Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 240 (2003) 57–75
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Ammonium based anion receptors

José M. Llinares, Douglas Powell, Kristin Bowman-James *

Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA

Received 23 August 2002; accepted 15 January 2003

Contents

Abstract

Selective anion recognition has been a tremendous challenge to chemists over the decades. However, with the advent of the concepts inherent in 'supramolecular chemistry,' the field now flourishes. Of the major types of receptors, polyamines have been studied widely as anion hosts by a number of researchers. Both electrostatic interactions and hydrogen bonds between protonated amines and the anion guests govern the binding in these systems. Exceptions to this rule are found in the quaternary ammonium systems, which utilize primarily electrostatic interactions and topological complementarity for binding purposes. This review focuses only on amine-based hosts, and is divided into acyclic and macrocyclic categories, the latter of which are based on cyclic dimension. The resulting four categories are: acyclic, monocyclic, bicyclic, and polycyclic. Within the major categories, binding is discussed according to the nature of the anion target, i.e. 'simple' inorganic anions, organic anions, and anionic metal complexes.

Keywords: Anion recognition; Polyammonium macrocycles; Azacryptands; Polycyclic amines; Quaternary ammonium receptors

1. Introduction

Selective anion recognition has been a tremendous challenge to chemists over the decades. However, with the advent of the concepts inherent in 'supramolecular chemistry,' the field now flourishes. The birth of 'anion coordination chemistry' might be considered to be the report by Park and Simmons in 1968 that simple bicyclic diaza katapinands could encapsulate halide ions [1], but the field lay dormant until the mid-1970s. At that time Lehn and co-worker began to explore the opportunities behind anion coordination chemistry in polyammonium

* Corresponding author. Tel.: +1-785-864-3669; fax: +1-785-864-5396.
E-mail address: kbowman-james@ku.edu (K. Bowman-James).

0010-8545/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0010-8545(03)00019-5

macrocycles [2]. A number of researchers are now involved in this fast evolving field, which includes a wide variety of different types of receptors.

Both electrostatic interactions and hydrogen bonds between protonated amines and the anion guests govern the binding in these systems. The protonation of the amines to their polyammonium forms increases the positive charge density and consequently affinities are higher. Since many of the macrocycles are multiply protonated at pH 7 (i.e. in the polyammonium form), the onset of significant binding occurs right around neutral conditions. Exceptions to this rule are found in the quaternary ammonium systems, which were largely explored by Schmidtchen [3], and where hydrogen bond interactions are absent. The rationale for examining the quaternary systems was to explore the contribution of hydrogen bonding to the observed affinities.

Information about binding is obtained by solution as well as solid state (crystallographic) data. Affinities between anions and their polyamine-based receptors are usually measured in aqueous solutions. These are the most challenging conditions for achieving significant binding and selectivity because of the strong solvation capabilities of water. Perhaps the most informative method used to calculate binding constants is potentiometric measurements, which have the capability of measuring binding over a range of pHs. In the polyammonium receptors, these measurements are complicated by a complex series of protonation steps and multiple equilibria. The necessity of using an electrolyte to maintain constant ionic strength further complicates the situation, as extraneous cations and anions can interfere with binding of the targeted species. Nuclear magnetic resonance (NMR) is another option for measuring binding. Here the ligand is titrated by additions of aliquots of anion salt, and binding is calculated from changes in chemical shifts of the ligand resonances. In NMR studies binding is determined at a preselected pH and usually entails monitoring ^{1}H chemical shifts. In some cases, however, depending on the system, chemical shifts of other nuclei such as ^{19}F can be followed. Other spectrophotometric methods are less commonly used and include UV–vis and fluorescence emission, when available.

This review focuses only on amine-based hosts, and is divided into acyclic and macrocyclic groups, the latter of which are based on cyclic dimension. The resulting four categories are: acyclic, monocyclic, bicyclic, and polycyclic. Within each category, binding will, when appropriate, be discussed according to the nature of the anion target, i.e. 'simple' inorganic anions, organic anions, and anionic metal complexes. In perspective views of crystal structures carbons are clear circles, nitrogens are parallel lines from bottom left to upper right, oxygens are either parallel lines from upper left to bottom right or cross-hatched depending on whether there are additional heteroatoms, the latter of which are cross-hatched.

