Coordination Chemistry of Lithium Ion: A Crystal and Molecular Structure Review

URIEL OLSHER*

Department of Chemical Services, The Weizmann Institute of Science, Rehovot, Israel 76100

REED M. IZATT,* JERALD S. BRADSHAW, and N. KENT DALLEY

Department of Chemistry, Brigham Young University, Provo, Utah 84602

Received August 8, 1990 (Revised Manuscript Received October 31, 1990)

Contents

I. Introduction

There has been much recent interest in lithium and lithium ionophores. This growing interest in lithium is mainly due to the actual and potential applications of Li^+ in science, medicine, and technology.[1] Lithium salts have been extensively and successfully used for the treatment of manic depression and other neurological and psychiatric disorders.[1-4] Lithium ions also exhibit antiviral activity against DNA type viruses.[5] However, the use of lithium salts as drugs is limited because of their side effects and toxicity.[3,4] The mechanisms by which Li^+ is involved in biological systems are unknown. No natural molecules are known, nor has any synthetic ionophore been prepared that would be selective enough to preferentially bind Li^+ in its physiological concentration. Therefore, the elucidation of coordination properties of Li^+ should lead both to an improved understanding of its biological activity and to the design of better ionophores for it. It is hoped that the elucidation of the properties presented here will be useful for those who are interested in industrial and technological applications of Li^+.

The coordination chemistry of lithium compounds, in general, and lithium ion complexes, in particular, has been reviewed partially as is seen in the following list. Several of these review articles deal with the molecular structures of organolithium compounds, such as lithium amides, lithium alkyls, etc.

1. W. N. Setzer and P. von Ragué Schleyer, X-Ray Structural Analyses of Organolithium Compounds. *Adv. Organomet. Chem.* **1985**, *24*, 353–451.[6] The review deals with the crystal structures of simple organolithium compounds, mixed-metal organolithium compounds, structures of lithium compounds without lithium–carbon bonds, and miscellaneous inorganic lithium compounds.

2. P. Hubberstey, Compounds of the Alkali Metals Containing Organic Molecules or Complex Ions. *Coord. Chem. Rev.* **1985**, *66*, 1–92.[7] The review deals with complexes of acyclic lipophilic ionophores, crown-ethers, salts of carboxylic acids, heterobimetallic complexes containing alkali metals, and organolithium compounds. The article includes molecular structure data published through December 1984.

3. P. Hubberstey, Compounds of the Alkali Metals Containing Organic Molecules or Complex Ions. *Coord. Chem. Rev.* **1986**, *75*, 1–99.[8] Crown-ether–lithium complexes, lithium salts of carboxylic and dithiocarbamic acids, and organolithium compounds through 1985 are reviewed. The major emphasis is on the organolithium compounds.

4. P. Hubberstey, Compounds of the Alkali Metals Containing Organic Molecules or Complex Ions. *Coord. Chem. Rev.* **1988**, *85*, 1–85.[9] Crown-ether, spherand, and cryptate lithium complexes, salts of carboxylic acids, and organolithium compounds through 1987 are reviewed. The major emphasis is on organolithium compounds.

5. B. O. Bach, Ed., *Lithium—Current Applications in Science, Medicine, and Technology*; Wiley-Interscience: New York, NY, 1985.[1] This book contains an excellent coverage of industrial and medical applications of lithium. No molecular structures of lithium compounds are presented.

6. D. Seebach, Structure and Reactivity of Lithium Enolates. From Pinacolone to Selective C-Alkylations of Peptides. Difficulties and Opportunities Afforded by Complex Structures. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624–1654.[10] The chemistry of lithium enolates is used to demonstrate lithium complex structures held together by noncovalent bonds. Detailed crystallographic structural data through 1987 of numerous Li enolates and analogous derivatives are presented.

7. G. Boche, The Structure of Lithium Compounds

0009-2665/91/0791-0137$09.50/0

Uriel Olsher was born in Raanana, Israel. He obtained B.S. and M.S. degrees in chemistry from Bar-Ilan University. He received his Ph.D. degree in 1980 under the direction of Professor J. Jagur-Grodzinski at The Weizmann Institute of Science. His main emphasis was coordination chemistry of lithium ions. After spending two years of postdoctoral work with Professor E. R. Blout at Harvard Medical School studying linear and cyclic peptides and lithium selective ionophores, he returned to Israel and continued to conduct research at The Weizmann Institute. In 1989–1990 he spent a sabbatical leave at Brigham Young University working on the coordination chemistry of lithium ion and the solvation and hydration of ionophores in general with particular emphasis on crown-ether-alcohols. He is a member of the Israel Chemical Society and the American Chemical Society. His research interests include the design of ionophores for alkali-metal cations, structure–function relationships in macromolecules, solvation of ionophores by water molecules, and chemical and biological applications of lithium ion.

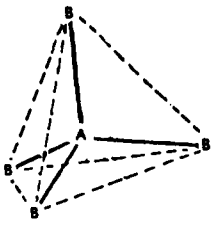
Reed M. Izatt was born in Logan, UT, and received his B.S. degree at Utah State University in 1951. He received his Ph.D. degree in 1954 with Professor W. Conard Fernelius in coordination chemistry at The Pennsylvania State University. After two years of postdoctoral work at Carnegie-Mellon University, he joined the Brigham Young University Chemistry Department in 1956. He delivered the Annual Sigma Xi lecture at BYU in 1966 and the Annual BYU Faculty Lecture in 1970 and was BYU Teacher of the Month in October 1974. He received the BYU Karl G. Maeser Research and Creative Arts Award in 1967 and was the recipient of an NIH Career Development Award (1967–1972), the Utah Award (American Chemical Society) in 1971, the Huffman Award (Calorimetry Conference) in 1983, the Willard Gardner Award of the Utah Academy of Sciences, Arts, and Letters in 1985, and the State of Utah Governor's Medal in Science in 1990. He is Chairman of the Organizing Committee for the annual International Symposium on Macrocyclic Chemistry. His research interests include the design of novel molecular recognition systems for the selective separation of cations, anions, and neutral species; calorimetry applied to metal–ligand and nonelectrolyte interactions over wide temperature and pressure ranges; and the compilation of thermodynamic data.

Jerald S. Bradshaw was born in Cedar City, UT, and received a B.A. degree in chemistry at the University of Utah in 1955. After four years as an officer in the U.S. Navy, he enrolled in a Ph.D. program at UCLA. He received the Ph.D. in 1963 with Professor Donald J. Cram on electrophilic substitution at saturated carbon. He received an NSF postdoctoral fellowship for the 1962–1963 academic year to work with Professor George S. Hammond at the California Institute of Technology. After three years as a research chemist at Chevron Research in Richmond, CA, he joined the faculty at Brigham Young University in 1966. He was named Professor of the Year at BYU in 1975. He was U.S. National Academy of Sciences Exchange Professor for the academic year of 1972–1973 and the summer of 1982, working with Professor Miha Tisler at the University of Ljubljana, Yugoslavia. He also was a visiting professor with Dr. J. F. Stoddart at the University of Sheffield, England, in 1978, and a National Science Foundation Cooperative Research Fellow with Dr. L. F. Lindoy at James Cook University, Townsville, Australia, in 1988. He is a member of the American Chemical Society. He received the 1989 Utah Award from the Salt Lake and Central Utah sections of the American Chemical Society. His research interests are the synthesis and cation complexation properties of macrocyclic multidentate compounds, the photochemical reactions of heterocyclic compounds, and the preparation of new polysiloxanes for chromatography uses.

N. Kent Dalley was born in Pontiac, MI. He obtained his B.S. and M.S. from Brigham Young University. He received his Ph.D. degree from The University of Texas at Austin in 1968. Research for his degree was performed at The University of Texas and also at Argonne National Laboratory where he performed neutron diffraction studies while he was a pre-doctoral Associate in the Metallurgy Division. His research was directed by Dr. S. H. Simonsen at Texas with assistance by Dr. M. H. Mueller at Argonne National Laboratory. Following receipt of his Ph.D. degree, he spent one year as a post-doctoral Associate in the Bio-medical Division at Argonne National Laboratory. He obtained a faculty position at Brigham Young University in 1968 where he is currently a professor in the Chemistry Department. He was a Visiting Associate Research Professor at the University of Utah in 1977. His major research interests are crystal structure studies of biologically active nucleosides and of macrocyclic ligands and their complexes.

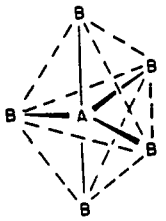
of Sulfones, Sulfoximides, Sulfoxides, Thioethers, and 1,3-Dithianes, Nitriles, Nitro Compounds and Hydrazones. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277–297.[11] A summary is presented of recent research into the structures of the title compounds. Crystal structure determinations are central to the review, but

1.1 Four-Fold Coordination.

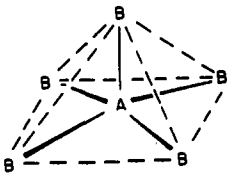


Tetrahedron (Td)

1.2 Five-Fold Coordination.

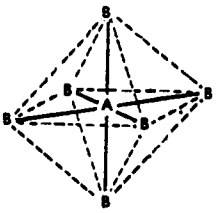


Trigonal bipyramid (TBP)



Square-pyramid (SP)

1.3 Six-Fold Coordination.



Octahedron (Oc)

1.3.1 Sketches showing the three principal types of distortion found in real octahedral complexes.

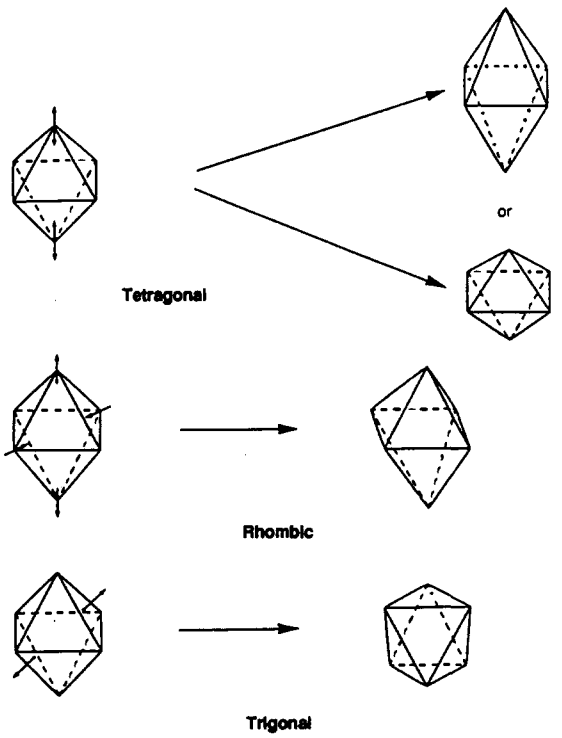
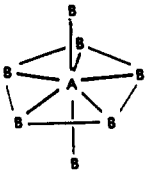
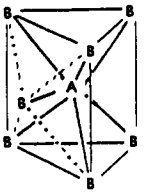


Figure 1. Coordination polyhedra.

1.4 Seven-Fold Coordination.

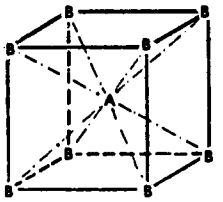


Pentagonal bipyramid (PBP)



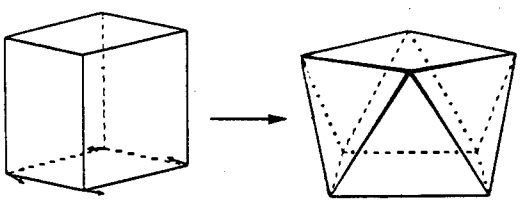
Insertion of a seventh atom above the center of one of the rectangular faces of a trigonal prism.

1.5 Eight-Fold Coordination.



Cube (Cb)

1.5.1 The two most important ways of distorting the cube are: (a) to produce a square antiprism (SA) ; (b) to produce a dodecahedron (Dh).



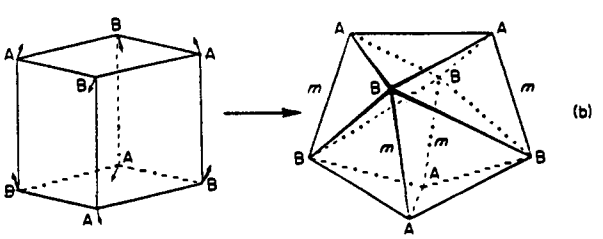


TABLE I. Radius (r_m) of the Minimal Cavity Enclosed by n Oxygen Atoms[16] and Fit of Li^+ to the Cavity[a]

coordination no., n (coordination geometry)	radius: r_m, Å	r_m/r_{Li^+}
2 (linear)	0.00	0
3 (triangular)	0.22	0.37
4 (tetrahedral)	0.31	0.52
4 (square)	0.58	0.97
5 (trigonal-bipyramidal)	0.58	0.97
5 (pyramidal)	0.64	1.07
6 (octahedral)	0.58	0.97
7 (symmetry C_{3v})	0.83	1.38
7 (pentagonal-bipyramidal)	0.98	1.63
8 (cubic)	1.02	1.70
9 (symmetry D_{3h})	1.02	1.70
12 (cubo-octahedral)	1.40	2.33

[a] Radius of a coordinating oxygen atom is equal to 1.40 Å.

TABLE II. Classification of Lewis Bases[a,17]

hard	borderline	soft
H_2O, OH^-, F^-, $CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-}, Cl^-, CO_3^{2-}, ClO_4^-, NO_3^-, ROH, RO^-, R_2O, NH_2, RNH_2, N_2H_4	R, N_3^-, Br^-, NO_2^-, SO_2^{2-}, N_2	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{2-}$, R_3P, R_3As, $(RO)_3P$, CN^-, RNC, CO, H^-, R^-

[a] The symbol R stands for an alkyl or aryl group.

these are supplemented by solution studies and by calculations of structures.

In the present review article, a tabulation is given, based on X-ray crystallographic data, of the bond lengths, geometry, coordination numbers, and solvent of crystallization of Li^+ complexes. The data included in the review extend from the earliest publications through February 1990. We have attempted in the text to draw the reader's attention to the various parameters involved in lithium–ligand interaction such as ligand coordination sites, ligand conformation changes, stereochemical arrangement of ligand binding sites, counterion effects, and solvent effects. In addition, discussion is included of lithium selective ionophores and of the involvement of Li^+ in biological cycles. Appropriate examples taken from the tables of data are used to illustrate the text. The compounds included in the review are listed by formula and abbreviation in Charts I–XVIII.

The approach we chose for this review is a structural one, centered on the examination of the three-dimensional crystal structures of lithium salts and complexes. The basic assumption is that the structures of these lithium complexes in the solid state resemble their structures in solution, and that similar structure–selectivity relationships exist, at least to some extent, in both media.

II. Coordination Numbers and Polyhedra

A. General

Although coordination compounds are of particular importance in the chemistry of transition elements, they also play a significant role in the chemistry of all elements having electropositive natures including the alkali and alkaline earth metal cations. Particular metal ions have characteristic coordination numbers and their coordination polyhedra have definite shapes or symmetries. It is important to realize that a given metal ion does not necessarily have a single characteristic coordination number and geometry. A brief summary of cation coordination numbers and polyhedra is now presented.[12] The coordination polyhedra discussed below are illustrated in Figure 1.

Coordination Number 2

Coordination number 2 is not common. Such complexes have linear arrangements of the metal ion and the two ligand atoms.

Coordination Number 3

Coordination number 3 is rare. The usual structure of these complexes is an approximately equilateral triangle of donor atoms with the cation in the center. The two most symmetrical arrangements are planar and pyramidal.

Tetrahedral 4 Coordination

Tetrahedral coordination is common among complexes of non-transition metal ions. The tetrahedral (Td) configuration is the most stable one for four coordination from an electrostatic point of view.

Coordination Number 5

Two forms of 5-fold coordination are common. In one, the ligands lie at the vertices of a trigonal bipyramid (TBP) while in the other, they lie at the vertices of a square pyramid (SP). In many real cases, however, the arrangement of ligands is not exactly either of these. Another important aspect of five coordinate species is the relative ease with which the TBP and SP configurations can be interconverted suggesting that the energy of interconversion is small.

Coordination Number 6

This is perhaps the most common coordination number, and the six ligands almost invariably lie at the vertices of an octahedron (Oc) or a distorted octahedron. Three principal forms resulting from distortion of the octahedron are tetragonal, rhombic, and trigonal.

Coordination Number 7

Three geometrical arrangements are known. The most regular is the pentagonal bipyramid. A second arrangement results from addition of a seventh atom at the center of one face of an octahedron. This addition results in the spreading apart of the three atoms defining this face. The third arrangement is derived by inserting a seventh atom above the center of one of the rectangular faces of a geometrical trigonal prism.

Coordination Number 8

The most symmetrical arrangement possible is the cube (Cb) but this seems to occur only in a few solid compounds. This is presumably because there are several ways in which the cube may be distorted so as to lessen repulsions between nonbonded atoms. The two principal ways in which the cube may become distorted are as the square antiprism (SA) and the dodecahedron (Dh). In general, there is little difference

between the energies of the square antiprism and the dodecahedral arrangements and the occurrence of both is common.

B. Lithium(I)

Lithium(I) compounds and complexes exhibit coordination numbers varying from 2 to 8.[6-10] The binding in organolithium compounds[6] and lithium(I) complexes[13,14] is predominately electrostatic. Therefore, since coulombic forces are undirected, the radius of Li^+ (0.6 Å)[15,16] plays an important role in determining the final structure of a given complex. The coordination number of Li^+ in a complex is determined primarily by the number of binding sites, usually anions (ion–ion interaction) and negative poles of the neutral ligand and solvent (ion–dipole interaction), that can be packed around the Li^+ ion. The small radius of Li^+ gives the possibility for versatile Li^+ coordination numbers and polyhedra. The mutual repulsion of n coordinating atoms precludes their contact with cations smaller than a certain critical radius.[13-16] For cations smaller than this minimal cavity radius (Table I), the interaction with the coordination sphere becomes independent of the cation radius. The minimal radius of the enclosed cavity increases gradually with the number of the coordination sites available. From the r_m/r_{Li^+} values, the most favorable coordination numbers for Li^+ are expected to be 4, 5, and 6.

