on each axial side with N of NCS; the latter probably aids location of the cation well into the cavity of the strained ring. Strontium in $Sr(NCS)_2(V) \cdot H_2O$, which is isostructural with the analogous Ba complex, chelates with all the donor sites of the ring and, uniquely, with both the NCS ions from the same axial side.[560] The two anions pull the cation from the ring significantly yet a molecule of water coordinates to the cation from the other axial side. Active participation of furan moieties in M^+ complexes of antibiotics has stimulated interest in M^+-template synthesis of some furan-based crowns.[555,564,565] Macrocycle VI has been synthesized employing Ca, Sr, or Ba as a template and the structure of $Sr(NCS)_2(VI) \cdot H_2O$ has been determined.[555] The furanyl oxygen is interacting. The Sr–O(water) and Sr–N(NCS) distances (2.58 and 2.63 Å, respectively) are shorter than the Sr–ring contacts (2.69–2.80 Å). As in the complex $Sr(NCS)_2(V) \cdot H_2O$,[560] both the NCS ions interact with the cation from the same axial side suggesting that unlike in complexes such as $Ca(NCS)_2(V)$,[560] $Ca(NCS)_2(18C6)$,[504] and $Ca(NCS)_2(B15C5)(H_2O$ or $MeOH)$[505] the nonlinear $Sr(NCS)_2$ gets complexed as an ion pair and becomes more angular. Work on the benzimidazolone-based macrocycle

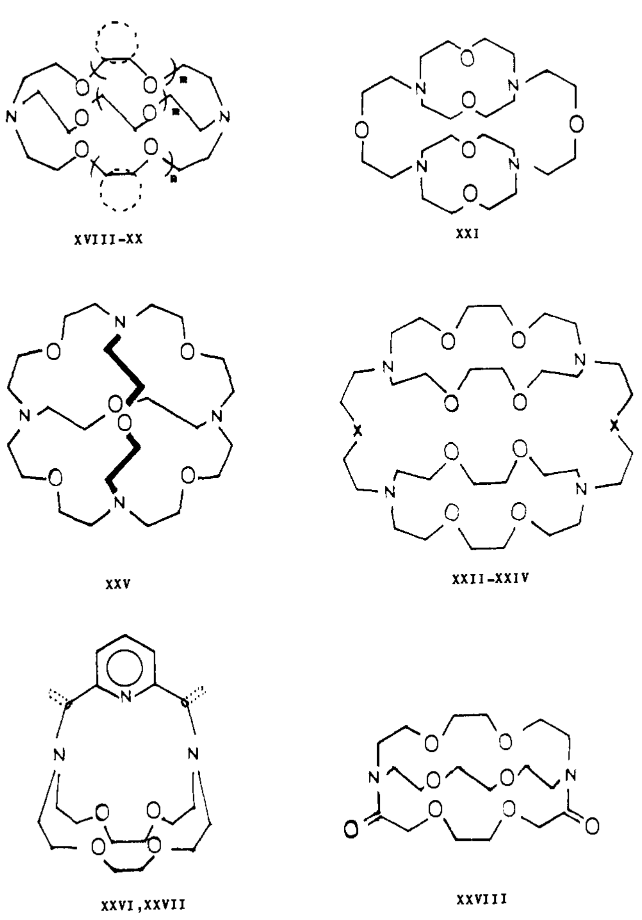


Figure 32. Cryptands (XVIII–XXVIII). XVIII (broken circles representing no attached nucleus): [1.1.1] form $m = n = 0$; [2.1.1] form $m = 0$, $n = 1$; [2.2.1] form $m = 1$, $n = 0$; [2.2.2] form $m = n = 1$; [3.2.2] form $m = 1$, $n = 2$. XIX: one broken circle representing benzo nucleus on [2.2.2] form of XVIII. XX: each broken circle representing benzo nucleus on [2.2.2] form of XVIII. XXI: a simple tricyclic cryptand. XXII: a cylindrical tricyclic cryptand with X = CH_2. XXIII: a cylindrical tricyclic cryptand with X = O. XXIV: a cylindrical tricyclic cryptand with X = C_6H_4. XXV: a spheroidal cryptand. XXVI: each broken rectangle representing carbonyl function. XXVII: broken rectangle representing no attached function. XXVIII: dilactam of [2.2.2] form of XVIII.

VII and related compounds has indicated that M^{z+} can be complexed but the efficiency of the ligand bears little relation to its hole size.[568]

Smid and co-workers report[12] on the ion-binding ability of various polymer macrocycles which, because of the attachment of a linear polymer moiety to a crown, may be treated as cyclic–acyclic macromolecules as is, for example, XI. Such molecules appear to represent all the possible structural features of a transport mediator operative within a cell membrane, and may develop into suitable models. The effect of a substitution as shown in XI is significantly greater than the effects arising from the change in the ring size of the macrocycle;[579a] complex formation constant of XI with K in acetone, for example, is eight times lower than the one with the analogous 4'-methyl derivative.

The intermolecularly bridged crowns, such as XII, bind cations to produce a sort of polyelectrolyte wherein formation constants are a function of the number of cations bound to the molecule.[579b] The intramolecularly bridged crowns, for example, XIII and XIV, resemble the cryptands in topology but differ from the latter in that the donor atoms are only oxygens. For M^+ the spherical cavity ligands XIII and XIV have been found[575] to be more strongly complexing than the ellipsoidal cavity ones.[574] Ligand XIII which carries a bridge of four oxygens on the DB14C4 ring has shown a Na(K)/Rb selectivity in water whereas XIV carrying a bridge of five oxygens shows a K(Rb)/Na selectivity in the same medium.[575] The log *K* values with XIII for Na and K (5.4–5.8) and XIV for K and Rb (4.3–4.4) are higher than those known for crowns of the comparable cavity[580] yet the values are lower than those known for [2.2.2] form of cryptand XVIII.[581]

Polyoxa-polyaza macrocycles derived from acetonitrile oxide,[576] for example, the hexamer XV and the heptamer XVI, render the $M(pic)_z$ (M^{z+} = Na, K, Rb, Cs, and Ba) and $M(NCS)_z$ (M^{z+} = Na, K, and Ba) salts soluble in chloroform. Solid complexes $KNCS(XV)_2$ and KNCS(XVI) can be synthesized, the stoichiometry of which may be compared with the products[478,488] of these salts with crowns of the comparable cavity, viz., B15C5 and 18C6, respectively. The 11-crown-5 analog XVII, which involves a phosphorus atom in the ring, undergoes 1:1 complexation with Li, Na, or K[577] and like 12C4[582] or 14C4[30] shows a high selectivity for Li.

C. Cryptands

The most potential cyclic multidentates synthesized so far are the Lehn's bicyclic and tricyclic ligands which are collectively called cryptands. The synthetic strategies and complexation abilities of these ligands have been reviewed in detail by Lehn.[13,19,24] Others[25,30,37,40–42,45] have also outlined some aspects of their complexation chemistry. Compared to the popular crowns, for example, cryptands show attractive selectivity patterns although with regard to the stoichiometry of their complexes the results are comparatively monotonous.[45] Complexes of M^{z+} with cryptands, called cryptates, are in general many orders of magnitude more stable than those with crowns,[583] for the cryptate effect[470] is stronger than the macrocyclic effect;[468,469] in MeOH, the K^+ complex of the [2.2.2] form of XVIII (Figure 32), for example, is about 10^4 times more stable than the K^+(DB18C6) complex.[13] Unlike the crowns, however, cryptands are more selective for M^{2+} than similar-sized M^+;[19] the Ba/K selectivity of [2.2.2], for example, is ca. 10^4.

