The Synthesis and Ion Binding of Synthetic Multidentate Macrocyclic Compounds

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Contents

I. Introduction

Although metal complexes of naturally occurring macrocyclic ligands have been known for over 50 years, *e.g.*, porphyrin and corrin ring derivatives and phthalocyanines, it is only during the past decade that a large number of synthetic macrocyclic compounds capable of binding cations or anions have been prepared and investigated. Many of these synthetic macrocyclic polyethers, polyamines, polythioethers, and other related molecules have been shown to possess very interesting and unusual ion binding properties. These novel macrocycles typically contain central hydrophilic cavities ringed with either electronegative or electropositive binding atoms and exterior flexible frameworks exhibiting hydrophobic behavior. They show a pronounced ability to bind a wide variety of cations or anions and in many cases to undergo marked conformational changes during binding. Their hydrophobic exteriors allow them to solubilize ionic substances in nonaqueous solvents and in membrane media. Particularly interesting is the strong affinity shown by the polyethers for alkali and alkaline earth metal ions and their selective binding of certain of these cations resulting in their use as models for carrier molecules in the study of active ion transport phenomena in biological systems. Also the possibility of using synthetic polyamines as models for more intricate biological macrocyclic systems has been recognized and presents intriguing possibilities.

This review deals with the synthesis of multidentate macrocyclic compounds and the chemistry of the reactions of these compounds with cations and anions. Only those macrocyclic compounds which meet the following criteria are included in the review: (1) synthetic in origin, (2) contain multiple donor atoms, and (3) exhibit ion binding properties. Classes of compounds not included are macrocycles of biological origin such as antibiotics (valinomycin, actins, etc.), ferrocenes, and porphyrins. Representative of the macrocyclic compounds reviewed here are those shown in Figure 1. The compounds shown in Figure 1 differ in type and number of ion binding sites and thus generally exhibit quite different affinities for a given ion.

Macrocyclic molecules have been shown to bind with a wide variety of cations including ammonium ion and in a few specific cases with anions. The factors affecting the formation and thermodynamic stabilities of these ion–macrocycle complexes include (1) the type(s) of binding sites in the ring, (2) the number of binding sites in the ring, (3) the relative sizes of the ion and the macrocyclic cavity, (4) the physical placement of the binding sites, (5) steric hindrance in the ring, (6) the solvent and extent of solvation of the ion and the binding sites, and (7) the electrical charge of the ion. Thus, there exist unusual opportunities for the synthesis of macrocyclic molecules which exhibit a high degree of selectivity in metal binding. For example, certain cyclic polyethers not only strongly bind particular alkali and alkaline earth metals but selectively bind one or more of these ions in preference to the others in each series.

This review covers the literature through December 1972. Section II contains information regarding the method used in this review for classifying the macrocycles according to donor atom together with a table containing both the structures of all macrocycles reviewed and a listing of those ions which have been shown to interact with the respective macrocycles. Section III reviews major methods of synthesizing the various classes of macrocycles. Section IV deals with the ion binding properties of macrocycles. A table containing the available thermodynamic data (log K, ΔH, ΔS, and ΔC_p) for macrocycle ion binding is included in section V. Sections VI and VII contain pertinent information concerning structure data and kinetic data involving macrocyclic complexes, respectively.

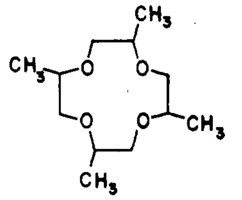
Although no general review article has been published covering all the macrocycles included here, several articles covering various aspects of the chemistry and ion binding of macrocyclic ligands have recently appeared. Christensen and coworkers[1] have discussed for several classes of macrocycles their unique ion binding properties and their present and future areas of application. Pedersen and Frensdorff,[2] Truter and Pedersen,[3] and Izatt and coworkers[4] have discussed the chemistry of oxygen-containing macrocycles, the structures of various macrocyclic complexes, and the thermodynamics of cation–macrocyclic complexation reactions, respectively. Curtis,[5] Busch,[6,7] and Lindoy and Busch[8] have described in detail the synthesis and properties of nitrogen-containing macrocycles and their complexes, mainly with the first row transition series metal ions.

II. List of Compounds and Nomenclature

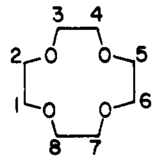
A. List of Compounds

The macrocyclic compounds covered in this review are classified and arranged in the text and tables according to the type of donor atoms available for ion binding. Macrocycles containing oxygen donor atoms are listed first followed in order by macrocycles containing nitrogen donor atoms, sulfur donor atoms, and mixed donor atoms. The mixed donor atoms are presented in the following order: nitrogen–oxygen, sulfur–nitrogen, sulfur–oxygen, nitrogen–sulfur–oxygen, and others. A total of 221 different macrocycles are included in the review.

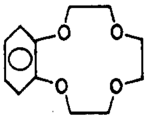
Table I contains a compilation of ion binding synthetic multidentate macrocyclic ligands together with the ions bound by each ligand. An ion was included in Table I whenever the data indicated that either the ion reacted with the free macrocycle to form a complex or that the ion was incorporated into the macrocycle during synthesis of the macrocycle. Each parent ligand structure as determined from the ring containing the donor atoms is represented by a structural formula. Specific ligands are indicated by the chemical groups attached to the basic structure and are identified by a number and letter. Thus the structure



is found in the table under the parent structure

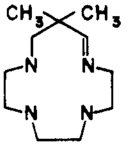


with the methyl groups indicated by the listing 2-methyl; 4-methyl; 6-methyl; and 8-methyl and is identified by number **1c**. Benzene and other ring structures attached to the basic structure are indicated by naming both the position or positions of attachment and the group attached. Thus **1a** has the benzo group indicated by the designation 1,2-benzo.



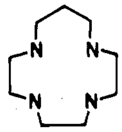
1a

Double bonds in a structure are designated by the symbol d. Two or more groups attached to the basic structure at the same place are indicated by naming each group separately. For example, the structure **17a**

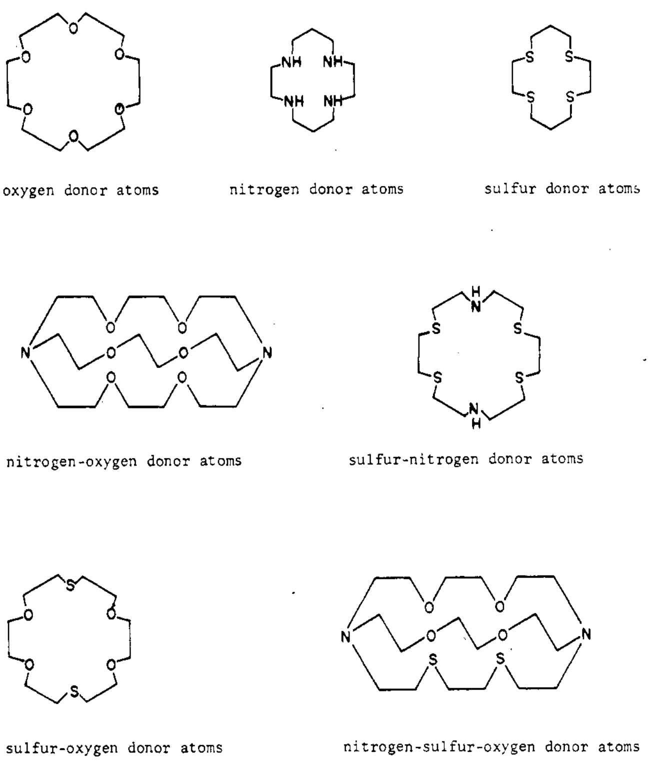


17a

is found in Table I under the parent structure



and is designated by the following: d_4; 2-methyl, methyl. Within each main group of macrocyclic compounds in Table I (*e.g.*, macrocycles containing oxygen donor groups), the ligands are listed in order of increasing number of donor groups in the basic structure ring. The metal ion order is that given in ref 121. Charges are given on the metal ions only where multiple valence states are common.



oxygen donor atoms
nitrogen donor atoms
sulfur donor atoms
nitrogen-oxygen donor atoms
sulfur-nitrogen donor atoms
sulfur-oxygen donor atoms
nitrogen-sulfur-oxygen donor atoms

Figure 1. Representative synthetic macrocyclic compounds.

B. Nomenclature

Conventional IUPAC rules for naming organic compounds result in the assignment of unequivocal, but extremely complicated names to macrocyclic compounds.[2,122] The number-letter designation given in Table I will therefore be used throughout this review for identification of specific compounds.

However, it should be noted that for the cyclic polyethers and related macrocycles a system of *ad hoc* names has been devised solely for their ready identification[122] and is used extensively. In this scheme, the use of cumbersome nomenclature is avoided by assigning common names to the polyethers based on the use of the term "crown" to represent the central ring. Several examples illustrating how names are derived from the side ring substituents or replacement donor atoms (if any), the total number of atoms in the polyether ring, the "crown," and the total number of donor atoms in the main ring are given in Table II. It should be kept in mind that these names are simple but not always unambiguous as is readily apparent in the case of the macrocycles *asym*-dibenzo-22-crown-6 and dithia-15-crown-5 given in Table II. The extension of this naming procedure beyond cyclic polyethers and certain mixed donor atom macrocycles containing oxygen donors is probably not desirable.

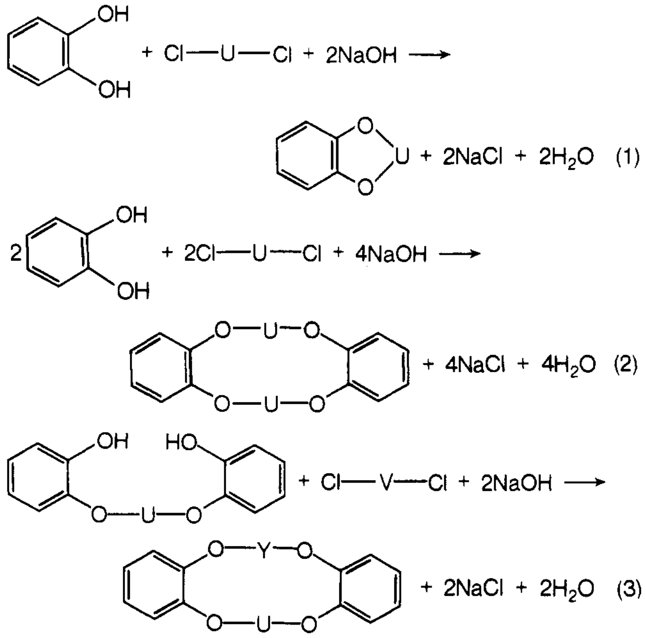
III. Synthesis of Free Macrocycles

Table III is a compilation of references reporting the synthesis of synthetic multidentate macrocyclic ligands. The table follows the order given in Table I in listing the ligands according to the types and number of donor atoms contained in the ring. Some of the ligands in Table III have not been shown to bind metal ions but have been included to give a more complete compilation of synthetic methods. Further information concerning the synthesis of specific macrocycles that bind metal ions can be found in Table I in those references in which an A appears in the "Other information column." Representative synthetic methods for the various classes of macrocycles are given below.

A. Cyclic Polyethers

The first cyclic polyether compound, **6g** (dibenzo-18-crown-6), was formed as an unexpected by-product during a preparation of bis[2-(*o*-hydroxyphenoxy)ethyl] ether from bis(2-chloroethyl) ether and the sodium salt of 2-(*o*-hydroxyphenoxy)tetrahydropyran which contained a small quantity of catechol.[122,135,136] Subsequently more than 60 macrocyclic polyethers have been synthesized.

The aromatic crown polyethers are prepared by straightforward condensation methods[2,122,135,136] exemplified by the stoichiometric equations 1–3, in which U and V represent divalent organic groups, generally of the type $-(CH_2CH_2O)_nCH_2CH_2-$. The condensations are typically run in 2-butanol under reflux for 12 to 24 hr. Method 1 can be used, for example, to prepare **3a**, benzo-15-crown-5 (n = 3, yield 62%); **1a**, benzo-12-crown-4 (n = 2, yield 4%); and **6b**, benzo-18-crown-6 (n = 4, yield 60%). Method 2 gives, for instance, **6g**, dibenzo-18-crown-6 (n = 1, yield 45%); **10b**, dibenzo-24-crown-8 (n = 2, yield 38%); or **11a**, dibenzo-30-crown-10 (n = 3, yield over 6%). The starting material for method 3 is made by attaching a base-stable protecting group, *e.g.*, benzyl or tetrahydropyranyl, to one of the hydroxyls of catechol, condensing 2 mol of this with Cl-U-Cl, and then removing the protecting groups. Method 3 is most convenient for synthesis of uneven-numbered polyether rings, *e.g.*, **8a**, dibenzo-21-crown-7.



Aromatic macrocyclic polyethers containing neutral substituents, such as alkyl or chloro, may be prepared by using suitably substituted aromatic vicinal diols.[2] Of course, the substituents must be inert toward sodium hydroxide and the open-chain dichloro polyether.

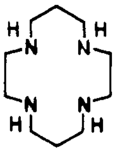
Saturated polyethers are prepared from the corresponding aromatic ones by catalytic hydrogenation, typically in 2-butanol at 100° and 7–10 atm over a ruthenium catalyst.[135] Recovery of the product is best done by column chromatography on alumina, and the yields are almost quantitative.

B. Cyclic Polyamines

1. Monocyclic

A large variety of cyclic polyamines having three to six functional groups in the ring have been synthesized. However, the majority have four functional groups which are more or less evenly spaced in a ring containing between 12 and 16 atoms. The macrocycles can be synthesized either "free" or bound to a given metal ion.

The preparation of the free macrocycle has certain advantages in many cases. Firstly, purification of the organic product may be more readily accomplished than purification of its complexes, and, secondly, the characterization by such physical techniques as gas-liquid chromatography, mass spectrometry, infrared spectroscopy, and nuclear magnetic resonance spectroscopy also tends to be less involved for the metal-free macrocycle. Further, the various spectra obtained for the free ligand are usually of great assistance in the interpretation of the corresponding metal-complex spectra. However, preparation of the free macrocycle also has the decided disadvantage in that the method usually gives only low yields of the desired products. An example of a metal free synthesis is the preparation of cyclic tetradentate secondary amine, **18a**, 1,4,8,11-tetraazacyclotetradecane (cyclam), by refluxing 1,3-bis(2′-aminoethylamino)propane with 1,3-dibromopropane in ethanol for 3 hr, treating the solution with alcoholic potassium hydroxide, and then refluxing for a further 1.5 hr.[137-139] It is then possible to isolate the free ligand by codistillation from the reaction mass with additional unreacted 1,3-bis(2′-aminoethylamino)propane. It is fortuitous that **18a** is only slightly soluble in the entraining linear tetraamine and separates from the distillate as a white crystalline solid. The yield varies from 0 to 3%. A second route to **18a** which provides a more deliberate but far more tedious synthesis of the compound has been published.[140]



18a

In general, cyclic polyamines are formed by one of a number of different kinds of condensation reactions in which a transition metal ion functions as a template, holding the condensing molecules in a suitable orientation to facilitate the formation of products.[5,6,8] This so-called coordination template effect figures heavily in the majority of the syntheses of macrocyclic ligands containing nitrogen binding atoms. An inherent disadvantage of most *in situ* syntheses is that a small excess of one or another of the organic reactants (which are often chelating agents themselves) may lead to contamination of the required product with acyclic impurities. It is also true that in some cases there remains an element of mystery con-

TABLE I. Compilation of Ion Binding Synthetic Multidentate Macrocyclic Ligands and of Ions Bound by Each Ligand