The experimental data presented in this review article support the above calculations. Most Li^+ complexes are 4- and 5-fold coordinated. The most selective Li^+ ionophores exhibit 4-fold tetrahedral coordination and 5-fold square pyramidal coordination.

III. Coordination Sites in Li^+-Ligand Complexes

A. General

In organic and inorganic complexes, Li^+ is usually bonded to the ligand via lithium–oxygen (Li–O) interactions. Li^+ is defined as a hard acid.[17,18] Most synthetic and natural ionophores, biological macromolecules, and solvents contain hard oxygen atoms[17,18] as potential donors in their binding sites (i.e., hydroxyl, keto, carbonyl, carboxylate, ethereal, ester, phosphate, silicate, carbonate, etc.) Thus, interaction of Li^+ with the oxygen atoms of the ligands is expected. To a lesser extent, Li^+ is coordinated to aliphatic and aromatic amines via nitrogen atoms. No interaction has been found between Li^+ and sulfur atoms.[19-22] Interactions between Li^+ and oxygen donor atoms (hard base) are strong while those with the softer nitrogen atoms are weaker. The classification of hard and soft bases is shown in Table II.

Using the hard and soft base scale in Table II, one can predict the preferred donor atoms in Li^+ complexes. Thus, the stability of Li^+ complexes decreases as the ligand donor atoms are changed as follows: O > N ≫ S.

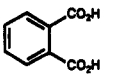
Krasne and Eisenman[23] and Olsher[24] have shown that the behavior of ligands is partially attributable to the properties of the individual ligand coordination or binding sites. The properties of these binding sites are considered to be a major factor in Li^+–ligand interaction, and therefore influence parameters such as selectivity, thermodynamic stability, and conformational changes in the ligand.[13,14] In addition, complexation of a cation by a ligand is affected by the nature of the solvent[24] and the anion present.[23-25] The complex which is formed in biological and artificial membranes results from the simultaneous interaction of the cation with ligand, solvent, and anion binding sites.[13,14,23-25] Thus, solvent molecules and counterions in addition to ligands are regarded as containing possible binding sites in the Li^+ complexes. Li^+ which is already bonded to a ligand molecule might interact with additional solvent molecule(s) and/or the counterion in order to saturate its coordination sphere.

Tables III–VII contain structural information for Li^+–ligand complexes of 4, 5, 6, 7, and 8-fold coordination. The structural information includes the counter anion, the formula of the complex, solvent(s) of crystallization, bond distances, geometry, and bonding atoms, and the reference. The following ligands are included in one or more of the tables: carboxylic acids, amines, amides and peptides, ethers, ketones, alcohols, carbamates, phosphates, picrate ion, nitrate ion, and nitronate ion.

CHART I. Carboxylic Acids

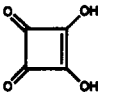
I, HCO_2H Formic acid
II, CH_3CO_2H Acetic acid
III, HO_2CCO_2H Oxalic acid
IV, $HO_2CCH_2CO_2H$ Malonic acid
V, $HO_2C(CH_2)_2CO_2H$ Succinic acid
VI, $HO_2C(CH_2)_4CO_2H$ Adipic acid
VII, $HO_2CCH{=}CHCO_2H$ Maleic acid
VIII, $HO_2CC{\equiv}CCO_2H$ Acetylenedicarboxylic acid
IX, $HOCH_2CO_2H$ Glycolic acid
X, $HO_2CCH(OH)CH_2CO_2H$ Malic acid
XI, $HO_2CCH(OH)CH(OH)CO_2H$ Tartaric acid
XII, $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$ Citric acid
XIII, $HO_2CCH_2OCH_2CO_2H$ Oxydiacetic acid

XIV



Phthalic acid

XV



Squaric acid

B. Carboxylic Acids

Stable complexes of Li^+ with mono-[26,27] di-[28-34,38-41,86,90] and hydroxy-[35-37,42,87-89,115] carboxylic acids in aqueous and nonaqueous solutions have been reported (Chart I). The coordination numbers of Li^+ in its complexes with carboxylic acids are 4, 5, and 6, and the coordination polyhedra are Td for 4-fold coordination Li^+, TBP and SP for 5-fold coordination Li^+, and distorted Oc for 6-fold coordinated Li^+. The average Li–O distances for the different coordination numbers and polyhedra are presented in Table VIII. The versatile coordination of Li^+ with carboxylates might be explained by the strong electrostatic ion–ion interaction between the hard Li^+ and the hard carboxylate oxygen donor atoms (see Table II). As shown in Table VIII, the average Li–O distance increases gradually with the number of the carboxylate groups available for coordination.

In most cases, the Li^+ is coordinated by carboxylate groups of more than one molecule. When the carboxylic acid has one of the conformations shown in Figure 2, it interacts with the Li^+ as a bidentate ligand.

A few of the crystal structures reported contain more than one kind of complex in the unit cell. For example, the lithium malonate,[30] lithium maleate,[33] and lithium hydrogen phthalate[38,40,41] crystal structures contain two crystallographically different complexes in the unit cell while there are four crystallographically different

TABLE III. Li^+ 4-Fold Coordination

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distances, Å			geometry, bonding atoms	ref
				Li^+–L	Li^+–S	Li^+–A^{n-}		
			Carboxylic Acids Bond					
I	formate	$CHO_2Li·H_2O$	H_2O	1.923 $(O)_{ca}$ 1.954 $(O)_{ca}$ 1.938 $(O)_{ca}$	1.974 $(O)_w$		Td, one O of three different formates and a water O	26
II	acetate	$C_2H_3O_2Li·2H_2O$	H_2O	1.895 $(O)_{ca}$ 1.895 $(O)_{ca}$	2.045 $(O)_w$ 2.045 $(O)_w$		Td, one O of two different acetates and two water O's	27
III	oxalate	$C_2O_4Li_2$	H_2O	2.071 $(O)_{ca}$ 2.030 $(O)_{ca}$ 1.996 $(O)_{ca}$ 1.931 $(O)_{ca}$			Td, two O's of two different oxalates	28
IV	hydrogen malonate	$C_6H_7O_8Li$	H_2O	1.978 $(O)_{ca}$ 2.042 $(O)_{ca}$ 1.977 $(O)_{ca}$ 2.010 $(O)_{ca}$			Td, two O's each of two different malonates	29
IV	malonate	$C_3H_2O_4Li_2$	H_2O	1.962 $(O)_{ca}$ 2.094 $(O)_{ca}$ 1.942 $(O)_{ca}$ 1.932 $(O)_{ca}$			Td,[a] one O of four different malonates	30
				1.907 $(O)_{ca}$ 1.950 $(O)_{ca}$ 2.043 $(O)_{ca}$ 1.911 $(O)_{ca}$			Td, one O of four different malonates	30
V	succinate	$C_4H_4O_4Li_2$	H_2O	1.954 $(O)_{ca}$ 1.943 $(O)_{ca}$ 1.945 $(O)_{ca}$ 1.961 $(O)_{ca}$			Td, one O of four different succinates	31
VI	hydrogen adipate	$C_6H_9O_4Li$	H_2O	1.940 $(O)_{ca}$ 1.896 $(O)_{ca}$ 1.955 $(O)_{ca}$ 1.977 $(O)_{ca}$			Td, one O of four different hydrogen adipates	32
VII	maleate	$C_4H_2O_4Li_2·2H_2O$	H_2O	1.911 $(O)_{ca}$ 2.015 $(O)_{ca}$ 1.935 $(O)_{ca}$	1.901 $(O)_w$		Td,[a] two O's of one ligand, one O of another ligand and one water O	33
				1.964 $(O)_{ca}$ 1.963 $(O)_{ca}$ 2.022 $(O)_{ca}$	1.962 $(O)_w$		Td, one O of three different ligands and one water O	33
VIII	acetylene dicarboxylate	$C_4HO_4Li·H_2O$	H_2O	1.926 $(O)_{ca}$ 1.976 $(O)_{ca}$ 1.979 $(O)_{ca}$	1.871 $(O)_w$		Td, one O of three different carboxylic acids and one water O	34
X	hydrogen malate	$C_4H_5O_5Li$	H_2O	1.997 $(O)_{ca}$ 1.917 $(O)_{ca}$ 1.930 $(O)_{ca}$ 1.973 $(O)_{OH}$			Td, one O of four symmetry-related hydrogen malates; three acid O's and one hydroxy O	35
XII	hydrogen citrate	$C_6H_6O_7Li(NH_4)·H_2O$	H_2O	1.894 $(O)_{ca}$ 1.917 $(O)_{ca}$ 1.977 $(O)_{ca}$ 2.012 $(O)_{ca}$			Td, one O of four different citrate ions	36
XII	citrate	$C_6H_5O_7Li_3·5H_2O$	H_2O–ethanol	1.959 $(O)_{ca}$ 1.959 $(O)_{ca}$ 1.957 $(O)_{ca}$			Td,[a] one O of four different citrate ions	37

				1.957 $(O)_{ca}$			
				1.894 $(O)_{ca}$	1.957 $(O)_{w}$		Td, one citrate O and three water O's	37
					1.931 $(O)_{w}$		
					1.946 $(O)_{w}$		
				1.883 $(O)_{ca}$	1.908 $(O)_{w}$		Td, one O of three different citrate ions and one water O	37
				1.960 $(O)_{ca}$			
				1.903 $(O)_{ca}$			
XIV	hydrogen phthalate	$C_8H_5O_4Li \cdot H_2O$	H_2O	1.933 $(O)_{ca}$			Td,[a] one O of four different ligands	38
				1.935 $(O)_{ca}$			
				1.954 $(O)_{ca}$			
				1.905 $(O)_{ca}$			
				2.069 $(O)_{ca}$	1.914 $(O)_{w}$		Td, one O of two different ligands and two water O's	38
				2.043 $(O)_{ca}$	1.931 $(O)_{w}$		
XIV	hydrogen phthalate	$C_8H_5O_4Li \cdot 2H_2O$	H_2O	1.895 $(O)_{ca}$	1.940 $(O)_{w}$		Td, one O of two different ligands and two water O's	39
				1.998 $(O)_{ca}$	1.940 $(O)_{w}$		
XIV	hydrogen phthalate	$C_8H_5O_4Li \cdot CH_3OH$	methanol	1.936 $(O)_{ca}$			Td,[a] one O of four different ligands	40, 41
				1.929 $(O)_{ca}$			
				1.931 $(O)_{ca}$			
				1.931 $(O)_{ca}$			
				2.059 $(O)_{ca}$	1.918 $(O)_{OH}$		Td, one O of two different ligands and an O of two different methanol molecules	40, 41
				2.050 $(O)_{ca}$	1.939 $(O)_{OH}$		
XV	hydrogen squarate	$C_4HO_4Li \cdot H_2O$	H_2O	2.057 $(O)_{OH}$	2.035 $(O)_{w}$		Td, one O of two different ligands and two water O's	42
				2.057 $(O)_{OH}$	2.057 $(O)_{w}$		
				Amines				
XVI	Br^-	$(C_2H_8N_2)_2LiBr$	ethylene-diamine	2.076 $(N)_{am}$			Td, one N of two two different solvent molecules and two N's of a bidentate solvent molecule	43
				2.076 $(N)_{am}$			
				2.060 $(N)_{am}$			
				2.060 $(N)_{am}$			
XVI	Cl^-	$[Li(C_2H_8N_2)_3]Cl$	ethylene-diamine	2.075 $(N)_{am}$			Td, one N of two mondentate solvent molecules and two N's of a bidentate solvent molecule	43
				2.075 $(N)_{am}$			
				2.067 $(N)_{am}$			
				2.067 $(N)_{am}$			
XVII	$C_5(CH_3)_5Lu(CH_3)_3^-$	$[Li(C_6H_{16}N_2)_2]$-$[C_5(CH_3)_5Lu(CH_3)_3]$	THF	2.02 $(N)_{am}$			Td, two N's of two different ligands	44
				2.02 $(N)_{am}$			
				2.27 $(N)_{am}$			
				2.27 $(N)_{am}$			
XVII	$CH_3Ni(C_2H_4)_2^-$	$[Li(C_6H_{16}N_2)_2]$-$[CH_3Ni(C_2H_4)_2]$	THF	2.12 $(N)_{am}$			Td two N's of two different ligands	45
				2.16 $(N)_{am}$			
				2.13 $(N)_{am}$			
				2.10 $(N)_{am}$			
XVII	$Si(CH_3)_3^-$	$[Li(C_6H_{16}N_2)_{1.5}$-$Si(CH_3)_3]_2$	Et_2O	2.16 $(N)_{am}$		2.70 (Si)	Td, two N's of one ligand, one of another bridging ligand, and a Si of the anion	46
				2.18 $(N)_{am}$			
				2.21 $(N)_{am}$			
XVII	$Si(CH_3)_3^-$	$[Li(C_6H_{16}N_2)_{1.5}$-$Si(CH_3)_3]_2$	Et_2O	2.16 $(N)_{am}$		2.69 (Si)	Td, two N's of one ligand, one of another bridging ligand, and a Si of the anion	46
				2.17 $(N)_{am}$			
				2.15 $(N)_{am}$			

TABLE III (Continued)

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distances, Å			geometry, bonding atoms	ref
				Li^+–L	Li^+–S	Li^+–A^{n-}		
XVIII	$Cu_5Ph_6^-$	$[Li(C_4H_8O)(C_8H_{23}N_3)][Cu_5Ph_6]$	THF	2.115 $(N)_{am}$ 2.178 $(N)_{am}$ 2.136 $(N)_{am}$	1.935 $(O)_{et}$		Td, three N's of a ligand and an O of the solvent	47
XIX	Cl^-	$[Li(C_5H_5N)_2(H_2O)Cl]$	pyridine	2.050 $(N)_{pyr}$ 2.060 $(N)_{pyr}$	1.939 $(O)_w$	2.329 (Cl)	Td, one N of two pyridine ligands, a solvent O, and the anion	48
XX	Ph(2-pyr)N^-	[Li[Ph(2-pyr)NH]-(HMPA)[Ph(2-pyr)N]]	hexane–HMPA	2.078 $(N)_{pyr}$ 2.111 $(N)_{pyr}$	1.815 (O)	2.091 (N)	Td, one pyridine N of two different ligands, one N from anion, and one solvent O	49
			Amides, Peptides, and Urea					
XXVI	Cl^-	$[Li(C_3H_7NO)_4]Cl$	*N*-methyl-acetamide	1.95 $(O)_{amide}$ (average value)			Td, one O of four different ligand molecules	50
XXVIII	$TpClPB^-$	$[Li(C_{28}H_{50}N_2O_2)_2]$-TpClPB	chloroform	1.883 $(O)_{amide}$ 1.883 $(O)_{amide}$ 1.889 $(O)_{amide}$ 1.889 $(O)_{amide}$			Td, two O's of two different ligand molecules	51
XXIX	I^-	$[Li[(NH_2)_2CO]_4]I$	H_2O	1.88 $(O)_{Ur}$ 1.88 $(O)_{Ur}$ 1.95 $(O)_{Ur}$ 1.95 $(O)_{Ur}$			Td, one O of four urea ligands	52
XXIX	SO_4^{2-}	$[Li_2[(NH_2)_2CO]_3SO_4]\cdot H_2O$		1.97 $(O)_{Ur}$ 1.93 $(O)_{Ur}$		1.93 (O) 1.94 (O)	Td, one O of two ligand molecules and two O's of an anion	53
XXX	Br^-	$[Li(C_4H_8N_2O_3)_4]Br$	H_2O	2.000 $(O)_{ca}$ 1.960 $(O)_{ca}$ 1.915 $(O)_{ca}$ 1.887 $(O)_{amide}$			Td, one O of four different peptide molecules	54
XXXI	Br^-	$[Li(C_5H_{10}N_2O_3)_3H_2O]$-Br-$H_2O$	H_2O	1.883 $(O)_{ca}$ 1.909 $(O)_{ca}$ 1.943 $(O)_{amide}$	1.916 $(O)_w$		Td, one O of three different peptides and one solvent O	55
XXXII	Br^-	$[Li(C_6H_{11}N_3O_4)_4]Br$	H_2O	1.956 $(O)_{amide}$ 1.969 $(O)_{ca}$ 1.933 $(O)_{ca}$ 1.993 $(O)_{ca}$			Td, one O of four different ligand molecules	56
XXXIII	ClO_4^-	$[Li(C_6H_{10}N_2O_2)_4]ClO_4$	ethyl acetate	1.952 $(O)_{amide}$ 1.937 $(O)_{amide}$ 1.906 $(O)_{amide}$ 1.892 $(O)_{amide}$			Td, one O of four different peptide molecules	57
			Ethers					
XXXV	$N(Si[CH_3]_3)_2^-$	$[Li[N[Si(CH_3)_3]]_2$-$(OC_4H_{10})]$	Et_2O	1.943 $(O)_{et}$		2.055 (N) 2.055 (N)	Three coordinate, one N of two different anions and one ligand O bridges two Li	58, 59
XXXV	4-CH_3-2,6-(*t*-Bu)$_2$-$C_6H_2O^-$	$[Li(OC_6H_2CH_3$-4-(*t*-Bu)$_2$-2,6)$(OEt_2)]_2$	Et_2O	1.96 $(O)_{et}$		1.86 $(O)_{aryl}$ 1.86 $(O)_{aryl}$	Three coordinate, one O from ligand and two aryl O's	60