In a bicyclic molecule such as XVIII each of *n* and *m* can be varied from 0 to 2 to obtain molecules of different cavity sizes so that cryptands of the sizes compatible with different cations are available. With regard to monopositive ions, for example, [1.1.1], [2.1.1.], [2.2.1], and [2.2.2] forms of XVIII are selective for H^+, Li^+, Na^+, and K^+, respectively.[470,584] The two donor oxygens of the N to N link can be replaced by NR,[585,586] S,[587] or CH_2,[24] but by doing so the complexing ability of the ligand is decreased. The molecule can also be made "thick skinned" by fusing one (XIX) or two (XX) benzo nuclei at the regions indicated by broken circles. By doing so the binding constants of the ligand for a cation[588] and the M^{2+}/M^+ selectivity both get modified; ligand XVIII or XIX shows a measurable Ba/K selectivity whereas XX does not distinguish between the two cations.[24,589]

The effects arising from variation in the cavity size of the ligand with respect to the size of the cation strongly modify the kinetics of complexation and decomplexation. When cavity size of the ligand suits the cation size, a slow cation exchange (compared to that in the M^{z+}–crown systems) is generally always observed.[19,41,436a,590–593] For the complexes [Na-2.2.1] and [K-2.2.2], for example, complexation constants are high and decomplexation constants are quite low.[583] However, for the cryptates wherein the cation size exceeds that of the cavity, such as [Na-2.1.1] and [K-2.2.1], complexation constants are either high (K) or low (Na), but decomplexation constants are constantly high.[583] This suggests that these misfit cation–ligand combinations, like [Cs-2.2.2],[594] produce exclusion complexes in which the cation is only partially encapsulated and factors related as well as unrelated to the ion-cavity radius concept are operative. In the case of the higher charge density Na, formation of the exclusion complex should in principle be unfavorable because of the involvement of the cation with anionic species so that the complexation constant should be low, and because of the conformation strain on the ligand the decomplexation constant has to be high as observed. For the rather polarizable K which is relatively less involved with the anionic species, the thermodynamic terms of the interaction should be favorable owing to effective ligand encapsulation (even for the formation of exclusion complexes) so that the complexation constant could be high, and because of the conformation strain on the ligand the decomplexation constant should also be high as observed. Activation parameters for the formation of some M^{2+}–cryptates, viz., of Ca with [2.1.1], [2.2.1], and [2.2.2], of Sr with [2.2.1] and [2.2.2], and of Ba with [2.2.2], have also been measured.[595] The ΔH, ΔS, and log K values (for Ca) have been found to be in agreement with those found potentiometrically[470] and calorimetrically,[596] but dissociation rates for M^{2+}–cryptates contrast with those for M^+–cryptates (M^+ = Na or K).[436b,593] Recent work on these ligands includes also calorimetric studies on the enthalpy of transfer of [2.2.2], [Na-2.2.2], and [K-2.2.2], and on the heat of M^+–[2.2.2] complexation.[597]

X-ray diffraction structural analysis has been performed on the complexes [Li-2.1.1]I,[598] [Na-2.2.1]NCS,[599] [K-2.2.1]-NCS,[599] [Na-2.2.2]I,[600,601] $[\text{Na-2.2.2}]_2[\text{Fe(CO)}_4]$,[602] [K-2.2.2]I,[600,603] [Rb-2.2.2]NCS·H_2O,[604,605] [Cs-2.2.2]NCS·H_2O,[600,605] $[\text{Ca-2.2.2}(H_2O)]Br_2 \cdot 2H_2O$,[606] [Ba-2.2.2(NCS)-($H_2O$)]NCS,[607,608] and $[\text{Ba-3.2.2}(H_2O)_2](NCS)_2$.[607,609] It has been found in general that the products are the complexes of the inclusion type (complete encapsulates) in the case of M^+ ions while ion-paired or incomplete encapsulates in the case of the M^{2+} ions.

The tricyclic cryptands have also been synthesized which are formed of two macrocycles connected by two bridges (XXI, for example).[610] By changing the dimensions of the top and the bottom cavities a tricyclic molecule can be modified into a so-called cylindrical cryptand (XXII to XXIV) so that formation of the 1:1 as well as 2:1 bimetallic encapsulates becomes possible;[13,611] in the case of 1:1 complexes an intersite cation exchange within the ligand molecule is exhibited.[612] X-ray molecular structure of the complex $[\text{2Na-XXIII}]I_2$[613] is known; each cation is charge separated (Na^+–I^- > 5 Å) and bonded to two nitrogens and five oxygens.

The so-called spheroidal cryptands (XXV, for example) yield only 1:1 complexes. With M^+,[13] the stability order with XXV in water is Rb > K ~ Cs; the stability of the Cs complex (log K = 3.4) is the highest for any complex of this cation known so far.[614]

The complexing ability of so-called modified cryptands (XXVI to XXVIII) has been studied.[530,615] While the affinity of ligands XXVI and XXVII for Na remains the same, XXVI shows a high K/Na selectivity and XXVII shows a low K/Na selectivity.[530] The overall ligating ability of these compounds, however, is comparable to that of the bicyclics discussed above. The [2.2.2]-dilactam XXVIII, which is a precursor of [2.2.2],[615] complexes M^+ (Li, Na, or Cs) but weakly compared to the latter.

D. Acyclic Multidentates

1. *Poly(oxyethylene) Derivatives*

The reported work, particularly with the poly(ethylene oxide) (PEO) molecules, is mostly of the qualitative nature carried out to note their interactions and relative interactions with alkali and alkaline earth salts. Some of the earlier observations include: (i) lowering of the melting point of nylon-6 in the presence of LiX,[616] (ii) disruption of the crystallinity of PEOs in the presence of a salt like KI,[617] (iii) change in the viscosity of PEOs in the presence of MX,[617] and (iv) enhanced solubility of the PEOs in MeOH in the presence of MX.[617] The PEO–MX (MX = KNCS, NaNCS, NaI, and LiI) complexes constitute solid phases different from those of the reactants (X-ray studies).[618] In the presence of the rather self-stabilized Ph_4B as counteranion, the high molecular weight PEOs complex also the M^{2+} ions.[619–622] Infrared features of the M^+–PEO products are new and comparable to those of the M^+–crown complexes,[618] suggesting M^+–O(PEO) complexation to be due to an ion–dipole type of interaction. This is understandable because a PEO molecule exists in a helical state[623] (wherein a turn is composed of about 7 units) and disposition of the donor oxygens can be compared with that of a crown such as 18C6. There is apparently a relationship between the number of the repeating units of the PEO molecule and the size of the cation (six for Na[624] and seven for K[625]), but later work[626,627] reveals that such a categorization is not rigid although, roughly, ligands with increased number of the repeating units show compatibility with increased size cations. Although PEOs and their esters behave[617,628,629a] nonspecific (compared to, for example, crowns), their binding powers are strong probably because of the cooperative effects operative between the oxygen atoms distributed on the ligand skeleton of the ligand.

The helical structure of these acyclics, i.e., outward disposition of the hydrophobic skeleton, enables them to act as efficient phase-transfer agents for MX_z (X^- = I or NCS) to the extent that PEO-1000 (23 repeating units) works more efficiently than 18C6 toward the extraction of $M(NCS)_2$ salts from water to dichloromethane.[625] Whereas a crown such as 18C6 efficiently extracts the M^+ ions,[510,625] PEO-1000 proves more efficient for the M^{2+} ions (Ba > Ca > Mg) under the same conditions.[625] The terminal OH groups play an important role in complexation[627] which suggests that in the present M^{2+} systems, –OH···NCS interaction might be operative so that even Mg is complexable (self-encapsulation); complexation is favored toward the large cation because M^{2+}–O contacts become increasingly facilitated and/or ligand encapsulation makes an increasing contribution.