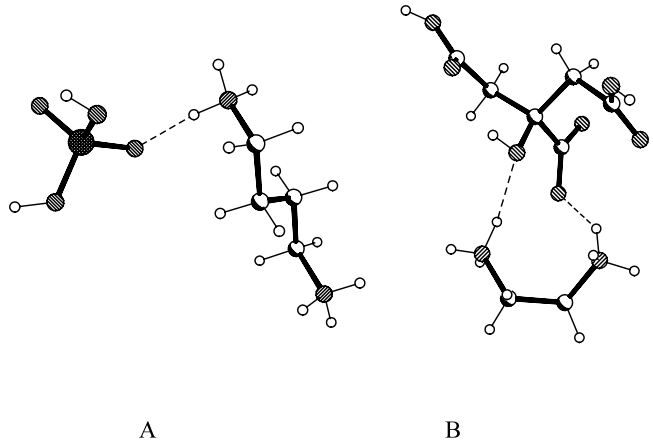


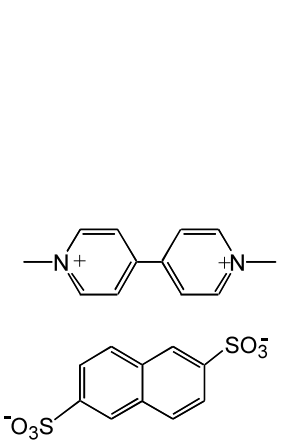
Fig. 1. (A) Complex of diprotonated putrescine with $H_2PO_4^-$ [8]. (B) Ethylenediammonium complex with citrate [10].

2. Acyclic ammonium receptors

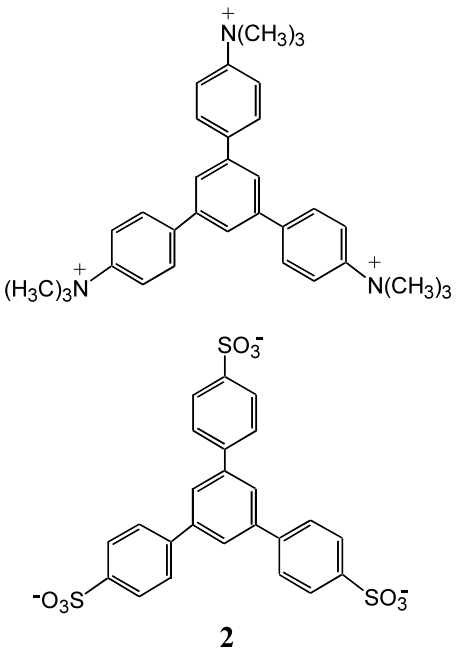
Included in the acyclic category are alkyl ammonium salts, admittedly the simplest receptors in terms of design. In their protonated form they can readily complex anions, and do so in biological systems. For example, the tetraamine spermine, $^{+}NH_3(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_3^+$, is utilized in nature to bind phosphate in yeast phenylalanine tranfer RNA [4–7]. The diprotonated extended chain diamine, putrescine (1,4-diamino-*n*-butane), binds $H_2PO_4^{2-}$ in what can be considered as a model for nucleic acid interactions with amines [8,9] (Fig. 1A). Even simple protonated ethylenediamine can form complexes, as seen in the crystal structure of the ethylenediammonium salt with citrate (Fig. 1B). Although not shown, when all of the hydrogen bonding interactions of a single ethylenediammonium receptor are considered, the dication binds four citrates in the solid state via hydrogen bonding interactions [10].

A study on ion pair formation was undertaken in an attempt to quantify the energies of noncovalent interactions so important in supramolecular chemistry [11]. The effects of noncovalent interactions, including both Coulomb and van der Waals, were examined for organic ion pairs, such as **1** and **2**, i.e. ions with rigid aromatic fragments. Results indicated an additivity of ΔG of ca. 5 kJ mol^{-1} for a single salt bridge and a van der Waals increment of about 1–2 kJ mol^{-1} for each aryl group.

An early foray into polyamine anion receptors with fluorescence capabilities was undertaken with the anthrylpolyamines, **3** and **4**. Interactions with oxo anion groups, carboxylate, phosphate, and sulfate were examined [12]. A later study focused on a variety of linear amines, **5**, of varying chain lengths with one or two