XXXV	$AsPh_2^-$	$[Li_2(C_4H_{10}O)_2(AsPh_2)_2]$	Et_2O	1.974 $(O)_{et}$ 1.997 $(O)_{et}$	2.708 (As) 2.757 (As)	Td, one O of two different solvent (or ligand) molecules and one As of two different anions	61
XXXV	$YbCl_2[C_5(CH_3)_5]_2^-$	$[Li(C_4H_{10}O)_2YbCl_2$-$[C_5(CH_3)_5]_2]$	Et_2O	1.924 $(O)_{et}$ 1.935 $(O)_{et}$	2.390 (Cl) 2.412 (Cl)	Td, one O of two different ligands and two anions	62
XXXVI	Ph-CO-P=C(O)Ph$^-$	$C_{16}H_{20}O_4PLi$	DME	1.944 $(O)_{et}$ 2.152 $(O)_{et}$	2.044 (O) 2.044 (O)	Td, one O of two different phosphide molecules and two O's of a solvent (or ligand) molecule	63
XXXVII	Cl^-	$Li(C_4H_8O_2)$·Cl	1,4-dioxane	1.88 $(O)_{et}$ 1.95 $(O)_{et}$	2.39 (Cl) 2.42 (Cl)	Td, two anions, one O of two different solvent (or ligand) molecules, and two anions bridge two Li^+'s	64
XXXVII	$AsPh_2^-$	$Li(C_4H_8O_2)_3(AsPh_2)$	1,4-dioxane	1.953 $(O)_{et}$ 1.931 $(O)_{et}$ 1.937 $(O)_{et}$	2.660 (As)	Td, three O's of three different ligand molecules and As of anion	61
XXXVIII	$[Fe_2(CO)_6[C(O)Ph]$-$(\mu_2\text{-}PPh_2)_2]^-$	$[Li(C_4H_8O)_3][Fe_2(CO)_5$-$[C(O)Ph](\mu_2\text{-}PPh_2)_2]$	THF	2.063 $(O)_{et}$ 2.002 $(O)_{et}$ 1.902 $(O)_{et}$	1.902 $(O)_{acyl}$	Td, one O of three solvent (or ligand) molecules and acyl O of anion	65
XXXVIII	$[U(C_2B_9H_{11})_2\text{-}Cl_2]$	$[Li(C_4H_8O)_3]$-$[U(C_2B_9H_{11})_2\text{-}Cl_2]_2$	THF	2.05 $(O)_{et}$ 1.88 $(O)_{et}$ 1.91 $(O)_{et}$ 1.90 $(O)_{et}$		Td,[a] an O of four different solvent (or ligand) molecules	66
				2.02 $(O)_{et}$ 1.88 $(O)_{et}$ 1.92 $(O)_{et}$ 1.86 $(O)_{et}$		Td, an O of four different solvent (or ligand) molecules	66
XXXVIII	$Ag[C[(Si(CH_3)_3]]_2^-$	$[Li(C_4H_8O)_4]$-$[Ag[C[Si(CH_3)_3]_3]_2]$	THF	1.83 $(O)_{et}$ 1.97 $(O)_{et}$ 1.98 $(O)_{et}$ 2.04 $(O)_{et}$		Td, an O of four different solvent (or ligand) molecules	67
XXXVIII	$Lu(C_8H_9)_4^-$	$[Li(C_4H_8O)_4]$-$[Lu(C_8H_9)_4]$	THF	1.87 $(O)_{et}$ 1.95 $(O)_{et}$ 2.02 $(O)_{et}$ 1.91 $(O)_{et}$		Td, an O of four different solvent (or ligand) molecules	68
XXXVIII	$Yb[CH[Si(CH_3)_3]_2]_3Cl^-$	$[Li(C_4H_8O)_4][Yb[CH$-$[Si(CH_3)_3]_2]_3Cl$	$THF\text{-}Et_2O$	1.949 $(O)_{et}$ 1.993 $(O)_{et}$ 1.935 $(O)_{et}$ 1.987 $(O)_{et}$		Td, an O of four different solvent (or ligand) molecules	69
XXXVIII	$Cu_5Ph_6^-$	$[Li(C_4H_8O)_4][Cu_5(Ph)_6]$	$THF\text{-}Et_2O$	1.88 $(O)_{et}$ 1.91 $(O)_{et}$ 2.01 $(O)_{et}$ 1.97 $(O)_{et}$		Td, an O of four different solvent (or ligand) molecules	47
XXXVIII	$Li[C[Si(CH_3)_3]_3]_2^-$	$[Li(C_4H_8O)_4]$-$[Li[C[Si(CH_3)_3]_3]_2]$	toluene–THF	1.83 $(O)_{et}$ 1.96 $(O)_{et}$ 1.98 $(O)_{et}$ 2.05 $(O)_{et}$		Td, one O from four different THF solvent (or ligand) molecules	70
XXXIX	NCS^-	$Li(C_9H_{24}O_3)NCS$	acetonitrile	1.910 $(O)_{et}$ 1.946 $(O)_{et}$ 1.940 $(O)_{et}$	1.958 $(N)_{NCS}$	Td, three O's of ligand and N of the anion	71, 72

TABLE III (Continued)

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distances, Å			geometry, bonding atoms	ref
				Li^+–L	Li^+–S	Li^+–A^{n-}		
XL	ClO_4^-	$Li(C_{15}H_{30}O_3)ClO_4$	acetonitrile	1.907 $(O)_{et}$ 1.908 $(O)_{et}$ 1.913 $(O)_{et}$		1.950 $(O)_{ClO_4}$	Td, three O's of ligand and an O of anion	71, 72
LII	picrate	$[Li(C_6H_2N_3O_7)\cdot 2H_2O]\cdot C_{14}H_{20}O_5$	H_2O		1.86 $(O)_w$ 1.87 $(O)_w$	1.92 $(O)_{ph}$ 2.04 $(O)_{NO_2}$	Td, two O's of anion and an O of two solvent molecules	73
LV	ClO_4^-	$[Li(C_{12}H_{24}O_6)\cdot(H_2O)_2]\cdot ClO_4$	ethanol–H_2O	2.070 $(O)_{et}$ 2.124 $(O)_{et}$	1.922 $(O)_w$ 1.906 $(O)_w$		Td, two O's of one ligand and an O of two solvent molecules	74
LV	NCS^-	$[Li(C_{12}H_{24}O_6)\cdot(H_2O)_2]\cdot SCN$	ethanol–H_2O	2.073 $(O)_{et}$ 1.995 $(O)_{et}$	1.966 $(O)_w$ 1.899 $(O)_w$		Td,[a] two O's of one ligand and an O of two solvent molecules	74
LV	NCS^-	$Li(C_{12}H_{24}O_6)(H_2O)\cdot(NCS)_2^-$	ethanol–H_2O	1.991 $(O)_{et}$	1.996 $(O)_w$	1.998 $(N)_{NCS}$ 2.011 $(N)_{NCS}$	Td, one O of ligand, one O of solvent molecule, and an N of two different anions	74
LVIII	ClO_4^-	$[Li(C_{21}H_{35}NO_8)\cdot[(NH_2)_2CO]]\cdot ClO_4$	ethanol–urea	2.20 $(N)_{am}$ 1.98 $(O)_{et}$	1.90 $(O)_{ur}$ 1.95 $(O)_{ur}$		Td, one ether O and one aromatic N of ligand and one O from two different urea molecules	75
			Ketones					
LIX	Br^-	$Li(C_3H_6O)Br$	acetone	2.01 $(O)_{ca}$ 1.91 $(O)_{ca}$		2.51 (Br) 2.55 (Br)	Td, one O of two different solvent (or ligand) molecules and two anions	76
LX	2,4-pentanedionato	$Li(C_5H_7O_2)_2$	hexane	1.923 $(O)_{ke}$ 1.941 $(O)_{ke}$ 1.926 $(O)_{ke}$ 1.926 $(O)_{ke}$			Td,[a] two O's of two different ligands	77
LX		$Li(C_5H_7O_2)_2$		1.953 $(O)_{ke}$ 1.955 $(O)_{ke}$ 1.967 $(O)_{ke}$ 1.953 $(O)_{ke}$			Td, two O's of two different ligands	
			Alcohols					
XXIII	Cl^-	$C_{15}H_{36}N_4O_4(LiCl)_2\cdot 2H_2O$	H_2O–ethanol	1.941 $(O)_{OH}$ 1.943 $(O)_{OH}$ 1.922 $(O)_{OH}$	1.927 $(O)_w$		Td, one O of three different ligand molecules and an O of a solvent molecule	78a
LXXXII	$C_6H_5CHNO_2^-$	$Li(C_6H_5CHNO_2)$	ethanol	1.919 $(O)_{NO_2}$ 1.925 $(O)_{NO_2}$ 1.927 $(O)_{NO_2}$	1.979 $(O)_{OH}$		Td, one O of three different ligand molecules and an O of a solvent molecule	78b
			Carbamates					
LXX	$C_3H_6NS_2^-$	$[Li(H_2O)_4]C_3H_6NS_2$	H_2O–ethanol		1.913 $(O)_w$ 1.907 $(O)_w$ 1.954 $(O)_w$ 1.941 $(O)_w$		Td, one O of four different water molecules	19
LXXI	$C_5H_{10}NS_2^-$	$[Li(H_2O)_4]C_5H_{10}NS_2$	H_2O		2.019 $(O)_w$ 2.049 $(O)_w$ 1.895 $(O)_w$ 1.897 $(O)_w$		Td, one O of four different water molecules	20

LXXII	$C_7H_{14}NS_2^-$	$[Li(H_2O)_4]C_7H_{14}NS_2$	H_2O		1.870 $(O)_w$ 2.031 $(O)_w$ 2.011 $(O)_w$ 1.877 $(O)_w$		Td, one O of four different water molecules	21
LXXIII	$C_5H_8NS_2^-$	$[Li(H_2O)_4]C_5H_8NS_2$	H_2O		1.907 $(O)_w$ 1.923 $(O)_w$ 1.906 $(O)_w$ 2.000 $(O)_w$		Td, one O of four different water molecules	22
				Phosphates				
LXXIV	I^-	$[Li(C_{18}H_{15}OP)_4]I$	diethyl ether–hexane	1.97 (O) (average value)			Td, one O of four different TTP molecules	79
LXXV	Cl^-	$[Li[OP[N(CH_3)_2]_3]-(H_2O)_2]Cl$	diethyl ether–hexane	1.984 $(O)_{HMPA}$ 2.013 $(O)_{HMPA}$	1.940 $(O)_w$ 1.936 $(O)_w$		Td, one O of two HMPA ligands bridging two Li^+'s and two different water O's	80
LXXV	$Li_5[N{=}CPh_2]_6^-$	$[Li[OP[N(CH_3)_2]_3]_4]-[Li_5(N{=}CPh_2)_6]-[O{=}P[N(CH_3)_2]_3]$	Et_2O–toluene	1.900 $(O)_{PO}$ 1.839 $(O)_{PO}$ 1.861 $(O)_{PO}$ 1.770 $(O)_{PO}$			Td, one O of four different ligands	81
LXXV	Cl^-	$[ClLi{\cdot}O{=}P[N(CH_3)_2]_3]_4$	hexane	1.858 $(O)_{PO}$		2.357 (Cl) 2.441 (Cl) 2.415 (Cl)	Td, one O of HMPA molecule and three Cl^-	82
LXXVII	$C_{21}H_{26}N_7O_{14}P_2^-$	$C_{21}H_{26}N_7O_{14}P_2Li{\cdot}2H_2O$	H_2O–methanol	2.13 $(N)_{ad}$ 1.92 $(O)_{PO}$ 1.88 $(O)_{PO}$ 1.86 $(O)_{PO}$			Td, one O of one ligand and one O and one adenine N of another ligand resulting in polymer	83, 84
LXXVIII	*cis*-$(CO)_4Mo(PhCO)-[EtOP(C_4H_9NO)_2]^-$	*cis*-$(CO)_4Mo(PhCOLi)-[EtOP(C_4H_9NO)_2]$	THF–benzene	1.93 $(O)_{pho}$ 2.12 $(N)_{am}$ 2.10 $(N)_{am}$		1.88 (O)	Td, two N's and O of phosphite ring and benzoylate O	85

[a] Crystal structure contains more than one molecule in the asymmetric unit.

TABLE IV. Li^+ 5-Fold Coordination

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distance ranges, Å			comments	ref
				Li^+–L	Li^+–S	Li^+–A^{n-}		
				Carboxylic Acids				
III	hydrogen oxalate	$HC_2O_4Li·H_2O$	H_2O	2.070 $(O)_{ca}$ 2.273 $(O)_{ca}$ 2.014 $(O)_{ca}$	2.055 $(O)_w$ 2.046 $(O)_w$		TBP, two O's of one anion and one O of another anion and two water O's	86
IX	glycolate	$C_2H_3O_3Li$	H_2O	1.952 $(O)_{ca}$ 2.357 $(O)_{OH}$ 1.988 $(O)_{ca}$ 1.998 $(O)_{OH}$ 2.020 $(O)_{ca}$			TBP, two O's of bidentate ligand one carboxylate O of two ligands and one hydroxy O of another ligand	87
XI	tartrate	$C_4H_4O_6LiNH_4·H_2O$	H_2O	1.957 $(O)_{ca}$ 2.036 $(O)_{ca}$ 2.199 $(O)_{OH}$ 2.060 $(O)_{ca}$	2.026 $(O)_w$		TBP, two O's of a bidentate ligand, one carboxylate O of two different ligands, and one solvent O	88
XI	tartrate	$C_4H_4O_6LiTl·H_2O$	H_2O	1.928 $(O)_{ca}$ 1.995 $(O)_{ca}$ 2.114 $(O)_{ca}$ 2.190 $(O)_{OH}$	2.049 $(O)_w$		TBP, two O's of bidentate ligand, one carboxylate O of two different ligands, and one solvent O	89
XIII	hydrogen oxydiacetate	$LiC_4H_5O_5$	H_2O	2.038 $(O)_{ca}$ 2.052 $(O)_{ca}$ 2.031 $(O)_{ca}$ 2.040 $(O)_{ca}$ 2.122 $(O)_{et}$			TBP, two O's of one bidentate ligand (one carboxylate, one ethereal) and one carboxylate O of three different ligands	90
				Amines				
XVIII	Br^-	$(C_8H_{23}N_3)Li(Br)_2$-$Li(C_9H_{23}N_3)$	hexane	2.16 $(N)_{am}$ 2.28 $(N)_{am}$ 2.19 $(N)_{am}$		2.51 (Br) 3.20 (Br)	TBP,[a] three N's of amine in equatorial positions, two B^- in axial positions	91
XVIII	Br^-	$(C_9H_{23}N_3)Li(Br)_2$-$Li(C_9H_{23}N_3)$		2.19 $(N)_{am}$ 2.31 $(N)_{am}$ 2.24 $(N)_{am}$		2.57 (Br) 2.87 (Br)	TBP, three N's of amine in equatorial positions, two Br^- in axial positions	91
XXI	ClO_4^-	$[Li(C_{14}H_{31}N_5]ClO_4$	methanol	2.008 $(N)_{am}$ 2.083 $(N)_{am}$ 2.037 $(N)_{am}$ 2.056 $(N)_{am}$ 2.015 $(N)_{am}$			SP, five N's of ligand	92
XXII	BPh_4^-	$[Li(C_{17}H_{25}N_5]BPh_4$	H_2O–methanol	2.14 $(N)_{am}$ 2.45 $(N)_{am}$ 2.21 $(N)_{am}$ 2.26 $(N)_{am}$ 2.26 $(N)_{am}$			SP, five N's of ligand	93
XXIII	Cl^-	$[Li(C_{16}H_{36}N_4O_4)]Cl$·$LiCl·2H_2O$	chloroform	2.079 $(N)_{am}$ 2.131 $(N)_{am}$ 2.346 $(N)_{am}$ 2.347 $(N)_{am}$ 1.948 $(O)_{OH}$			SP, four N's and one side arm O of ligand	78
				Amides and Peptides				
XXXIV	Br^-	$[Li(C_{64}H_{78}N_{10}O_{10})$-$CH_3CN]Br·2CH_3CN$	acetonitrile	2.09 $(O)_{amide}$ 2.12 $(O)_{amide}$ 2.04 $(O)_{amide}$ 2.24 $(O)_{amide}$	2.07 $(N)_{AN}$		SP, four carbonyl O's of ligand and N of solvent	94, 95