The aryl-substituted PEO, XXIXA (Figure 33), undergoes complexation with NaNCS, KNCS, and $Ca(NCS)_2$;[517] crystal structures of NaNCS(XXIXA) and $[\text{KNCS(XXIXA)}_2]_2 \cdot CHCl_3$ have been solved.[629b] Sodium in its complex is ion-paired and is seven-coordinated through five oxygens of one ligand molecule in a plane while NCS occupies one axial position from the N end and one diol oxygen of the neighboring molecule completes the pentagonal bipyramid. Potassium in its dimeric complex, on the contrary, is charge separated and ten-coordinated through five oxygens (including a diol oxygen) of each ligand. The larger PEO, XXIXB, fails to complex NaNCS.[517] In ligands XXX to XXXII, one or both terminal groups are nonhydroxyl. The ester ligand XXXII works better than its acid analog XXXI; synthesis of complexes with the latter and other carboxy ligands is not possible particularly with the salts of high charge density cations, probably because of[45] their metathetical reactivity.

The nonionic surfactants, e.g., nonylphenoxypoly(oxyethylene)ethanols (NPOE) complex with M^{z+} [510,619,621,622] and have been investigated for their possible use in ion-selective electrodes.[630–636] Some nonstoichiometric $M(Ph_4B)_2$–NPOE complexes have been synthesized from water.[510] Phase-transfer studies with $M(pic)_z$ salts show same extraction sequences as for other neutral macrocycles.[537] Extraction is possible employing MCl_z–picH–NPOE systems,[510] which indicates that even MCl_z is complexable with NPOE and that the electrostatically destabilized Cl in the product $M(NPOE)_nCl_z$ causes deprotonation of picH so as to produce the extractable $M(NPOE)_n(pic)_z$ as has also been found for similar systems involving B15C5.[518]

The PEO ethers, glymes in particular, interact with $M(fl)_z$ salts in a medium of low polarity (THF) to yield loose–tight ion pairs depending upon M^{z+} and the nature of glyme.[22a,637a] X-ray analysis of the complex $NaNCS[MeO(C_6H_4)O(CH_2CH_2O)_3(C_6H_4)OMe]$ reveals that the ion-paired cation is chelated through all the six oxygens of the ligand.[637b] The aromatic analogs of the glymes, viz., $PhO(CH_2CH_2O)_nPh$ (n = 4, 6–10) have been studied.[624] The n = 6 to 10 ligands complex Na in MeOH for which stability values enhance with the value of n; a crystalline product

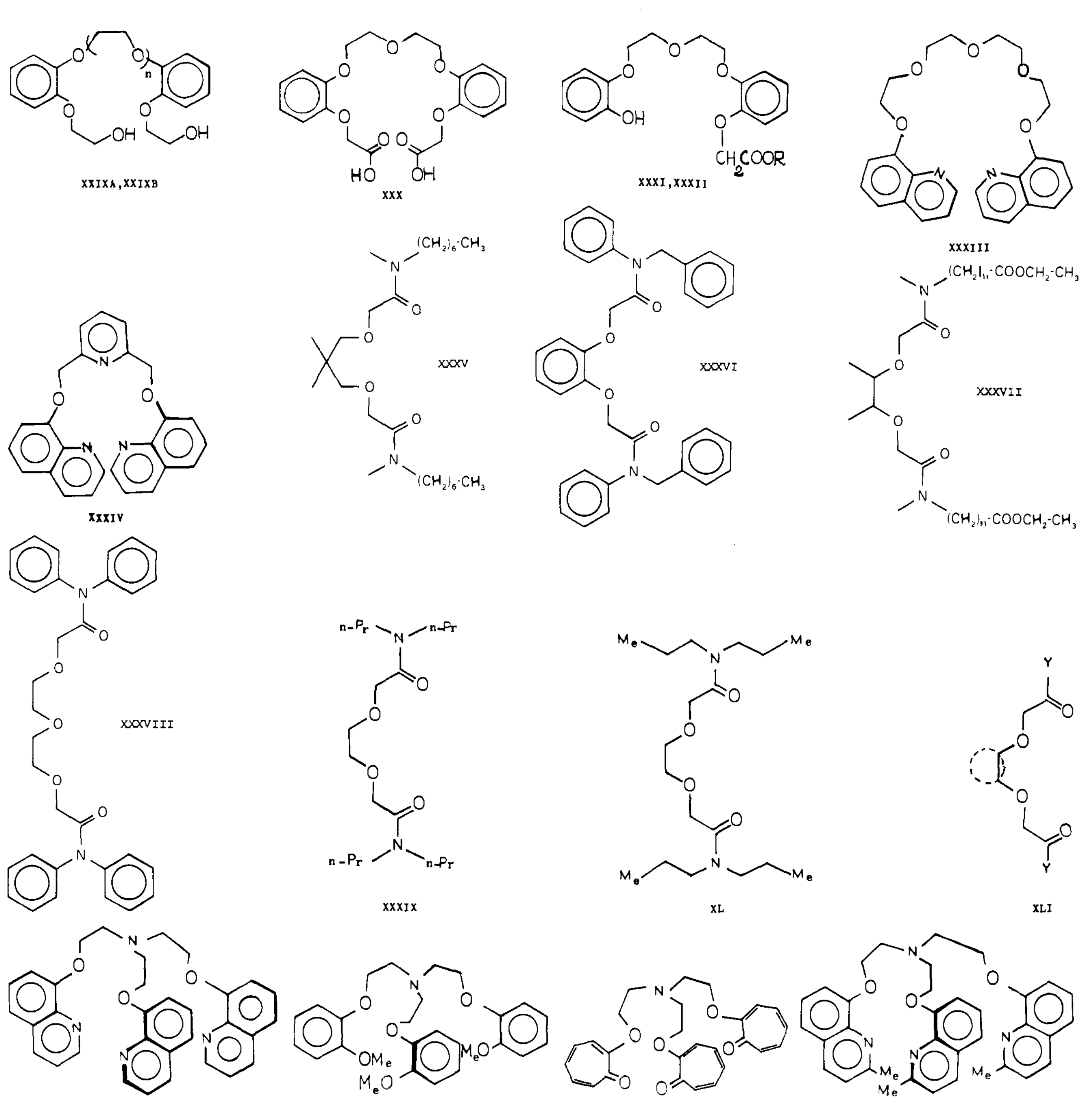


Figure 33. Acyclic multidentates (XXIX–XLV). XXIXA: $n = 1$; XXIXB: $n = 2$; XXXI: R = H; XXXII: R = Et; XLI: Y = Cl, $N(n\text{-}Pr)_2$, or $N(Me)(CH_2)_5(CO_2Et)$, broken circle representing benzo-, naphtho-, cyclohexano-, or *t*-Bu(cyclohexano) nucleus.

has been characterized for which the composition is $\{[PhO(CH_2CH_2O)_6Ph]_2Na_2\}[Co(NCS)_4]$.[624] Crystalline 1:1 $Ba(NCS)_2$ complexes have been synthesized with $n = 5$ to 7 ligands.[638] The ligands $NaphO(CH_2CH_2O)_nNaph$ yield 1:1 crystalline complexes with $Ba(NCS)_2$ ($n = 5$ or 7) or $NaClO_4$ ($n = 6$).[638] These results are significant in view of the fact that the analogous glymes such as GLYME-6 fail to produce solid complexes with M^{z+}.[88,639]