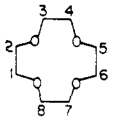
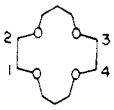
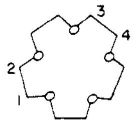
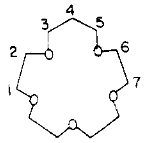
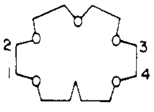
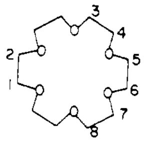
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
	1,2-Benzo	**1a**		A	122
	1,2-Benzo; 5,6-benzo	**1b**		A	122
	2-Methyl; 4-methyl; 6-methyl; 8-methyl	**1c**	Na, K		9
			Na		180
	1,2-Cyclohexyl	**1d**		A	122
			Li, Na, K, Rb		177
	1,2-Benzo; 3,4-benzo	**2a**	Li	A	122
			Na		165
	1,2-Butylbenzo; 3,4-butylbenzo	**2b**		A	122
				B	160
			Li, Na, K, Rb		177
	1,2-Cyclohexyl; 3,4-cyclohexyl	**2c**		A	122
			Na, K		180
	1,2-Butylcyclohexyl; 3,4-butylcyclohexyl	**2d**		A	122
			Li, Na, K	B	160
	1,2-Benzo	**3a**	Na	A	122
			Na, K, NH_4, Cs, Ba, Ag^+		163
			Na, K		10
			K, Rb		11
			Li, Na, K, Rb, Cs	A	12
			Na		203
			Na		169
	1,2-Butylbenzo	**3b**	Li, Na, K	A	122[c]
	1,2-Naphtho	**3c**		A	122
	1,2-Cyclohexyl	**3d**	Na	A	122
			Li, Na, K, Cs		180
			Na, K		179[d]
	1,2-Butylcyclohexyl	**3e**	K	A	122
			Li, Na, K, Cs		160
	1,2-Decalyl	**3f**		A	122
	1,2-Benzo; 3,4-benzo	**3g**		A	122
			K		163
	1,2-Vinylbenzo (polymer)	**3h**		A	13
			Li, Na, K, Rb, Cs	A	12
	1,2-Cyclohexyl; 3,4-cyclohexyl	**3i**		A	135
	1,2-4-Methylbenzo	**3j**	Na, K		9
			Na, K	A	14
	1,2-Benzo; 6,7-benzo	**4a**	Na		165
				A	122
	1,2-Cyclohexyl; 6,7-cyclohexyl	**4b**		A	135
	3,4,5-Naphthyl	**4c**	Na, K, Sr, Ba, Ag^+	A	135
	1,2-Benzo; 3,4-benzo	**5a**		A	122
			Li, Na, K, Rb		177
		**6a**		A, B	122
			Na, K, Cs, NH_4, Ag^+		180
	1,2-Benzo	**6b**	K	A	122
			K, Cs		163
			Li, Na, K, Rb, Cs		12
	1,2-Cyclohexyl	**6c**	NH_4, Ba	A	122
			Li, Na, K, Cs, NH_4, Ba, Ag^+		180
	1,2-4-Methylbenzo	**6d**	Na, K		14
	1,2-*tert*-Butylbenzo	**6e**	K, Sr	A	122
	1,2-*tert*-Butylcyclohexyl	**6f**	K	A	122
	1,2-Benzo; 5,6-benzo	**6g**	Na		169
			Li, Na, K, Rb, Cs, NH_4, RNH_3, Ag^+, Mg, Ca, Ba, Cd, Hg^{2+}, Pb^{2+}	A, B	122
			Na, K, Cs		180
			K		10
			Rb		15
			Rb		166
			Na, K		200

TABLE I (continued)

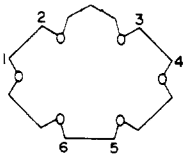
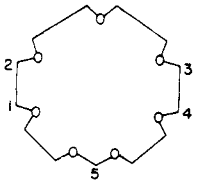
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
		6g	Li, Na, K, Rb, Cs, NH_4, RNH_3, Ca, Sr^{2+}, Ba, Cd, Hg^{2+}, Pb^{2+}, La^{3+}, Ce^{3+}, Tl^+	A	136
			Na	C	16
			Na, K		17
			K		18
			Na, K, Rb, Cs, Tl^+		19
			Na		204
			K, Rb, Cs		163
			Li, Na, K, Cs		160
			Na, K		177
			K, Rb		11
	1,2-Cyclohexyl; 5,6-cyclohexyl	**6h**	K, RNH_3	C	20
			K, Cs	B	21
			K, Rb, Cs		162
			Li, Na, K, Cs	B	165
			Na, K, Cs, NH_4	A	122
			Te^{3+}, V^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+}	B	167
			K, Rb, Cs		163
			Li, Na, K, Cs, NH_4, Ag^+		180
			Li, Na, K, Rb, Cs		178
			Na, K		177
			Na, K, Rb, Cs		174
			Li, Na, K, Rb, Cs, NH_4, RNH_3, Ca, Ba, Ag^+, Cd, Hg^+, Sr, La^{3+}, Hg^2,$^+$ Pb^{2+}, Tl^+, Ce^{3+}		136
			Ba		202
			Na, K, Cs		200
			Li, Na, K, Cs, Rb, NH_4		22
			Na, K		18
			Na, K, Cs		17
			Na, K, Rb, Cs, Tl^+		19
			Na, K		14
			Na, K		179
			K, Rb, Cs, NH_4, Sr, Ba, Ag^+		161
			Na, K, Rb, Cs, NH_4, Sr, Ba, Ag^+		10
			Li, Na, K, Cs		160
	1,2-Benzo; 5,6-cyclohexyl	**6i**		A	135
	1,2-Benzo; 3,4-benzo	**6j**		A	122
	1,2-Methylbenzo; 5,6-methylbenzo	**6k**		B	165
			Ba		164
			Na, K		9
	1,2-Butylbenzo; 5,6-butylbenzo	**6l**	K	A	122
			Cs		163
	1,2-*tert*-Butylcyclohexyl; 5,6-*tert*-butylcyclohexyl	**6m**		A	122
			Li, Na, K, Cs, NH_4		180
			Li, Na, K, Rb, NH_4, Ca		23
	1,2-Benzo; 3,4-benzo; 7,8-benzo	**6n**		A	122
			Li, Na, K, Rb		177
	1,2–2,3-Naphtho	**6o**		A	122
	1,2–2,3-Naphtho; 5,6–2,3-naphtho	**6p**		A	122
	1,2-Vinylbenzo (polymer)	**6q**	Li, Na, K, Rb, Cs		12
	1,2-Benzo; 3,4-benzo	**7a**	K	A	122
	1,2-Benzo; 3,4-benzo; 5,6-benzo	**7b**		A	122
	1,2-Benzo; 3,4-benzo	**8a**	K, Cs	A	135
	1,2-Benzo; 3,4-benzo; 5-pentamethylene	**8b**		A	135
	1,2-Benzo; 3,4-benzo; 5-oxygen	**8c**	Na, K, Cs, NH_4	A	135

TABLE I (continued)

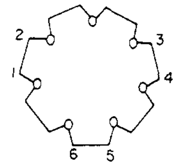
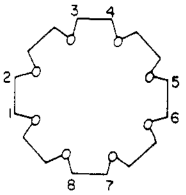
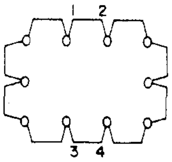
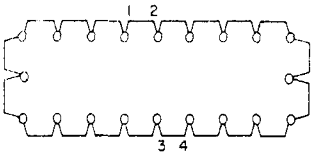
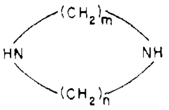
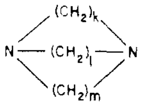
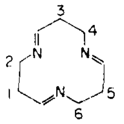
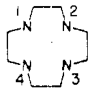
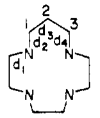
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
		**9a**	K, Cs		180
	1,2-Benzo; 3,4-benzo	**9b**		A	122[c]
			Cs		163
			Na, K, Cs		180
	1,2-Cyclohexyl; 3,4-cyclohexyl	**9c**		A	122
			Li, Na, K, Cs		160
			Cs		180
			Li, Na, K, Rb		177
	1,2-Benzo; 3,4-benzo; 5,6-benzo	**9d**		A	122
		**10a**	K, Cs		180
	1,2-Benzo; 5,6-benzo	**10b**	K	A	122[c]
			Cs		163
			K, Cs		180
			K		168
	1,2-Cyclohexyl; 5,6-cyclohexyl	**10c**		A	122
			Li, Na, K, Cs		160
			Cs		180
			Na, K		179
			Li, Na, K, Rb		177
	1,2-Benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**10d**		A	122
	1,2–2,3-Naphtho; 5,6–2,3-naphtho	**10e**		A	122
	1,2-Benzo; 3,4-benzo	**11a**	K	A	122
			Na, K		180
			K, Rb		11
			Na, K, Rb, Cs, NH_4, Tl^+	C	24
			K		205
			K		169
	1,2-Cyclohexyl; 3,4-cyclohexyl	**11b**		A	122
			Li, Na, K, Rb		177
	1,2-Benzo; 3,4-benzo	**12a**		A	122
			K		180
	1,2-Cyclohexyl; 3,4-cyclohexyl	**12b**		A	122
	(*n*,*m*) = (4,6), (5,6), (6,6), (7,6), (8,6), (9,6), (10,6), (13,6), (4,4), (5,4), (6,4), (7,4), (8,4), (9,4), (10,4), (6,2), (10,2)	**13a–q**		A	10
	(*n*,*m*) = (3,3)	**13r**	Ni		181
	(*k*,*l*,*m*) = (7,7,7), (8,8,8), (9,9,9), (10,10,10), (6,6,8), (6,8,10), (8,8,10)	**14a–g**		A, B	142
				B, C	25
		14a–d	Cl, Br, I		185
	1,2-Benzo; 3,4-benzo; 5,6-benzo	**15a**	Ni		6
			Ni	A, B	26
			Ni	A, B	27
			Ni		28
			Co^{3+}	A, B	29
			Co^{3+}		30
		**16a**	Co^{3+}, Rh^{3+}	A, B	31
	1-CH_2-benzo; 2-CH_2-benzo; 3-CH_2-benzo; 4-CH_2-benzo	**16b**	Ni	A, B	32
	d_4; 2-methyl, methyl	**17a**	Ni	A	5
	d_4; 1-methyl; 3-methyl	**17b**	Ni		6
			Ni	A, B	33
			Ni	A	34
			Ni	A	35
			Ni	A, B	36
	d_4; 1-methyl; 3-trifluoromethyl	**17c**	Ni	A	35
			Ni	A, B	36
	d_4; 1-ethyl; 2-methyl	**17d**	Ni		6
			Ni	A, B	33
	d_4; 1-propyl; 2-ethyl	**17e**	Ni		6
			Ni	A, B	33

TABLE I (continued)

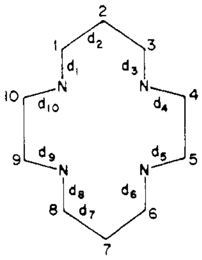
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
	d_4; 1-methyl, methyl; 3-methyl	**17f**	Ni, Cu^{2+}		6
			Ni, Cu^{2+}	A, B	33
			Ni, Cu^{2+}	A, B	37
			Ni	A	5
			Ni	A	38
	d_2; d_4; 1-methyl; 3-methyl	**17g**	Cu^{2+}	A	39
	d_3; d_4; 1-methyl, 3-methyl	**17h**	Cu^{2+}	A, B	39
	d_1; d_3, d_4; 1-methyl; 3-methyl	**17c**	Ni^{2+}	A, B	40
		**18a**	Co^{3+}	A, C	138
			Cr^{3+}	A, B	41
			Ni^{2+}, Ni^{3+}	A	42
			Ni^{2+}	B	43
			Ni^{2+}		213
			Co^{3+}	A, C	44
			Co^{3+}	B, C	45
			Co^{3+}	C	139
			Co^{3+}	A, B	46
			Co^{3+}	A, B	137
			Ni^{2+}	A, B	47
	1-Methyl; 3-methyl, methyl; 6-methyl; 8-methyl, methyl	**18b**	Ni^{2+}	A, B	48
			Rh^{3+}	A, B	49
			Cu^{2+}	A	50[e]
			Co^{3+}	A, B	125[f]
			Co^{3+}	A, B	52
			Cu^{+}, Cu^{2+}, Cu^{3+}	A, B	53
			Ni^{2+}	A, B	54
			Ni^{+}, Ni^{2+}, Ni^{3+}	A, B	181
			Fe^{2+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}	A	34
			Co^{3+}	A, B	55
			Co^{3+}	A, B	56
			Ni^{2+}		6
			Ni^{2+}, Cu^{2+}	A, B	57
			Ni^{2+}		210
			Ni^{2+}, Cu^{2+}	B	58
			Cu^{2+}		182
			Cu^{2+}	C	59
			Co^{3+}	B, C	60
			Co^{3+}	B, C	61
			Ni^{3+}	B	62
			Co^{3+}	A, C	63
			Fe^{2+}	A	64
			Co^{+}, Co^{2+}, Co^{3+}	A, B	65
			Co^{3+}	A, C	66
			Ni^{3+}	A	42
	1-Methyl, methyl; 3-methyl; 6-methyl; 8-methyl, methyl	**18c**	Ni^{3+}	A	42
			Ni^{2+}	A	67
			Ni^{+}, Ni^{2+}, Ni^{3+}	A, B	181
			Co^{3+}	A, B	52
	1-Methyl, methyl; 3-methyl, methyl; 6-methyl, methyl; 8-methyl	**18d**	Ni^{2+}	A, B	68
	1-Methyl; 3-methyl, methyl; 4-methyl; 6-methyl; 8-methyl, methyl; 9-methyl	**18e**	Ni^{2+}	A, C	34
	d_3; 1-methyl; 3-methyl	**18f**	Ni^{2+}	A, C	34
	d_1; d_6; 1-methyl; 3-methyl, methyl; 6-methyl; 8-methyl, methyl	**18g**	Ni^{2+}, Cu^{2+}		6
			Ni^{2+}, Cu^{2+}	A	5
			Ni^{2+}, Cu^{2+}	A, B	69
			Ni^{+}, Ni^{2+}, Ni^{3+}		181
			Cu^{+}, Cu^{2+}, Cu^{3+}	A, B	53
			Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	A, B	70
			Cu^{2+}	A	50
			Ni^{2+}	B	71
			Co^{3+}	B, C	60
			Co^{3+}	B, C	61
			Co^{+}, Co^{2+}, Co^{3+}	A, B	65
			Co^{3+}		72
			Ni^{2+}, Cu^{2+}		7

TABLE I (continued)

Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
		18g	Ni^{2+}, Cu^{2+}		58
			Ni^{2+}	A	38
			Ni^{2+}	A, B	73
			Fe^{2+}, Fe^{3+}	B	74
			Fe^{2+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}	A	34
			Cu^{2+}	C	59
			Co^{3+}	A, B	51
			Ni^{2+}	A, B	75
			Ni^{2+}		211
			Co^{3+}	A, C	66
			Ni^{2+}, Cu^{2+}	A, B	76
	d_1; d_6; 1-ethyl; 3-methyl, ethyl; 6-ethyl; 8-methyl, ethyl	**18h**	Cu^{2+}		6
			Ni^{2+}	A	5
			Cu^{2+}	A, B	76
			Ni^{2+}, Cu^{2+}	B	58
	d_1; d_6; 1-methyl; 3-methyl, methyl; 5-methyl, 6-methyl; 8-methyl, methyl; 10-methyl	**18i**	Ni^{2+}, Cu^{2+}		6
			Ni^{2+}	A	5
			Ni^{2+}, Cu^{2+}	B	58
			Ni^{2+}, Cu^{2+}	B	214
	d_1; d_6; 1-methyl; 3-methyl, methyl; 4-methyl; 6-methyl, 8-methyl, methyl; 9-methyl	**18j**	Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	A	5
			Ni^{2+}	A	33
			Co^{2+}, Ni^{2+}		34
	d_1; d_6; 1-methyl; 3-methyl, methyl; 5-methyl; 6-methyl; 8-methyl, methyl; 9-methyl	**18k**	Cu^{2+}	A, B	76
	d_9; d_{10}; 9-methyl; 10-methyl	**18l**	Co^{3+}	A, C	63
	d_1; d_8; 1-methyl; 3-methyl; 6-methyl, methyl; 8-methyl	**18m**	Ni^{2+}	A	38
	d_1; d_8; 1-methyl; 3-methyl, methyl; 6-methyl, methyl; 8-methyl	**18n**	Ni^{+}, Ni^{2+}, Ni^{3+}	A, B	181
			Ni^{2+}	A, B	73
			Ni^{2+}	A, B	75
			Ni^{2+}		77
			Co^{3+}		206
			Co^{2+}	A, B	78
			Ni^{2+}		216
			Ni^{2+}		211
			Ni^{2+}		212
	d_1; d_8; 1-methyl; 3-methyl, methyl; 6-methyl; 8-methyl, methyl	**18o**	Ni^{2+}	A	5
			Ni^{2+}		212
			Ni^{2+}	B	71
			Co^{3+}	A, C	63
	d_1; d_8; 1-methyl; 3-methyl, methyl; 6-methyl; 8-methyl, methyl; 10-methyl	**18p**	Cu^{2+}	A	5
	d_1; d_8; 1-methyl; 3-methyl, methyl; 5-methyl; 6-methyl; 8-methyl, 10-methyl	**18q**	Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	A	5
	d_3; d_6; 1,2-benzo; 7,8-benzo	**18r**	Co^{2+}, Ni^{2+}, Cu^{2+}	A, B	215
	d_3; d_6; 1,2-benzo; 4,5-benzo; 7,8-benzo	**18s**	Co^{2+}, Ni^{2+}	A, B	215
	d_2; d_3; d_{10}; 1-methyl; 3-methyl	**18t**	Ni^{2+}	A, B	40
	d_4; d_5; d_9; d_{10}; 4-methyl; 5-methyl; 9-methyl; 10-methyl	**18u**	Co^{3+}	A, C	63
	d_1; d_4; d_5; d_8; 1-methyl; 3-methyl, methyl; 6-methyl, methyl; 8-methyl	**18v**	Ni^{2+}		207
			Ni^{2+}	A, B	79
	d_1; d_4; d_6; d_9; 1-methyl; 3-methyl, methyl; 6-methyl; 8-methyl, methyl	**18w**	Ni^{2+}	A, B	79
	d_2; d_3; d_6; d_7; 4,5-benzo; 9,10-benzo	**18x**	Co^{2+}, Ni^{2+}, Cu^{2+}	A, B	80
	d_2; d_3; d_6; d_7; 2-$COCH_3$, 3-methyl; 4,5-benzo; 6-methyl; 7-$COCH_3$; 9,10-benzo	**18y**	Ni^{2+}		6
	d_2; d_3; d_6; d_7; 2,3-oxocyclohexane; 6,7-oxocyclohexane	**18z**	Ni^{2+}, Cu^{2+}	A	81