				Ethers				
XLI	SCN^-	$Li(C_8H_{16}O_4)NCS$	acetonitrile	2.08 $(O)_{et}$ 2.06 $(O)_{et}$ 2.05 $(O)_{et}$ 2.14 $(O)_{et}$		1.960 (N)	SP, four ethereal O's of ligand and N of anion	96
XLI	$N[Si(CH_3)_3]_2^-$	$[Li(C_8H_{16}O_4)N-[Si(CH_3)_3]_2]$	THF–Et_2O–hexane	2.332 $(O)_{et}$ 2.393 $(O)_{et}$ 2.094 $(O)_{et}$ 2.108 $(O)_{et}$		1.965 (N)	SP, four ethereal O's of ligand and N of anion	97
XLII	SCN^-	$[Li(C_{13}H_{18}O_4)NCS]$	methanol–Et_2O	2.164 $(O)_{et}$ 2.033 $(O)_{et}$ 2.059 $(O)_{et}$ 2.012 $(O)_{et}$		1.945 (N)	SP, four ethereal O's of ligand and N of anion	98
XLV	SCN^-	$[Li(C_{18}H_{20}O_4)NCS]$	2,2,2-trifluoro-ethanol	2.033 $(O)_{et}$ 2.033 $(O)_{et}$ 2.054 $(O)_{et}$ 2.054 $(O)_{et}$		1.960 (N)	SP, four ethereal O's of ligand and N of anion	99
XLV	ClO_4^-	$[Li(C_{18}H_{20}O_4)H_2O]ClO_4$	2,2,2-trifluoro-ethanol	2.03 $(O)_{et}$ 2.01 $(O)_{et}$ 2.02 $(O)_{et}$ 2.04 $(O)_{et}$	1.92 $(O)_w$		SP, four ethereal O's of ligand and water O	100
XLV	I^-	$[Li(C_{18}H_{20}O_4)H_2O]I$	2,2,2-trifluoro-ethanol	2.07 $(O)_{et}$ 2.04 $(O)_{et}$ 2.07 $(O)_{et}$ 2.11 $(O)_{et}$	2.80 $(O)_w$		SP, four ethereal O's of ligand and water O	100
				2.12 $(O)_{et}$ 2.27 $(O)_{et}$ 2.04 $(O)_{et}$ 1.85 $(O)_{et}$	1.78 $(O)_w$		SP, four ethereal O's of ligand and water O	100
XLV	picrate	$Li(C_{18}H_{20}O_4)(C_6H_2O_7N_3)$	methanol–Et_2O	2.048 $(O)_{et}$ 2.032 $(O)_{et}$ 2.025 $(O)_{et}$ 2.038 $(O)_{et}$		1.916 $(O)_{pic}$	SP, four ethereal O's of ligand and phenolate O of anion	101
XLVI	SCN^-	$Li(C_{18}H_{20}O_5)NCS$	acetonitrile	1.971 $(O)_{et}$ 2.004 $(O)_{et}$ 2.014 $(O)_{et}$ 2.024 $(O)_{et}$		2.014 (N)	SP,[a] four ethereal O's of ligand and N of anion	102
XLVI	SCN^-	$Li(C_{18}H_{20}O_5)SCN$		1.980 $(O)_{et}$ 2.004 $(O)_{et}$ 2.018 $(O)_{et}$ 2.046 $(O)_{et}$		1.974 (N)	SP, four ethereal O's of ligand and N of anion	
XLVIII	SCN^-	$Li(C_{18}H_{20}O_6)SCN$	acetonitrile	1.999 $(O)_{et}$ 2.001 $(O)_{et}$ 2.049 $(O)_{et}$ 2.068 $(O)_{et}$		2.000 (N)	SP, four ethereal O's of ligand and N of anion	102
XLIX	SCN^-	$Li(C_{19}H_{22}O_5)SCN$	acetonitrile	2.007 $(O)_{et}$ 2.018 $(O)_{et}$ 2.025 $(O)_{et}$ 2.036 $(O)_{et}$		1.983 (N)	SP, four ethereal O's of the ligand N of anion	102
XLIX	NO_3^-	$Li(C_{19}H_{22}O_5)NO_3$	acetonitrile	2.043 $(O)_{et}$ 2.046 $(O)_{et}$ 2.048 $(O)_{et}$ 2.016 $(O)_{et}$		1.936 $(O)_{nit}$	SP, four ethereal O's of the ligand and one nitrate O	

TABLE IV (Continued)

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distance ranges, Å			comments	ref
				Li^+–L	Li^+–S	Li^+–A^{n-}		
L	carboxylate of ligand	$C_{20}H_{21}O_7Li\cdot7.5H_2O$	H_2O–methanol	2.077 $(O)_{et}$ 2.068 $(O)_{et}$ 2.067 $(O)_{et}$ 2.038 $(O)_{et}$	1.908 $(O)_w$		SP, four ethereal O's of ligand and water O	103
LIII	SCN^-	$[Li(C_{12}H_{24}O_4)NCS]$	methanol	2.08 $(O)_{et}$ 2.07 $(O)_{et}$ 2.08 $(O)_{et}$ 2.09 $(O)_{et}$		2.04 (N)	SP, four ethereal O's of ligand and N of anion	104
LIV	picrate	$Li(C_{28}H_{38}O_4)(C_6H_2N_3O_7)$	chlorobenzene + 1% THF	2.101 $(O)_{et}$ 2.105 $(O)_{et}$ 2.080 $(O)_{et}$ 2.088 $(O)_{et}$		1.883 $(O)_{pic}$	SP, four ethereal O's of ligand and phenolate O of anion	105
LVI	picrate	$C_{32}H_{48}O_{12}\cdot Li_2(C_6H_2N_3O_7)_2\cdot 2H_2O$	acetonitrile–petroleum ether	2.234 $(O)_{et}$ 1.983 $(O)_{et}$ 2.067 $(O)_{et}$	1.962 $(O)_w$	1.936 $(O)_{pic}$	TBP for both Li^+, three ethereal O's, one solvent O and, one phenolate O of anion for each Li^+	106
LVII	I^-	$C_{25}H_{52}O_{14}\cdot 2LiI\cdot 4H_2O$	ethyl acetate–acetone	1.98 $(O)_{et}$ 2.21 $(O)_{et}$ 2.12 $(O)_{et}$	1.96 $(O)_w$ 1.93 $(O)_w$		TBP for both Li^+, three ethereal O's of ligand and by two water O's for each Li^+	107
LXI	ClO_4^-	$Li(C_{21}H_{18}N_2O_2)ClO_4$	chloroform	2.17 $(O)_{et}$ 2.17 $(O)_{et}$ 2.12 $(N)_{am}$ 2.12 $(N)_{am}$		2.00 (O)	SP, two O's and two N's of one ligand and one O of anion	108
LXIV	SCN^-	$Li(C_{33}H_{58}N_2O_4)NCS$		1.950 $(O)_{amide}$ 1.979 $(O)_{amide}$ 2.229 $(O)_{et}$ 2.085 $(O)_{et}$		2.032 (N)	SP, four O's of ligand and the N of the anion	109
LXV	I^-	$[cyclo(C_{12}H_{20}O_{12})_6]_2\cdot LiI_3\cdot I_2\cdot 8H_2O$	H_2O–methanol	not reported			SP, four hydroxyl groups of two glucoses provide the basis of a square pyramid, the apex being formed by a water O	110
LXVII	$FeCl_4^-$	$[Li[(CH_3C_6H_2O)(CH_3C_6H_2OCH_3)(CH_2)_3(CH_3C_6H_2O)]_2]FeCl_4$	THF–benzene	2.036 $(O)_{et}$ 2.003 $(O)_{et}$ 2.007 $(O)_{et}$ 2.085 $(O)_{et}$ 2.052 $(O)_{et}$			TBP, five ethereal O's of the ligand	111, 112
			Phosphates					
LXXIX	$[C_{41}H_{40}NO_7P_2Mo]^-$	$[C_{41}H_{40}NO_7P_2Mo]Li]\cdot CH_2Cl_2$	CH_2Cl_2–pentane	2.02 $(O)_{pho}$ 2.09 $(O)_{pho}$ 2.01 $(O)_{pho}$ 2.23 $(N)_{am}$		1.92 $(O)_{ca}$	TBP, the three ethereal O's, a N, and a carboxylate O, all of one ligand	113
LXXX	picrate	$Li(C_6H_2N_3O_7)_2(H_2O)$	methanol	2.043 $(O)_{NO_2}$ 2.030 $(O)_{NO_2}$ 1.934 $(O)_{phn}$ 1.930 $(O)_{phn}$	1.959 $(O)_w$		SP,[a] one nitro O and one phenolate O from two different anions and one water O	114
LXXX	picrate	$Li(C_6H_2N_3O_7)_2(H_2O)$		2.032 $(O)_{NO_2}$ 2.039 $(O)_{NO_2}$ 1.979 $(O)_{phn}$ 1.986 $(O)_{phn}$	1.928 $(O)_w$		SP, one nitro O and one phenolate O from two different anions and one water O	114

[a] Crystal structure contains more than one molecule in the asymmetric unit.

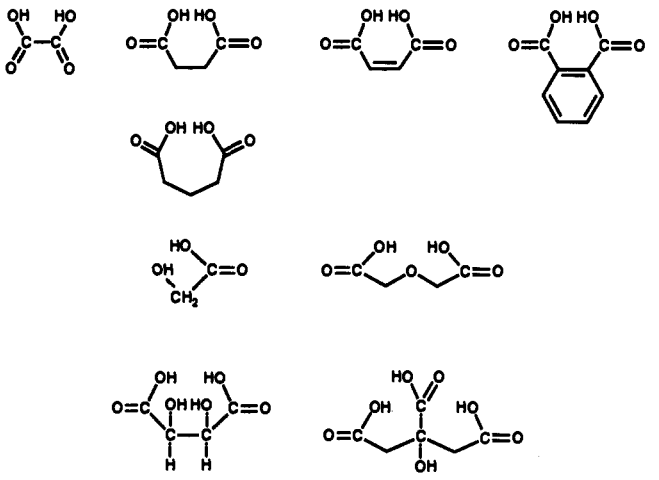


Figure 2. Carboxylic acids that function as polydentate ligands.

CHART II. Amines

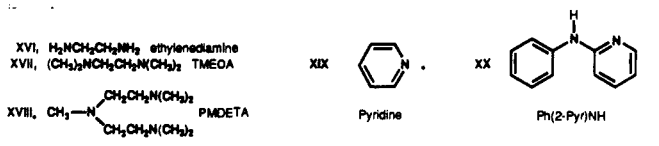
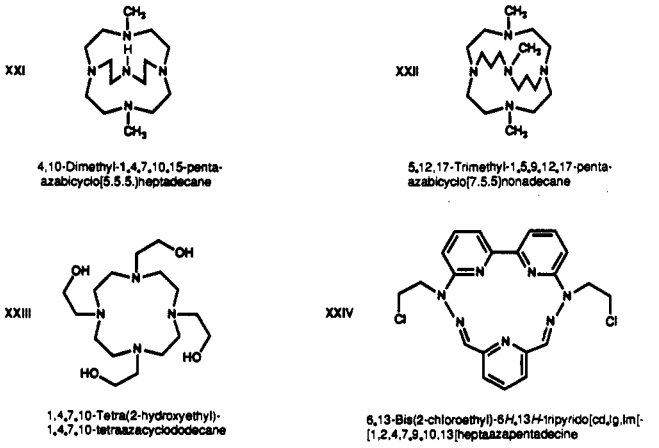


CHART III. Cyclic Polyamines



complexes in the crystal structure of lithium citrate.[37] Sometimes the complexes are chemically similar as in the case of lithium malonate[30] where the two complexes have tetrahedral geometry with each of the four coordinating sites occupied by an oxygen of four different malonates. However, in some cases the complexes are chemically different. For example, in the lithium citrate structures three of the complexes have tetrahedral geometry. In one of these the coordinating sites are occupied by an oxygen from four monodentate citrates while the other two complexes each contain one citrate oxygen and three water oxygens in their coordination sites. In the fourth complex, the Li^+ is Oc coordinated to four oxygen atoms from two ligands and two solvent molecules. Sometimes polymorphs are formed. An example is found in the lithium tartrate system in which one polymorph contains a complex with trigonal bipyramidal geometry[88] while the other contains a complex with square pyramidal geometry.[89] The above findings can be explained by the availability of flexible ligands with hard base donor atoms which provide one or more binding sites available for interactions with Li^+ as well as the ability of lithium to form complexes with solvent and anionic ligands. The existence of polymorphs in the Li^+–tartrate system may provide an example of the relative ease with which the TBP and SP geometries can be interconverted.

Two facts suggest that carboxylate binding sites in biological systems will not be selective for Li^+. First, there are a large variety of carboxylate conformations for complexations (see Figure 2). Second, all of the alkali metal ions as well as some other cations present in biological systems interact strongly with hard bases (e.g. carboxylate oxygens) and so will compete with Li^+ for these sites.

C. Amines

Li^+ forms stable complexes with aliphatic[43-47,78,91-93,116] and aromatic[48,49,117] mono- and polyamines in nonaqueous solutions (Charts II and III). The coordination of Li^+ by amine nitrogens might be explained as the result of interaction of the hard Li^+ with the hard amine base nitrogen (see Table II), and the ion (Li^+)–dipole (amine nitrogen) interaction. The coordination numbers of Li^+–amine complexes are 4, 5, and 6, and the coordination polyhedra are Td for 4-fold coordination, TBP and SP for 5-fold coordination, and distorted Oc and pentagonal based pyramidal for 6-fold coordination. The average Li–N distances for the different coordination numbers and polyhedra are presented in Table IX.

The minimal radius of the enclosed cavity increases gradually with the number of the amine nitrogens available for coordination. When the amine has one of the conformations shown in Figure 3 it interacts with the Li^+ as a polydentate ligand.

The strong interaction of Li^+ with aromatic nitrogens[48,83,84] might elucidate, at least in part, the binding of Li^+ in biological systems.

D. Amides and Peptides

Li^+ forms complexes with amides[50,52,53,118] diamides,[51,109,118] linear peptides,[54-56] and cyclic peptides,[57,94,95] (Charts IV–VI). The linear peptide complexes are formed in aqueous solution, while the remaining complexes are formed in nonaqueous solutions. The coordination numbers of Li^+ complexes with amide and peptide carbonyl oxygens are 4, 5, and 6, and the coordination polyhedra are Td, SP, and distorted Oc for 4-fold, 5-fold, and 6-fold coordination, respectively. The average Li–O distances for the different coordination numbers and polyhedra are presented in Table X.

The interaction between amides and Li^+ is of the ion–dipole type[13,14] with the interaction energies becoming larger with increasing dipole moments of the ligands.[134,135] The strength of interaction of Li^+ increases from primary to secondary to tertiary amides, and as the number of methyl groups in a given amide ligand increases. The heat of interaction of a metal ion with the amide is more negative than that with water, and the heats of interaction with amides decrease in the sequence $Li^+ > Na^+ > K^+$.[134,135] These findings might explain the effectiveness of lithium salts as protein denaturating agents[136] and the nonselective binding of Li^+ to protein molecules in different biological systems.[1]

TABLE V. Li^+ 6-Fold Coordination

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distance ranges, Å			comments	ref
				Li^+–L	Li^+–S	Li^+–A^{n-}		
				Carboxylic Acids				
XII	dihydrogen citrate	$C_6O_7H_7Li$	H_2O	1.96 $(O)_{ca}$ 2.12 $(O)_{ca}$ 2.17 $(O)_{ca}$ 2.10 $(O)_{ca}$ 2.22 $(O)_{OH}$ 2.49 $(O)_{OH}$			Oc, two O's of two bidentate ligands and one O of two monodentate ligands	115
XII	citrate	$C_6H_5O_7Li_3{\cdot}5H_2O$	H_2O–ethanol	1.998 $(O)_{ca}$ 1.998 $(O)_{ca}$ 2.198 $(O)_{OH}$ 2.198 $(O)_{OH}$	2.222 $(O)_w$ 2.222 $(O)_w$		Oc, two O's of two bidentate ligands and two water O's	37
				Amines				
XVI	I^-	$[Li(C_2H_8N_2)_3]I$	ethylenediamine	2.20 $(N)_{am}$ (average value)			Oc, two N's of three different ligand molecules	116
XXIV	PF_6^-	$[Li(C_{21}H_{20}Cl_2N_7)(CH_3OH)]PF_6$	CH_3OH	2.160 $(N)_{am}$ 2.257 $(N)_{am}$ 2.152 $(N)_{am}$ 2.148 $(N)_{am}$ 2.271 $(N)_{am}$	2.041 $(O)_{OH}$		pentagonal-based pyrimide, five N's of ligand and one solvent molecule	117
				Amides				
XXV XXVII	ClO_4^-	$[Li(CH_3CONH_2)_{1.5}{\cdot}(CH_3CONHCOCH_3)]ClO_4$	methanol	1.99 $(O)_{amide}$ 2.02 $(O)_{amide}$ 2.16 $(O)_{amide}$ 2.11 $(O)_{amide}$ 2.03 $(O)_{amide}$		2.77 $(O)_{ClO_4}$	Oc, two O's from one diacetamide ligand, one O from three different acetamide ligands, and one O from an anion	118
XXXVI	$C_{18}H_{24}B^-$	$[Li(C_4H_{10}O_2)_2C_{18}H_{24}B]$	DME	2.353 $(O)_{et}$ 2.353 $(O)_{et}$ 2.000 $(O)_{et}$ 2.000 $(O)_{et}$		2.06 (H) 2.06 (H)	Oc, two O's from two different solvent (or ligand) molecules and two hydric H from anion	119
				Ethers				
XLII	ClO_4^-	$Li(C_{13}H_{18}O_4)ClO_4$	2,2,2-trifluoroethanol	2.14 $(O)_{et}$ 2.08 $(O)_{et}$ 2.03 $(O)_{et}$ 1.98 $(O)_{et}$		1.91 (O) 2.05 (O)	Oc, four ethereal O's of ligand and two O's of bidentate anion	120
XLII	picrate	$Li(C_{13}H_{18}O_4)(C_6H_2N_3O_7)$	methanol–Et_2O	2.15 $(O)_{et}$ 2.05 $(O)_{et}$ 2.09 $(O)_{et}$ 2.01 $(O)_{et}$		1.96 $(O)_{phn}$ 2.26 $(O)_{NO_2}$	Oc, four ethereal O's of ligand and two O's of bidentate anion	101
XLIII	NO_3^-	$Li(C_{14}H_{20}O_4)NO_3$	acetonitrile–toluene	2.040 $(O)_{et}$ 2.011 $(O)_{et}$ 2.098 $(O)_{et}$ 2.051 $(O)_{et}$		2.300 (O) 2.072 (O)	SP, equatorial positions occupied by four ethereal O's of ligand and axial position occupied by two O's of bidentate NO_3^-	121
XLIV	NO_3^-	$Li(C_{16}H_{24}O_4)NO_3$	acetonitrile–toluene	2.041 $(O)_{et}$ 2.021 $(O)_{et}$ 2.099 $(O)_{et}$ 2.052 $(O)_{et}$		2.074 $(O)_{nit}$ 2.286 $(O)_{nit}$	SP, equatorial positions occupied by four ethereal O's of ligand and axial position occupied by two O's of bidentate NO_3^-	122