With a view to determine the role of the terminal groups, Vogtle et al.[530,638–641] synthesized and studied various acyclic poly(oxyethylene) derivatives (e.g., XXXIII and XXXIV) which may be termed as acyclic crowns[640] or crown-type acyclics,[530] or substituted glymes and related compounds. Ligand XXXIII is the most highly studied of all its group members. It preferentially complexes, in general, the larger M^+ (which are only weakly involved with anionic species) both in solution[530] and in the solid state;[640–642] X-ray analysis reveals the RbI(XXXIII) complex to be charge separated.[642] The comparatively rigid XXXIV, on the contrary, exhibits a Na/K selectivity.[530] For the comparatively stable K–XXXIII and Na–XXXIV systems, kinetics of complexation have been carried out employing temperature-jump relaxation techniques.[530] Ligand XXXIII has also been used to aid chromatographic separation of M^+ ions.[643] Interestingly, like 8-hydroxyquinoline[644] and other N donors, XXXIII shows a Mg/Na (or K) selectivity in MeOH.[530] The possible use of such ligands as models for acyclic antibiotics in the transport reactions of M^+ has been argued.[530,642]

2. Sensors

The most important of the acyclic multidentates are the "sensors" (Figure 33, XXXV–XLI) which, too, possess a hydrophobic exterior and a polar interior so that M^{z+} can be effectively bound and screened from the decomplexing environments. The main aim of studying these ligands has neither been to discover the complexation characteristics of M^{z+} nor to study the conformation aspect of the molecule but to standardize different sensors for the selective complexation of different M^{z+}

so that ion selective electrodes of use in the analytical chemistry of the concerned cations can be developed;[44] those shown (XXXV to XXXVIII) are selective for Li,[645] Na,[646] Ca,[647] and Ba,[648] respectively. Except for a study on some,[649] serious efforts have not been made to synthesize solid M^{z+}-sensor complexes.

Structural aspects of the sensors and the medium profoundly modify the selectivity behavior of a sensor toward M^{z+}.[26,44] The complexing ability of XXXIX with Na, K, Ca, and Ba in different media has been investigated in detail employing ^{13}C chemical shift and spin-lattice relaxation time measurements.[650] The stoichiometry of interaction is influenced by the solvent medium while donor site participation changes from cation to cation. In CD_3CN and CD_3OD, for example, 1:1 complexes are formed involving all the four oxygens. In $CDCl_3$, each of K, Ca, and Ba gives a 1:2 product while Na forms 1:1 as well as 1:2 products; in the 1:2 products of M^+ only one amide carbonyl is involved whereas in the M^{2+} products of the same stoichiometry both the carbonyl functions are involved.

The complex $[Ca(XL)_2]Cl_2$ constitutes a rare example of a sensor complex on which X-ray analysis has been carried out.[651] In the lattice, a pair of symmetry-equivalent ligands constitute a trigonal dodecahedron around the cation. The four ethereal oxygens from the apices of an elongated tetrahedron (2.46 Å) and the four carbonyl oxygens from those of a flattened tetrahedron (2.36 Å) make contacts with the cation. The ethereal oxygens make longer bonds probably because of the structural strain experienced by the complexed molecules as also argued for the NaNCS–nonactin complex.[652] The chloride ions fill the space between the lipid cations and are separated from calcium. Previous knowledge does not help to understand why a complex of calcium should be charge separated. If the mysterious peak (noticed at about 3.1 Å from chloride) is due to a water molecule and if nitrogen atoms projecting the coordinating carbonyls are polarized enough to provide the possible stabilization to the Cl ions, then the charge separation is understandable. Some more work on analogous systems appears required before commenting on the role of the torsion of the C–O (ether) bonds toward the selectivity of XL for Ca, however. While it is not definite what could actually be responsible for charge separation, charge separation could well be the reason for a high selectivity of XL for Ca.

Recently,[653] the ethylenedioxydiacetamide group of acyclic ligands (represented by XLI) has been developed. Employing extraction studies on $M(pic)_z$ salts, they have been found to be more selective for M^{2+} ions.

3. Acyclic Cryptands

Acyclic cryptands (XLII to XLV), also called pseudocryptands, have been added recently to the list of the acyclic multidentates.[654] Though acyclic, these ligands behave like the cyclic cryptands in view of their complexation with M^{z+}. Solid 1:1 complexes XLII (*NaNCS*, KNCS, or RbI), XLIII (NaNCS), XLIV (*BaI*$_2$), and XLV (KNCS, RbI, or *BaI*$_2$) have been synthesized[654] with MX_z shown in parentheses; salts shown in italics yield monohydrated complexes with the concerned ligand. ^1H NMR and potentiometric solution studies indicate that XLII is selective for Na over any of K and Li unlike most cyclic crowns and crown-related ligands. Ligand XLII exhibits a peak selectivity for Mg while XLIV shows a pronounced M^{2+}/M^+ selectivity.

E. Antibiotics

The antibiotics of relevance to the present subject have been reviewed quite often (refs 25, 26, 28, 29, 32, 34, 37, 43, 45, 272, 655). The molecules (Figure 34) which interact with the concerned cations are: (i) cyclic neutral antibiotics of the types depsipeptides, macrotetrolides (depsides or nactins), and cyclic polypeptides; (ii) acyclic ionizable carboxy antibiotics; and (iii) neutral molecules which can be classed as cyclic as well as acyclic.

1. Cyclic Neutral Antibiotics

a. Depsipeptides

The most well-known antibiotic of this group is valinomycin, an antibiotic of a rigid conformation because of an extensive intramolecular hydrogen bonding. The degree of the bonding and hence the cavity size of the ligand are strongly influenced by the polarity of the solvent medium so that selectivities (toward, e.g., M^+) are dependent on coordinative characteristics of the cation as well as the medium of investigation. Although analogs of valinomycin, which involve different degrees of intramolecular hydrogen bonding, can show any of the sequences Na > K > Cs, K > Cs > Na, and Cs > K > Na,[37] yet the general sequence of M^{+} with valinomycin is K > Rb > Cs > Na > Li;[656-659] the K/Na selectivity can be as high as 10^5. Conformation of the ligand has been widely studied, for example, in solid K–valinomycin complexes[660-662] and for M^+–valinomycin (M^+ = Na or K) complexes in solution;[655,663] the structure of the Na complex is solvent dependent unlike the K analog.[655] For K, even a 1:2 sandwich formation in solution has been reported[664] which suggests that in addition to the ion-cavity radius considerations the coordinative characteristics of the cation are involved and that in this particular case ligand encapsulation is operative.

Enniatin A, enniatin B, and beauvericin are other well-known antibiotics of this group which have a common structure except for a substitution (isobutyl, isopropyl, and benzyl in this order) in an amino acid moiety of the repeating unit. They constitute a 18-membered ring and, unlike valinomycin, do not involve intramolecular hydrogen bonding, and are therefore flexible. Under normal conditions they undergo 1:1 complexation with M^+ ions[657-659,665] but with larger M^+ excess antibiotic can produce 2:3 (Cs–enniatin B (2:3)[666,667]) or 1:2 (K–enniatin B (1:2)[666]) complexes. In each type of complex the M^+–antibiotic moiety constitutes a disk-shaped entity. These antibiotics show a similar selectivity pattern as valinomycin but stabilities and selectivities are both low. Most results can be attributed to the monotonous conformation that these antibiotics show for different cations under different conditions.[668,669] With $Ba(pic)_2$, beauvericin yields a 2:2 complex[670] which is unique for an antibiotic and for this cation. The cation is bound through three amide carbonyls and holds pic ions in the same manner that Rb and Cs hold the NCS ions in the 2:2 ion-paired sandwiches RbNCS(18C6)[481] and CsNCS(18C6).[482]

For monamycins, which are also 18-membered depsipeptide antibiotics,[655] water-insoluble M^+ complexes (M^+ = Na, K, Rb, or Cs) are reported formed.[671]

b. Macrotetrolides (Nactins)

The antibiotics of this group (nonactin, monactin, dinactin, trinactin, and tetranactin) differ from one another by the number of ethyl substituents on a common skeleton. They complex M^{z+} in polar media,[672] induce transport through a membrane,[673] and produce crystalline complexes suitable for X-ray diffraction studies.