TABLE I (continued)

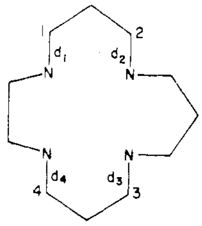
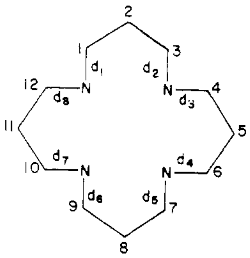
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
	d_1; d_3; 1-methyl; 2-methyl, methyl; 3-methyl; 4-methyl, methyl	**19a**	Ni^{2+}	A	5
			Ni^{2+}	A	38
	d_2; d_3; 1-methyl, methyl; 2-methyl; 3-methyl; 4-methyl; methyl	**19b**	Ni^{2+}, Cu^{2+}	A	5
	1-Methyl, methyl; 3-methyl, methyl; 7-methyl, methyl; 9-methyl	**20a**	Ni^{2+}	A, B	65
	2,3-Benzo; 5,6-benzo; 8,9-benzo; 11,12-benzo	**20b**	Ni^{2+}		6
			Ni^{2+}		82
			Ni^{2+}	A, B	83
	d_1; d_5; 1-methyl; 3-methyl, methyl; 7-methyl; 9-methyl, methyl	**20c**	Ni^{2+}, Cu^{2+}		6
			Ni^{2+}, Cu^{2+}	A	69
			Ni^{2+}	A	5
			Ni^{2+}	A	38
			Fe^{2+}	B	84
	d_1; d_5; 2,3-benzo; 4-methoxide; 5,6-benzo; 8,9-benzo; 10-methoxide; 11,12-benzo	**20d**	Ni^{2+}, Cu^{2+}		82
			Ni^{2+}	A, B	120
	d_1; d_5; 2,3-benzo; 4-ethoxide; 5,6-benzo; 8,9-benzo; 10-ethoxide; 11,12-benzo	**20e**	Ni^{2+}		6
			Ni^{2+}	A, B	120
	d_2; d_4; d_6; 1-methyl, methyl; 3-methyl; 7-methyl, methyl; 9-methyl	**20f**	Ni^{2+}	A, B	85
	d_2; d_4; d_6; d_8; 1-methyl, methyl; 3-methyl; 7-methyl, methyl; 9-methyl	**20g**	Ni^{2+}	A, B	85
			Fe^{2+}	B	84
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 7,8-benzo; 10,11-benzo	**20h**	Ni^{2+}		6
			Co^{2+}, Ni^{2+}, Cu^{2+}		7
			Ni^{2+}, Cu^{2+}		26
			Ni^{2+}		86
			Ni^{2+}, Cu^{2+}	A, B	87
			Co^{3+}, Ni^{2+}, Cu^{2+}		88
			Co^{2+}, Co^{3+}, Ni^{+}, Ni^{2+}, Cu^{+}, Cu^{2+}		82
			Ni^{2+}		209
			Co^{3+}	A, B	89
			Cu^{2+}, Cu^{3+}	A, B	83
			Co^{2+}		90
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-NH_2; 7,8-benzo; 10,11-benzo; 12-NH_2	**20i**	Ni^{2+}	A, B	197
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-$N(CH_3)_2$; 7,8-benzo; 10,11-benzo; 12-$N(CH_3)_2$	**20j**	Ni^{2+}, Cu^{2+}	A, B	197
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-$N(C_2H_5)_2$; 7,8-benzo; 10,11-benzo; 12-$N(C_2H_5)_2$	**20k**	Ni^{2+}	A, B	197
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-$N(CH_3)CH_2CH_2NH(CH_3)$; 7,8-benzo; 10,11-benzo; 12-$N(CH_3)CH_2CH_2NH(CH_3)$	**20l**	Ni^{2+}	A, B	197
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-$N(CH_3)CH_2CH_2N(CH_3)_2$; 7,8-benzo; 10,11-benzo; 12-$N(CH)_3$-$CH_2CH_2N(CH_3)_2$	**20m**	Ni^{2+}	A, B	197
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-$NHCH_2CH_2CH_2NH_2$; 7,8-benzo; 10,11-benzo; 12-$NHCH_2CH_2CH_2NH_2$	**20n**	Ni^{2+}	A, B	197
	d_2; d_4; d_6; d_8; 1,2-benzo; 4,5-benzo; 6-$NH(CH_2)_3NH_2$; 7,8-benzo; 10,11-benzo; 12-$NH(CH_2)_3NH_2$	**20o**	Ni^{2+}	A, B	197

TABLE I (continued)

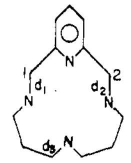
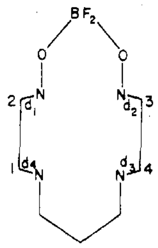
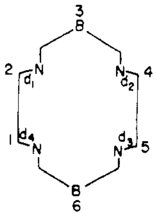
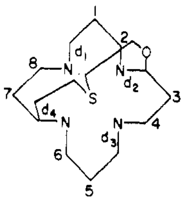
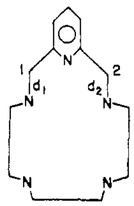
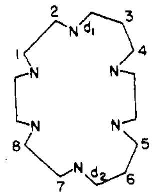
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
	d$_2$; d$_4$; d$_6$; d$_8$; 1,2-benzo; 4,5-benzo; 6-O(CH$_2$)$_5$OH; 7,8-benzo; 10,11-benzo; 12-O(CH$_2$)$_5$OH	**20p**	Ni^{2+}	A, B	197
	d$_2$; d$_4$; d$_6$; d$_8$; 1,2-benzo; 4,5-benzo; 6-O(CH$_3$)$_2$; 7,8-benzo; 10,11-benzo; 12-O(CH$_2$)$_5$OH	**20q**	Cu^{2+}	A, B	197
		**21a**	Fe^{2+}	B	84
	1-Methyl; 2-methyl	**21b**	Ni^{2+}		6
			Co^{3+}	A, B	91
			Cu^{2+}	A, B	92
			Ni^{2+}		93
			Ni^{2+}	A, B	94
			Ni^{2+}		217
	d$_2$; 1-methyl; 2-methyl	**21c**	Ni^{2+}	A	93
	d$_1$; d$_2$; 1-methyl; 2-methyl	**21d**	Co^{2+}, Ni^{2+}, Cu^{2+}		6
			Co^{3+}	A, B	95
			Ni^{2+}	A, B	96
			Co^{2+}	A, B	97
			Ni^{2+}		208
			Cu^{2+}	A, B	92
			Ni^{2+}		93
	d$_1$; d$_2$; d$_3$; 1-methyl; 2-methyl	**21e**	Ni^{2+}	A	93
	d$_1$; d$_2$; d$_3$; d$_4$; 1-methyl; 2-methyl; 3-methyl; 4-methyl	**22a**	Ni^{2+}		6
	d$_1$; d$_2$; d$_3$; d$_4$; 1-methyl; 2-methyl; 3-fluoride, fluoride; 4-methyl; 5-methyl; 6-fluoride, fluoride	**23a**	Ni^{2+}		6
			Ni^{2+}	A	98
			Ni^{2+}		7
	d$_1$; d$_2$; d$_3$; d$_4$; 1-methyl; 2-methyl; 3-ethyl, ethyl; 4-methyl; 5-methyl; 6-ethyl, ethyl	**23b**	Ni^{2+}	A	99
	d$_1$; d$_2$; d$_3$; d$_4$; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo; 9-methyl	**24a**	Ni^{2+}, Cu^{2+}	A, B	197
			Ni^{2+}, Cu^{2+}		198
	d$_1$; d$_2$; 1-methyl; 2-methyl	**25a**	Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}		6
			Fe^{3+}		7
			Fe^{3+}		100
			Fe^{3+}	A, B	101
			Fe^{3+}	A, B	102
			Fe^{3+}		103
	d$_1$; d$_2$; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**26a**	Fe^{2+}, Zn^{2+}	A, B	196

TABLE I (continued)

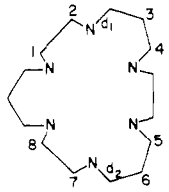
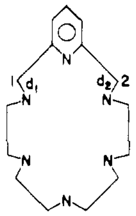
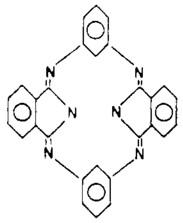
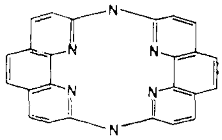
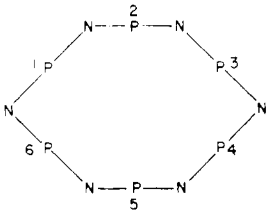
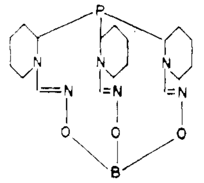
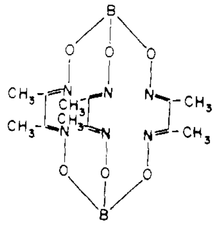
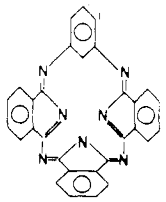
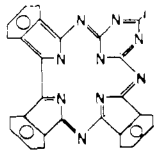
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
	d_1; d_2; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**27a**	Fe^{2+}, Zn^{2+}	A, B	196
	d_1; d_2; 1-methyl; 2-methyl	**28a**	Co^{2+}, Ni^{2+}, Cu^{2+}		6
			Fe^{3+}		7
			Fe^{3+}	A, B	101
			Fe^{3+}		103
		**29a**	Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	B	104
		**30a**	Cu^{2+}	A	105
	1-NMe, NMe; 2-NMe, NMe; 3-NMe, NMe; 4-NMe, NMe, 5-NMe, NMe; 6-NMe, NMe	**31a**	Cu^{2+}		215
		**32a**	Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	A, B	183
		**33a**	Co^{3+}	A, B	184
			Co^{2+}, Co^{3+}		106
		**34a**	Co^{2+}, Ni^{2+}, Cu^{2+}	B	104
			Co^{2+}, Ni^{2+}, Cu^{+}, Cu^{2+}	A, B	107
	1-Methyl	**34b**	Co^{2+}, Ni^{2+}, Cu^{+}, Cu^{2+}	A, B	107
	1-Methyl	**35a**	Cu^{2+}	A	108

TABLE I (continued)

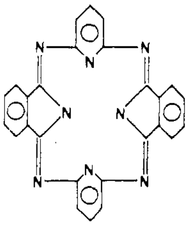
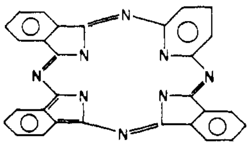
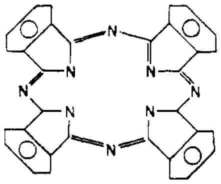
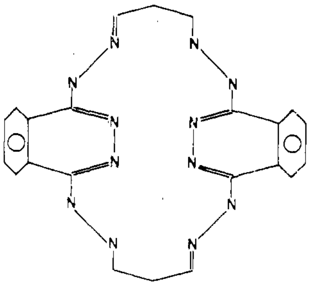
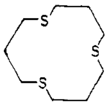
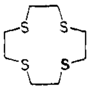
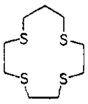
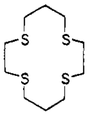
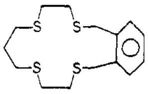
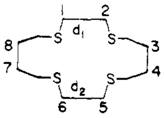
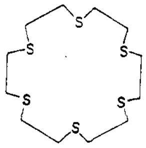
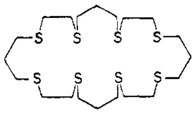
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
		**36a**	Mn^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}		6
			Mn^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}	A, B	109
		**37a**	Ni^{2+}, Cu^{2+}, Au^{3+}	A, B	110
		**38a**	Ni^{2+}		6
			Sn^{4+}	A	111
			Li, Na, K, Be, Mg, Ca, La, Ti, Zr, Hf, Th, V, Cr, U, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb	A, B	141
		**39a**	Ni^{2+}	A, B	112
		**40a**	Ni^{2+}	A, B	147
		**41a**	Ni^{2+}	A, B	147
		**42a**	Ni^{2+}	A, B	147
		**43a**	Ni^{2+}	A	145
			Ni^{2+}	A, B	144
		**44a**	Ni^{2+}	A, B	144
	3,4-Benzo; 7,8-benzo	**45a**		A, B	113
	d$_1$; d$_2$; 1-phenyl; 2-phenyl; 3,4-benzo; 5-phenyl; 6-phenyl; 7,8-benzo	**45b**	Ni^{2+}	A	186
		**46a**	Co^{2+}, Ni^{2+}	A, B	148
		**47a**	Ni^{2+}, Pd^{2+}		146

TABLE I (continued)

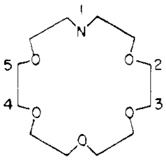
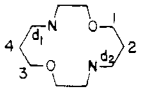
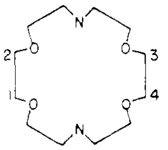
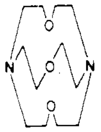
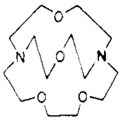
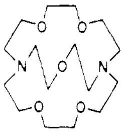
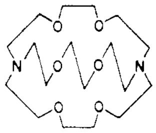
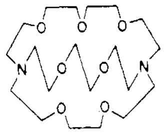
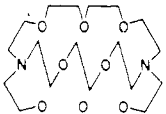
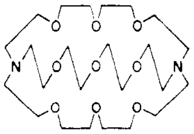
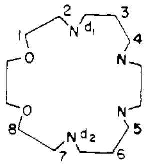
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b].	Ref
		**48a**	K, Ag$^+$		180
	2,3-Benzo; 4,5-benzo	**48b**	K		180
	1-n-C_8H_{17}; 2,3-benzo; 4,5-benzo	**48c**	K		180
	d_1; d_2; 1,2-benzo; 3,4-benzo	**49a**	Ni^{2+}	A	188
			Ni^{2+}		187
		**50a**		A	151
			K, Ag$^+$		180
			K, Rb, Cu^{2+}	A	149
			Cu^{2+}		189
	1,2-Benzo; 4,5-benzo	**50b**	K		180
	3-Methyl, 6-methyl	**50c**	Na, K, Ba		114
	3,6-C_8H_{16}	**50d**	Na, K, Ba		114
		**51a**	H, Li	A, B, C	115
		**52a**	Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba		191
			Li, Na, K, Ca, Sr		195
		**53a**	Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba		191
			Li, Na, K, Rb, Cs, Ca, Sr, Ba		195
		**54a**	Na, K, Cs		193
			Ba		194
			Rb		192[g]
			Na, K, Rb, Ca, Sr, Ba, Tl$^+$	B, C	190
			Li, Na, K, Rb, Cs, Ca, Sr, Ba	B	150
				A, B	149
			Sr		117
			Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba		191
			Na, K, Ba		114
			Li, Na, K, Rb, Cs, Ca, Sr, Ba		195
	1,2-Benzo	**54b**	Na, K, Ba		114
	1,2-Benzo; 3,4-benzo	**54c**	Na, K, Ba		114
		**55a**		A	149
			Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba		191
			Na, K, Rb, Cs, Ca, Sr, Ba,		195
			Ba		194
		**56a**		A	149
			Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba		191
			Li, Na, K, Rb, Cs, Ca, Sr, Ba		195
		**57a**		A	149
			Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba		191
			Li, Na, K, Rb, Cs, Ca, Sr		195
	d_1; d_2; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**58a**	Ni^{2+}	A, B	196

TABLE I (continued)