LI	$[In(CH_3)_3Cl]^-$	$Li(C_{13}H_{29}O_5)(In(CH_3)_3Cl)$	benzene	2.09 $(O)_{et}$ 2.28 $(O)_{et}$ 2.24 $(O)_{et}$ 2.29 $(O)_{et}$ 2.27 $(O)_{et}$		2.40 (Cl)	Oc, five ethereal O's of ligand and Cl^- of anion	123
LXII	SCN^-	$[Li(C_{14}H_{28}N_2O_4)NCS]\cdot 0.5H_2O$	methanol	2.255 $(O)_{et}$ 2.222 $(O)_{et}$ 2.161 $(O)_{et}$ 2.151 $(O)_{et}$ 2.205 $(N)_{am}$ 2.210 $(N)_{am}$			Oc, four ethereal O's of ligand and two N's	124
LXIII	I^-	$[Li(C_{14}H_{28}N_2O_4)]I$	acetone	2.288 $(N)_{am}$ 2.288 $(N)_{am}$ 2.173 $(O)_{et}$ 2.173 $(O)_{et}$ 2.081 $(O)_{et}$ 2.081 $(O)_{et}$			Oc, four O's and two N's of ligand	125
				Spherands				
LXVI	Cl^-	$[Li(C_{48}H_{48}O_6)]Cl$	THF–Benzene	2.138 $(O)_{et}$ (average value)			Oc, six ethereal O's of ligand	111, 112
				Natural Ionophores				
LXIX	carboxylate	$[Li(C_{35}H_{59}O_{11})]\cdot H_2O$	methanol	2.098 $(O)_{et}$ 2.099 $(O)_{et}$ 2.097 $(O)_{et}$ 2.098 $(O)_{et}$ 2.162 $(O)_{OH}$ 2.038 $(O)_{OH}$			Oc, four ethereal O's and two hydroxy O's of ligand	126
				Lithium Salts				
LXXXI	NO_3^-	$LiNO_3\cdot 3H_2O$	H_2O		2.082 $(O)_w$ 2.082 $(O)_w$ 2.082 $(O)_w$ 2.082 $(O)_w$	2.206 $(O)_{nit}$ 2.206 $(O)_{nit}$	Oc, one O of four different waters and one O of two different NO_3^-	127

TABLE VI. Li^+ 7-Fold Coordination for Spherands

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distance ranges, Å Li^+–L	comments	ref
LXVIII	Cl^-	$[Li(C_{52}H_{52}O_7)]Cl$	THF–benzene	2.291 $(O)_{et}$ 2.030 $(O)_{et}$ 2.062 $(O)_{et}$ 2.262 $(O)_{et}$ 2.393 $(O)_{et}$ 2.334 $(O)_{et}$ 2.430 $(O)_{et}$	seven coordinate, seven ethereal O's of ligand	111, 112

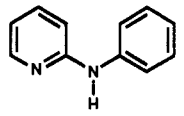


Figure 3. Amines that function as polydentate ligands.

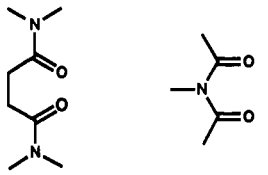


Figure 4. Amides that function as polydentate ligands.

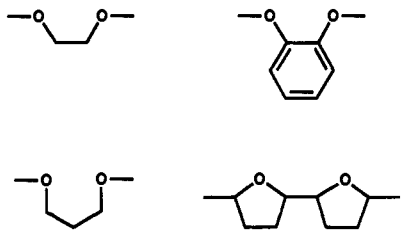


Figure 5. Ethers that function as polydentate ligands.

The radius of the enclosed cavity increases gradually with the number of the amide carbonyl oxygens available for coordination. When the amide has one of the conformations shown in Figure 4 it interacts with Li^+ as a bidentate ligand. Unprotected C-terminal peptides have additional carboxylate binding sites which provide intramolecular counterions.

E. Ethers, Ketones, and Alcohols

Li^+ forms stable complexes with monoethers,[58-61,64-71,48-55] diethers,[61,63] linear polyethers,[62,119] and cyclic polyethers[72-75,96-107,109,111,112,120-126,128-133] in nonaqueous solutions (Charts VII, VIII, and X–XV). The interaction between ethers and Li^+ is of the ion–dipole type.[12,23] Ethereal oxygens are hard bases[16-18] that interact strongly with Li^+. The coordination numbers of Li^+ in its complexes with ethers are 3, 4, 5, 6, 7, and 8, and the coordination polyhedra are pyramidal for 3-fold, Td for 4-fold, SP and TBP for 5-fold, distorted Oc for 6-fold, modified trigonal prism for 7-fold, and square antiprism for 8-fold coordination. The average Li–O distances for the different coordination numbers and polyhedra are presented in Table XI.

The radius of the enclosed cavity increases gradually with the number of the ethereal oxygen atoms available

CHART IV. Amides

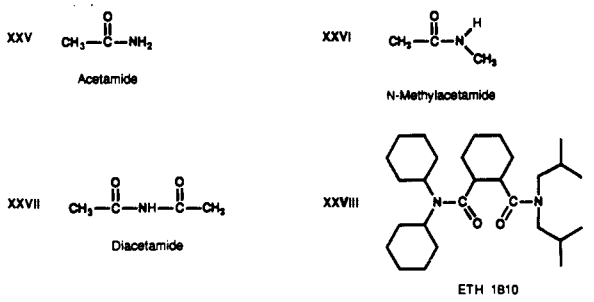
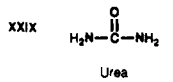


CHART V. Urea



for coordination. The most favorable distance, r, for Li–O interaction should be $r \leq r_{Li^+} + r_{O^{2-}} = 0.6 + 1.40 = 2.00$ Å.[15,16] This r value is obtained when the coordination number is 4 or 5, and the coordination geometries are Td, SP, or TBP.[15,16] These findings might explain why the most selective ionophores for Li^+ have coordination numbers 4[14,15,137] and 5[109,138-140] and their coordination geometries are Td[14,51,137] and SP.[109,138-140] When the ether has one of the conformations shown in Figure 5 it interacts with Li^+ as a polydentate ligand. THF molecules coordinate Li^+ more effectively than other monoethers. THF units are building blocks of the natural antibiotic monensin, which forms a stable complex with Li^+.[126]

There are few crystal structures of Li^+ ketone complexes[76,77] (Chart IX). In those reported the Li^+ is Td coordinated by the carbonyl oxygens of the keto groups. The average Li–O distance is 1.946 Å. The complexes are formed in nonaqueous solutions.

Crystal complexes of Li^+ with alcohols are rare.[78a,78b,110] The Li^+ is Td and SP coordinated to the hydroxyl oxygen atoms. The average Li–O distance is 1.935 Å for the 4-fold Td coordinated Li^+.

F. Phosphates

Li^+ forms stable complexes with phosphates[79-84,113] (Chart XVI). The Li^+ is 4-fold Td coordinated in all complexes,[79-84] except one,[113] in which it is 5-fold coordinated. The average Li–O distance is 1.911 Å. The complexes are formed in nonaqueous solutions. This information has important biological implications since Li^+ is reported to associate with phosphate nucleotides such as ATP, ADP, AMP, GTP, IMP, IDP, and ITP.[5,141] The nature of these and other Li^+–phosphate interactions of biological importance may be better understood by reference to the structural data contained herein.

TABLE VII. Li^+ 8-Fold Coordination for Ethers

ligand, L	anion, A^{n-}	complex formula	solvent(s) of crystallization	distance ranges, Å Li^+–Li	comments	ref
XLI	PPh_2^-	$[Li(C_8H_{16}O_4)_2]PPh_2$	THF–Et_2O	2.478 $(O)_{et}$ 2.323 $(O)_{et}$ 2.361 $(O)_{et}$ 2.308 $(O)_{et}$ 2.323 $(O)_{et}$ 2.430 $(O)_{et}$ 2.315 $(O)_{et}$ 2.457 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	128, 129
XLI	$AsPh_2^-$	$[Li(C_8H_{16}O_4)_2]AsPh_2$	THF–Et_2O	2.436 $(O)_{et}$ 2.269 $(O)_{et}$ 2.420 $(O)_{et}$ 2.418 $(O)_{et}$ 2.430 $(O)_{et}$ 2.399 $(O)_{et}$ 2.287 $(O)_{et}$ 2.284 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	128, 129
XLI	$CHPh_2^-$	$[Li(C_8H_{16}O_4)_2]CHPh_2$	THF–Et_2O	2.415 $(O)_{et}$ 2.423 $(O)_{et}$ 2.398 $(O)_{et}$ 2.295 $(O)_{et}$ 2.287 $(O)_{et}$ 2.411 $(O)_{et}$ 2.374 $(O)_{et}$ 2.400 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	129, 130
XLI	CPh_3^-	$[Li(C_8H_{16}O_4)_2]CPh_3$	THF–Et_2O	2.401 $(O)_{et}$ 2.411 $(O)_{et}$ 2.396 $(O)_{et}$ 2.375 $(O)_{et}$ 2.297 $(O)_{et}$ 2.287 $(O)_{et}$ 2.371 $(O)_{et}$ 2.395 $(O)_{et}$	SA, sandwich complex, four ethereal O's two different ligands	129, 130
XLI	$SbPh_2^-$	$[Li(C_8H_{16}O_4)_2]SbPh_2 \cdot 0.33C_4H_8O$	THF–Et_2O	2.439 $(O)_{et}$ 2.268 $(O)_{et}$ 2.422 $(O)_{et}$ 2.417 $(O)_{et}$ 2.430 $(O)_{et}$ 2.400 $(O)_{et}$ 2.288 $(O)_{et}$ 2.285 $(O)_{et}$	Sa, sandwich complex, four ethereal O's of two different ligands	61
XLI	$Sb_3Ph_4^-$	$[Li(C_8H_{16}O_4)_2]Sb_3Ph_4$	THF–Et_2O	2.479 $(O)_{et}$ 2.324 $(O)_{et}$ 2.360 $(O)_{et}$ 2.309 $(O)_{et}$ 2.322 $(O)_{et}$ 2.431 $(O)_{et}$ 2.316 $(O)_{et}$ 2.455 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	61
XLI	$2,4,6\text{-}(CH_3)_3C_8H_2\cdot P\cdot B[2,4,6\text{-}(CH_3)_3C_6H_2]_2^-$	$[Li(C_8H_{16}O_4)_2]2,4,6\text{-}(CH_3)_3C_6H_2\cdot P\cdot B(2,4,6\text{-}(CH_3)_3C_6H_2)_2$	THF–Et_2O	2.275 $(O)_{et}$ 2.263 $(O)_{et}$ 2.285 $(O)_{et}$ 2.401 $(O)_{et}$ 2.355 $(O)_{et}$ 2.297 $(O)_{et}$ 2.361 $(O)_{et}$ 2.268 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	131
XLI	$Ph_3SiNSiPh_3^-$	$[Li(C_8H_{16}O_4)_2]Ph_3SiNSiPh_3$	THF–Et_2O	2.266 $(O)_{et}$ 2.265 $(O)_{et}$ 2.220 $(O)_{et}$ 2.259 $(O)_{et}$ 2.266 $(O)_{et}$ 2.205 $(O)_{et}$ 2.220 $(O)_{et}$ 2.259 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	132
XLI	$B(2,4,6\text{-}(CH_3)_3C_6H_2)_3^-$	$[Li(C_8H_{16}O_4)_2]B[2,4,6\text{-}(CH_3)_3C_8H_2]$	THF–Et_2O	2.255 $(O)_{et}$ 2.400 $(O)_{et}$ 2.423 $(O)_{et}$ 2.393 $(O)_{et}$ 2.423 $(O)_{et}$ 2.393 $(O)_{et}$ 2.254 $(O)_{et}$ 2.400 $(O)_{et}$	SA, sandwich complex, four ethereal O's of two different ligands	133

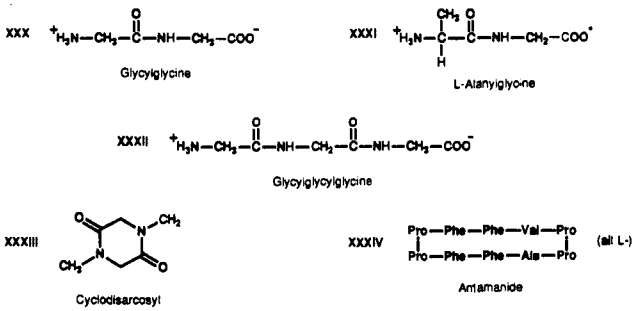
TABLE VIII. Average Li–O Distances of Li^+-carboxylic Acid Binding Sites Involved in Li^+ Complexation

coordination no., n	coordination geometry	average Li–O distance, Å
4	Td	1.957
5	TBP	2.071
5	SP	2.057
6	distorted Oc (tetragonal)	2.145

TABLE IX: Average Li–N Distances in Lithium–Amine Complexes

coordination no., n	coordination geometry	average Li–N distance, Å: aliphatic nitrogen	average Li–N distance, Å: aromatic nitrogen
4	Td	2.089	2.080
5	TBP	2.228	
5	SP	2.247	
6	distorted Oc (tetragonal)	2.348	
6	pentagonal based pyramid		2.198

CHART VI. Peptides



G. Water Molecules

Li^+ forms stable complexes with water molecules,[19-22] in which the cation is coordinated by four water molecules in Td geometry. In many other cases, water molecules are included in the coordination sphere of Li^+ in order to saturate its coordination sphere or because of incomplete replacement of the water molecules of the hydration shell by the ligand binding sites. Water molecules are involved in Li^+ complexes with coordination numbers 4, 5, and 6, and coordination polyhedra of Td, SP, TBP, and Oc. The average Li–O distances for the different coordination numbers and polyhedra are presented in Table XII. From the table, it is seen that the average Li–O distance is independent of the number of H_2O molecules in the hydration shell in 4-fold Td geometry. The same phenomenon is found in 5-fold TBP coordinated Li^+ complexes, when either one or two water molecules are coordinated to the Li^+.

H. Other Inorganic Anions

Valuable information about the coordination of Li^+ is obtained from the crystal structures of inorganic lithium salts (Table XIII). In general, these crystal structures resemble those of sodium salts. A coordination number of 6 is common. In some structures, the coordination number drops to 4. In an octahedral hole in a NaCl-type lattice comprised of large anions, Li^+ may rattle around, e.g., in LiI, so that the instantaneous number of nearest neighbors is less than six. Lithium

TABLE X. Average Li–O Distances in Lithium–Amide and –Peptide Complexes

coordination no., n	coordination geometry	average Li–O distance, Å
4	Td	1.923
5	SP	2.036
6	distorted Oc (tetragonal)	2.180

CHART VII. Ethers

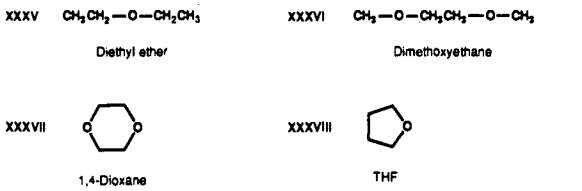
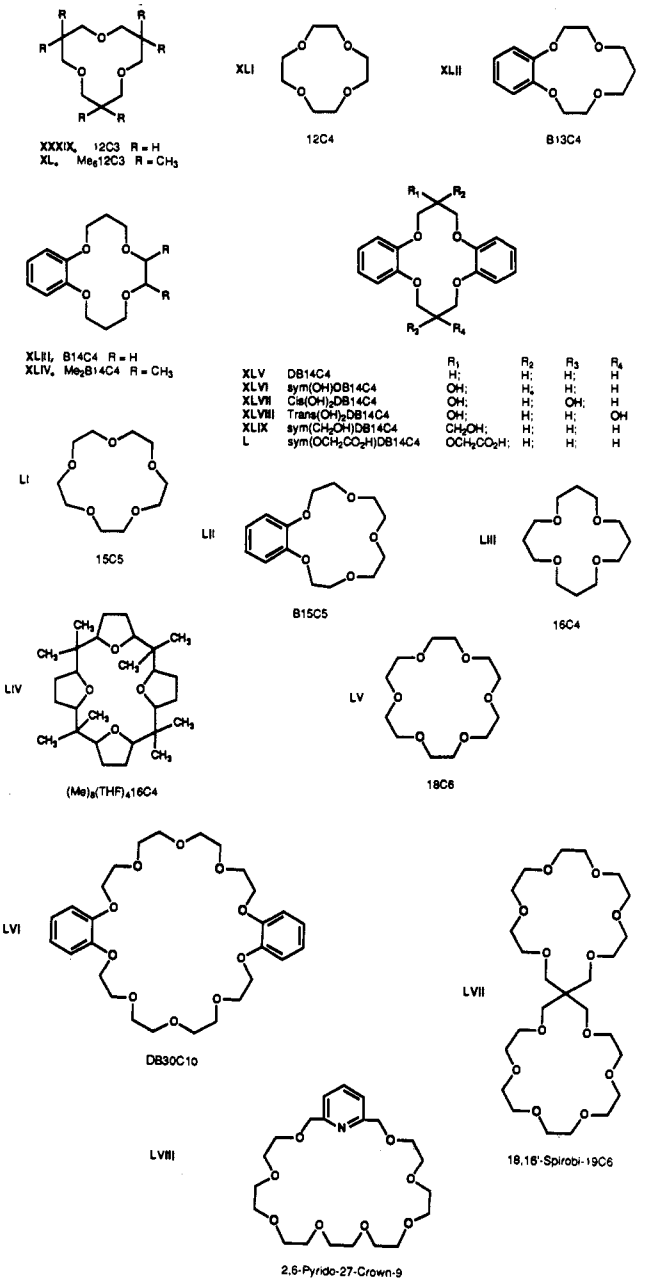


CHART VIII. Crown-Ethers



can replace either Na^+ or Mg^{2+} in a six-coordinate hole, but it prefers a somewhat smaller hole than does Na^+. It is unlikely to compete with K^+ or ions larger than