Molecular structures of [Na(nonactin)]NCS,[652] [K(nonactin)]NCS,[674,675] [Cs(nonactin)]NCS,[676] [Na(tetranactin)]NCS,[677,678] [K(tetranactin)]NCS,[677,678] [Rb(tetranactin)]NCS,[677,678] and [Cs(tetranactin)]NCS[676] have been solved. A general observation is that nonactin is a more deformable molecule than tetranactin. Each listed complex is a complete encapsulate involving an eight-coordinated cation; in each system furanyl and carbonyl oxygens participate in coordination. The M^+–O(furanyl) bonds are in general longer than the M^+–O(carbonyl) bonds; the difference is particularly pronounced for the Na–nactin complexes because the cubic coordination around Na is markedly distorted. In the Cs–nactin complexes, on the contrary, the

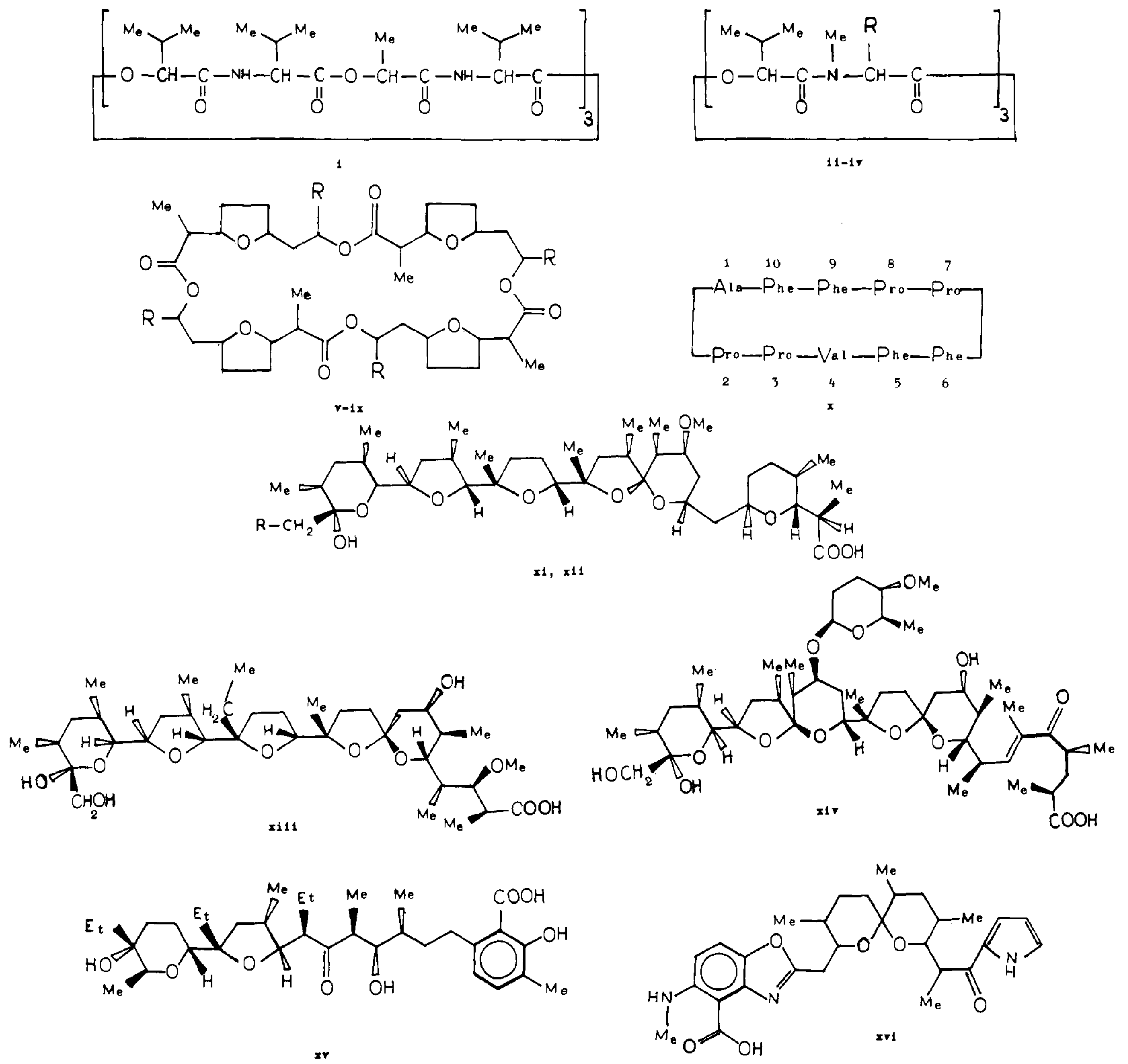


Figure 34. Antibiotics. (i) Valinomycin; (ii) enniatin A: R = CH(Me)Et; (iii) enniatin B: R = $CH(Me)_2$; (iv) beauvericin: R = CH_2Ph; (v) nonactin: $R_1 = R_2 = R_3 = R_4$ = Me; (vi) monactin: $R_1 = R_2 = R_3$ = Me, R_4 = Et; (vii) dinactin: $R_1 = R_3$ = Me, $R_2 = R_4$ = Et; (viii) trinactin: R_1 = Me, $R_2 = R_3 = R_4$ = Et; (ix) tetranactin: $R_1 = R_2 = R_3 = R_4$ = Et; (x) antamanide; (xi) grisorixin: R = H; (xii) nigericin: R = OH; (xiii) monensin; (xiv) dianemycin; (xv) X-537 A; (xvi) A23187.

Cs–O(carbonyl) bonds are longer by about 0.04 Å and in the cavity of each ligand Cs makes a strainful entry; of all the M^+-tetranactin complexes, for instance, only in the Cs complex are the M^+–O bonds shorter than the sum of the radius of the cation and van der Waals radius of oxygen.[676] The strainful fit of Cs also appears to take place in solution, for ^1H NMR shift of the methine protons for the Cs–tetranactin complex is appreciably different from that for the analogous Na and K complexes.[679] The destabilization effect of this conformation strain for Cs is so pronounced that the Cs–tetranactin complex (in aqueous acetone) behaves less stable than even the Na–tetranactin complex.[679]

The general selectivity sequence for M^+ with nactins in solution is K > Rb > Cs ~ Na > Li[680] which is the same as that with the 36-atom cavity valinomycin[32] and the 30-atom cavity DB30C10.[529a] This happens despite the fact that hydration energies (Figure 1) increase in the order Cs to Li. This suggests that the hydration energy criterion alone cannot be considered to explain the selectivity sequences in such systems as attempted earlier.[679] Two distinct points about the observed sequence are that (i) the sequence for the larger three cations is opposite to their hydration and anionphilicity terms, and (ii) the most highly anion-involved Na and Li form complexes of the lowest stability. This indicates that superimposed on the ion-cavity size factor are (i) contribution from the self-encapsulating ability for the larger cations which increases in the order Cs to K, and (ii) the adverse effect of the cation–anion involvements which discriminates Na and particularly Li from the larger cations.

c. Antamanide

This decapeptide antibiotic is unlike other antibiotics being discussed in this review in that it has poor ionophoric properties[655] and in that with M^{2+} ions it gives selectivity orders Li < Na > K > Rb > Cs, and Ca > Sr > Ba > Mg.[681,682] NMR and CD studies[664] show that both Na and Ca interact with antamanide to produce 1:1 as well as 1:2 complexes in solution.[655] Interestingly, the low charge density K, Rb, and Cs, though well known for their ability to form 1:2 sandwiches (with crowns), undergo only 1:1 complexation with antamanide.