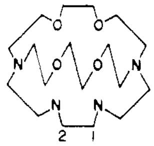
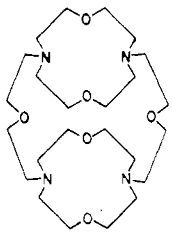
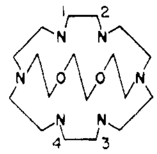
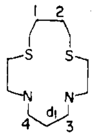
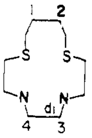
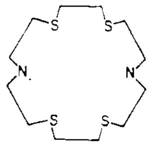
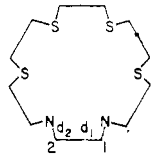
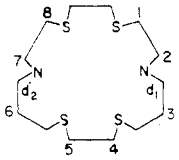
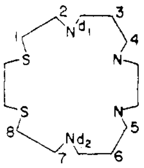
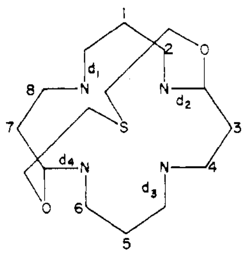
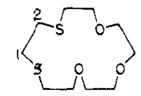
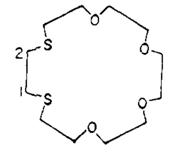
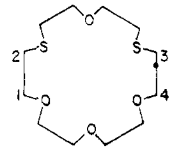
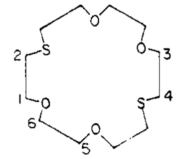
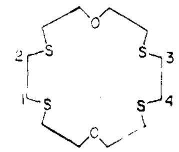
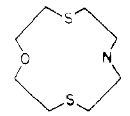
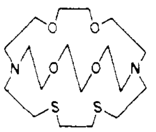
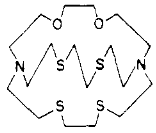
Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
		**59a**	Na, K, Cd	A	118
	1-Methyl; 2-methyl	**59b**	K, Ag	A	118
	1-Tosylate; 2-tosylate	**59c**	Ag	A	118
		**60a**	Na, K, Rb, Cs, Ca, Sr, Ba, La, Ag^+, Tl^+, Pb^{2+}	A	119
		**61a**	K	A	118
	1-Methyl; 2-methyl; 3-methyl; 4-methyl		K	A	118
	d_1; d_2; 1,2-benzo; 3-methyl; 4-methyl	**62a**	Ni^{2+}		7
			Ni^{2+}	A, B	154
	d_1; d_2; 1,2-benzo; 3-methyl; 4-ethyl	**62b**	Ni^{2+}		6
			Ni^{2+}	A, B	154
			Ni^{2+}	B, C	155
	d_1; d_2; 1,2-benzo; 3-methyl; 4-pentyl	**62c**	Ni^{2+}	A, B	154
	d_1; 1,2-benzo; 3-methyl; 4-methyl, methyl	**63a**	Ni^{2+}		6[h]
		**64a**		A	151
			Co^{2+}, Ni^{2+}		152
	d_1; d_2; 1-methyl; 2-ethyl	**65a**	Ni^{2+}		6
	d_1; d_2; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**66a**	Co^{2+}, Ni^{2+}		153
			Co^{2+}, Ni^{2+}	A	156
	d_1; d_2; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**67a**	Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	A, B	196
	d_1; d_2; d_3; d_4; 1,2-benzo; 3,4-benzo; 5,6-benzo; 7,8-benzo	**68a**	Ni^{2+}, Cu^{2+}	A, B	197
			Ni^{2+}, Cu^{2+}		198

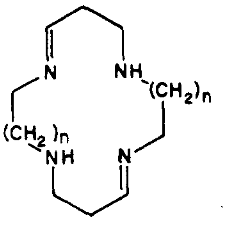
TABLE I (continued)

Basic structure	Attached groups[a]	No.	Ions bound by ligand	Other information[b]	Ref
	1,2-4-Methylbenzo	**69a**	K, Ag	A, B	199
	1,2-4-Methylbenzo	**70a**	K, Ag	A, B	199
	1,2-Benzo; 3,4-benzo	**71a**	K, Ag	A, B	199
		**72a**	K, Ag		180
	5,6-Benzo	**72b**	K, Ag		199
	1,2-Benzo; 3,4-benzo	**72c**	K, Ag		199
		**73a**		A, B	148
			Na, K, Ag	A, B	199
	1,2-Methylbenzo; 3,4-methylbenzo	**73b**	Na, K, Ag	A, B	199
		**74a**	Co^{2+}, Ni^{2+}		148
		**75a**	Na, K, Rb, Ba, Pb^{2+}, Ag^{+}, Tl^{+}	A, B	151
		**76a**	Li, Na, Co^{2+}, Ag^{+}	A, B	151

[a] Numbers designate where group is attached to basic structure; *i.e.*, d designates a double bond. [b] Other pertinent information contained in reference concerning complex and/or macrocycle are designated as follows: A, synthesis; B, spectra; C, kinetic. [c] See also ref 4. [d] See also ref 15. [e] See also ref 84. [f] See also ref 51. [g] See also ref 44. [h] See also ref 20.

cerning the actual sequence of reactions and the exact nature of the metal ion effects.

Typical of macrocycles prepared by condensation in the presence of transition metal salts are those formed by reaction of certain metal-amine complexes with aliphatic carbonyl compounds.[5,8] For example, with acetone as the carbonyl compound and diaminoethane as the amine complex, a cyclic complex characterized by the formula given by I where $n = 2$, is obtained (the methyl side groups are not indicated in the formula). This reaction provides a covnvenient route to complexes of macrocyclic ligands with four nitrogen donor atoms. The macrocycle ring size can be changed by replacing one or both of the diaminoethane residues by 1,3-diaminopropane residues or by cyclization of triethylenetetramine complexes by a single amine-imine bridge. The ring substituents can be changed by replacement of acetone by some other aliphatic carbonyl compound. The macrocyclic complexes formed have two imine and two secondary amine donor groups, but it is possible to vary the unsaturation of the macrocycle from the tetraimine to the tetraamine by oxidation or reduction, respectively. The direct condensation between metal-amine complexes and carbonyl compounds is satisfactory only for nickel(II) and copper(II), but by isolation of some of the macrocycles from the nickel(II) complexes it has been possible to prepare complexes of other metal ions. Several reviews and papers have been published describing the synthesis of cyclic polyamines.[5-8,141]

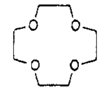
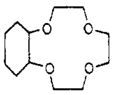
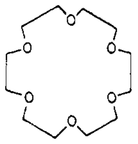
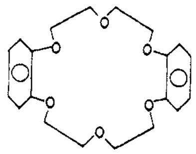
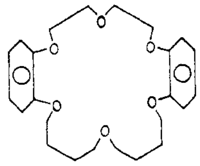
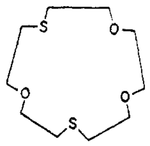


I

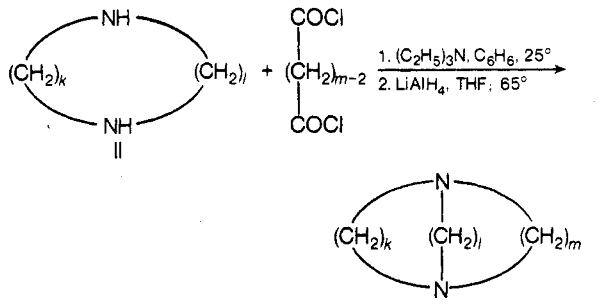
2. *Bicyclic*

Simmons and Park[142] have made a series of macrobicyclic diamines of type **14a–g.** 1,(k + 2)-Diazacycloal-

TABLE II. Some Representative Cyclic Polyethers Together with Their Crown Names

Compound	Crown name
	12-Crown-4
	Cyclohexyl-12-crown-4
	18-Crown-6
	Dibenzo-18-crown-6
	*asym*-Dibenzo-22-crown-6
	Dithia-15-crown-5

kanes (II) were prepared by the procedure of Stetter and Marx[143] and converted by an extension of the same method to the crystalline 1,(k + 2)-diazabicyclo[$k.l.m$]alkanes (III).



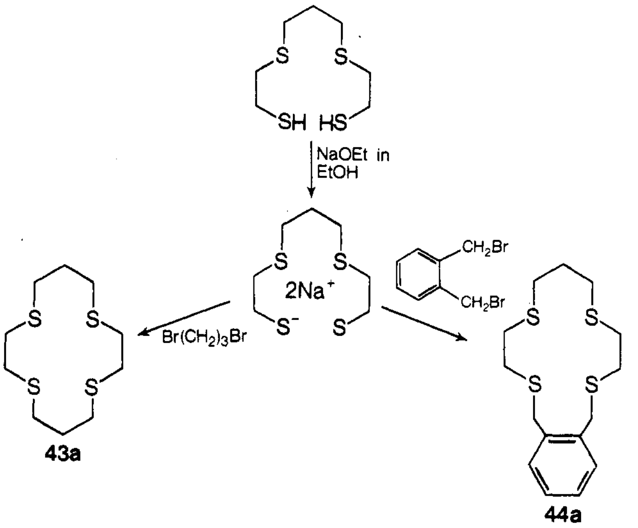
(4)

Overall yield based on amines of type II, which were prepared in 50–70% yields, were 20 to 75%. They found that, as originally made, the lone pairs, or the protons in the protonated form, were on the outside and called this the *out–out* form. When the hydrochlorides are left in solution, there is a drastic change in the proton nmr signal, attributed to a change in the formation of the ligand at the nitrogen atoms resulting in the protons being on the inside of the cavity to give the *in–in* form.

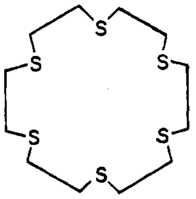
C. Cyclic Polythioethers

Rosen and Busch[8,144,145] have used the reaction sequence in Scheme I to prepare the quadridentate macrocycles **43a** and **44a.** The final ring-closing step gave a 38% yield. Initially the corresponding yield of **43a**, the sulfur analog of cyclam, was 7.5%, although the reaction was performed at moderate dilution. Subsequently this yield was improved by diluting threefold the alcohol solution used in the original preparation.

SCHEME I



Four other sulfur-containing macrocycles have been synthesized[146,147] by procedures similar to Scheme I. Black and McLean[148] report the synthesis of an 18-membered ring, **46a**, by reaction of 1,2-dibromoethane with the disodium salt of 3-thiapentane-1,5-dithiol in ethanol at high dilution with a yield of 31%.



46a

D. Mixed Donor Macrocycles

1. Nitrogen–Oxygen

A series of mono- and bicyclic macrocycles containing both nitrogen and oxygen atoms has been synthesized by Dietrich, Lehn, and Sauvage.[149-151] The procedure used is outlined in Scheme II for the synthesis of **50a** and **54a.**

Starting from the required dioxa diamine and dicarboxylic acid dichloride the macrocyclic diamine is obtained in 75% yield by condensation under high dilution conditions followed by reduction (lithium aluminum hydride or diborane) of the diamides obtained. Condensation (high

SCHEME II

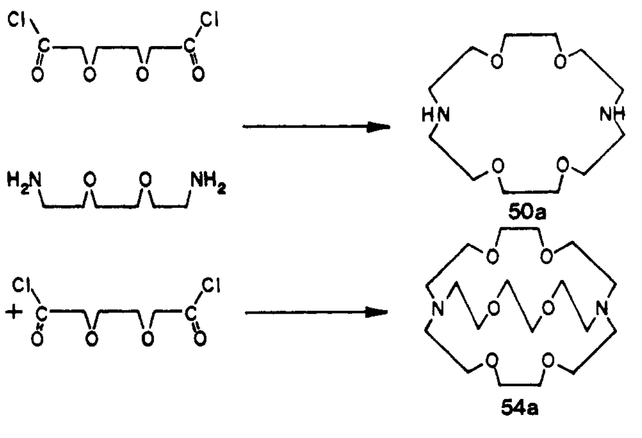


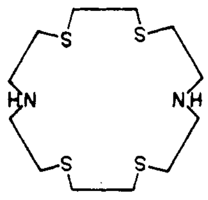
TABLE III. Compilation of Reference Reporting Synthesis of Synthetic Multidentate Macrocyclic Ligands

Number of donor atoms	References
	Oxygen Donor Atoms
2	123–126
3	113, 122, 125
4	122–128
5	12–14, 122, 135
6	122, 125, 128, 135, 136
7	122, 135
8	122, 135
10	122
16	122
20	122
	Nitrogen Donor Atoms
2	10, 124, 142
3	26, 27, 29
4	5, 31–42, 44, 46–48, 50–57, 63–70, 73, 75, 76, 78–81, 83, 85, 87, 89, 91–99, 120, 130, 137, 138, 181, 197, 214, 215
5	101, 102
6	101, 105, 196
7	107, 108
8	109–112, 141
	Sulfur Donor Atoms
3	147
4	113, 131, 132, 144, 145, 147, 186
6	133, 148
8	134, 146
	Mixed Donor Atoms
	Nitrogen–Oxygen
1–5	180
2–2	188
2–3	115
2–4	149, 151
2–5	149
2–6	149
2–7	149
2–8	149
2–9	149
4–2	196
6–3	183
	Sulfur–Nitrogen
1–4	197
2–2	154
2–4	196
4–2	151, 156
6–2	151
	Sulfur–Oxygen
1–2	157
1–3	157
1–4	157
1–7	199
2–1	157
2–2	157
2–3	157, 199
2–4	157, 199
3–1	157
4–2	148, 157, 199
	Nitrogen–Sulfur–Oxygen
1–2–1	148
2–2–2	151
2–2–4	151
2–4–2	151

dilution) of **50a** with the acid chloride followed by reduction (diborane) of the intermediate diamide led to the macrobicyclic diamine **54a** in 25% yield from the starting materials.

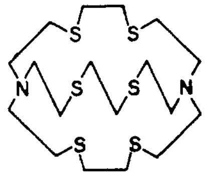
2. *Sulfur–Nitrogen*

Dietrich, Lehn, and Sauvage,[151] using the procedure outlined in Scheme II but with sulfur replacing the oxygen atoms, synthesized a mono-



64a

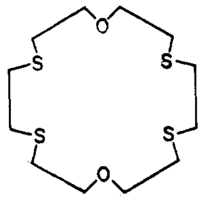
and a bicyclic thia macrocyclic diamine.



Compound **64a** has also been prepared in 8% yield by the reaction of the disodium salt of ethane-1,2-dithiol and di(2-bromoethyl)amine in ethanol at high dilution.[148,152] Busch and coworkers[8,153–156] have synthesized several sulfur–nitrogen containing macrocycles by *in situ* methods where a metal ion is present, yielding the metal complex directly.

3. *Sulfur–Oxygen*

A tetrathioether, **73a**, has been synthesized[148] by reaction of 1,2-dibromoethane with the disodium salt of 3-

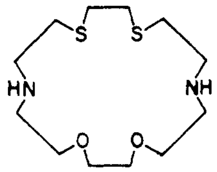


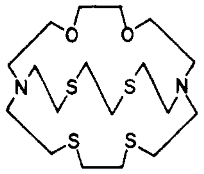
73a

oxapentane-1,5-dithiol in ethanol at high dilution with a yield of 7%. Bradshaw, *et al.*,[157] have prepared 11 different thioethers in a manner similar to that reported by Dann, Chiesa, and Gates,[158] in which the appropriate oligo ethylene glycol dichloride was allowed to react with a dithiol or sodium sulfide. Yields were generally low (5–30%) owing to extensive polymer formation.

4. *Nitrogen–Sulfur–Oxygen*

Monocyclic and bicyclic macrocycles as typified by the following two structures were synthesized[151] by the



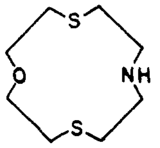


method described in Scheme II. Starting with the required dithia diamine and dicarboxylic acid dichloride, the monocyclic compounds were obtained in 55% yield. Subsequent condensation with the required diacid dichloride followed by reduction of the intermediate diamides led to the bicyclic macrocycle with an overall yield of about

TABLE IV. Diameters of Selected Cations and Cyclic Polyether Cavities[160,163]

Cation	Ionic diameter, Å	Polyether	Diameter of cavity, Å
Lithium	1.20	All 14-crown-4	1.2–1.5
Sodium	1.90	All 15-crown-5	1.7–2.2
Potassium	2.66	All 18-crown-6	2.6–3.2
Ammonium	2.84	All 21-crown-7	3.4–4.3
Rubidium	2.96		
Cesium	3.34		
Silver	2.52		
Barium	2.70		

20%. Macrocycle **74a** has been prepared by the reaction of the disodium salt of 3-oxapentane-1,5-dithiol with di(2-bromoethyl)amine in ethanol at high dilution.[148,159]



74a

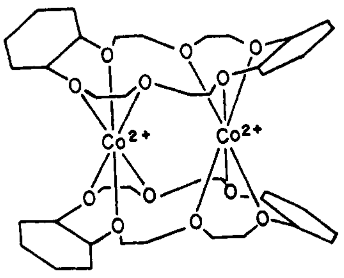
IV. Ion Binding Properties

A. Cyclic Polyethers

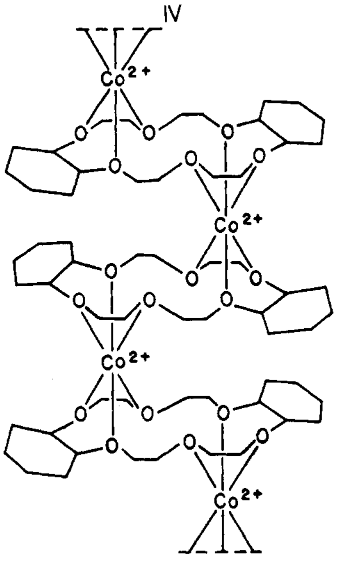
The cyclic polyethers have been found to form primarily 1:1 metal:polyether complexes with a large array of metal ions.[122,135,160-162] However, depending on the ratio of the diameter of the cavity and metal ion diameter, 1:2 and 2:3 complexes are also formed.[163]

The 1:1 complexes are generally assumed to consist of the metal ion bound in the cavity of the polyether ring (ref 122, 135, 160, 164, 165). This "metal in the hole" picture has been substantiated by X-ray crystallographic studies of several metal–cyclic polyether complexes (see section VI for table giving structures of metal–cyclic polyether complexes). However, caution should be used in determining the composition of the complex in solution from the crystal composition. The first cyclic polyether complex to be investigated by X-ray crystal structure analysis[166] had a 2:3 crystal stoichiometric composition of two ribidium thiocyanate units to three polyethers **6g** (dibenzo-18-crown-6), but the complex was found to have 1:1 structure. An extra uncoordinated molecule of ligand was present in the crystal for every two molecules of the complex.