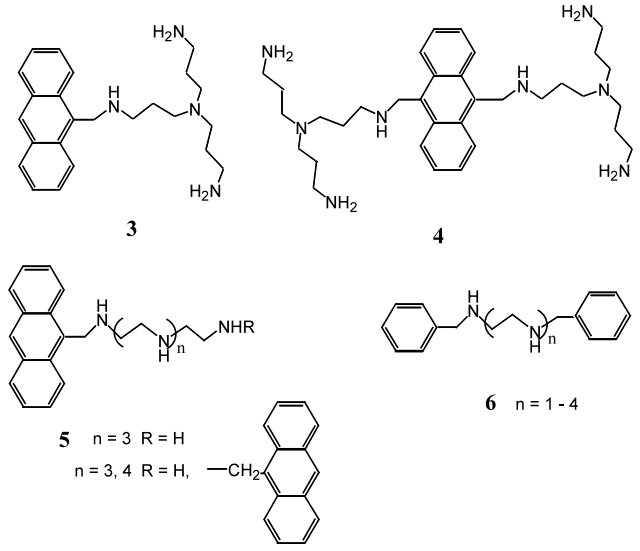


1



2

terminal anthracenes as fluorescence-signaling receptors for ATP, ADP and AMP. The findings indicated that the binding of ATP compared to the other nucleotides was significantly higher ($\log K$ $K_{[H_5L\cdot ATP]/[H_5L][ATP]}$ = 8.1–9.9) [13].



3 4

5 n = 3 R = H
n = 3, 4 R = H, —CH2

6 n = 1 - 4

The ability of dibenzylated linear amines, **6**, to bind $Co(CN)_6^{3-}$ was also examined [14]. Binding constants measured by quenching of the steady-state fluorescence emission indicated a range of $\log K_s$ from 2.41 for the shortest to 2.60 for the longest chain. Irradiation experiments indicated a decrease in the photoaquation quantum yields, as also observed for macromonocycles and discussed in greater detail in Section 3.3.

Other workers have utilized transition metal complexes to anchor polyamine receptors in appropriate binding geometries to add the capability of signaling binding of the desired anions. Included in this category are *tris*-bipyridineruthenium(II) complexes as well as ferrocene- and cobaltocene-based receptors. These receptors are discussed in another review in this issue, and so will not be included here [15].

3. Monocyclic ammonium receptors

Discussion of the binding of anions with monocylic ammonium receptors will be divided according to the identity of the target anion. The first category, simple inorganic anions, includes primarily halides, pseudohalides (e.g. $-SCN^-$, N_3^-), other halogen-containing species (e.g. BF_4^-) and oxo anions. A second series of anions, investigated even more extensively with monocycles, includes organic ions such as carboxylates and nucleotides. Transition metal anionic complexes comprise a third subset of target anions.

3.1. Simple inorganic anions

Polyammonium macromonocycles in general do not form highly selective complexes with simple inorganic anions. The first crystallographic foray in this area, vis-à-vis anion binding, was reported for the 18-membered system [18]aneN_6 [16], **7A** [17]. Potentiometric results indicated relatively weak binding for nitrate and chlo-