CHART IX. Ketones

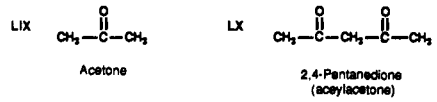


CHART X. Amino Ethers and Cryptands

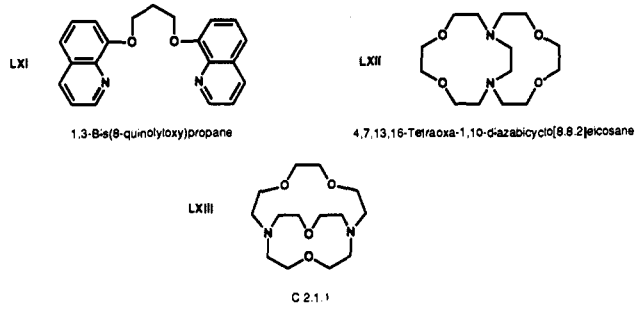


CHART XI. Amido Ethers

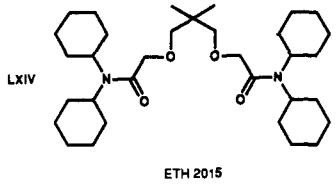


CHART XII. Cyclodextrins

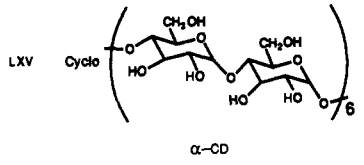


CHART XIII. Spherands

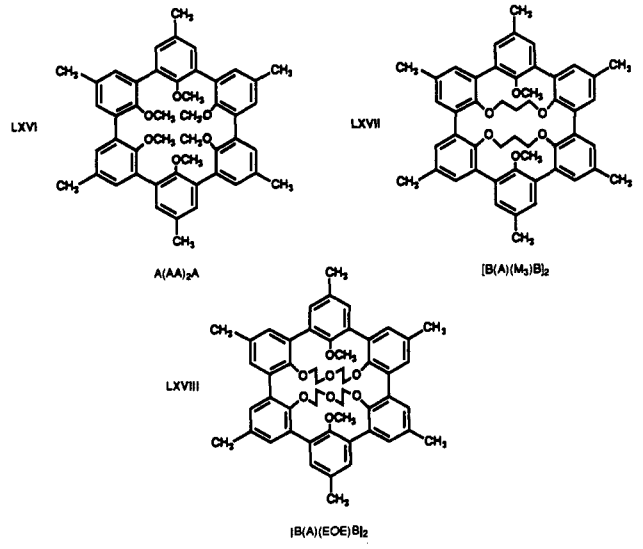


CHART XIV. Natural Ionophores

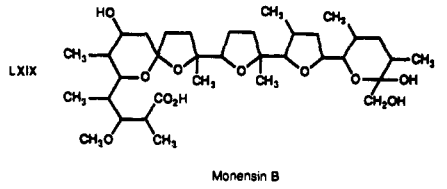


CHART XV. Dithiocarbamates

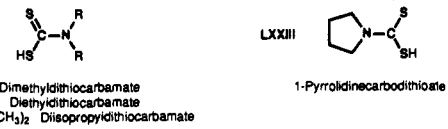


CHART XVI. Organophosphorus Compounds

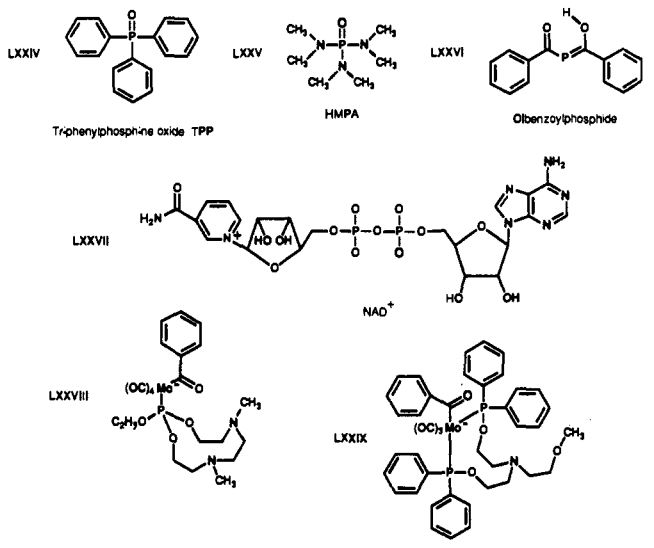


TABLE XI. Average Li–O Distances in Lithium–Ether Complexes

coordination no., n	coordination geometry	average Li–O distance, Å
3	pyramidal	1.951
4	Td	1.962
5	SP	2.032
5	TBP	2.099
6	distorted Oc (tetragonal)	2.265
7	modified trigonal prism	2.257
8	square antiprism	2.341

TABLE XII. Average Li–O Distances in Lithium–H_2O Complexes

coordination no., n	coordination geometry	no. of H_2O molecules in hydration shell	average Li–O distance, Å
4	Td	1	1.933
		2	1.948
		3	1.945
		4	1.944
5	TBP	1	1.994
		2	1.998
	SP	1	1.906
6	distorted Oc (tetragonal)	2	2.222
		4	2.082

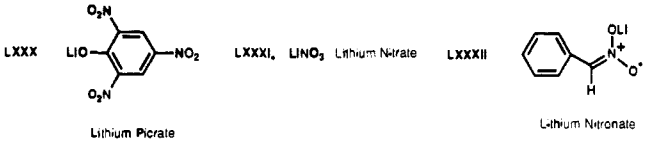
Ca^{2+} as the latter cations have a higher coordination number (≥8). In order to have six neighbors at ionic bond distances, such that the anions and cations are in contact, the anions must be small relative to the cations, otherwise, lower coordination numbers (4 and 5) are favorable. This reflects the Pauling "radius-ratio" effect,[16] that small cations fit best in a lattice of small anions. The picture is more complicated when anions of higher charge are involved, for example, O^{2-}, CO_3^{2-}, PO_4^{3-}. Although some of these anions are large they produce a large charge field because of their high

TABLE XIII. Crystal Structures of Lithium Inorganic Salts[142,143]

compd	coordination no., n	coordination geometry	Li–anion distance, Å	range of distances, Å
LiCl	6	Oc	2.565	
LiBr	6	Oc	2.748	
LiI	6	Oc	3.001	
LiH	6	Oc	2.043	
LiD	6	Oc	2.033	
Li_2O	6	Oc	2.050	
Li_2O_2	6	Oc	1.962	
Li–O[a]	6	Oc	2.16(average)	1.96–2.41
Li_2S	6	Oc	2.504	
$(Li_2SiO_3)_x$	4	Td	2.103	
Li_3PO_4	4	Td	1.955	
$Li_2SO_4 \cdot H_2O$	4	Td	2.015	
Li–O[a]	4	Td	1.98(average)	1.86–2.05

[a] Range of Li–O distances in lithium inorganic salts.

CHART XVII. Lithium Salts



charge.[144] The anions require more than one monovalent cation, e.g., in M_3PO_4, so that small cations have great packing advantage. Li^+ and Mg^{2+} have a preference for anions with small radius, r, and high charge, z, i.e., anions with high z/r. This explains why Na^+ occurs in nature as a chloride, but Li^+ and Mg^{2+} occur mainly as silicates. This difference introduces an additional restriction in the biological availability of Li^+ and Mg^{2+} from the soil, for while chlorides are water soluble silicates are not. The above results might explain the strong interactions between Li^+ and phosphate nucleotides, e.g., ATP, ADP, AMP, IMP, and ITP. The Li–O distances in inorganic salts are similar to those of organic complexes in Td and Oc coordination geometries.

IV. Conformational Changes of Linear and Cyclic Ligands in Lithium Complexes

The coordination number of lithium complexes with linear ligands varies from 2 to 6, while that with cyclic ligands varies from 4 to 8. This difference is due to the structures of the ligand molecules involved. Linear molecules have one or more binding sites available for variable coordination numbers of interaction with Li^+ due to the molecule flexibility. Li^+ is either 4-fold Td[28] or 5-fold TBP[86] when coordinated to oxalic acid, Td[36,37] and Oc[37,115] when coordinated to citric acid, and Td[43] and Oc[116] when coordinated to ethylenediamine. Cyclic ligands have restricted flexibility, and their possible conformational changes are limited. The conformations of the Li^+ complexes of these ligands are dictated by those of the free ligands. The three oxygen atoms in 12C3 crown ethers provide a basis for a trigonal-pyramidal structure.[72] Most of the crown ether molecules[96–105] and the cyclic peptides[94,95] which possess four donor oxygen atoms, provide a basis for SP coordination. The DB14C4 molecule is preorganized for SP coordination with Li^+. Biycyclic and spherand ligands provide optimal preorganized cages for Li^+ binding. Coordination numbers found with these ligands are 5,[92,93,111,112] 6,[111,112,125] and 7.[111,112] Eight-fold coordination is achieved by the formation of a sandwich complex of Li^+ with two 12C4 molecules in aprotic organic media.[128–133] Trace amounts of H_2O cause the decomposition of the complex. The use of cyclic ligands allows the positioning of more donor atoms close to the Li^+ than is possible with noncyclic ligands. The structural data show that both linear and cyclic ligands can bind Li^+ in its favorable 4 and 5 coordination numbers. Linear ligands may have the advantage of rapid complexation and decomplexation rates of their Li^+ complexes. This feature has resulted in the use of linear ligands in lithium selective electrodes. The large equilibrium constants for the interaction of Li^+ with cyclic and bicyclic ligands makes these viable candidates for diagnostic uses.

V. Counterion Effects

Transport of cations by ionophoric carrier molecules from one aqueous phase to another aqueous phase through hydrophobic membranes is important because of possible biological[23] and industrial[1] applications. Complexation occurs between the cation and the binding sites of the ionophore. In the case of neutral carrier molecules, the cation flux has a strong inverse dependence on the solvation energy of the accompanying counterion.[145] Successful transport depends, therefore, on the readiness of the anion to leave its aqueous environment and enter the organic phase. Common practice is to employ large, poorly hydrated anions that may interact by polar and dispersion forces with the membrane medium,[145] picrate being the favorite anion chosen for this purpose.[146] This simple picture is obscured, however, by the additional effect of ion pairing between the cation and the anion(s).[145–150] In water and other highly solvating media, the charged complex and the anion are separately solvated.[147,151–153] In poorly solvating media, such as hydrophobic organic solvents, pronounced ion pairing occurs and complexed ion pairs or ligand separated ion pairs are formed. Water molecule(s) from the cation and solvent molecule(s) from the anion first solvation shells are probably displaced in this ion pairing if it leads to a contact pair.[147,150] The extent of the electrostatic cation–anion interactions, which are typical of Li^+ complexes, depends on the following properties of the anion: charge, ionic radius, shape, polarizability, and lipophilicity.[147] These properties are extremely important for the dis-

TABLE XIV. Coordination of Lithium Picrate and Its Complexes with Crown-Ethers

coordination			coordination sites in lithium picrate complexes								
			ethereal oxygens		phenolate oxygens		o-nitro oxygens		H_2O		
ligand	no.	symmetry	no. of sites	Li···O, Å, average	no. of sites	Li···O, Å, average	no. of sites	Li···O, Å, average	number of sites	Li···O, Å, average	ref
LXXX	5	SP	–	–	2	1.982	2	2.035	1	1.928	114
XLV	5	SP	4	2.035	1	1.916	–	–	–	–	101
LIV	5	SP	4	2.092	1	1.883	–	–	–	–	105
LII	4	Td	–	–	1	1.925	1	2.040	2	1.865	73
XLII	6	distorted Oc	4	2.087	1	1.960	1	2.26	–	–	101
LVI	5	TBP	3	2.095	1	1.936	–	–	1	1.962	106
average Li···O (Å) distance				2.077		1.933		2.112		1.918	–

solution of the complex in solvents of low polarity. The contribution of the anion to the transport selectivity is also important. It was recognized that the presence of lipophilic anions in the membrane phase gives rise to significant changes in the cation selectivity of neutral carrier based sensors.[51,154,155] Solvent polymeric membranes containing DB14C4 are most selective for lithium ions.[156] Incorporation of lipophilic anions, such as tetra-(*p*-chlorophenyl)borate, into the membrane leads to an improvement in lithium selectivity. Bulky polarizable soft anions in aprotic nonpolar organic solvents form ligand separated Li^+ ion pairs.[61,128-133] For example, in one case, the Li^+ is in a sandwich complex of two 12C4 molecules.[61,128-133] Trace amounts of moisture decompose the complexes. In other cases, solvent-separated Li^+ ion pairs are formed, e.g., hydrates of lithium carbamates,[19-22] and THF-solvated lithium salts of $U(C_2B_9H_{11})_2Cl_2^-$,[65] $Ag[C[Si(CH_3)_3]_3]_2^-$,[66] $AsPh_2^-$,[61] $Lu(C_8H_9)_4^-$,[68] and $Cu_5Ph_6^-$.[70] There are examples of soft spherical anions that form separate ion pairs with the Li^+ complexes, and the coordination sphere of the Li^+ is saturated by the ligand binding sites and solvent molecules, such as H_2O,[55,73,74,78,100,103,104] CH_3OH,[117] CH_3CN,[94,95] THF,[47] and urea.[75] No crystal structures of separated ion pairs of Li^+ complexes with hard anions have been reported.

Anions of dicarboxylic acids, such as succinate,[31] malonate,[29,30] maleate,[33] phthalate,[38-41] and oxalate[28,86] which function as bidentate ligands, enhance Li^+ transport in erythrocytes by an anionic cation transport mechanism.[4] Lithium ion forms crystal complexes with the above carboxylate ions. In all of these structures, the carboxylate ions function as bidentate ligands suggesting a similarity between crystal and solution structures of Li^+ complexes.

The counterion effect is illustrated by the coordination chemistry of lithium picrate with crown ethers. Examples are presented in Table XIV. The Li^+ has coordination numbers 4, 5, and 6, and coordination geometries of Td, SP, TBP, and distorted Oc, respectively. The picrate in some complexes is a monodentate ligand[101,105,106] binding through the phenolic oxygen. In other cases, it is a bidentate ligand[73,114] where the additional binding site is an oxygen of an *o*-nitro group. Whether the picrate ion is monodentate or bidentate appears to depend upon whether one or two donor sites are needed to saturate the coordination sphere. When there are constraints because of the ligand molecule conformation, additional water molecules interact with the Li^+ in order to saturate its coordination sphere.[67,106,114] The mono- and bidentate property of the picrate ion may have implications on extraction and selectivity studies of alkali picrates in solution. Crystal structure studies of lithium thiocyanate[99] and lithium picrate[101] complexes of DB14C4 reveal that the Li^+ is SP coordinated. The four ethereal oxygens of DB14C4 provide the basis of a square pyramid, and the apical site is occupied by the anion. Replacement of the chelating anions thiocyanate and picrate by the nonchelating bulky spherical anions iodide[100] and perchlorate[100] causes the formation of separate ion pairs in which the complexed cation is separated from the anion by a water molecule. It is assumed that complex formation in these cases is by a stepwise replacement mechanism presented in the following equations:

$$M^{z+}(S)_m + L = M^{z+}S_{m-1}L + S(\text{solvent}) \quad (1)$$

$$M^{z+}S_{m-1}L + L = M^{z+}S_{m-2}L_2 + S \text{ etc.} \quad (2)$$

$$M^{z+}SL_{n-1} + L = M^{z+}L_n + S \quad (3)$$

$$M^{z+} + nL = M^{z+}L_n \quad (4)$$

Equilibria 1 and 2 would be predominant when the cations are nearly fully solvated. Further ligand binding occurs, until the solvent (S) molecules in the solvation shell of the cation (M^{z+}) are replaced by the ligand (L) binding sites (equilibria 3 and 4).

The solvent molecules are replaced by the ligand binding sites. The replacement of each water molecule in the hydration sphere requires the contribution of much energy.[13,157-159] By changing the anion, it is possible to change the coordination sphere of the Li^+,[100-103,120] a parameter that affects the kinetics and thermodynamics of Li^+ complexation.