The fact that a metal ion forms a 1:1 complex with a cyclic polyether does not always indicate that the metal ion is located in the cavity of the polyether. The metal ion may have directed valencies which preclude bonding to all the oxygen atoms or it may be too large or too small to fit "exactly" in the hole. Apparently, the former is the case for the solid complex of cobalt dichloride and the cyclic polyether **6h** (dicyclohexyl-18-crown-6), where, based on infrared and magnetic moment data,[167] two possible structures were postulated: a sandwich-type structure with two cobalt ions located between two cyclic polyether molecules, IV, and a chain-type polymer with an alternating array of cobalt cations and cyclic polyether molecules, V. These structures are possible only if each cyclic polyether contributes three oxygen atoms to each cobalt ion to form an octahedral complex. In the absence of X-ray crystallographic data, it cannot be predicted which, if either, of these structures is correct.



IV



V

There is also structural evidence indicating that in many cases the relative sizes of the polyether cavity and the metal ion control the stoichiometry of the resulting complex. The ionic diameters of some cations and the estimated sizes of the holes of selected cyclic polyethers are given in Table IV. The alkali metal–thiocyanate complexes of the cyclic polyethers **6g** (dibenzo-18-crown-6) were found[163] to have, for a given metal, the following metal/polyether ion ratios: potassium, 1:1; rubidium, 1:1 and 1:2; and cesium, 1:2 and 2:3. A "sandwich" structure, in which the metal ion is located between two cyclic polyether molecules, was suggested as the most probable one for the 1:2 complex. A "club sandwich" structure was postulated for the 2:3 complex where three polyether molecules are arranged flatwise in three tiers, each separated from the next by a metal ion. Rough approximations of these structures are depicted in Figure 2a (sandwich complex) and Figure 2b (club sandwich complex).

Similarly, where the metal ion was larger than the hole in the ring, other cyclic polyethers have been found[163,168] to give 1:2 and 2:3 complexes with various metal ions. Thus, it seems evident that the relative sizes of the hole and the metal ion have much to do with determining the stoichiometry of the complex. However, it has also been found that silver forms a 1:1 complex with the cyclic polyether **3a** (benzo-15-crown-5), yet the silver ion diameter is larger than the diameter of the hole in the cyclic polyether (Table IV) and that potassium forms a 1:1 complex with **11a** (dibenzo-30-crown-10), in which the ligand is wrapped around the metal.[169] This indicates that relative size is not the only factor influencing the configuration of the complexes.

One of the most interesting features of the cyclic polyethers is the ability of these compounds to selectively bind various cations. Solvent extraction studies[160] indicate preferential metal ion binding of alkali metal ions by cyclic polyethers as shown in Table V.

The most extensive work has been reported for the reaction of mono- and bivalent cations with the two isomers of the ligand **6h** (dicyclohexyl-18-crown-6) in aque-

TABLE V. Preferential Metal Ion Binding Exhibited by Cyclic Polyethers

Alkali metal ion	Cyclic polyether[a]	Ligand no.[b]	Approx ratio[c]	Ref
Lithium	Bis(*tert*-butylcyclohexyl)-14-crown-4	**2d**	0.89	170
Sodium	*tert*-Butylcyclohexyl-15-crown-5	**3e**	0.97	170
Potassium	Dicyclohexyl-18-crown-6	**6h**	0.90	170
Rubidium	*asym*-Dicyclohexyl-21-crown-7	**9c**	0.77	160
Cesium	Dicyclohexyl-24-crown-8	**10c**	0.83	160

[a] Which shows a preference for a given alkali metal ion over other alkali metal ions. [b] See Table I. [c] Of metal ion diameter to hole diameter. See Table IV for diameters of metal ions and polyether cavities.

ous solution.[161,162] The results are shown in Figure 3 for monovalent and bivalent cations, the optimum being at a somewhat smaller cation size in the case of the divalent cations. Also, **6h** was shown to be extremely selective toward certain cations. For example, the difference in stability constants between the Ca^{2+} and Pb^{2+} complexes of **6h** is about 10^5. In addition, **6h** has no measurable affinity for Cd^{2+} or Zn^{2+}, but high affinity for Hg^{2+}. The stability sequence for the alkali metal ion complexes with **6h** was found to be potassium > rubidium > cesium $\simeq$ sodium > lithium, which is essentially the same as the permeability sequence of the alkali metal ions in the presence of certain antibiotics for the transport of metal ions through natural and synthetic membranes and also the same as the binding sequence of metals ions by certain antibiotics.[171-179]

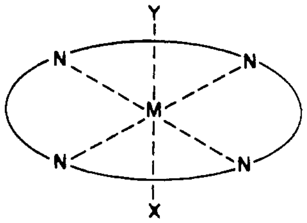
Frensdorff[180] has investigated the relationship between ring size and cation size by determining log *K* values for the reaction in methanol of several cyclic polyethers with Na^+, K^+, and Cs^+. The log *K* values are plotted in Figure 4 where several trends are evident. The relationship between ring size and cation size changes from $Na^+ > K^+$ for **2c** (dicyclohexyl-14-crown-4) to $Na^+ \sim K^+ > Cs^+$ for **3d** (cyclohexyl-15-crown-5) to $K^+ \sim Cs^+ > Na^+$ for **9b** (dibenzo-21-crown-7), and to $Cs^+ > K^+$ for **10b** (dibenzo-34-crown-8). It is evident that the change from preferred complexing with Na^+ to that with Cs^+ is very much dependent on the size of the cyclic polyether cavity. Values for ionic diameters of the alkali metal ions and ligand hole sizes are given in Table IV. For a given ring size, there is close correspondence between the cation diameter for which maximum stability is found and the macrocycle hole diameter.

Izatt, *et al.*,[4] have discussed the variations in ion binding properties with respect to cation size and charge, ligand cavity size, donor atom number and type, and ring type and conformation.

B. Cyclic Polyamines

1. Monocyclic

The majority of the monocyclic complexes have structures similar to VI where four more or less equivalent ni-



IV

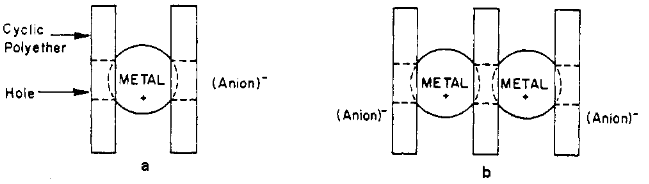


Figure 2. Possible structures of metal–cyclic polyether compounds.

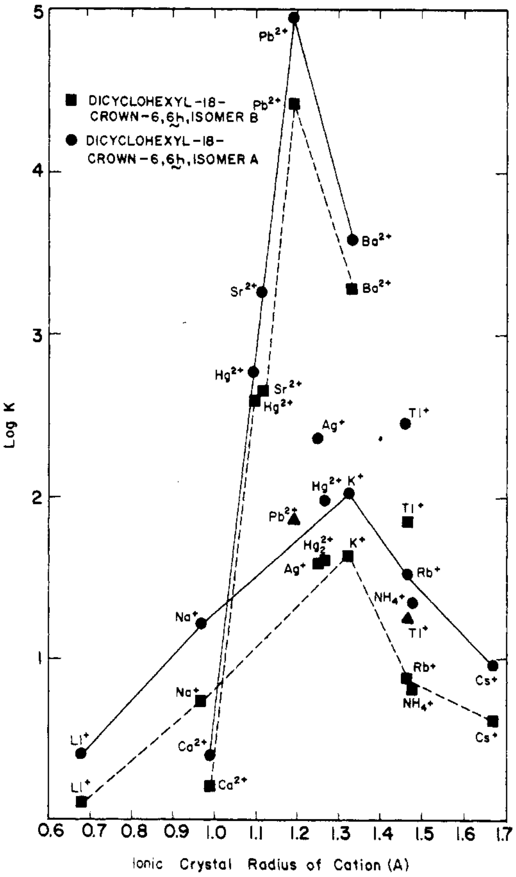


Figure 3. Relation between magnitude of binding constant and metal ion radius for the cyclic polyether **6h** (dicyclohexyl-18-crown-6) in aqueous solution. Diameter of cavity is approximately 3.0 Å (Table IV).

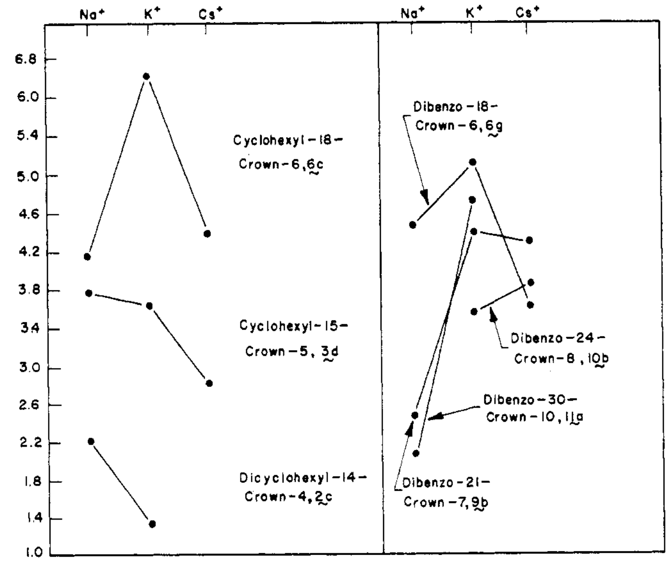


Figure 4. Log *K* values for the reaction in methanol of several cyclic polyethers of varying ring sizes and number of donor atoms with Na, K, and Cs.

TABLE VI. Log *K* Values for the Formation of Several 1:1 Cu^{2+}-Tetramine Complexes

Ligand	Log *K*	Temp, °C
Macrocyclic		
18b (blue)	20	25
18b (red)	28	25
Noncyclic		
$N[(CH_2)_3NH_2]_3$	13.1	25
$NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$	17.3	20
$N[(CH_2)_2NH_2]_3$	18.8	20
$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	20.1	25
$NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$	23.9	25

trogen atoms are coordinated in a single plane about the metal ion while two variable ionic groups are bound in the axial sites above and below that plane.

X-Ray crystallographic analysis on several macrocycles containing four and five nitrogen atoms indicates that the metal ion is located in the cavity of the ring (see section VI for table giving structures of metal-cyclic polyamine complexes). The complexes of only a small number of metal ions, mostly first row transition metal ions in their usual oxidation states, have been studied in any detail.[8] Examples of pentadentate, sexadentate, and higher polydentate macrocycles are rare, and such ligands have been used to prepare only a relatively small number of metal complexes. Relatively little has been done to measure metal binding constants in the cases of these macrocycles or to investigate the various factors which affect these constants. This is due partially to the covalent bonding between the nitrogen atoms and the metal ion which because of the template effect results in a macrocycle being synthesized with a strongly bonded metal ion in the cavity. The complexes are in general remarkably inert to dissociation, and in many cases it is not possible to obtain the metal free macrocycle. It has been suggested that because of the high stability of the complexes it might be possible to trap some of the more uncommon oxidation states of the transition metals by reduction or oxidation of the complexes containing the metals in their normal oxidation states.[181] In some cases, the free macrocycle can be obtained by introduction of a stronger metal binding molecule. For example, **18b**, L, can be readily removed intact from nickel(II) ion by the action of aqueous cyanide ion.[6]

$$\mathrm{Ni(L)^{2+} + 4CN^- \longrightarrow Ni(CN)_4{}^{2-} + L} \qquad (4)$$

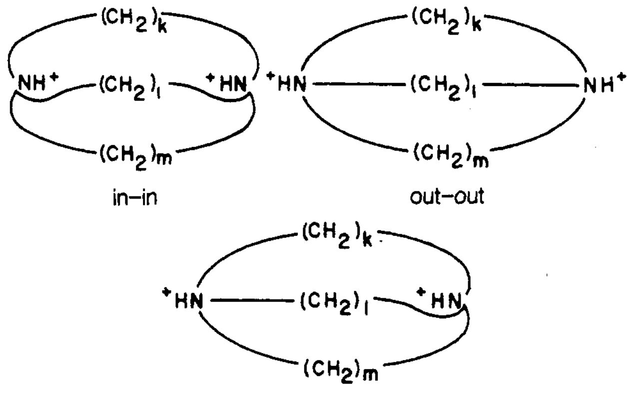
This reaction also establishes the binding constant for the nickel macrocycle complex to be less than that for the $Ni(CN)_4{}^{2-}$ complex which has a log *K* value of 30.1.

The binding constants for the red and blue forms of the copper(II) complex of the macrocycle **18b** have been measured and compared with similar constants for copper binding with noncyclic nitrogen-containing molecules.[182] These results are given in Table VI and indicate the high stability of the red form of macrocycle **18b**.

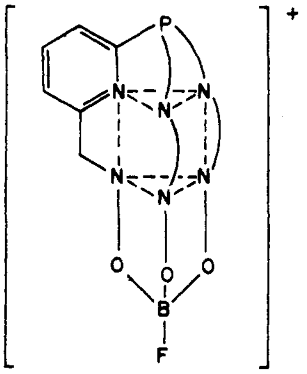
The effect of increased stability of a metal complex coordinated to a tetramine macrocyclic ligand over that of similar noncyclic tetramine ligands has been called the macrocyclic effect.[182] Aside from the above study, little has been reported with respect to the effect of the various factors which determine the thermodynamic stability of the complexes formed between metals and cyclic polyamines.

2. *Bicyclic*

SCHEME III

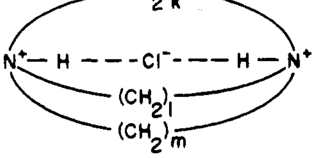


Several macrobicyclic complexes of the general type shown by **32a** have been synthesized containing completely encapsulated metal ions.[183,184] Rigid cage structures are characteristic of this class of complexes with the complexes having a 1:1 metal to ligand ratio. The metal free ligand was not obtained and no metal binding constants have been reported.



32a

Macrobicyclic diamines with bridgehead nitrogen atoms have been reported[185] to exhibit an unprecedented ion pairing phenomenon. These macrocycles can exist in the three configurations illustrated in Scheme III.[25,142] Nmr studies indicate that the out-out isomer (Scheme III, $k = l = m = 9$, **14c**) dissolved in 50% deuteriotrifluoroacetic acid was slowly converted to the in-in isomer until an equilibrium condition was reached which gave an equilibrium constant, K = in-in/out-out, equal to 0.41. Also, halide ions react with the in-in form to produce a new cation consistent with the encapsulation of the halide ions in the molecular cavity of the bicyclic amine.[185] This process, which involves the diffusion of halide ions into the cavity of a bicyclic amine, has been defined as katapinosis, and the resulting ion pairs have been termed katapinate ions. The katapinate ion formed by the encapsulation of chloride ion by the macrobicyclic diamine has the structure VII. The binding constants for halide ion encapsulation by these macrocyclic compounds are given in section V. It was postulated[185] that the stability of the complexes must be in part due to the high positive potential of the hole with respect to anions and from hydrogen bonding within the cavity. It was found that for chloride ions the encapsulated chloride ion exchanged rapidly with the external chloride ion.