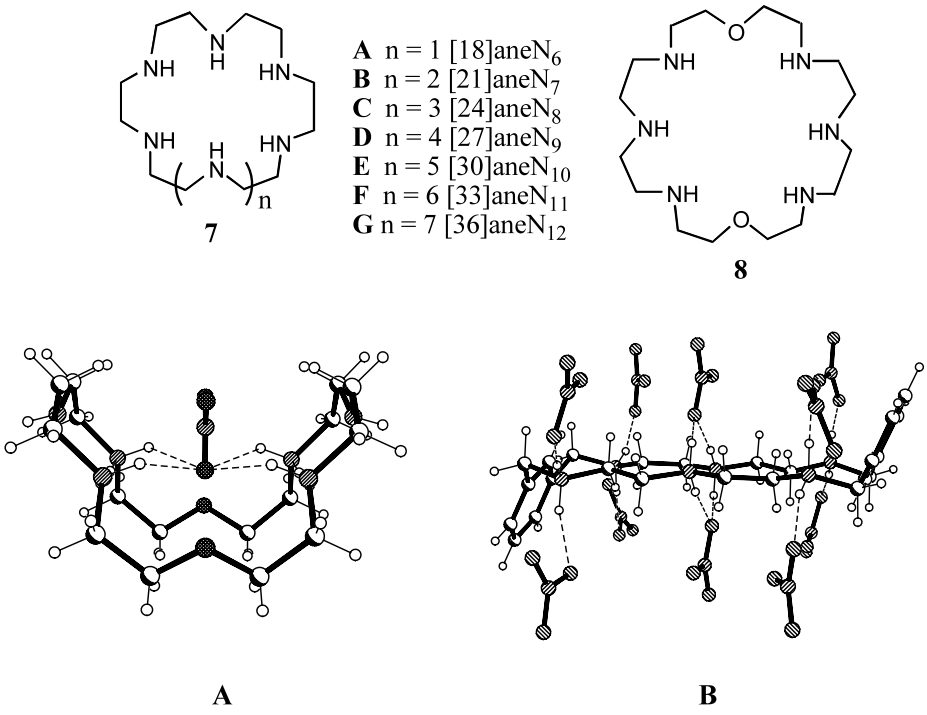


Fig. 2. (A) Encapsulation of nitrate in the complex of $H_4\mathbf{8}^{4+}\cdot 4NO_3^-$ [18]. (Only the encapsulated nitrate is shown.) (B) Layered structure of the nitrate complex of $H_6\mathbf{9A}^{6+}\cdot 6NO_3^-$ [22]. (Eight surrounding nitrates are shown.)

ride (K_s ca. 10^2), and X-ray crystallography showed layers of macrocycles interspersed with anions. Subsequent studies with a larger mixed polyammonium macrocycle [24]aneN$_6$O$_2$, **8**, indicated a folded structure for the tetraprotonated macrocycle with an encapsulated nitrate (Fig. 2A) [18]. Molecular dynamics studies on **8** and several related systems indicated that in solution solvation effects come into play, and the folded structure is very flexible [18–20].

More recently, some researchers have shifted their synthetic strategies to receptors readily obtainable by simple Schiff base condensations followed by borohydride reductions (Fig. 3) [21]. Many of these aza monocycles (Route A) also tend to show layered structures, including complexes of **9A** with nitrate [22], sulfate [22], bromide [23] and fluoride [24]. An example is the nitrate structure of **9A** (Fig. 2B), where two 'layers' of nitrates are shown.

Flexible, linear oxo anions such as pyrophosphate and triphosphate appear to more readily 'thread' monocycles, as observed crystallographically for **9A** and **B** with pyrophosphate (Fig. 4) [23,25] and for triphosphate with **9B** [26]. In the latter structure, both threaded and unthreaded triphosphates were observed. In the pyrophosphate structure with the smaller 18-membered **7A**, the pyrophosphates lie above and below the macrocyclic plane [27]. In the two structures shown, however, hydrogen bonding by both ends of the anion

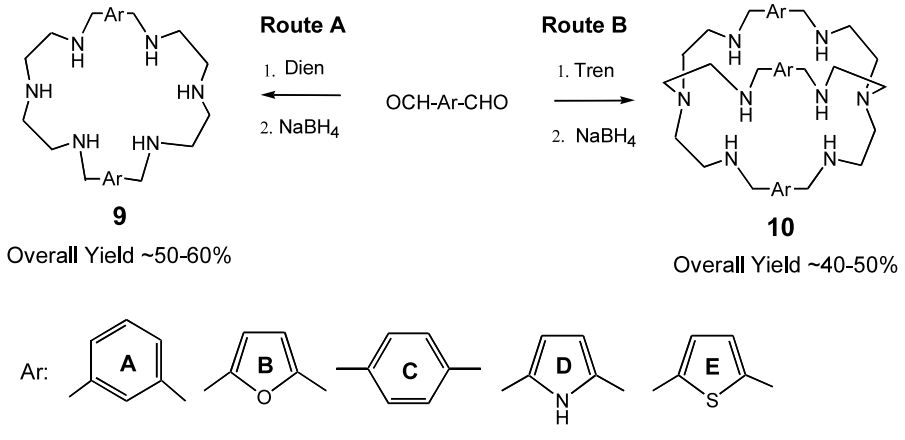
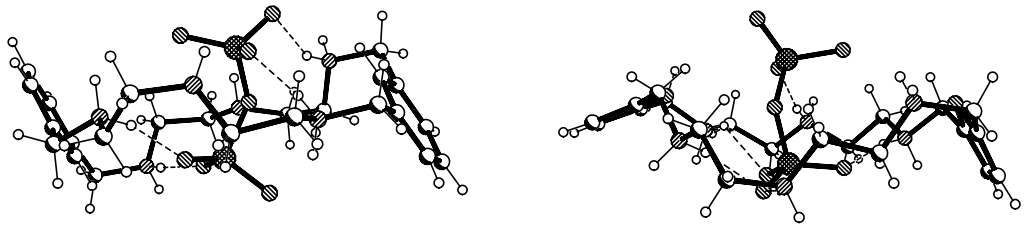


Fig. 3. Synthetic route to polyaza macrocycles and aza cryptands using Schiff base methodology [21].