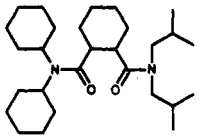
VI. Solvent Effects

Cation binding and selectivity by ionophores are affected by the nature of the solvent.[13,14,147,153,154,160,161] In general, oxygen-donor solvents and nitriles solvate hard acceptors well and soft ones poorly. On the other hand, amines and sulfur-donor solvents solvate soft acceptors strongly and hard acceptors poorly. The thermodynamic stability of a complex is, in general, inversely proportional to the solvation of the ligand and of the metal ion or complex. Complex formation will, therefore, be weaker in solvents where the acceptor is strongly solvated. When the dielectric constant is lower than 10, ion-pair formation with its resultant neutralization of charge becomes important, and the stabilities of neutral complexes increase dramatically.[147,153] The solvation of anions follows a quite different pattern than that of cations. The donor properties of the solvents are of minor importance for the solvation of anions,

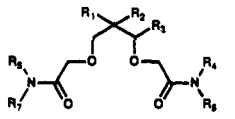
CHART XVIII. Lithium-Selective Ionophores

Linear Amides

1 (XXVIII)*



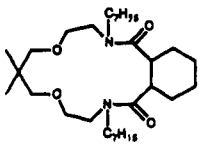
Linear Amido - Ethers



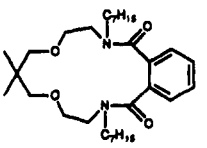
	R_1	R_2	R_3	R_4	R_5	R_6	R_7
2	CH_3	CH_3	H	CH_3	$n\text{-}C_7H_{15}$	CH_3	$n\text{-}C_7H_{15}$
3	C_2H_5	$n\text{-}C_4H_9$	H	CH_3	$n\text{-}C_7H_{15}$	CH_3	$n\text{-}C_7H_{15}$
4	CH_3	CH_3	$iso\text{-}C_3H_7$	CH_3	$n\text{-}C_7H_{15}$	CH_3	$n\text{-}C_7H_{15}$
5	H	H	H	CH_3	$n\text{-}C_7H_{15}$	CH_3	$n\text{-}C_7H_{15}$
6 (LXIV)*	H	H	H	cyclohexyl	cyclohexyl	cyclohexyl	cyclohexyl
7	CH_3	CH_3	H	$n\text{-}C_7H_{15}$	$C_2H_4\text{-}O\text{-}C_2H_5$	$n\text{-}C_7H_{15}$	$C_2H_4\text{-}O\text{-}C_2H_5$

Cyclic Amido-Ethers

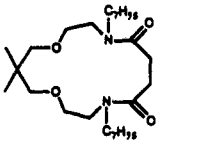
8



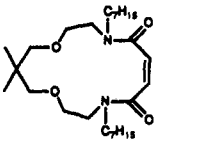
9



10

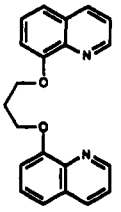


11

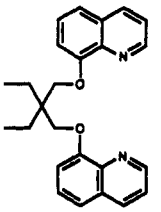


Linear Amino Ethers

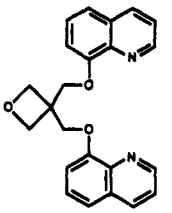
12 (LXI)*



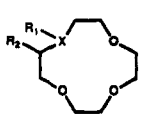
13

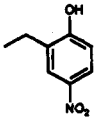
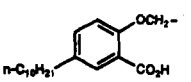


14



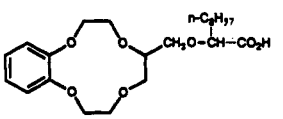
12-Crown-4 derivatives



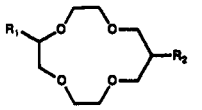
	X	R_1	R_2
15 (XLI)*	O	•	H
16	N		H
17	O		

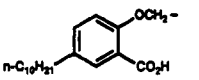
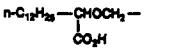
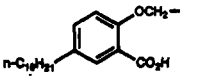
Benzo-12-Crown-4 derivatives

18



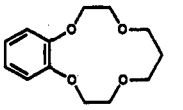
13-Crown-4 derivatives



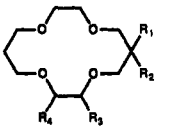
	R_1	R_2
19		H
20		H
21	H	

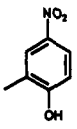
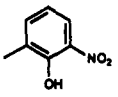
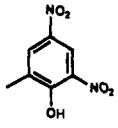
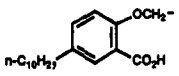
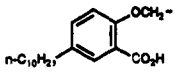
Benzo-13-Crown-4

22 (XLII)*



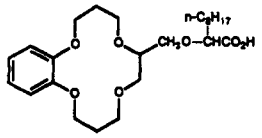
14-Crown-4 derivatives



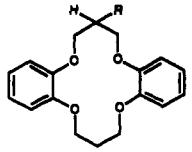
	R_1	R_2	R_3	R_4
23	H	$C_{12}H_{25}$	H	H
24	$n\text{-}C_8H_{17}$	$n\text{-}C_8H_{17}$	H	H
25	CH_3	$n\text{-}C_{12}H_{25}$	H	H
26	$n\text{-}C_{12}H_{25}$	$n\text{-}C_{12}H_{25}$	H	H
27	$PHCH_2$	$n\text{-}C_{12}H_{25}$	H	H
28	$PHCH_2$	$PhCH_2$	H	H
29	$CH_2CON(C_2H_5)_2$	$n\text{-}C_{12}H_{25}$	H	H
30	H		H	H
31	H		H	H
32	H		H	H
33	H		H	H
34	H	H	$CON(C_4H_9)_2$	$CON(C_4H_9)_2$
35		H	H	H
36	H	H		H

Benzo-14Crown-4 derivatives

37



Dibenzo-14-Crown-4 derivatives



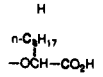
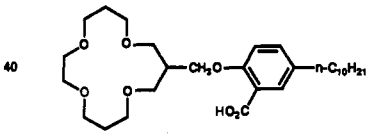
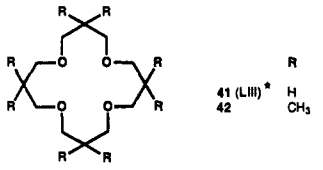
	R
38 (XLV)*	H
39	

CHART XVIII (Continued)

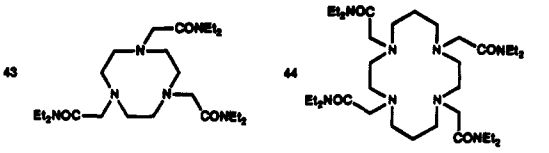
15-Crown-4 derivatives



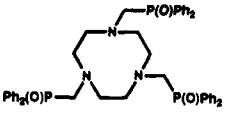
16-Crown-4 derivatives



Amide-armed Azamacrocycles



Diphenylphosphinyl-armed Azamacrocycles



which are donors themselves. The halides are especially strongly solvated in solvents capable of forming hydrogen bonds. The strength of the hydrogen bonds formed by the halides decreases in the order $Cl^- > Br^- > I^-$. Bulky, spherical hydrophobic anions may interact with the solvent molecules by polar and dispersion forces.[147]

By using solvents with different properties, such as dielectric constant, donicity, etc.,[153] one may have different complexes involving the same ligand molecule and cation salt. Lithium hydrogen phthalate crystallizes from aqueous solution in a Td coordination in which two of the binding sites are phthalate carboxylate oxygen atoms and the other two are H_2O molecules.[38] By changing the solvent to methanol, the two H_2O molecules in the coordination sphere of Li^+ are replaced by two CH_3OH molecules.[40] The combination of highly solvating solvents such as H_2O, THF, HMPA, and soft polarizable anions causes the formation of solvent-separated ion pairs. Examples are the lithium tetrahydrate carbamates in aqueous solutions,[19-22] the tetra-THF-solvated Li^+ in THF solutions[67-71] and tetra-HMPA-solvated Li^+ in Et_2O–toluene solution.[81] As was shown in the previous section, it is difficult to differentiate between the counterion and the solvent effects. Both factors contribute to the formation of the complex. Both the anion and the solvent molecules compete with the ligand binding sites for the saturation of the Li^+ coordination sphere. Mainly, the Li^+ is coordinated by the ligand binding sites and the counterion, but there are examples where the counterion is replaced by solvent molecules, such as H_2O,[55,73,74,78,100,103,107] CH_3OH,[117] CH_3CN,[94,95] THF,[47] and urea.[75] Water molecules are involved in the coordination sphere, when Li^+ is 4, 5, or 6 coordinated. The presence of trace amounts of H_2O prevents the formation of Li^+ complexes with coordination numbers lower than 4 and higher than 6. The replacement of solvent molecules by the ligand binding sites upon cation complex formation is illustrated in equations 1–4. The stepwise mechanism is affected by both the anion and the solvent molecules.[147,153]

VII. Lithium-Selective Ionophores

There has been much recent interest in lithium-selective ionophores primarily because of their possible biological and medical applications. No natural ionophores have been identified that exhibit significant preference toward Li^+, and, in fact, no synthetic ionophore has been prepared that would be selective enough to preferentially bind Li^+ in its physiological concentration.[3,4] Therefore, it is desirable to elucidate the basic principles of lithium coordination, which, hopefully, may lead both to the design of better ionophores for Li^+ and to the understanding of its biological activity. There are both linear[51,108,109,162-165,168,175] and cyclic[138-140,156,166,167,169-179] synthetic ionophores for Li^+ (see Chart XVIII).

The most effective and favorable binding sites in Li^+ selective ionophores are amide and ethereal oxygens. It is probably due to the fact that both amide and ethereal oxygens are hard bases that can form Td and SP coordination polyhedra with optimal cavity radius for Li^+ binding. It is important that all of the Li^+ ionophores except one (compound 1) have four or five binding sites. The crystal structures of compounds 1, 6, 12, 15, 22, 38, and 41 show that compound 1 forms a sandwich complex with Li^+ in Td geometry, while all of the other ligands are pentacoordinated to the Li^+ in SP geometry. These results are consistent with the theoretical calculations[16] and the experimental data[15] of optimal cavity radius for Li^+ binding. Hexadentate Li^+ selective ligands are achieved by the synthesis of rigid-cage molecules with very small cavity radius,[15,16] such as, cryptands[92,93,125,160,161] and spherands.[101,102] Otherwise, hexadentate ligands are an unlikely choice for Li^+ selective complexation, because they might also bind Na^+ effectively. The coordination number and geometry around the Li^+ is dictated by the ligand. Since two molecules of 1 provide four donor oxygen atoms in a Td geometry, there is no possibility for other geometrical arrangements. The linear amino and amido ethers 6 and 12 provide the square basis of the 5-fold SP coordination. Model structures of these ligands show that their participation in TBP geometry is unfavorable. All of the cyclic polyethers having four ethereal oxygens (15, 22, 38, 41) provide the square basis for 5-fold SP coordination.[179] The coordination number and geometry around the Li^+ is dictated by the ligand. In all of the pentacoordinated complexes, when the ligand provides four binding sites, the fifth site is occupied by either the anion[96-99,102,104,105,108,109] or solvent molecule.[100,103] In the Li^+ ionophores, both the linear and the cyclic compounds are relatively rigid, and it appears that the coronand lithium complexes in the crystal resemble their structure in solution. Additional

support for this assumption comes from the correlation between crystal structure studies[28-31,33,38-41,86] and enhancement of Li^+ transport through erythrocyte membranes[4] by Li^+–dicarboxylic acid complexes. Therefore, similar structure–selectivity relationships exist in both media.

VIII. Lithium Ions in Biological Systems

The effect of lithium on behavior has been established beyond doubt during the past several decades. Lithium ions have been effective in the treatment of human mania,[1,2] and sometimes even of human depression.[1] Some biochemical reactions influenced by Li^+, such as inhibition of carbohydrate transport,[180-181] influence on cyclic AMP metabolism,[182,183] the combined effect with dopamine and vanillyl mandelic acid,[184] inositol phospholipid metabolism,[141] and activity against DNA type viruses[5] have been reported. However, the physiological effect of Li^+ is still not well understood.[1,3,4,185,186]

Lithium ions form stable solution complexes with nucleosides,[187] uramildiacetic acid and its homologue,[188] ATP,[5] ADP,[5] pyrophosphate,[5] and the antibiotic lasalocid A.[189] Of particular interest is the interaction between Li^+ and carboxylic acids. Succinate, malonate, maleate, phthalate and oxalate enhance Li^+ transport through erythrocyte membranes.[4] Lithium ions form crystal complexes with most of the carboxylic acids that are involved in the citric acid cycle,[190] citrate,[36,37,115] malate,[35] succinate,[31] malonate,[29,30] acetate,[27] formate,[26] glycolate,[87] and NAD^+.[83,84] The formation of stable complexes with the building blocks of the citric acid cycle and NAD^+ on one side and the interaction with ADP and ATP on the other side suggests that Li^+ may interfere with the most essential biological metabolic cycles of living cells. The strong interaction with amides[50-53,118] and peptides[54-57,94,95] might explain the effectiveness of Li^+ as a denaturating agent of proteins.

Acknowledgments. The Cambridge Crystallographic Data Center, the American Chemical Society Microforms & Back Issues Office, and the International Union of Crystallography were invaluable sources of references for this article, but many colleagues also provided valuable information. We thank, in particular, W. Simon, D. J. Cram, K. N. Trueblood, J. Dale, P. Groth, P. Brown, K. Hiratani, G. Shoham, and F. Frolow. Appreciation is expressed to the State of Utah Centers of Excellence Program and the U.S. Department of Energy, Basic Energy Sciences (Grant No. DE-FG02-86ER-13463) for financial support of this work.

Abbreviations

ad	adenine
am	amine
AN	acetonitrile
A^{n-}	anion
B	benzo
12C3	12-crown-3
14C4	14-crown-4
ca	carboxylate
Cb	cube
α-CD	α-cyclodextrin
Dh	dodecahedron
DME	dimethoxyethane
Et	ethyl
et	ether
Et_2O	diethyl ether
HMPA	hexamethylphosphoramide
L	ligand
NAD	nicotinamide adenine dinucleoside
nit	nitrate
Oc	octahedron
OH	hydroxyl
PBP	pentagonal bipyramid
Ph	phenyl
phn	phenolate
pho	phosphine
pic	picrate
PO	phosphate
pyr	pyridine
S	solvent
SA	square antiprism
SP	square pyramid
Td	tetrahedron
TBP	trigonal bipyramid
t-Bu	*tert*-butyl
THF	tetrahydrofuran
TpClPB	tetra-(*p*-chlorophenyl) borate
TPP	triphenylphosphine oxide
Ur	urea
w	water

References

(1) *Lithium—Current Applications in Science, Medicine, and Technology*; Bach, R. O., Ed.; Wiley-Interscience: New York, NY, 1985.
(2) Tosteson, D. *Sci. Am.* **1981**, *244*, 164–175.
(3) Lazarus, J. H.; Collard, K. J. *Endocrine and Metabolic Effects of Lithium*; Plenum: New York, NY, 1986.
(4) Emrich, H. M.; Aldenhoff, J. B.; Lux, H. D., Eds. *Basic Mechanisms in the Action of Lithium*; Proceedings of a Symposium held at Schloss Ringberg, Bavaria, FRG, October 4–6, 1981; Elsevier Science Publishing Co., Inc.: New York, NY, 1982.
(5) Bach, R. O. *Med. Hypotheses* **1987**, *23*, 157–169.
(6) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353–451.
(7) Hubberstey, P. *Coord. Chem. Rev.* **1985**, *66*, 1–92.
(8) Hubberstey, P. *Coord. Chem. Rev.* **1986**, *75*, 1–99.
(9) Hubberstey, P. *Coord. Chem. Rev.* **1988**, *85*, 1–85.
(10) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624–1654.
(11) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277–297.
(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience Publishers, J. Wiley & Sons: New York, 1988; pp 10–18.
(13) Lehn, J. M. *Struct. Bond* **1973**, *16*, 1–70.
(14) Simon, W.; Morf, W. E.; Meier, P. C. *Struct. Bond* **1973**, *16*, 113–160.
(15) Shannon, R. D. *Acta Crystallogr. A.* **1976**, *32*, 751–767.
(16) Pauling L. *The Nature of the Chemical Bond*; 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(17) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581–587.
(18) Marcus, Y. *Israel J. Chem.* **1972**, *10*, 659–683.
(19) Ymên, I. *Acta Crystallogr. C.* **1984**, *40*, 33–34.
(20) Ymên, I. *Acta Crystallogr. C.* **1984**, *40*, 241–243.
(21) Oskarsson, A.; Ymên, I. *Acta Crystallogr. C.* **1984**, *40*, 30–32.
(22) Ymên, I. *Acta Crystallogr. C.* **1983**, *39*, 570–572.
(23) Krasne, S.; Eisenman, G. In *Membranes*; Eisenman, G., Ed.; Marcel Dekker: New York, 1973; Vol. 2.
(24) Olsher, U. *Biophys. J.* **1982**, *40*, 61–68.
(25) Truter, M. R. *Struct. Bond* **1973**, *16*, 71–112.
(26) Enders-Beumer, A.; Harkema, S. *Acta Crystallogr. B.* **1973**, *29*, 682–685.
(27) Galigné, J. L.; Mouvet, M.; Falgueirettes, J. *Acta Crystallogr. B.* **1970**, *26*, 368–372.
(28) Beagley, B.; Small, R. W. H. *Acta Crystallogr.* **1964**, *17*, 783–788.