VII

C. Cyclic Polythioethers

Metal chelates, primarily nickel(II) and cobalt(III), of several cyclic polythioethers containing three, four, six, and eight sulfur atoms have been reported.[146-148,186] The metal free cyclic polythioether ligand can usually be obtained from the complexes by reaction with water or ethanol to liberate the free ligand. The configuration of the metal ion-ligand complex is a function of the ring size and number of sulfur groups. A tridentate macrocycle, **40a**, with nickel(II), gave a complex with a 2:1 ligand/metal ratio, indicating the formation of a sandwich-type structure with the metal ion located between the two ligands.[147] Tetradentate macrocycles were found to contain the metal ion in the plane of the ring for ring size over 14 members[144,145] but to form complexes with 3:2 ligand/metal ratios for ring sizes of 13 members or less. Sexadentate ligands having 18 and 20 member rings were found[148] to have four of the sulfur atoms in a plane with the metal ion with the other two sulfur atoms occupying positions above and below the plane (octahedral geometry). An octadentate thioether was found to yield nickel(II) complexes in which the ligand was able to circumscribe completely two metal ions.[146] Spectral evidence indicates that each nickel(II) ion is located in a plane of the four sulfur atoms coordinated to it. With palladium(II) and platinum(II), however, the complexes formed had a metal to ligand ratio of 4:1, indicating that two sulfur atoms bind with each metal ion.

D. Mixed Donor Macrocycles

1. *Nitrogen-Oxygen Donor Groups*

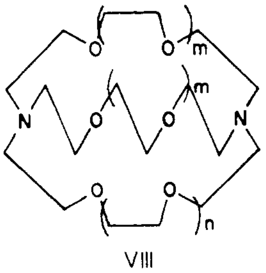
a. Monocyclic

Several macrocycles and metal complexes containing both nitrogen and oxygen donor groups have been reported.[180,187-189] The complexes formed with various metal ions were all 1:1 metal/ligand with the metal ion located in the cavity of the macrocycle.

The effect of substituting nitrogen for oxygen on the metal binding properties of the cyclic polyethers **6a** (18-crown-6) and **6g** (dibenzo-18-crown-6) with potassium and silver ions has been studied,[180] and the results are shown in Table VII. Complexing of potassium is weakened appreciably as nitrogen is substituted in the ring, the stability constant falling in the order of decreasing electronegativity of the substituted group, O > NR > NH. The effects on silver(I) complexing were exactly the opposite with the stability increasing with substitution. It was concluded that only electrostatic bonding exists in the potassium complexes whereas the silver(I) complexes have both electrostatic and covalent bonding.[180]

b. Bicyclic

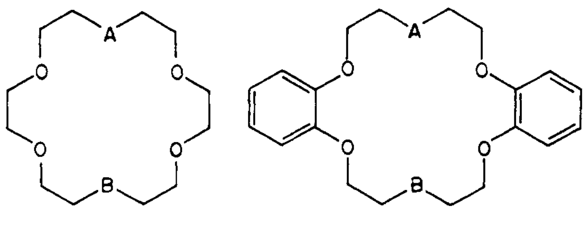
Several polyoxa macrobicyclic diamines represented by the structure VIII, where $m = n = p = 1$; $m = n = 1$, $p = 2$; $m = 1$, $n = p = 2$; and $m = n = p = 2$ have recently been reported.[149-151,190,191] These compounds are able to form metal ion complexes in which the metal ion is located within the central cavity of the macrocycle. The crystal structure of several metal complexes of **54a**[192,193] and of one metal complex of **55a**[194] have been determined by X-ray crystallography. In all cases it was found that the metal ion was located in the cavity of the macromolecule and that the two nitrogen atoms participated with the oxygen atoms in bonding to the metal atom. Binding constants for the formation of several metal complexes of **52a-57a** have been measured[150,191,195] and are given in section V. The complexes all showed 1:1 stoichiometry with the metal positioned in the center of the ligand cavity. These macrocycles demonstrate a very strong tendency to form remarkably stable complexes with, and to differentiate between, various metal ions.



VIII

Ligand	*m*	*n*
52a	0	1
53a	1	0
54a	1	1
55a	1	2
56a	2	1
57a	2	2

TABLE VII. Equilibrium Constants for the Interaction of Potassium and Silver(I) with Mixed Dentate Macrocycles at 25°



type 1 type 2

Ligand no.	Ligand type	A	B	Log *K*: K in methanol	Log *K*: Ag(I) in water
6a	1	O	O	6.10	1.60
6b	2	O	O	5.00	
48c	2	NR[a]	O	4.10	
48a	1	NH	O	3.90	3.3
48b	2	NH	O	3.20	
50a	1	NH	NH	2.04	7.8
50b	2	NH	NH	1.63	

[a] R = *n*-octyl.

The aqueous stability constants for the bicyclic ployoxa amines with a given metal ion are two or more decades above the constants for similar cyclic polyether derivatives.[191] Higher metal ion selectivity compared with monocyclic ligands was also found.[191]

2. *Sulfur-Nitrogen Donor Groups*

Metal complexes of mainly nickel(II) and cobalt(II) with macrocyclic ligands containing two sulfur and two nitrogen donors,[6,7,154,155] four sulfur and two nitrogen donors,[151-153,156] two sulfur and four nitrogen donors,[196] and one sulfur and four nitrogen donors[197,198] have been synthesized, and in some cases the metal-free ligand has also been obtained. The metal complexes of ligands of the type **66a** (four sulfur and two nitrogen donors) have four sulfur atoms lying in an equatorial plane with the two nitrogen atoms occupying trans positions.[152,153] However, the metal complexes of a ligand having two sulfur and four nitrogen donors (**67a**) have the metal located in the cavity octahedrally bound by the six donor atoms[196] (two sulfur atoms and two nitrogen atoms lying in an equatorial plane with two nitrogen atoms occupying trans positions). Apparently no metal binding constants have been reported for this class of macrocycles.

3. *Sulfur-Oxygen*

Macrocyclic polyether sulfides containing two to four sulfur atoms and two to four oxygen atoms have been found to form 1:1 complexes with alkali, alkaline earth, and silver cations.[180,199,200]

TABLE VIII. Log K, ΔH, ΔS, and ΔC_p Values for the Interaction of Ions with Synthetic Multidentate Macrocyclic Compounds

Cation	Log K	Method[a]	ΔH, kcal/mol	Method[a]	ΔS, cal/(mol deg)	ΔC_p, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
Oxygen Donor Atoms										
1c, M + L = ML										
Na^+	1.41	P					25	MeOH	10^{-4}–10^{-2}	180
2a, MF + L = MLF (F = fluorenyl ion)										
Na^+	2.176	S						Tetrahydrofuran		165
2c, M + L = ML										
Na^+	2.18	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	1.30	P					25	MeOH	10^{-4}–10^{-2}	180
3a, M + L = ML										
Na^+	0.72	C	−1.77	C	−2.6		25	20/80 wt % MeOH/H_2O	0	10
	1.17	C	−2.63	C	−3.5		25	40/60 wt % MeOH/H_2O	0	10
	1.64	C	−3.78	C	−5.2		25	60/40 wt % MeOH/H_2O	0	10
	1.99	C	−3.82	C	−3.7		25	70/30 wt % MeOH/H_2O	0	10
	2.26	C	−8.32	C	−17.6		25	80/20 wt % MeOH/H_2O	0	10
K^+	1.22	C	−1.8	C	−0.5		25	20/80 wt % MeOH/H_2O	0	10
	1.92	C	−2.51	C	0.4		25	40/60 wt % MeOH/H_2O	0	10
	2.54	C	−3.52	C	−0.2		25	60/40 wt % MeOH/H_2O	0	10
	2.93	C	−3.67	C	1.1		25	70/30 wt % MeOH/H_2O	0	10
	2.82	C	−10.20	C	−21.3		25	80/20 wt % MeOH/H_2O	0	10
	0.97	P					25	50/50 vol % tetrahydrofuran/H_2O		11
Rb^+	0.46	P					25	50/50 vol % tetrahydrofuran/H_2O		11
3d, M + L = ML										
Li^+	<1.0	P					25	H_2O	10^{-4}–10^{-2}	180
Na^+	<0.3	P					25	H_2O	10^{-4}–10^{-2}	180
	3.71	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	0.6	P					25	H_2O	10^{-4}–10^{-2}	180
	3.58	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	2.78	P					25	MeOH	10^{-4}–10^{-2}	180
3d, ML + L = ML_2										
K^+	1.88	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	1.91	P					25	MeOH	10^{-4}–10^{-2}	180
3j, FML = FLM (F = fluorenyl ion)										
Na^+	−0.284	S					25	Tetrahydropyran		14
	0.255	S					25	Tetrahydrofuran		14
3j, FM + L = FML (F = fluorenyl ion)										
Na^+	3.964	S					25	Tetrahydrofuran		14
3j, FM + L = FLM (F = fluorenyl ion)										
Na^+	4.217	S					25	Tetrahydrofuran		14
3j, FML + L = FLML (F = fluorenyl ion)										
Na^+	0.447	S					25	Tetrahydropyran		14
	0.544	S					25	Tetrahydrofuran		14
K^+	3.236	S					25	Tetrahydrofuran		14
4a, FM + L = FLM (F = fluorenyl ion)										
Na^+	3.845	S					25	Tetrahydrofuran		165
6a, M + L = ML										
Na^+	<0.3	P					25	H_2O	10^{-4}–10^{-2}	180
	4.32	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	2.06	P					25	H_2O	10^{-4}–10^{-2}	180
	6.10	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	0.8	P					25	H_2O	10^{-4}–10^{-2}	180
	4.62	P					25	MeOH	10^{-4}–10^{-2}	180
NH_4^+	1.1	P					25	H_2O	10^{-4}–10^{-2}	180
Ag^+	1.6	P					25	H_2O	10^{-4}–10^{-2}	180
6a, ML + L = ML_2										
Cs^+	1.30	P					25	MeOH	10^{-4}–10^{-2}	180
6c, M + L = ML										
Li^+	<0.7	P					25	H_2O	10^{-4}–10^{-2}	180
Na^+	0.8	P					25	H_2O	10^{-4}–10^{-2}	180
	4.09	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	1.90	P					25	H_2O	10^{-4}–10^{-2}	180
	5.89	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	0.8	P					25	H_2O	10^{-4}–10^{-2}	180
	4.30	P					25	MeOH	10^{-4}–10^{-2}	180
NH_4^+	1.1	P					25	H_2O	10^{-4}–10^{-2}	180
Ag^+	1.7–1.9	P					25	H_2O	10^{-4}–10^{-2}	180

TABLE VIII (continued)

Cation	Log *K*	Method[a]	Δ*H*, kcal/mol	Method[a]	Δ*S*, cal/(mol deg)	ΔC_p, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	*μ*	Ref
6c, $M + L = ML_2$										
Cs^+	1.52	P					25	MeOH	10^{-4}–10^{-2}	180
6d, FML = FLM (F = fluorenyl ion)										
K^+	−0.260	S					25	Tetrahydropyran		14
	−0.032	S	−3.0	T	−10.4		25	Tetrahydrofuran		14
6g, $M + L = ML$										
Na^+	3.18	Con					0	*N*,*N*-Dimethylformamide	10^{-3}	16
	5.17	Con					10	Acetonitrile	<0.004 *M* ($NaBPh_4$)	17
	4.62	Con					10	MeOH	<0.004 *M* (NaCl)	17
	2.97	Con					15	*N*,*N*-Dimethylformamide	10^{-3}	16
	5.04	Con					25	Acetonitrile	<0.004 *M* ($NaBPh_4$)	17
	4.36	P					25	MeOH	10^{-4}–10^{-2}	180
	4.16	Con					25	MeOH	<0.004 *M* (NaCl)	17
	2.69	Con					30	*N*,*N*-Dimethylformamide	10^{-3}	16
	2.58	Con					40	*N*,*N*-Dimethylformamide	10^{-3}	16
			−6	T	−7		10–40	*N*,*N*-Dimethylformamide	10^{-3}	16
6g, $M + L = ML$										
	5.04	Con					10	Acetonitrile	<0.004 *M* ($KBPh_4$)	17
K^+	4.83	Con					25	Acetonitrile	<0.004 *M* ($KBPh_4$)	17
	2.5	C	−5.5	C	−6.9		25	Dimethyl sulfoxide	0	10
	5.00	P					25	MeOH	10^{-4}–10^{-2}	180
	4.57	Con					25	MeOH	<0.004 *M* (KCl)	17
	1.87	P					25	50 vol % tetrahydrofuran 50 vol % H_2O		11
	5.04	Pol					—	0.2 *M* tetramethylammonium chloride in H_2O		19
Cs^+	3.55	P					25	MeOH	10^{-4}–10^{-2}	180
Rb^+	1.35	P					25	50 vol % tetrahydrofuran 50 vol % H_2O		11
6g, $ML + L = ML_2$										
Cs^+	2.92	P					25	MeOH	10^{-4}–10^{-2}	180
6h (Isomer A), $M + L = ML$										
Li^+	0.6	P					25	H_2O	10^{-4}–10^{-2}	180
Na^+	1.5–1.8	P					25	H_2O	10^{-4}–10^{-2}	180
	4.08	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	2.15	C	−4.14	C	−4.8		10	H_2O	0	10, 161
	2.02	C	−3.88	C	−3.8	20	25	H_2O	0	10, 161, 162
	2.18	P					25	H_2O	10^{-4}–10^{-2}	180
		P	−10.12	C			25	Acetone	≃0	22
	6.01	P					25	MeOH	10^{-4}–10^{-2}	180
	1.91	C	−3.58	C	−2.7		40	H_2O	0	10, 161
Rb^+	1.61	C	−3.43	C	−4.8		10	H_2O	0	10, 161
	1.52	C	−3.33	C	−4.2	5	25	H_2O	0	10, 161, 162
	1.40	C	−3.29	C	−4.1		40	H_2O	0	10, 161
Cs^+	1.00	C	−2.40	C	−3.9		10	H_2O	0	10, 161
	0.96	C	−2.41	C	−3.7	0	25	H_2O	0	10, 161, 162
	1.25	P					25	H_2O	10^{-4}–10^{-2}	180
	4.61	P					25	MeOH	10^{-4}–10^{-2}	180
	0.96	C	−2.38	C	−3.2		40	H_2O	0	10, 161
NH_4^+	1.33	C	−2.16	C	−1.2		25	H_2O	0	10, 161
	1.4	P					25	H_2O	10^{-4}–10^{-2}	180
Ba^{2+}	3.84	C	−4.97	C	0.0		10		0	10, 161
	3.57	C	−4.92	C	−0.2	4	25		0	10, 161
	3.47	C	−4.85	C	0.4		40		0	10, 161
Sr^{2+}	3.43	C	−3.68	C	2.7		10		0	10, 161
	3.24	C	−3.68	C	2.5	0	25		0	10, 161
	3.16	C	−3.70	C	2.6		40		0	10, 161
Ag^+	2.3	P					25		10^{-4}–10^{-2}	180
6h (Isomer A), $ML + L = ML_2$										
Cs^+	0.59	P					25	MeOH	10^{-4}–10^{-2}	180

TABLE VIII (continued)

Cation	Log K	Method[a]	ΔH, kcal/mol	Method[a]	ΔS, cal/(mol deg)	ΔCp, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
6h (Isomer A), FML = FLM (F = fluorenyl ion)										
K^+	0.255	S	−3.9	T	−11.7		25	Tetrahydrofuran		14
6h (Isomer B), M + L = ML										
Na^+	1.7	C	−2.5	C	−0.6		25	Dimethyl sulfoxide	0	10, 161
	∼4.5	C	∼−8.6	C			25	EtOH	0	10, 161
			−5.6	C	−1.9		25	MeOH	0	10, 161
	1.2–1.6	P					25	H_2O	10^{-4}–10^{-2}	180
	3.68	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	1.79	C	−5.78	C	−12.2		10	H_2O	0	10, 161
	1.63	C	−5.07	C	−9.6	53	25	H_2O	0	10, 161, 162
	2.7	C	−7.7	C	−13.5		25	Dimethyl sulfoxide	0	10, 161
	>6.0	C	∼−12.6	C			25	EtOH	0	10, 161
			−10.5	C	−10.5		25	MeOH	0	10, 161
	1.78	P					25	H_2O	10^{-4}–10^{-2}	180
			−11.06	C			25	Acetone	Low	22
	5.38	P					25	MeOH	10^{-4}–10^{-2}	180
	1.54	C	−4.19	C	−6.5		40	H_2O	0	10, 161
Rb^+	0.95	C	−4.6	C	−11.9		10	H_2O	0	10, 161
	0.87	C	−3.97	C	−9.3	44	25	H_2O	0	10, 161
	0.86	C	−3.30	C	−6.6		40	H_2O	0	10, 161
Cs^+	3.49	P					25	MeOH	10^{-4}–10^{-2}	180
NH_4^+	0.80	C	−3.41	C	−7.8		25	H_2O	0	10, 161
	0.80	P					25	H_2O	10^{-4}–10^{-2}	180
Ba^{2+}	3.44	C	−6.82	C	−8.3		10	H_2O	0	10, 161
	3.27	C	−6.20	C	−5.8	35	25	H_2O	0	10, 161
	3.12	C	−5.78	C	−4.2		40	H_2O	0	10, 161
Sr^{2+}	2.80	C	−3.45	C	0.6		10	H_2O	0	10, 161
	2.64	C	−3.16	C	1.5	17	25	H_2O	0	10, 161
	2.56	C	−2.91	C	2.4		40	H_2O	0	10, 161
Ag^+	1.59	C	−2.09	C	0.3		25	H_2O		10, 161
	1.8	P					25	H_2O	10^{-4}–10^{-2}	180
6h (Isomer B), ML + L = ML_2										
Cs^+	0.9	P					25	H_2O	10^{-4}–10^{-2}	180
6h (Isomer B), FML = FLM (F = fluorenyl ion)										
K^+	−0.097	S	−3.1	T	−10.7		25	Tetrahydrofuran		14
6h (Mixture Isomers A + B), M + L = ML										
Li^+			−3.87	C			25	Acetone	Low	22
			∼0	C			25	Dimethyl sulfoxide	Low	22
			∼0	C			25	Tetrahydrofuran	Low	22
Na^+			−6.43	C			25	NaI in acetone	Low	22
			−5.99	C			25	$NaB(C_6H_5)_4$ in acetone	Low	22
	5.20	Con					25	Acetonitrile	<0.004 *M* ($NaBPh_4$)	17
			−0.48	C			25	NaI in dimethyl sulfoxide	Low	22
	4.05	Con					25	MeOH	<0.004 *M* (NaCl)	17
			−4.78	C (Method 1)			25	$NaB(C_6H_5)_4$ in tetrahydrofuran	Low	22
			−5.03	C (Method 2)			25	$NaB(C_6H_5)_4$ in tetrahydrofuran	Low	22
	4.21	Pol						0.2 *M* tetramethylammonium chloride in H_2O		19
K^+			−9.71	C			25	KI in acetone	Low	22
			−9.29	C			25	$KB(C_6H_5)_4$ in acetone	Low	22
	5.63	Con					25	Acetonitrile	<0.004 *M* ($KBPh_3$)	17
			−7.53	C			25	KNO_3 in dimethyl sulfoxide	Low	22
			−7.45	C			25	$KB(C_6H_5)_4$ in dimethyl sulfoxide	Low	22
			−7.39	C			25	KI in dimethyl sulfoxide	Low	22
			−6.52	C			25	KI in dimethyl sulfoxide	Low	22
	5.35	Con					25	MeOH	<0.004 *M* (KCl)	17
	5.97	Pol						0.2 *M* tetramethylammonium chloride in H_2O		19