A B

Fig. 4. Pyrophosphate structures showing threaded anions: (A) $H_4\mathbf{9A}^{4+}\cdot H_2P_2O_7^{2-}$ [22]; and (B) $H_5\mathbf{9B}^{5+}\cdot H_2P_2O_7^{2-}$ [25].

with the macrocycle help to hold the anion in place. Oxalate was also found to thread through **9B** [25].

Binding constants are normally obtained by potentiometric and/or NMR techniques. Protonation constants obtained for these polyamines from potentiometric measurements can vary depending on the supporting electrolyte. Nonetheless, for singly charged anions with monocycles, binding constants are usually small if even measurable. Affinity tends to increase, however, with increasing charge on the anion as shown for **9A** (Table 1) [22–24]. For the various phosphate species, determination of binding is complicated since the oxo anions become protonated at near neutral pH [23,26]. For example, the first two protonation constants of phosphate are 11.74 and 6.80 [26], meaning that PO_4^{3-} is essentially nonexistent within the pH range that these receptors actively bind. While it can be seen from Table 1 that a direct correlation is not observed between simple anionic charge and magnitude of binding (e.g. a comparison of SO_4^{2-} and HPO_4^{2-}), binding tends to decrease with increasing degree of protonation within a given polyprotic species.

Table 1
Binding constants (log K_s) in aqueous solutions for inorganic anions with **9A**

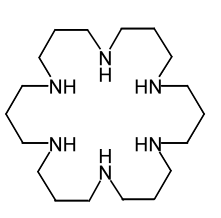
Anion	log K_s	Equilibrium
F^- [a]	~2 (NMR)	$H_6LF/H_6L\cdot F$
NO_3^- [b]	n.o. [d]	$H_6LNO_3/H_6L\cdot NO_3$
SO_4^{2-} [b]	4.36	$H_6LSO_4/H_6L\cdot SO_4$
HPO_4^{2-} [c]	7.36	$H_7LPO_4/H_6L\cdot HPO_4$
$H_2PO_4^-$ [c]	3.86	$H_7LPO_4/H_5L\cdot H_2PO4$
$P_2O_7^{4-}$ [c]	13.07	$H_6LP_2O_7/H_6L\cdot P_2O_7$
$HP_2O_4^{3-}$ [c]	6.14	$H_7LP_2O_7/H_6L\cdot HP_2O_7$
$H_2P_2O_4^{2-}$ [c]	n.o. [d,e]	$H_8LP_2O_7/H_6L\cdot H_2P_2O_7$
$P_3O_{10}^{5-}$ [c]	14.19	$H_6LP_3O_{10}/H_6L\cdot P_3O_{10}$
$HP_3O_{10}^{4-}$ [c]	11.06	$H_7LP_3O_{10}/H_6L\cdot HP_3O_{10}$
$H_2P_3O_{10}^{3-}$ [c]	7.57	$H_8LP_3O_{10}/H_6L\cdot H_2P_3O_{10}$

[a] In 0.1 M NaOTs [24].
[b] In 0.1 M NaOTs [22].
[c] In 0.1 M KCl [23].
[d] Not observed.
[e] This log K_s is 4.53 for **9B** and 4.86 for **8**.

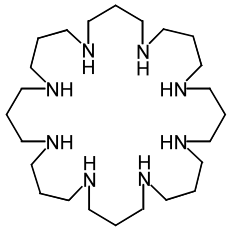
3.2. Organic anions

3.2.1. Carboxylates

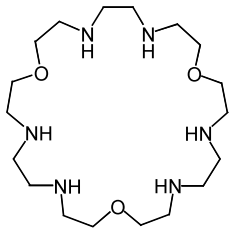
Macromonocycles have also been found to bind organic ions, including carboxylates and nucleotides [28–32]. A seminal paper by Lehn and co-workers in 1981 described the interaction of three different polyamine macromonocycles, **11**–**13**, with a series of organic anions (as well as with sulfate, nucleotides and transition metal anionic complexes) [28]. In addition to the large polyaza ring systems, penta-, hexa- and heptaamine macrocycles such as **14A**–**C** [29] and **7A** and **B** [30], among others, bind polycarboxylates. A comparison of the binding of selected carboxylates with a variety of macromonocycles is depicted in Table 2.