(29) Soriano-Garcia, M.; Parthasarathy, R. *J. Chem. Soc., Perk. Trans. 2* **1978**, 668–670.
(30) Soriano-Garcia, M.; Rao, S. N. *Acta Crystallogr. C.* **1983**, *39*, 850–852.
(31) Klapper, V. H.; Küppers, H. *Acta Crystallogr. B.* **1973**, *29*, 21–26.
(32) He, X.; Craven, B. M. *Acta Crystallogr. C.* **1984**, *40*, 1157–1159.
(33) Town, W. G.; Small, R. W. H. *Acta Crystallogr. B.* **1973**, *29*, 1950–1955.
(34) Mattes, R.; Plescher, G. *Acta Crystallogr. B.* **1981**, *37*, 697–699.
(35) Van Havere, W.; Lenstra, A. T. H. *Acta Crystallogr. B.* **1980**, *36*, 1483–1486.
(36) Gabe, E. J.; Glusker, J. P.; Minkin, J. A.; Patterson, A. L. *Acta Crystallogr.* **1967**, *22*, 366–375.
(37) Rossi, M.; Rickles, L. F.; Glusker, J. P. *Acta Crystallogr. C.* **1983**, *39*, 987–990.
(38) Küppers, H. *Acta Crystallogr. B.* **1978**, *34*, 3763–3765.
(39) Gonschorek, W.; Küppers, H. *Acta Crystallogr. B.* **1975**, *31*, 1068–1072.
(40) Adiwidjaja, G.; Küppers, H. *Acta Crystallogr. B.* **1978**, *34*, 2003–2005.
(41) Küppers, H.; Kvick, Å.; Olovsson, I. *Acta Crystallogr. B.* **1981**, *37*, 1203–1207.
(42) Semmingsen, D. *Acta Chem. Scand. A.* **1976**, *30*, 808–812.
(43) Durant, F.; Piret, P.; Van Meerssche, M. *Acta Crystallogr.* **1967**, *23*, 780–788.
(44) Schumann, H.; Albrecht, I.; Pickardt, J.; Hahn, E. *J. Organomet. Chem.* **1984**, *276*, C5–C9.
(45) Jonas, K.; Pörschke, K. R.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 621–622.
(46) Teclé, B.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1982**, *1*, 875–877.
(47) Edwards, P. G.; Gellert, M. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072–2073.
(48) Durant, F.; Piret, P.; Van Meerssche, M. *Acta Crystallogr.* **1967**, *22*, 52–57.
(49) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc. Chem. Comm.* **1984**, 469–470.
(50) Haas, D. J. *Nature* **1964**, *201*, 64–65.
(51) Metzger, E.; Ammann, D.; Schefer, U.; Pretsch, E.; Simon, W. *Chimia* **1984**, *38*, 440–442.
(52) Verbist, J.; Meulemans, R.; Piret, P.; Van Meerssche, M. *Bull. Soc. Chim. Bel.* **1970**, *79*, 391–396.
(53) Suleimanov, K.; Sergienko, V. S.; Kipkalova, N.; Sulaimankolov, K. *Koord. Khim.* **1979**, *5*, 1732–1736; *Chem. Abstr.* **1980**, *92*, 50423k.
(54) Meulemans, R.; Piret, P.; Van Meerssche, M. *Bull. Soc. Chim. Bel.* **1971**, *80*, 73–81.
(55) Declercq, J. P.; Meulemans, R.; Piret, P.; Van Meerssche, M. *Acta Crystallogr. B.* **1971**, *27*, 539–544.
(56) Meulemans, R.; Piret, P.; Van Meerssche, M. *Acta Crystallogr. B.* **1971**, *27*, 1187–1190.
(57) Takahashi, N.; Tanaka, I.; Yamane, T.; Ashida, T. *Acta Crystallogr. B.* **1977**, *33*, 2132–2136.
(58) Lappert, M. F.; Slade, M. J.; Singh, A. *J. Am. Chem. Soc.* **1983**, *105*, 302–304.
(59) Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. H. *J. Chem. Soc. Dalton Trans.* **1983**, 1671–1673.
(60) Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086–2088.
(61) Bartlett, R. A.; Dias, H. V. R.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6921–6926.
(62) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271–3278.
(63) Becker, G.; Birkhahn, M.; Massa, W.; Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 741–742.
(64) Durant, F.; Gobillon, Y.; Piret, P.; Van Meerssche, M. *Bull. Soc. Chim. Bel.* **1966**, *75*, 52–69.
(65) Ginsburg, R. E.; Berg, J. M.; Rothrock, R. K.; Collman, J. P.; Hodgson, K. O.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 7218–7231.
(66) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769–1775.
(67) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Comm.* **1984**, 870–871.
(68) Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Comm.* **1972**, 1225–1226.
(69) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Comm.* **1978**, 140–142.
(70) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Comm.* **1983**, 827–828.
(71) Dale, J.; Fredriksen, S. B. *Pure Appl. Chem.* **1989**, *61*, 1587–1592.
(72) Dale, J.; Eggestad, J.; Fredriksen, S. B.; Groth, P. *J. Chem. Soc., Chem. Comm.* **1987**, 1391–1393.
(73) Bhagwat, V. W.; Manohar, H.; Poonia, N. S. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 373–375.
(74) Groth, P. *Acta Chem. Scand. A.* **1982**, *36*, 109–115.
(75) Aarts, V. L. M. J.; van Staveren, C. J.; Grootenhius, P. D. J.; van Eerden, J.; Kruise, L.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5035–5036.
(76) Amstutz, R.; Dunitz, J. D.; Laube, T.; Schweizer, W. B.; Seebach, D. *Chem. Ber.* **1986**, *119*, 434–443.
(77) Schröder, V. F. A.; Weber, H. P. *Acta Crystallogr. B.* **1975**, *31*, 1745–1750.
(78) (a) Groth, P. *Acta Chem. Scand. A.* **1983**, *37*, 71–74. (b) Klebe, G.; Böhn, K. H.; Marsch, M.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 78–79.
(79) Yasin, Y. M. G.; Hodder, O. J. R.; Powell, H. M. *Chem. Comm.* **1966**, 705–706.
(80) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Comm.* **1984**, 974–975.
(81) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Comm.* **1984**, 226–227.
(82) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Comm.* **1984**, 79–80.
(83) Reddy, B. S.; Saenger, W.; Mühlegger, K.; Weimann, G. *J. Am. Chem. Soc.* **1981**, *103*, 907–914.
(84) Saenger, W.; Reddy, B. S.; Mühlegger, K.; Weimann, G. *Nature* **1977**, *267*, 225–229.
(85) Powell, J.; Ng, K. S.; Ng, W. W.; Nyburg, S. C. *J. Organomet. Chem.* **1983**, *243*, C1–C4.
(86) Thomas, J. O. *Acta Crystallogr. B.* **1972**, *28*, 2037–2045.
(87) Gabe, E. J.; Taylor, M. R. *Acta Crystallogr.* **1966**, *21*, 418–421.
(88) Hinazumi, H.; Mitsui, T. *Acta Crystallogr. B.* **1972**, *28*, 3299–3305.
(89) Kay, M. I. *Ferroelectrics* **1978**, *19*, 159–164.
(90) Herbertsson, H. *Acta Crystallogr. B.* **1976**, *32*, 2381–2384.
(91) Hall, S. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1983**, *22*, 4070–4073.
(92) Bencini, A.; Bianchi, A.; Borselli, A.; Ciampolini, M.; Micheloni, M.; Nardi, N.; Paoli, P.; Valtancoli, B.; Chimichi, S.; Dapporto, P. *J. Chem. Soc., Chem. Comm.* **1990**, 174–175.
(93) Bencini, A.; Bianchi, A.; Borselli, A.; Ciampolini, M.; García-España, E.; Dapporto, P.; Micheloni, M.; Paoli, P.; Ramírez, J. A.; Valtancoli, B. *Inorg. Chem.* **1989**, *28*, 4279–4284.
(94) Karle, I. L. *J. Am. Chem. Soc.* **1974**, *96*, 4000–4006.
(95) Karle, I. L.; Karle, J.; Wieland, T.; Burgermeister, W.; Faulstich, H.; Witkop, B. *Proc. Nat. Acad. Sci. U.S.A.* **1973**, *70*, 1836–1840.
(96) Groth, P. *Acta Chem. Scand. A.* **1981**, *35*, 463–465.
(97) Power, P. P.; Xiaojie, X. *J. Chem. Soc., Chem. Comm.* **1984**, 358–359.
(98) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Am. Chem. Soc.* **1983**, *105*, 1247–1252.
(99) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Chem. Soc., Chem. Comm.* **1983**, 208–209.
(100) Olsher, U.; Shoham, G. Manuscript in preparation.
(101) Olsher, U.; Shoham, G. Manuscript in preparation.
(102) Olsher, U.; Dalley, N. K.; Bartsch, R. A. Manuscript in preparation.
(103) Shoham, G.; Christianson, D. W.; Bartsch, R. A.; Heo, G. S.; Olsher, U.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 1280–1285.
(104) Groth, P. *Acta Chem. Scand. A.* **1981**, *35*, 460–462.
(105) Van Beylen, M.; Roland, B.; King, G. S. D.; Aerts, J. *J. Chem. Res., Part S* **1985**, 388–389, *J. Chem. Res., Part M* **1985**, 4201–4289.
(106) Doughty, S. M.; Stoddart, J. F.; Colquhoun, H. M.; Slawin, A. M. Z.; Williams, D. J. *Polyhedron* **1985**, *4*, 567–575.
(107) Czugler, M.; Weber, E. *J. Chem. Soc., Chem. Comm.* **1981**, 472–473.
(108) Ueno, K.; Hiratani, K.; Taguchi, K.; Okado, T.; Sugihara, H. *Chem. Lett.* **1987**, 949–952.
(109) Metzger, E.; Aeschimann, R.; Egli, M.; Suter, G.; Dohner, R.; Ammann, D.; Dobler, M.; Simon, W. *Helv. Chim. Acta* **1986**, *69*, 1821–1828.
(110) Noltemeyer, M.; Saenger, W. *J. Am. Chem. Soc.* **1980**, *102*, 2710–2722.
(111) Cram, D. J.; Kaneda, T.; Helgeson, R. C.; Brown, S. D.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 3645–3657. Cram, D. J.; Lein, G. M. *J. Am. Chem. Soc.* **1985**, *107*, 3657–3668.
(112) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 6228–6232.
(113) Powell, J.; Nyburg, S. C.; Smith, S. J. *Inorg. Chim. Acta* **1983**, *76*, L75–L77.
(114) Olsher, U.; Frolow, F. Manuscript in preparation.
(115) Glusker, J. P.; Van Der Helm, D.; Love, W. E.; Dornberg, M. L.; Minkin, J. A.; Johnson, C. K.; Patterson, A. L. *Acta Crystallogr.* **1965**, *19*, 561–572.
(116) Gillier-Pandraud, H.; Jamet-Delcroix, S. *Acta Crystallogr. B.* **1971**, *27*, 2476–2479.
(117) Constable, E. C.; Chung, L.-Y.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Comm.* **1986**, 1719–1720.
(118) Gentile, P. S.; White, J. G.; Cavalluzzo, D. D. *Inorg. Chim. Acta* **1976**, *20*, 37–42.

(119) Hooz, J.; Akiyama, S.; Cedar, F. S.; Bennett, M. J.; Tuggle, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 274–276.
(120) Olsher, U.; Shoham, G. Manuscript in preparation.
(121) Holt, E. M.; Malpass, G. D., Jr.; Ghirardelli, R. G.; Palmer, R. A.; Rubin, B. *Acta Crystallogr. C.* **1984**, *40*, 394–396.
(122) Holt, E. M.; Malpass, G. D., Jr.; Ghirardelli, R. G.; Palmer, R. A.; Rubin, B. *Acta Crystallogr. C.* **1984**, *40*, 396–398.
(123) Stark, P. C.; Huff, M.; Babaian, E. A.; Barden, L. M.; Hrncir, D. C.; Bott, S. G.; Atwood, J. L. *J. Inclusion Phenom.* **1987**, *5*, 683–688.
(124) Alfheim, T.; Dale, J.; Groth, P.; Krautwurst, K. D. *J. Chem. Soc., Chem. Comm.* **1984**, 1502–1504.
(125) Moras, D.; Weiss, R. *Acta Crystallogr. B.* **1973**, *29*, 400–403.
(126) Walba, D. M.; Hermsmeier, M.; Haltiwanger, R. C.; Noordik, J. H. *J. Org. Chem.* **1986**, *51*, 245–247.
(127) Hermansson, K.; Thomas, J. O.; Olovsson, I. *Acta Crystallogr. B.* **1977**, *33*, 2857–2861.
(128) Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1984**, *106*, 819–821.
(129) Power, P. P. *Acc. Chem. Res.* **1988**, *21*, 147–153.
(130) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174–2175.
(131) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817–6819.
(132) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 6509–6510.
(133) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 4235–4236.
(134) Balasubramanian, D.; Goel, A.; Rao, C. N. R. *Chem. Phys. Lett.* **1972**, *17*, 482–485.
(135) Balasubramanian, D.; Shaikh, R. *Biopolymers* **1973**, *12*, 1639–1650.
(136) Harrington, W. F.; Sela, M. *Biochim. Biophys. Acta* **1958**, *27*, 24–41.
(137) Morf, W. E.; Simon, W. *Helv. Chim. Acta* **1971**, *54*, 794–810.
(138) Kitazawa, S.; Kimura, K.; Yano, H.; Shono, T. *J. Am. Chem. Soc.* **1984**, *106*, 6978–6983.
(139) Kimura, K.; Yano, H.; Kitazawa, S.; Shono, T. *J. Chem. Soc. Perk. Trans. 2* **1986**, 1945–1951.
(140) Kimura, K.; Oishi, H.; Miura, T.; Shono, T. *Anal. Chem.* **1987**, *59*, 2331–2334.
(141) Rawis, R. L. *Chem. Eng. News* **1987**, *65* (Dec 21), 26–39.
(142) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, UK, 1968; Vol. III, p 258.
(143) *Lithium: Its Role in Psychiatric Research and Treatment*; Gershon, S., Shopsin, B., Eds.; Plenum Press: New York, 1973.
(144) Eisenman, G. *Glass Electrode for Hydrogen and Other Cations*; Marcel Dekker: New York, 1967.
(145) Christensen, J. J.; Lamb, J. D.; Izatt, S. R.; Starr, S. E.; Weed, G. C.; Astin, M. S.; Stitt, B. D.; Izatt, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 3219–3220.
(146) Takeda, Y. *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1984; pp 1–38.
(147) Marcus, Y. *Ion Solvation*; J. Wiley & Sons: New York, 1985.
(148) Blasius, E.; Janzen, K. P. *Pure Appl. Chem.* **1982**, *54*, 2115–2128.
(149) Blasius, E.; Janzen, K. P. *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1981; pp 163–189.
(150) Basolo, F. *Coordin. Chem. Rev.* **1968**, *3*, 213–223.
(151) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth & Co. Ltd.: Washington, DC, 1959.
(152) Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience: New York, 1968.
(153) Persson, I. *Pure Appl. Chem.* **1986**, *58*, 1153–1161.
(154) Güggi, M.; Fiedler, U.; Pretsch, E.; Simon, W. *Anal. Lett.* **1975**, *8*, 857–866.
(155) Meier, P. C.; Morf, W. E.; Läubli, M.; Simon, W. *Anal. Chim. Acta* **1984**, *156*, 1–8.
(156) Olsher, U. *J. Am. Chem. Soc.* **1982**, *104*, 4006–4007.
(157) Eigen, M. *Pure Appl. Chem.* **1963**, *6*, 97–115.
(158) Halliwell, H. F.; Nyburg, S. C. *Trans. Farad. Soc.* **1963**, *59*, 1126–1140.
(159) Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513–522.
(160) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271–339.
(161) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1384–1389.
(162) Kirsch, N. N. L.; Funck, R. J. J.; Pretsch, E.; Simon, W. *Helv. Chim. Acta* **1977**, *60*, 2326–2333.
(163) Metzger, E.; Dohner, R.; Simon, W.; Vonderschmitt, D. J.; Gautschi, K. *Anal. Chem.* **1987**, *59*, 1600–1603.
(164) Hiratani, K. *J. Chem. Soc., Chem. Comm.* **1987**, 960–961.
(165) Margalit, R.; Shanzer, A. *Biochim. Biophys. Acta* **1981**, *649*, 441–448.
(166) Attiyat, A. S.; Ibrahim, Y. A.; Kadry, A. M.; Xie, R. Y.; Christian, G. D. *Fresenius' Z. Anal. Chem.* **1987**, *329*, 12–17.
(167) Hruska, Z.; Petranek, J. *Polymer Bull.* **1987**, *17*, 103–106.
(168) Hiratani, K. *Analyst* **1988**, *113*, 1065–1068.
(169) Gadzekpo, V. P. Y.; Christian, G. D. *Anal. Lett.* **1983**, *16*, 1371–1380.
(170) Aalmo, K. M.; Krane, J. *Acta Chem. Scand. A.* **1982**, *36*, 227–234.
(171) Kimura, K.; Sakamoto, H.; Kitazawa, S.; Shono, T. *J. Chem. Soc., Chem. Comm.* **1985**, 669–670.
(172) Katayama, Y.; Fukuda, R.; Hiwatari, K.; Takagi, M. *Asahi Garasu Kogyo Gijutsu Shoreikai* **1986**, *48*, 193–199; *Chem. Abst.* **1987**, *107*, 32225w.
(173) Kataky, R.; Nicholson, P. E.; Parker, D. *Tetrahedron Lett.* **1989**, *30*, 4559–4562.
(174) Kataky, R.; Nicholson, P. E.; Parker, D. *J. Chem. Soc. Perk. Trans. 2* **1990**, 321–327.
(175) *Selectophore, Ionophores for Ion-Selective Electrodes*; Fluka Chemie: Neu-Ulm, Switzerland, 1988.
(176) Bartsch, R. A.; Czech, B. P.; Kang, S. I.; Stewart, L. E.; Walkowiak, W.; Charewicz, W. A.; Heo, G. S.; Son, B. *J. Am. Chem. Soc.* **1985**, *107*, 4997–4998.
(177) Olsher, U.; Jagur-Grodzinski, J. *J. Chem. Soc. Dalton Trans.* **1981**, 501–505.
(178) Tsukube, H.; Adachi, H.; Morosawa, S. *J. Chem. Soc. Perk. Trans. 1* **1989**, 1537–1538.
(179) Yatsimirskii, K. B.; Kabachnik, M. I.; Sinyavskaya, E. I.; Medved', T. Y.; Polikarpov, Y. M.; Shcherbakov, B. K. *Russian J. Inorg. Chem.* **1984**, *29*, 510–512, Yatsimirskii, K. B.; Sinyavskaya, E. I.; Tsymbal, L. V.; Medved', T. Y.; Shcherbakov, B. K.; Polikarpov, Y. M.; Kabachnik, M. I. *Russ. J. Inorg. Chem.* **1984**, *29*, 512–516.
(180) Speziali, G. A. G.; Van Wijk, R. *Biochim. Biophys. Acta* **1971**, *235*, 466–472.
(181) Bosackovâ, J.; Crane, R. K. *Biochim. Biophys. Acta* **1965**, *102*, 423–435.
(182) Dousa, T.; Hechter, O. *Life Sci.* **1970**, *9*, 765–770.
(183) Birch, N. J. *Nature* **1976**, *264*, 681.
(184) Messiha, F. S.; Agallianos, D.; Clower, C. *Nature* **1970**, *225*, 868.
(185) Pearson, I. B.; Jenner, F. A. *Nature* **1971**, *232*, 532–533.
(186) Kertesz, D.; De Körösy, F. *Separatum Experientia* **1972**, *28*, 1338.
(187) Plaush, A. C.; Sharp, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 7973–7980.
(188) Irving, H.; Da Silva, J. J. R. F. *J. Chem. Soc.* **1963**, 458–465.
(189) Shastri, B. P.; Easwaran, K. R. K. *Int. J. Biol. Macromol.* **1984**, *6*, 219–223.
(190) Stryer, L. *Biochemistry*; W. H. Freeman & Co.: New York, 1988; pp 373–396.