TABLE VIII (continued)

Cation	Log *K*	Method[a]	ΔH, kcal/mol	Method[a]	ΔS, cal/(mol deg)	ΔC_p, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
Rb^+	4.43	Pol						0.2 *M* tetramethylammonium chloride in H_2O		19
Cs^+			−8.40	C			25	$CsB(C_6H_5)_4$ in acetone	Low	22
	4.26	Con					25	Acetonitrile	<0.004 *M* ($CsBPh_4$)	17
			−6.94	C			25	CsI in dimethyl sulfoxide	Low	22
	3.85	Con					25	MeOH	<0.004 *M* (CsCl)	17
	4.25	Pol						0.2 *M* tetramethylammonium chloride in H_2O		19
NH_4^+			−9.98	C			25	NH_4I in acetone	Low	22
			−4.15	C			25	NH_4I in dimethyl sulfoxide	Low	22
Tl^+	5.20	Pol						0.2 *M* tetramethylammonium chloride in H_2O		19
					6m, M + L = ML					
Li^+	<0.6	Con					25	H_2O	10^{-4}–10^{-2}	23
Na^+	1.42	Con					25	H_2O	10^{-4}–10^{-2}	23
K^+	2.08	Con					25	H_2O	10^{-4}–10^{-2}	23
Cs^+	0.9	Con					25	H_2O	10^{-4}–10^{-2}	23
Rb^+	1.53	Con					25	H_2O	10^{-4}–10^{-2}	23
NH_4^+	1.28	Con					25	H_2O	10^{-4}–10^{-2}	23
					9a, M + L = ML					
K^+	4.41	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	5.02	P					25	MeOH	10^{-4}–10^{-2}	180
					9b, M + L = ML					
Na^+	2.40	P					25	MeOH	10^{-4}–10^{-2}	180
K^+	4.30	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	4.20	P					25	MeOH	10^{-4}–10^{-2}	180
					9b, ML + L = ML_2					
Cs^+	1.9	P					25	MeOH	10^{-4}–10^{-2}	180
					9c, M + L = ML					
Cs^+	1.9	P					25	H_2O	10^{-4}–10^{-2}	180
					10a, M + L = ML					
K^+	3.48	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	4.15	P					25	MeOH	10^{-4}–10^{-2}	180
					10b, M + L = ML					
K^+	3.49	P					25	MeOH	10^{-4}–10^{-2}	180
Cs^+	3.78	P					25	MeOH	10^{-4}–10^{-2}	180
					10c, M + L = ML					
Cs^+	1.9	P					25	H_2O	10^{-4}–10^{-2}	180
					11a, M + L = ML					
Na^+	2.0	P					25	MeOH	10^{-4}–10^{-2}	180
	2.114	S	−4	T			25	MeOH	0.15 *M* (LiCl)	24
K^+	4.60	P					25	MeOH	10^{-4}–10^{-2}	180
	4.568	S	−11.5	T			25	MeOH	0.15 *M* (LiCl)	24
	1.35	P					25	50 vol % tetrahydrofuran 50 vol % H_2O		11
Rb^+	4.643	S	−12.7	T			25	MeOH	0.15 *M* (LiCl)	24
	1.56	P					25	50 vol % tetrahydrofuran 50 vol % H_2O		11
Cs^+	4.230	S	−11.2	T			25	MeOH	0.15 *M* (LiCl)	24
NH_4^+	2.431	S	−5.5	T			25	MeOH	0.15 *M* (LiCl)	24
Tl^+	4.505	S	−11	T			25	MeOH	0.015 *M* (tetrabutylammonium perchlorate	24
					12a, M + L = ML					
K^+	3.90	P					25	MeOH	10^{-4}–10^{-2}	180
					Nitrogen Donor Atoms					
					14a, out-out = in-in					
	−0.071						23	50% trifluoroacetic acid		142
					14b, out-out = in-in					
	>2						23	50% trifluoroacetic acid		142
					14c, Halide + L = Halide(L)					
Cl^-	0.602	Pmr					23	50% aq trifluoroacetic acid		185
Br^-	0	Pmr					23	50% aq trifluoroacetic acid		185

TABLE VIII *(continued)*

Cation	Log K	Method[a]	ΔH, kcal/mol	Method[a]	ΔS, cal/(mol deg)	ΔC$_p$, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
14c, out-out = in-in										
	−0.383						23	50% aq trifluoroacetic acid		142
14d, out-out = in-in										
	0.518						23	50% aq trifluoracetic acid		142
14e, out-out = in-in										
	3.80						23	50% aq trifluoroacetic acid		142
14f, out-out = in-in										
	−0.155						23	50% aq trifluoroacetic acid		142
14g, out-out = in-in										
	0.176						23	50% aq trifluoroacetic acid		142
18a, *cis*-$[M(H_4L)(H_2O)_2]^{3+}$ = *cis*-$[M(H_3L)(H_2O)_2]^{2+} + H^+$										
Co^{3+}	4.9	P					25	0.5 *M* $NaClO_4$ in H_2O		45
Cr^{3+}	3.8	P					20	H_2O	0.1	41
18a, *trans*-$[M(H_4L)(H_2O)_2]^{3+}$ = *trans*-$[M(H_3L)(H_2O)_2]^{2+} + H^+$										
Co^{3+}	2.9	P					25	0.5 *M* $NaClO_4$ in H_2O		45
Cr^{3+}	3.05	P					20	H_2O	0.1	41
18a, *cis*-$[M(H_3L)(H_2O)_2]^{2+}$ = *cis*-$[M(H_2L)(H_2O)_2]^{+} + H^+$										
Co^{3+}	8.0	P					25	0.5 *M* $NaClO_4$ in H_2O		45
Cr^{3+}	7.0	P					20	H_2O	0.1	41
18a, *trans*-$[M(H_3L)(H_2O)_2]^{2+}$ = *trans*-$[M(H_2L)(H_2O)_2]^{+} + H^+$										
Co^{3+}	7.2	P					25	0.5 *M* $NaClO_4$ in H_2O		45
Cr^{3+}	6.6	P					20	H_2O	0.1	41
18b (Meso Isomer), M + L = ML										
H^+	12.6	Sol					25	H_2O		182
	11.6	P					25	H_2O		56
18b (Meso Isomer), ML + M = M_2L										
H^+	10.4	P					25	H_2O		182
	10.7	P					25	H_2O		56
18b (Meso Isomer), M_2L + M = M_3L										
H^+	0.8	P					25	H_2O		182
	2.7	P					25	H_2O		56
18b (Meso Isomer), M_3L + M = M_4L										
H^+	~0	(est)					25	H_2O		182
	2.3	P					25	H_2O		56
18b (Meso Isomer), $ML^{2+} + CN^- = MLCN^+$										
Cu^{2+}	2.949	S					22	H_2O	0	58
18b (Meso Isomer), M + L = ML										
Cu^{2+}	20	S					25	H_2O (blue complex)	0.1 *M* (HCl)	182
	28	S					25	H_2O (red complex)	0.1 *M* (HCl)	182
18b (Racemic Isomer), M + L = ML										
H^+	>11	P					25	H_2O		56
18b (Racemic Isomer), ML + M = M_2L										
H^+	10.5	P					25	H_2O		56
18b (Racemic Isomer), M_2L + M = M_3L										
H^+	2.2	P					25	H_2O		56
18b (Racemic isomer), M_3L + M = M_4L										
H^+	<2	P					25	H_2O		56
18g, $ML^{2+} + I^- = MLI^+$										
Cu^{2+}	0.892	S					25	H_2O	1	50
18g, $ML^{2+} + CN^- = MLCN^+$										
Cu^{2+}	2.681	S					22	H_2O	0	58
Ni^{2+}	1.398	S					22	H_2O	0	58
18g, $ML^{2+} + SCN^- = MLSCN^+$										
Cu^{2+}	0.778	S					25	H_2O	1	50
18g, $ML^{2+} + S_2O_3^{2-} = MLS_2O_3$										
Cu^{2+}	1.491	S					25	H_2O	1	50
18h, $ML^{2+} + CN^- = MLCN^+$										
Cu^{2+}	2.415	S					22	H_2O	0	58
18i, $ML^{2+} + CN^- = MLCN^+$										
Cu^{2+}	2.477	S					22	H_2O	0	58
Sulfur Donor Atoms										
43a, $ML^{2+} + I^- = MLI^+$										
Ni^{2+}	3.602							Nitromethane		144, 145
43a, $MLI^+ + I^- = MLI_2$										
Ni^{2+}	1.223							Nitromethane		144, 145

TABLE VIII (continued)

Cation	Log K	Method^a	ΔH, kcal/mol	Method^a	ΔS, cal/(mol deg)	ΔC$_p$, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
Mixed Donor Atoms: Oxygen-Nitrogen										
48a, M + L = ML										
K^+	3.90	P					25	MeOH	10^{-4}–10^{-2}	180
Ag^+	3.3	P					25	H_2O	10^{-4}–10^{-2}	180
48b, M + L = ML										
K^+	3.20	P					25	MeOH	10^{-4}–10^{-2}	180
48c, M + L = ML										
K^+	4.10	P					25	MeOH	10^{-4}–10^{-2}	180
50a, M + L = ML										
K^+	2.04	P					25	MeOH	10^{-4}–10^{-2}	180
Ag^+	7.8	P					25	H_2O	10^{-4}–10^{-2}	180
50b, M + L = ML										
K^+	1.63	P					25	MeOH	10^{-4}–10^{-2}	180
50c, M + L = ML										
Na^+	3.26	P					25	95.5% MeOH 4.5% H_2O		114
K^+	4.38	P					25	95.5% MeOH 4.5% H_2O		114
Ba^{2+}	6.67	P					25	95.5% MeOH 4.5% H_2O		114
50d, M + L = ML										
Na^+	3.0	P					25	95.5% MeOH 4.5% H_2O		114
K^+	4.35	P					25	95.5% MeOH 4.5% H_2O		114
Ba^{2+}	<2.0	P					25	95.5% MeOH 4.5% H_2O		114
52a, M + L = ML										
Li^+	4.30	P	−4.6	C	4		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Na^+	2.70	P	−4.7	C	−4		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		195
	2.80	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	2.55	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	2.7	P					25	4–8 × 10^{-2} *M* NMe_4Br in MeOH		191
K^+	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	<1.0	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Rb^+	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
Cs^+	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
Ca^{2+}	2.80	P	0	C	13		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Ba^{2+}	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
Sr^{2+}	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
53a, M + L = ML										
Li^+	2.50	P	0.4	C	13		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Na^+	5.40	P	−3.2	C	14		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	5.30	P	−4.7	C	8		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		195
	>9.0	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in MeOH		191
K^+	3.95	P	−5.9	C	−2		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
	3.9	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
Rb^+	2.55	P	−3.2	C	1		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Cs^+	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
Ca^{2+}	6.95	P	−1.7	C	26		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	6.95	P	−2.7	C	23		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		195
Mg^{2+}	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
Ba^{2+}	6.30	P	−5.1	C	12		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Sr^{2+}	7.35	P	−5.0	C	17		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
54a, M + L = ML										
Li^+	~0	P					20	H_2O		150
	<2.0	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
Na^+	3.6	P					20	H_2O		150
	3.90	P	−5.8	C	−2		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191, 195
	3.70	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	>9.0	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in MeOH		191
	6.95	P					25	95.5% MeOH, 4.5% H_2O		114
K^+	5.1	P					20	H_2O		150
	5.30	P	−11.1	C	−13		25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		195
	5.40	P					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	5.0	P(sie)^b					25	4–8 × 10^{-2} *M* NMe_4Br in H_2O		191
	9.45	P					25	95.5% MeOH, 4.5% H_2O		114

TABLE VIII (continued)

Cation	Log K	Method^a	ΔH, kcal/mol	Method^a	ΔS, cal/(mol deg)	ΔC_p, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
Rb$^+$	3.7	P					20	H$_2$O		150
	4.35	P	−10.5	C	−15		25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191, 195
	4.8	P(sie)^b					25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191
Cs$^+$	−0.7	P					20	H$_2$O		150
	<2.0	P					25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191, 195
Ca^{2+}	4.1	P					20	H$_2$O		150
	4.40	P	−0.15	C	20		25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191, 195
Mg^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191
Ba^{2+}	>15	P					20	H$_2$O		150
	9.50	P	−12.9	C	0		25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191, 195
	11.5	P					25	95.5% MeOH, 4.5% H$_2$O		114
Sr^{2+}	13.0	P					20	H$_2$O		150
	8.00	P	−8.1	C	9		25	$4–8 \times 10^{-2}$ M NMe$_4$Br in H$_2$O		191, 195
54b, M + L = ML										
Na$^+$	7.4	P					25	95.5% MeOH, 4.5% H$_2$O		114
K$^+$	9.05	P					25	95.5% MeOH, 4.5% H$_2$O		114
Ba^{2+}	11.05	P					25	95.5% MeOH, 4.5% H$_2$O		114
54c, M + L = ML										
Na$^+$	7.3	P					25	95.5% MeOH, 4.5% H$_2$O		114
K$^+$	8.6	P					25	95.5% MeOH, 4.5% H$_2$O		114
Ba^{2+}	8.5	P					25	95.5% MeOH, 4.5% H$_2$O		114
55a, M + L = ML										
Li$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Na$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
	1.65	P(sie)^b					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
	4.80	P(sie)^b					25	$4–8 \times 10^{-2}$ M LiCl in MeOH		191
K$^+$	2.2	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
	2.1	P(sie)^b	−6.2	C	−11		25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Rb$^+$	2.05	P(sie)^b	−5.4	C	−9		25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Cs$^+$	2.20	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
	1.8	P(sie)^b	−6.5	C	−14		25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Ca^{2+}	2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Mg^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
Ba^{2+}	6.00	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Sr^{2+}	3.40	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
56a, M + L = ML										
Li$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Na$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
	2.80	P(sie)^b					25	$4–8 \times 10^{-2}$ M LiCl in MeOH		191
K$^+$	1.60	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		195
	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
Rb$^+$	≤0.7	P(sie)^b					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Cs$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Ca^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Mg^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
Ba^{2+}	3.65	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Sr^{2+}	2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191
	1.8	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		195
57a, M + L = ML										
Li$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Na$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
K$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Rb$^+$	≤0.5	P(sie)^b					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Cs$^+$	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Ca^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Mg^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
Sr^{2+}	<2.0	P					25	$4–8 \times 10^{-2}$ M LiCl in H$_2$O		191, 195
60a, M + L = ML										
Na$^+$	4.5	P(sie)^b					25	MeOH		119
K$^+$	5.8	P(sie)^b					25	MeOH		119
Rb$^+$	6.2	P(sie)^b					25	MeOH		119
Cs$^+$	>6.0	P(sie)^b					25	MeOH		119
Ag$^+$	6.0	P(sie)^b					25	H$_2$O		119
	>9.5	P(sie)^b					25	MeOH		119
60a, ML + M = M$_2$L										
Ag$^+$	>6.0						25	MeOH		119

TABLE VIII (continued)

Cation	Log *K*	Method[a]	Δ*H*, kcal/mol	Method[a]	Δ*S*, cal/(mol deg)	ΔC_p, cal/(mol deg)	Temp, °C	Supporting electrolyte/solvent	μ	Ref
						72a, M + L = ML				
K^+	1.15	P					25	MeOH	10^{-4}–10^{-2}	180
Ag^+	4.34	P					25	H_2O	10^{-4}–10^{-2}	180

[a] Method used to determine log *K* values: P, potentiometric; S, spectrophotometry; C, calorimetry; Con, conductance; Pol, polarography; Sol, solvent extraction. [b] sie = selective ion electrode.