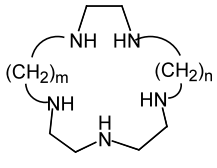
11
[24]aneN$_6$



12
[32]aneN$_8$



13
[27]aneN$_6$O$_3$



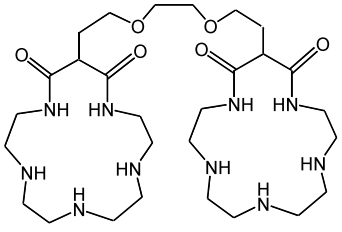
14 **A** m = n = 0
[15]aneN$_5$
B m = 0, n = 1
[16]aneN$_5$
C m = n = 1
[17]aneN$_5$

Table 2
Log K values for binding of carboxylates with selected aza macromonocycles in aqueous solutions

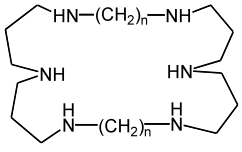
L	Malonate $(HO_2C)_2CH_2$	Succinate $HO_2C(CH_2)_2CO_2H$	Citrate $(HO_2CCH_2)_2C(OH)(CO_2H)$
7A · $3H^+$ [a]	1.5	1.2	2.4
11 · $6H^+$ [b]	3.3	2.4	4.7
12 · $8H^+$ [b]	3.9	3.6	7.6
13 · $6H^+$ [b]	3.8	2.8	5.8
14A · $5H^+$ [a]	n.o.	n.o.	1.7
14B · $5H^+$ [a]	0.8	2.1	2.4
14C · $5H^+$ [a]	0.4	1.0	3.0
16A · $6H^+$ [c]	2.75 (3.80)	3.40 (4.30)	n.r. [d]
16B · $6H^+$ [c]	3.80 (4.05)	3.0 (3.15)	n.r. [d]

[a] $I = 0.2$ M, Tris buffer [29].
[b] In 0.1 M Me_4NCl [28].
[c] In 0.01 or 0.1 M Me_4NCl, the latter in parentheses [32].
[d] Not reported.

As much of the focus on carboxylate binding has been for dicarboxylates, the introduction of ditopic receptors was a natural extension of ligand design. One method is to attach two monotopic macrocyclic receptors together as was done to obtain **15** [31]. The result is more effective binding of dicarboxylates, but only by a factor of about two over the monocyclic analog. Rather than linking together two separate macrocycles, another strategy for introducing ditopic binding is to place two binding sites at opposite ends of a macrocycle separated by a bridging chain or 'spacer', **16** [32]. By fitting an appropriate spacer on the receptor to the length of the substrate, it is possible to control the selectivity to a certain extent. For example, for $O_2C(CH_2)_mCO_2^{2-}$, affinity maximizes for **16A** at $m = 2$ and 3 ($\log K_s = 4.3$ and 4.4, respectively) and for **16B** at $m = 5$ and 6 ($\log K = 4.4$ and 4.25, respectively).



15



16

A n = 7, [32]aneN$_6$
B n = 10, [38]aneN$_6$

3.2.2. Nucleotides and organic phosphates

Polyammonium macromonocycles also bind nucleotides with high affinity [28,33] and can catalyze nucleotide hydrolysis in aqueous solutions, acting as mimics of the ATPases [34–43]. The mechanistic pathway for hydrolysis of ATP catalyzed by **8** was observed to proceed via initial 1:1 complex formation between **8** and ATP (Fig. 5A). ^{31}P-NMR studies of **8** indicate that in addition to a simple hydrolysis pathway (k_2/k_{-2}), another pathway at neutral pHs involves a macrocyclic phosphoramidate intermediate (k_3/k_{-3}), which is obtained via nucleophilic attack of a lone pair from a macrocyclic amine (Fig. 5B) [34,35].

Further studies of the chemistry between ATP and polyammonium macrocycles of varying ring sizes indicate an important correlation between size of the macrocycle and hydrolysis rate [36–38]. The highest rate occurs in macrocycles with 21- and 24-membered rings. Other effects such as methylation and introduction of rings were also found to modify rates of hydrolysis [37–42]. The addition of pendant chains to **8** was found to impede the catalytic reaction [43]. Covalent attachment of an additional recognition site consisting of one or two pendant acridine units, was found to enhance binding via a π stacking effect, although catalysis was diminished [44]. The acridine-modified receptor also binds NADPH very strongly ($K > 3 \times 10^8$), and shows a high selectivity for NADPH over $NADP^-$ [45]. Monocycles such as **7B**, [21]aneN$_7$, bind dinucleotides, and molecular dynamics studies indicate that the mode of interaction is primarily between the diphosphates and the protonated macrocycle [46].