X-ray analysis of Li(antamanide)Br·MeCN[160] (Figure 2) and Na(antamanide analog-Phe^4,Val^6)Br·EtOH[161] complexes has been carried out. In both the systems the cation is five-coordinated to produce an incomplete encapsulate while the bromide is bonded on the exterior of the antibiotic with the -NH function. Despite the availability of the space, neither cation gets well into the cavity. The double action shown by antamanide in these complexes is unique for M^{z+}-antibiotic systems and is probably related to the unique selectivity sequences it shows for M^{z+} ions.[45]

2. *Acyclic Ionizable Antibiotics*

Each member of this group carries an ionizable -COOH group which undergoes hydrogen bonding in a head-to-tail fashion with a suitable function at the other end of the molecule. Because of the $-COO^- \cdots HO$ (as in the ionized nigericin, monensin, dianemycin, grisorixin, and X-537A) or $-COOH \cdots N$ (as in un-ionized A23187) type of bonding, the uncomplexed antibiotic as well as M^{z+}-antibiotic complexes adopt a sort of cyclic conformation while projecting hydrophobic moieties on the exterior.[25,26,37,662] Consequent to this, the antibiotics as well as their complexes are insoluble in water but soluble in nonpolar organic solvents.

X-ray studies on metal derivatives Ag^+(monensin)$^-$ [683] (which is isomorphous in one form with the Na salt and in the other with the K salt), Ag^+(nigericin)$^-$ [684] (which is isomorphous with the analogous Na and K salts), M^+(dianemycin)$^-$ [685] (M^+ = Na or K), the dimeric $Na_2^+(X\text{-}537\ A)_2^-$,[686] and $Ba_2^{2+}(X\text{-}537\ A)_4^- \cdot 2H_2O$,[687] $Ca^{2+}(A23187)_2^-$,[688] $Ca^{2+}(A23187)_2^- \cdot H_2O$,[689] $Mg^{2+}(A23187)_2^-$ (which is isomorphous with the analogous anhydrous Ca salt),[662] and the less familiar $Na^+(A204A)^-$ [690] and Na^+(monensin)Br^- [691] have been carried out. In each system the cation is held at the anionic site of the antibiotic and for the purpose of its coordinative saturation is also coordinated with the various neutral donor sites of the anionic ligand. The cation is rather completely encapsulated except for Ca in its derivatives which appears relatively exposed probably because of restricted (unfavored) contacts with the neutral sites. Compared to the sugar complexes discussed in sections III.B.4 and III.C.3 the coordination number of Ca in the present systems is lower (6[688] or 7[689]). Dimerization of the X-537A complexes does not appear to be the characteristic property of the concerned cations because the analogous Ag complex is also dimeric.[692] It probably takes place because X-537A is a small ligand and dimerization is necessary for complete encapsulation of the cation. The complex Na^+(monensin)Br^- [691] is unique in that the involved antibiotic is un-ionized but charge separation of Na^+Br^- is still possible, and that unlike the aforesaid monensin derivatives (which are dihydrated) the product is anhydrous. A speciality of A23187 is that acid salt derivatives (compare ML,HL products of the high p*K* organic acids discussed in section III.B.2.a) can also be synthesized for M^+ ions.[693]

With a view to knowing whether intramolecular hydrogen bonding is a prerequisite for complexation with the concerned antibiotics, structural features of a synthetic open-chain dicarboxy crown, XXX, have been investigated employing X-ray diffraction technique on the complex K(pic)(XXX).[694] The complex dimerizes in the lattice while there is no intramolecular bonding within the ligand. This, however, does not mean that complexation with other synthetic acyclics should also not involve intramolecular bonding or that the role of such bonding is ruled out for complexation of the concerned antibiotics.

Solution stabilities shown by monensin (Na > K > Rb > Cs > Li; $M^+ > M^{2+}$),[771] nigericin (K > Rb > Na > Cs > Li),[696] dianemycin (Na $\gtrsim$ K $\gtrsim$ Rb),[695] A23187 (Li > Na > K; Ca > Mg > Sr > Ba; $M^{2+} > M^+$),[693] and X-537A ($M^{2+} > M^+$)[37] depict unrelated orders and appear difficult to rationalize even if an equal amount of work is put in addition. For some solution study results of M^+-monensin systems in anhydrous MeOH, see Hoogerheide and Popov.[697] Anteunis has recently studied solution conformation of the anionic antibiotics in the complexes $Mg(A23187)_2$,[698] Na(monensin A),[699] Na(A-204A),[700] Na(carriomycin),[772] and Na(lonomycin).[773]

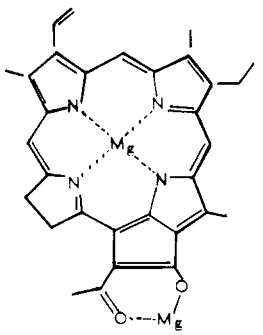


Figure 35. Showing central as well as peripheral complexation of Mg in a chlorophyll system on which substitutions are not fully shown.

3. *Cyclic/Acyclic Antibiotics*

The antibiotics of this category are relatively less known. Alamethicin is one such antibiotic which is believed to be cyclic[701,702] as well as acyclic[703] and is capable of inducing transport of alkali cations into a nonpolar organic phase.[704] Gramicidins, also believed to be cyclic[705] as well as acyclic,[706] alter ion conductance characteristics of the transporting membranes.

F. Other Macromultidentates

Studies have been carried out on various synthetic cyclic peptides with a view to understand the chemistry of the M^{z+}(peptide-antibiotic) systems, and on Mg complexes of the tetrapyrrole-based macrocycles for gaining insight into the chemistry of chlorophylls and related pigments.

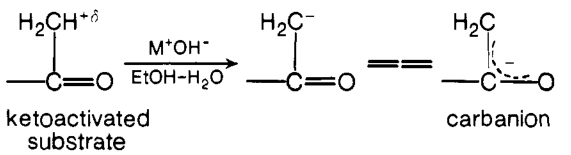
The rather small *N*,*N'*-dimethyldiketopiperazine (cyclodisarcosyl), unlike its linear analog, produces crystalline complexes with salts such as $LiClO_4$ and $Ba(ClO_4)_2$.[707] X-ray analysis of the complex $Li(cyclodisarcosyl)_2ClO_4$ reveals Li to be charge separated and four-coordinated in two types of tetrahedra (Li-O, ~1.90 and ~1.95 Å, respectively) through carbonyl groups while there are no Li-N interactions.[707] The results employing the synthetic hexapeptide *cyclo*-(L-Pro-Gly)$_3$ with M^{z+} are in line with[708] those obtained with antamanide in that the peptide is selective for Li and Na over the larger M^+ and for Mg and Ca compared to Ba; for Mg, three distinct complexes, 1:2, 1:1, and 2:1, are reported. However, *cyclo*-(L-Val-Sar)$_3$ (an analog of enniatins)[664] and *cyclo*-(D-Val-L-Pro-L-Val-D-Pro)$_3$ (an analog of valinomycin)[709] show selectivity for Li and Na over K which is unlike the natural analogs. The bicyclic *S*,*S'*-bis[*cyclo*-(Gly-L-Cys-Gly-Gly-L-Pro)], where the two macrocycles are cystine-bridged, displays the sequence K > Na > Li > Ca.[32] The dodecapeptide *cyclo*-(L-Val-Gly-Gly-L-Pro)$_3$ in MeCN shows M^{2+}/similar-sized M^+ and larger/smaller ion of the same charge selectivities.[710]

The Mg complexes of the natural origin, viz., the chlorophylls and the related pigments, form a vast field of study and have been investigated in solution as well as in the solid state.[711,712] The cation can be bound "centrally" in the tetrapyrrole cavity or "peripherally" with suitable donor sites located on the hydrophobic exterior of the macromolecule as shown in Figure 35. The central complexation determines the basic chemistry of the pigment while the peripheral interactions influence other physico-chemical characteristics such as molecular aggregation and their spectral features;[713] intermolecular peripheral coordination of a centrally coordinated cation is common but the same can be prevented by blocking the fifth (axial) coordination position of the cation in the tetrapyrrole cavity with say an imidazole moiety which forms the part of the macromolecule.[714] Aggregation and hence spectral properties of the pigments can also be competitively counteracted by strong donor solvents such as MeOH.[715] Although peripheral complexation is of the chelate type, yet such interactions are weaker than those of the central type.[713] Despite this, peripheral complexes of Mg with, say, methyl pheophorbides *a* and *b*, are stronger compared to the analogous complexes of the soft cations such as Zn and Cu.[713]