TABLE IX. Structures of Metal–Macrocycle Complexes

Macrocycle, L	Metal	Anion	Structure	Method	Ref
			Oxygen Donor Atoms		
3a (benzo-15-crown-5)	Na^+	I^-	NaLI: Na atom located equidistant from and slightly out of plane of O atoms	X-Ray	203 169
6g (dibenzo-18-crown-6)	Na^+	Br^-	$NaLBr\cdot 2H_2O$: Na atom located in plane of O atoms	X-Ray	204 169
	Rb^+, Na^+	SCN^-	$(Rb_{0.55}Na_{0.45})LSCN$: only one metal atom bonded to a given cyclic polyether. Metals are located in planes of O atoms	X-Ray	15 166
6h (isomer A) (dicyclohexyl-18-crown-6)	Ba^{2+}	SCN^-	$BaL(SCN)_2$: Ba atom located in plane of O atoms	X-Ray	202
	Co^{2+}	Cl^-	$Co_2L_2Cl_4$: sandwich structure having two Co atoms located equidistant between two cyclic polyethers with each Co atom coordinated to three O atoms in each polyether $[Co_2L_2Cl_4]_n$: polymeric structure consisting of alternate cyclic polyethers and Co atoms with the Co atoms coordinated to three O atoms from each of two polyethers	Spectral and magnetic data	167
10b (dibenzo-24-crown-8)	K^+	SCN^-	$K_2L(SCN)_2$: two K atoms located in plane of O atoms with each K atoms coordinated to five O atoms	X-Ray	168
11a (dibenzo-30-crown-10)	K^+	I^-	KLI: K atom located in loop of O atoms which are essentially equidistant from K	X-Ray	205 169
			Nitrogen Donor Atoms		
15a	Ni^{2+}	NO_3^-	$NiL(H_2O)(NO_3)_2$: Ni octahedrally coordinated with three N atoms, two H_2O molecules, and one nitrate; Ni is above plane of N atoms and equidistant from them	X-Ray	28
	Co^{3+}	I^-	CoL_2I_3: Co coordinated to six N atoms, three from each macrocycle; the three N in each macrocycle define planes which are parallel to one another with the Co sandwiched midway between	X-Ray	30
18a	Ni^{2+}	Cl^-	$NiLCl_2$: Ni atom position is a slight tetrahedral distortion from square-planar coordination	X-Ray	213
18b (tet b)	Ni^{2+}	ClO_4^-	$[NiLAcO]ClO_4$: four N atoms coordinated to adjacent octahedral sites of Ni atom with Ac groups occupying the two remaining sites	X-Ray	210
18i	Ni^{2+}	ClO_4^-	NiLClO: Ni atom coordination is square planar	Pmr spectra	214
	Cu^{2+}	ClO_4^-	$CuLClO_4$: Cu atom coordination is square planar	Pmr spectra	214
18n	Ni^{2+}	ClO^{4-}	$NiL(ClO_4)_2$: Ni atom position is a slight tetrahedral distortion from square-planar coordination	X-Ray	211 212 216
	Co^{3+}	CN^-	$[CoL(CN)_2]ClO_4$: stereochemical arrangement about the central Co atom is approximately octahedral with CN groups above and below the macrocycle	X-Ray	206
18v (*cis*-tetene)	Ni^{2+}	ClO_4^-	$NiL(ClO_4)_2$: Ni atom position is a slight tetrahedral distortion from square-planar coordination	X-Ray	207
20h (TABB)	Ni^{2+}	I^-	$NiLI_2\cdot H_2O$: Ni atom position is tetragonally coordinated to N atoms with opical positions occupied by an I atom and a H_2O atom	X-Ray	209
	Ni^{2+}	BF_4^-	$NiL(BF_4)_2$: Ni atom coordination is square planar	X-Ray	209
21b	Ni^{2+}	Br^-	$NiLBr_2\cdot H_2O$: stereochemical arrangement about the central Ni atom is approximately square pyramidal with Br atom at the apex	X-Ray	217
25a	Fe^{3+}	ClO^{4-}	$[(H_2O)LFe–O–FeL(H_2O)](ClO_4)_4$: dimer, with each Fe located in plane of five N atoms of one macrocycle	X-Ray	103

TABLE IX (continued)

Macrocycle, L	Metal	Anion	Structure	Method	Ref
	Fe^{3+}	SCN^-	$[FeL(NCS)_2]ClO_4$: Fe atom located in plane of N atoms	X-Ray	103
31a	Cu^{2+}	Cl^-	$[CuLCl]^+[CuCl_2]^-$: Cu bonded to four N atoms and to one Cl atom; Cl occupies the opical position of a distorted square pyramid	X-Ray	215
38a (phthalocyanine)	Ni^{2+} Pt^{2+} Be^{2+} Mn^{2+} Fe^{2+} Co^{2+} Cu^{2+}		Metal ion located in plane of N atoms (square-planar coordination)	X-Ray	141
			Mixed Donor Atoms: Nitrogen-Oxygen		
49a	Ni^{2+}	I^-	$NiLI_2$: Ni lies in plane defined by N and O atoms; I atoms occupy opical positions from Ni atom	X-Ray	187
50a	Cu^{2+}	Cl^-	$CuLCl_2$: Cu located in cavity of macrocycle bound by two N and two O atoms; two atoms are not coordinated to the Cu	X-Ray	189
54a	Na^+	I^-	NaLI: Na located in cavity of macrocycle bound by two N and six O atoms	X-Ray	193
	K^+	I^-	KLI: K located in cavity of macrocycle bound by two N and six O atoms	X-Ray	193
	Rb^+	SCN^-	$RbLSCN \cdot H_2O$: Rb located in cavity of macrocycle bound by two N and six O atoms	X-Ray	192
	Cs^+	SCN^-	$CsLSCN \cdot H_2O$: Cs located in cavity of macrocycle bound by two N and six O atoms	X-Ray	193
	Ba^{2+}	SCN^-	$BaL(SCN)_2 \cdot H_2O$: Ba located in cavity of macrocycle bound by two N and six O atoms of the macrocycle, an O atom of a water molecule, and the N atom of a thiocyanate group	X-Ray	194
55a	Ba^{2+}	SCN^-	$BaL(SCN)_2 \cdot 2H_2O$: Ba located in cavity of macrocycle bound by two N and seven O of the macrocycle and two water O atoms	X-Ray	194
			Mixed Donor Atoms: Sulfur-Nitrogen		
67a	Fe^{2+}	ClO_4^-	$FeL(ClO_4)_2 \cdot CH_3OH$: Fe located in cavity of macrocycle octahedrally bound by two S and four N atoms	X-Ray	196

A symmetrical macrocycle having two sulfur and four oxygen atoms, **72a**, has been synthesized, and log *K* values have been reported for the Ag^+ and K^+ complexes in aqueous solution.[180] A fourfold increase in the binding constant for Ag^+ over that for K^+ was found and attributed to the ability of Ag^+ to form both ionic bonds with oxygen atoms and covalent bonds with the sulfur atoms, whereas the K^+ can form only ionic bonds.

4. *Nitrogen–Sulfur–Oxygen*

a. Monocyclic

A 12-membered macrocycle, **74a,** containing one oxygen, two sulfur, and one nitrogen donor atoms was found to readily form 1:1 metal complexes with nickel(II) and cobalt(II) with the metal and ligand located not in a plane but in an octahedral configuration[148] where the other two bonding positions were occupied by unidentate groups (Cl or Br). This configuration was at least partially attributed to the relatively small hole available in the ring for insertion of the metal.

b. Bicyclic

Macrobicyclic diamines containing oxygen, sulfur, and nitrogen atoms, **75a** and **76a**, have been found to form predominantly 1:1 type complexes with a series of metal ions in water and in chloroform.[151] No equilibrium constants have been reported for the reaction of metal ions with macrocycles containing three different donor groups.

V. Thermodynamic Data

The thermodynamic quantities (log *K*, ΔH, ΔS, and ΔC_p) for the interaction of ions with synthetic multidentate macrocyclic molecules together with the methods and conditions used in their determination are given in Table VIII. The data in Table VIII are arranged according to the order in which the macrocycles appear in Table I with macrocycles containing oxygen donor atoms first followed by nitrogen, sulfur, and mixed donor atoms in that order. Within each such group the ligands are listed in order of increasing numbers of donor atoms. The metal ion order is that given in ref 121. Consecutive reactions are given first, followed by overall and unspecified reactions in that order. The log *K* and ΔH values are listed in order according to first, temperature; second, solvent; and third, ionic strength. The data valid at the lowest temperature are given first, followed by data obtained at higher temperatures. At each temperature the data valid in aqueous solution are given first followed by those determined in other solvents arranged alphabetically according to the solvent. For each solvent the data are arranged in order of ionic strength with those valid at the lowest ionic strength given first.

The most numerous thermodynamic data included in Table VIII are equilibrium constants. Relatively few ΔH and ΔS and very few ΔC_p values have been reported. The equilibrium constant determinations have been made under a variety of temperature, ionic strength, and solvent conditions, and in some cases one or more of these

TABLE X. Kinetic Data for the Interaction of Cations with Synthetic Multidentate Macrocyclic Compounds

Cation	k_f, M^{-1} sec^{-1}	k_r, sec^{-1}	Method	ΔE_f, kcal/mol	ΔE_r, kcal/mol	Temp, °C	Supporting electrolyte/solvent	μ	Ref
Oxygen Donor Atoms									
6g, M + L = ML									
Na^+	6×10^7	1×10^5	^{23}Na nmr spectroscopy	6.5	12.6	25	Measurements performed in *N,N'*-dimethylformamide containing 0.3–1.9 *M* NaSCN and 0.1–0.2 *M* L in temp range −60 to 80°	0	16
11a, M + L = ML									
Na^+	$>1.6 \times 10^7$	$>1.3 \times 10^5$	Spectrophotometry[a]			25	MeOH	0.15 *M* (LiCl)	24
K^+	6×10^8	1.6×10^4	Spectrophotometry[a]			25	MeOH	0.15 *M* (LiCl)	24
Rb^+	8×10^8	1.8×10^4	Spectrophotometry[a]			25	MeOH	0.15 *M* (LiCl)	24
Cs^+	8×10^8	4.7×10^4	Spectrophotometry[a]			25	MeOH	0.15 *M* (LiCl)	24
NH_4^+	$>3 \times 10^7$	$>1.1 \times 10^5$	Spectrophotometry[a]			25	MeOH	0.15 *M* (LiCl)	24
Tl^+	8×10^6	2.5×10^4	Spectrophotometry[a]			25	MeOH	0.015 *M* (tetrabutylammonium perchlorate)	24
54a, $ML^+ + Cl^- = MLCl$									
Na^+		27			14.2	3	D_2O containing 10% L		190
54a, $ML^+ + F^- = MLF$									
K^+		38			15.8	36	D_2O containing 10% L		190
54a, $ML^+ + Cl^- = MLCl$									
K^+		38			15.8	36	D_2O containing 10% L		190
54a, $ML^+ + Br^- = MLBr$									
K^+		42			15.7	35	D_2O containing 10% L		190
54a, $ML^+ + Cl^- = MLCl$									
Rb^+		38			14.4	9	D_2O containing 10% L		190
54a, $MLCl^+ + Cl^- = MLCl_2$									
Ca^{2+}		<20			>17	>100	D_2O containing 10% L		190
54a, $MLCl^+ + Cl^- = MLCl_2$									
Ba^{2+}		<18			>17	>100	D_2O containing 10% L		190
54a, $MLCl^+ + Br^- = MLBr_2$									
Sr^{2+}		<15			>17	>100	D_2O containing 10% L		190
54a, $ML^+ + Cl^- = MLCl$									
Tl^+		51			15.8	39	D_2O containing 10% L		190
		64			15.7	40	D_2O containing 10% L		190
54a, $ML^+ + NO_3^- = MLNO_3$									
Tl^+		51			13.5	−6	D_2O containing 10% L		190

[a] Absorbance change at isosbestic point.

quantities have not been reported. The wide range of solvents used is understandable in terms of the range of solubilities and of reactivities exhibited by the various macrocycles. It should be realized that the thermodynamic values are valid only at the specific experimental conditions and are not necessarily comparable with data obtained under different conditions. It is also well to realize that often the substance used as the added electrolyte interacts to a significant extent with the ligand or metal being studied so that competing reactions take place which can affect the values obtained. A further complication is encountered in the determination of ΔH values by calorimetric procedures where use of added electrolyte can result in errors which are often undetected. The hydration sphere of the reacting metal (and in some cases the ligand also) is changed in the presence of added electrolyte to contain some (usually unknown) number of coordinated electrolyte ions. Heat effects involved in the replacement of these ions could be significantly different from those involved in replacing the solvent molecules. Thus, in most cases, neither the log *K* nor ΔH value is known for the reaction of the added electrolyte, leaving the ΔH value for the formation of the metal complex in error by some unknown amount.

The ΔH values in Table VIII have often been calculated from the variation of the equilibrium constant with temperature. This method involves a differentiation process and results in a certain loss in accuracy which can be minimized if careful work is done at many temperatures. Therefore, one should be careful not to attach undue significance to the very small standard deviations often reported for ΔH values calculated by this method. The errors propagated through differentiation in calculating ΔH values from equilibrium constant data as a function of temperature have been discussed.[201] In general, the direct methods of calorimetry are preferable to temperature-dependent methods for the determination of ΔH values.

Enthalpy changes, ΔS, and ΔC_p values provide information regarding sites of binding and interactions of the metal ion with the macrocycle and the effect of the solvent on these interactions. The magnitude of the ΔH values are indicative of (a) the type and number of binding sites (*i.e.*, oxygen, nitrogen, sulfur, etc.). The magnitudes of the ΔS values are indicative of solvent–solute interaction and supply information about relative degrees of hydration of the metal ion, macrocycle and complex, the loss of degrees of freedom of the macrocycle when complexed with the metal ion, and charge types involved in the reaction. In addition, comparison of the ΔH and ΔS values for systems give rise to analogies among such systems. Izatt and coworkers[4] have extensively discussed the variation of thermodynamic quantities in cation–macrocycle interaction with respect to cation parameters (size, type, and charge) and macrocycle parameters (size of cavity, type and number of donor atoms, type and number of rings, and conformation of ring).

VI. Structural Data

The structures of metal macrocyclic complexes are presented in Table IX. The structures are arranged according to the order in which the macrocycles appear in Table I with macrocycles containing oxygen donor atoms first, followed by nitrogen, sulfur, and mixed donor atoms. Both the metal forming the complex and the predominant the metal forming the complex and the predominant anion are given together with the free macrocycle. A description of the complex is given from the point of view of describing the general location of the metal in the cavity of the macrocycle. The crystal structure data indicate that polyether macrocycles in general form complexes with alkali metal salts in which the metal is held in the center of a ring formed by the coplanar oxygen atoms for rings containing four, five, and six oxygen atoms (ref 15, 166, 167, 169, 202–204). Larger rings can apparently accommodate more than one metal ion, as a ring containing eight O atoms was found[168] to form a 2:1 metal–macrocycle complex. As the ring gets even larger, however, the macrocycle tends to form 1:1 complexes in which the ligand is wrapped around the metal ion. This latter configuration was found for a ring containing ten oxygen atoms.[169,205]

Metal–ligand complexes formed by transition metal ions and macrocycles containing four nitrogen atoms have the metal located in the center of a ring formed by four coplanar nitrogen atoms.[206–217]

Polyoxa macrobicyclic diamines appear from crystal structure data to bind both alkali and alkaline earth metal ions in the cavity formed by the nitrogen and oxygen atoms.[192–194] The metals are bound to both the nitrogen and oxygen atoms and are located approximately equidistant from the oxygen atoms and from the nitrogen atoms.

VII. Kinetic Data

Kinetic data for the interaction of metal ions with macrocyclic molecules and for the interaction of metal–macrocyclic complexes with anions are given in Table X. The macrocycles are arranged in Table X according to the order in which they appear in Table I. Where available, both forward and reverse reaction rates are given as well as forward and reverse energies of activation.

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