Polyaza macromonocycles exhibit other characteristics of the naturally occurring enzymes, such as regulation (in modifying the course of the reaction) and phosphoryl transfer capabilities to other substrates. For example, an increased amount of the phosphoramidate intermediate of **8** was observed by the addition of certain metal ions such as magnesium (operative in the natural ATPases), calcium, or lanthanum ions [47,48]. Under those conditions pyrophosphate formation is also observed, and occurs from nucleophilic attack of inorganic phosphate in solution on the phosphoramidate intermediate (regulation) (Fig. 5C). Pyrophosphate formation is also observed in polyammonium macrocyclic-catalyzed hydrolysis of acetyl phosphate [49,50].

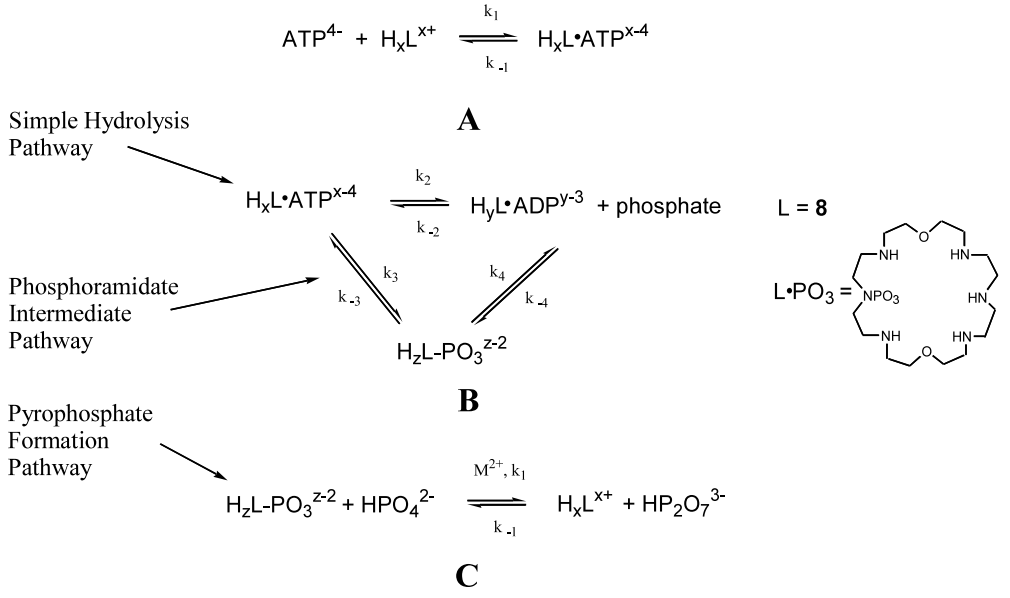


Fig. 5. (A) Equilibrium for 1:1 complex formation between ATP^{4-} with **8**. (B) Mechanistic pathways for hydrolysis of ATP catalyzed by **8**. (C) Pyrophosphate formation from the macrocyclic phosphoramidate and HPO_4^{2-}.

An additional hydrolytic pathway is observed for macrocycle-catalyzed cleavage of formyl phosphate [51–53]. Nucleophilic attack on formyl phosphate by the receptor **8** also occurs at the carbonyl carbon resulting in an N-*formylated* macrocycle which stable to hydrolysis. These findings led to an experiment designed to mimic N^{10}-formyltetrahydrofolate synthetase, the enzyme that brings formate into the one-carbon metabolic pool. The enzymatic mechanism is believed to occur by nucleophilic attack of formate on the terminal phosphate of ATP to yield a formyl phosphate intermediate. This formyl group is subsequently transferred to the N^{10}-position of tetrahydrofolate. The proposed mechanism for the mimic, **8**, is shown in Fig. 6. In this case, the initial step is the formation of the macrocyclic phosphoramidate (**Step 1**) followed by nucleophilic attack of the format on the phosphoramidate (**Step 2**). N-Formylation of the macrocycle occurs in the final step with attack by **8** on the formyl phosphate intermediate (**Step 3**).

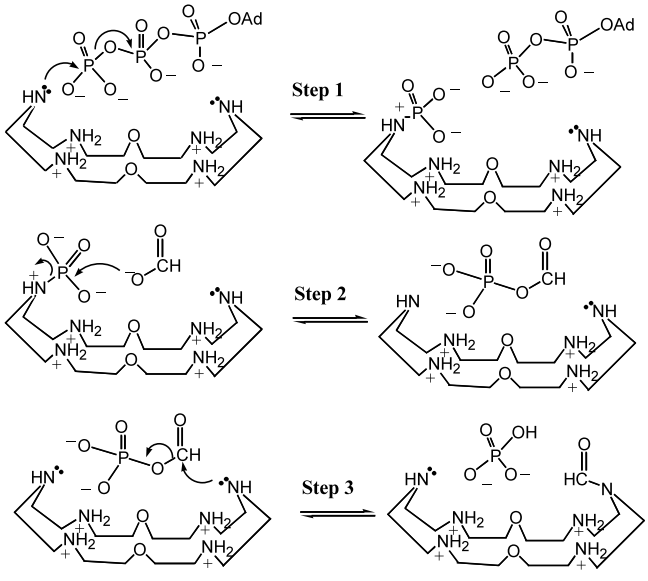


Fig. 6. Multistep pathway of formate activation by **8** in a route mimicking the enzyme N^{10}-formyltetrahydrofolate synthetase [52].