Metal-porphyrin interactions have been followed spectroscopically (^{1}H NMR) in solvents such as pyridine and stability values for Mg are as fairly strong as, for example, with *Zn*.[716] To gain insight into the bonding modes of the cation in the natural molecules,[717-719] X-ray analysis has been performed on natural molecules such as ethyl chlorophyllide a·2H_2O[720] as well as on the synthetic ones such as Mg(tetraphenylphthalocyanine)·H_2O[721] and Mg(phthalocyanine)(pyridine)$_2$·H_2O.[722] Axial coordination of the centrally complexed Mg with a molecule of water and the displacement of the cation from the tetrapyrrole cavity is a common feature. The displacement (0.49 Å) is maximum in the last complex wherein pyridine is "coordinated" to the polar proton of the coordinated water molecule and the water molecule displays a sort of double action.

V. Coordinative Interactions of M^{z+} during Organic Reactions

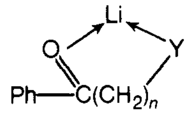
Coordinative participation of M^{z+} during various basic organic reactions has frequently been pointed out (e.g., refs 723–735). While discussing reduction of aldehydes and ketones with $MAlH_4$(M^+ = Li or Na), Uelzmann[733] argued that the difference in the reduction caused by the change of the cation can only be explained if a direct participation of the latter in the reaction takes place through coordination with carbonyl group of the substrate. He went on "it can be expected that many other reactions of complex ionic bonds follow a similar mechanism, particularly, in those cases where exposed reactive atoms are negatively polarized and, therefore, are subject to cationic activation." Such viewpoints are upheld even today.[736-738] We argued[737,738] that a very basic organic reaction, viz., production of a carbanion by an alkali hydroxide in an organic medium (eq 5), cannot take place unless M^+ is consumed (stabilized through coordination) with the "activating" (coordinating) carbonyl. This is because OH^- has no reason to part with a formally charged M^+ in preference to a feebly polarized hydrogen atom of an alkyl group;[737] in the absence of the $-C{=}O{\rightarrow}M^+$ coordination, charge separation of M^+OH^- in a medium which is rather nonionizing, and rupture of the H_2C–H bond, which is dominantly covalent, would be energetically unfavorable. In the following text, we highlight the coordinative role of M^{z+} in general with the help of selected organic reactions.



(5)

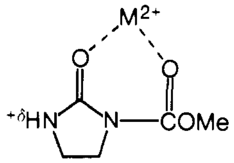
During base-catalyzed condensations of formaldehyde, which lead to the formation of sugars and sugar alcohols (the "formose reaction"), by say $Ca(OH)_2$, the initially formed C_2 and C_3 products such as glyceraldehyde, glycolaldehyde, and dihydroxyacetone are believed to complex with Ca for the purpose of undergoing a rapid condensation.[739] The Fischer glycosidation of sugars can be influenced by the presence of Ca and Sr ions.[740,741] This observation has been used successfully[742] for the synthesis of glycosides such as methyl α-D-erythrofuranoside using Ca (as chloride) in the reaction mixture.

While discussing stereoselective deuteration and methylation of α-lithiobenzylmethyl sulfoxide[743,744] and stereospecific methylation of cyclic α-lithio sulfoxides,[745] Li-chelated structures have been proposed and spectroscopically evidenced. The enantioselective reduction of ω-substituted alkyl phenyl ketones, $PhCO(CH_2)_nY$, with lithium tri-1-menthoxy aluminum hydride is facilitated[746] when Y is a donor group such as MeO. This strongly suggests coordination of the substrate through Y with the reducing agent as follows:



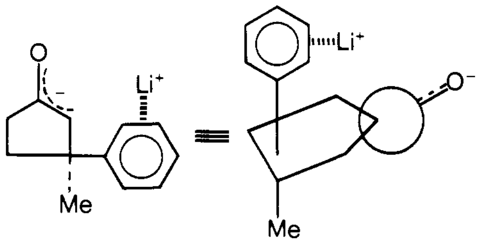
The coordinative role of Li in the formation of "dipole-stabilized carbanions" and "homoenolate intermediates", $C{=}O{\rightarrow}Li^+ \rightleftharpoons \underline{C\ldots}O\ Li^+$, is discussed.[747,748]

The transfer of methoxycarbonyl group of 1-methoxycarbonyl-2-imidazolidinone (and related compounds) to butylamine, by a direct reaction of the reactants, becomes possible in the presence of Ca and especially Mg ions and has been attributed[749] to chelation of the imidazolidinones in the fashion

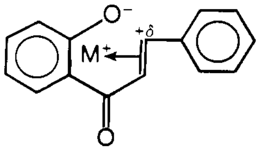


so that electrophilic reactivity of the methoxycarbonyl group is enhanced and it leaves nitrogen-1 of the heterocycle.

Regiospecific generation of an enolate of a 3-arylcyclopentanone in the presence of lithium diisopropylamide has been attributed[750] to the formation of a Li–arene π-coordination complex (eq 6), and cyclization of a 2′-hydroxychalcone in the presence of an alkali hydroxide has been attributed[738] to π-bonding of M^+ with the unsaturated chain as follows:

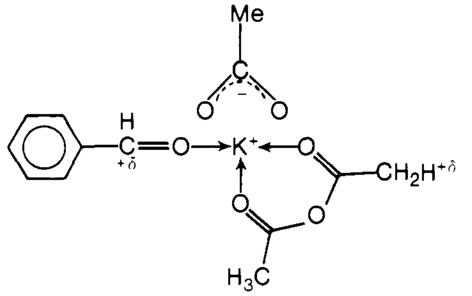


(6)



In both the reactions the yield of the product can be controlled by changing the solvent medium which influences the complexing ability of M^+.

During the reaction of PhCHO, Ac_2O, and KOAc (Perkin reaction, synthesis of cinnamic acid) without the use of any other medium,[751] acetate cannot be visualized as an "available" nucleophile for the production of carbanion from Ac_2O unless K is consumed through coordination with the reactants in the fashion:[752]



Through such a coordination of K, not only can acetate become available for the reaction due to loosening of the KOAc ion pair, but PhCHO also develops a carbonium character and Ac_2O gets its α-hydrogen polarized, both of which are required for the efficiency of the reaction.

The change in the nature of the cation, which forms a part of one of the reactants, may change the route of an organic reaction. Thus, for the acetophenone–phenylalkali reaction, the product is $C_6H_5C(CH_2)OM$ when phenylalkali is PhNa or PhK but is $(C_6H_5)_2C(CH_3)OM$ when PhLi or Ph_2Mg is used.[730] This is understandable because the cation regulates the nucleophilicity of the phenyl counterpart. Employing a kojic acid–dimethyl sulfate–MOH reaction mixture in water, the phenolic hydroxyl group can be selectively methylated when 1:1:1 reaction is carried out with KOH but, on the contrary, the alcoholic group can be selectively methylated when a 1:1.2:3 reaction is carried out employing LiOH.[377,753]

The accidental synthesis of the cyclic polyether DB18C6 through the interaction of catechol (present as impurity in the reaction) with bis(2-chloroethyl) ether, without recourse to the high dilution technique, led Pedersen to believe[754] that Na ions (present in the reaction owing to the use of NaOH) interacted with an intermediate of the reaction (an open-chain product (Figure 36) of an ether and two catechol molecules or of a catechol and two ether molecules) to facilitate the interaction of the fourth required molecule to produce the polyether. This type of "aid" of a spherical cation is now believed to be due to the incorporation of ion–dipole interactions between the cation and the reactants and/or reaction intermediates: template effect. Numerous cyclization reactions employing the template effect have by now been investigated (see refs 7, 39, 511, 555, 558–560, 564, 565, 754–761).

VI. Concluding Remarks

The Lewis acid role of M^{z+} in diverse systems including various organic reactions and their coordinative interactions have been noted widely and were perhaps of the earliest phenomena to be recorded. The coordinative principles of these cations, however, have never been adequately rationalized. Some salient features in this context, discussed in this review, are as follows.

The ligand action of a solvent (solvation or coordination) toward an ion pair in solution or at the surface of a solid is a direct function of the charge density difference of the constituting ions. The cation solvation is in general enhanced in the order neutral, basic, and hydrogen-bonding solvents which is also the statistical order of their participation in the composition of the solvated lattices and in causing charge separation of the concerned ions (formation of solvent complexes). The M^{z+}–ligand coordination, where ligand can also be a solvent, is counteracted by the charge neutralizing anion in accordance with its nucleophilicity. However, during formation of the charge-separated complexes with double action ligands (which stabilize the cation and its counteranion simultaneously), the process can be aided by the anion in accordance with its nucleophilicity because of enhanced anion–ligand interactions.

The ligation of an anion with M^{z+} is much more pronounced than with M^{n+} (HSAB concept). A monodentate and mononegative anion like bromide can make more than one contact with cations in the system which is of significance. During interaction of ML with HL or HL' and the consequent formation of $ML(HL)_n$ or $ML(HL')_n$, the driving force is the L⋯HL or L⋯HL' conjugation and the resulting acid anion then coordinates the cation extensively and even renders the latter soluble in nonpolar media. The higher charge density M^{z+} form anionic complexes with potentially chelating anions like β-diketonates while the lower charge density M^{z+} serve as overall charge neutralizers. The M^{z+}–carbanion species of particularly Li and Mg behave fairly stable and are covalent characterized wherein the cation usually involves chelation with a basic solvent. Whereas $ML(HL)_n$ formation is essentially a characteristic property of the lowest charge density K, Rb, and Cs, the ability to form stable anionic and π-carbanion complexes is bestowed to Na and particularly Li and Mg.

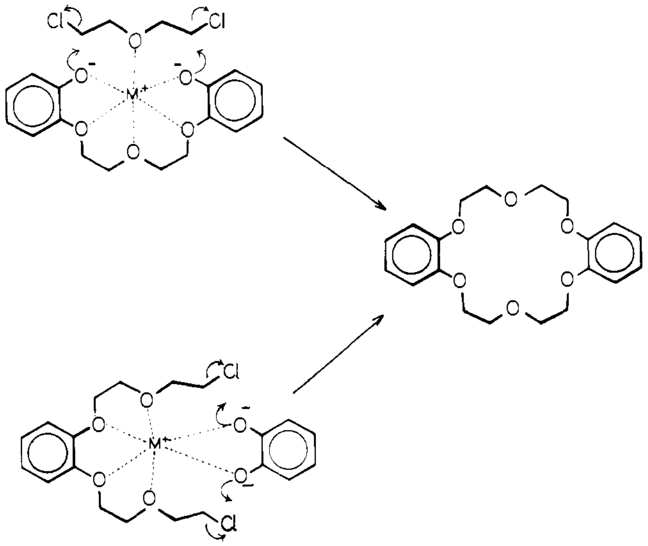


Figure 36. Showing the template cyclization for the formation of DB18C6.

For double action and particularly reinforced ligands, complexes of a high ligand/M^{z+} ratio can be synthesized which are usually charge separated; like the formation of the solvent complexes, interaction with the reinforced ligands is in general a property of the higher charge density Na, Li, Ca, and Mg. For the simple ligands not only is the ratio low but the ligand in the complex is also relatively uncomfortable because of direct involvement of the anion in the coordination sphere of the cation. The bulky sugars, which behave rather Ca-philic, yield charge-separated complexes of a low sugar/M^{z+} ratio despite their double action ability. This is at least partly due to steric and conformation reasons. On complexation, a neutral sugar undergoes a greater conformation change than an anionic sugar. Amides and related ligands cause charge separation through coordination of the cation with carbonyl functions and stabilization of the counteranion with the rather cationized amino functions.

Of the cyclic multidentates, crowns have provided maximum information on discrimination of M^{z+} through recognition of the coordinative characteristics of the latter; only the small and large crowns such as B15C5 and DB30C10 can discriminate cations such as Na and K whereas the nature of the products with the middle-sized crowns such as DB18C6 and DB24C8 is comparable. Complexation and discrimination of M^{2+} are relatively less rationalized; Mg and Ca in particular undergo complexation only when the crown is of a small cavity and when the counteranion is large (weakly interacting) and/or stabilized in the reaction by foreign proton donors such as water. Indeed, M^{z+}–MMM complexation, M^{z+}/MMM ratio in the complex, and conformation of

MMM in the complex are all strongly a function of the nature of the counteranion. For the larger M^+ ions, favored synthesis of the 1:2 charge-separated complexes with smaller cavity (with respect to size of M^+) crowns appears to be essentially due to an extensive polarization of the cation whereas that of 2:2 ion-paired sandwiches for the MNCS salts of Rb and Cs with the 18C6-cavity crowns may be due to a medium-order anionphilicity of the complexed cation toward NCS.

Solution stability values of the M^{z+}–macrocycle systems is a function of the size of M^{z+} with respect to that of the donor ring, of the substituents on the ring, and of the interactive preferences of the cation for the anionic species vis-à-vis the macrocycle. The coordinative characteristics of M^{z+} can be evaluated better through complexation with large-ring macrocycles, for under these conditions interaction of M^{z+} with other competing nucleophiles is shown up. For the highly basic crowns of a small ring or of a flexible ring, the crown–solvent interaction exercises a strong effect on the stability of the M^{z+}–crown system.

Cryptands are too strongly complexing to permit an understanding of the coordinative characteristics of M^{z+}. These ligands so strongly display the size effect that both chemistry and kinetics of complexation are dependent on the ion–cavity size relationship. The higher diols and related ligands, perhaps due to their hydrophobic exterior and the possible double action, appear to promise as efficient transfer agents for M^{z+}. Structural tailoring and extensive solution phase studies of the amide-group acyclics with M^{z+} have led to the discovery of "sensors" for the selective estimation of different M^{z+} ions. Of the naturally occurring cyclic and acyclic antibiotics, depsipeptides, nactins, and the ionizable nigericin show K/Na selectivity, although this and the general selectivity orders for M^{z+} are strongly a function of the solvent medium with which their conformation is influenced: antamanide and the ionizable monensin display a high Na/K selectivity under most conditions. Whether cyclic or acyclic, each antibiotic in the lattice of the complex has been found to encapsulate the cation of its anion.

Lastly, the chemistry of M^{z+} does not grade monotonously from Li to Cs and from Mg to Ba. The low charge density M^+ ions (K, Rb, and Cs in this order) and the high charge density M^{z+} ions (Li and Mg, and also Be), for example, show enhanced interaction with neutral ligands like water (Figure 1) and DMF (Figure 19) as against the medium charge density Na and Ca. This confirms that as with the macromolecular ligands,[45] Na and Ca behave rather anionphilic under the conditions that the low charge density ions are effectively polarized by the ligand (ligand complexation) and the high charge density ions cause polarization on the ligand (self complexation); for these reasons cations like Li and Mg behave profoundly "solventphilic" even under the counteracting effect of the charge-neutralizing anion and give rise to various stable solvates of the solvent complex type.

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