3.3. Anionic metal complexes

In what can be called 'second sphere coordination,' large ring polyammonium monocycles with six or more nitrogens form complexes with anionic transition metal complexes [28,54,55]. Polyaza macrocycles of a variety of ring sizes, **7**, **11**, and **12**, have been examined with square planar (e.g. $PdCl_4^{2-}$ and $Pt(CN)_4^{2-}$), and octahedral (e.g. $M(CN)_6^{n-}$, M = Fe, Co, Cr, and Ru, $n = 3$ and 4) complexes. In general 1:1 complex formation is observed. Affinity tends to increase with increasing degree of protonation of the macrocycle as seen in Fig. 7, where the logarithms of the equilibrium constants are plotted versus the number of protons present in the macrocyclic receptors for binding of $[Fe(CN)_6]^{4-}$ [28,55–60]. From the plot it is also evident that for a given degree of protonation the smaller macrocycles bind more effectively. At least penta-protonation is needed for significant interaction to be observed for the largest receptor in the series, **7G** [36]aneN_{12}.

When binding of $Co(CN)_6^{3-}$ is examined with these receptors, the most striking observation is the diminished binding, by almost five orders of magnitude (Fig. 8) [28,55–59]. Less effective binding is anticipated since the magnitude of binding in these receptors tends to decrease with decreasing charge on the substrate as well

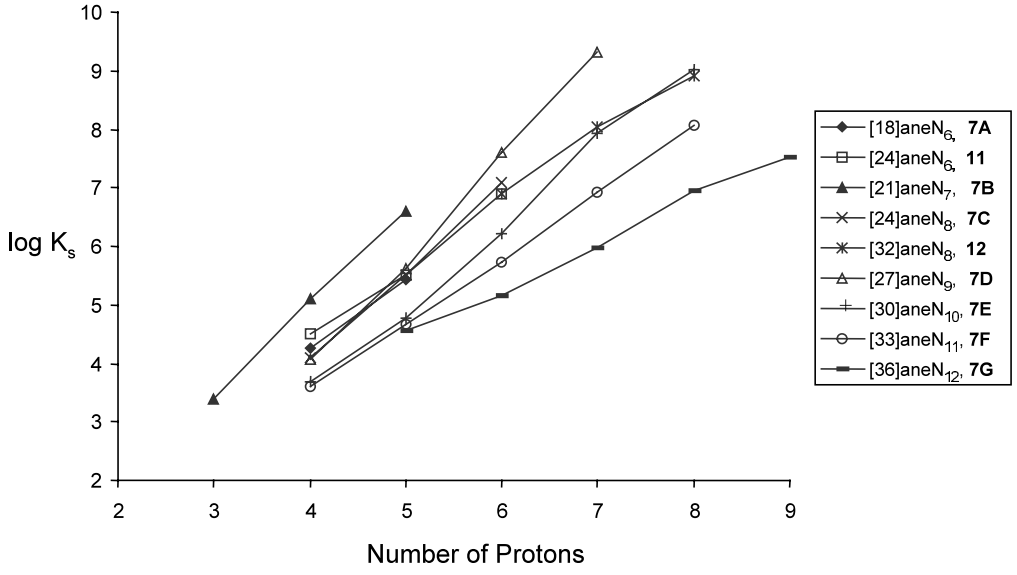


Fig. 7. Binding of $[Fe(CN)_6]^{4-}$ with selected aza macrocycles in aqueous solution: **7A**, in 0.1 M KCl [56]; **11**, in 0.1 M NMe_4Cl [28]; **7B**, in 0.15 M $NaClO_4$ [57]; **7C**, in 0.1 M NMe_4Cl [58]; **12**, in 0.1 M NMe_4Cl [59]; **7D** and **7E**, in 0.15 M. $NaClO_4$ [59,60]; **7F** and **7G**, in 0.15 M $NaClO_4$ [55].

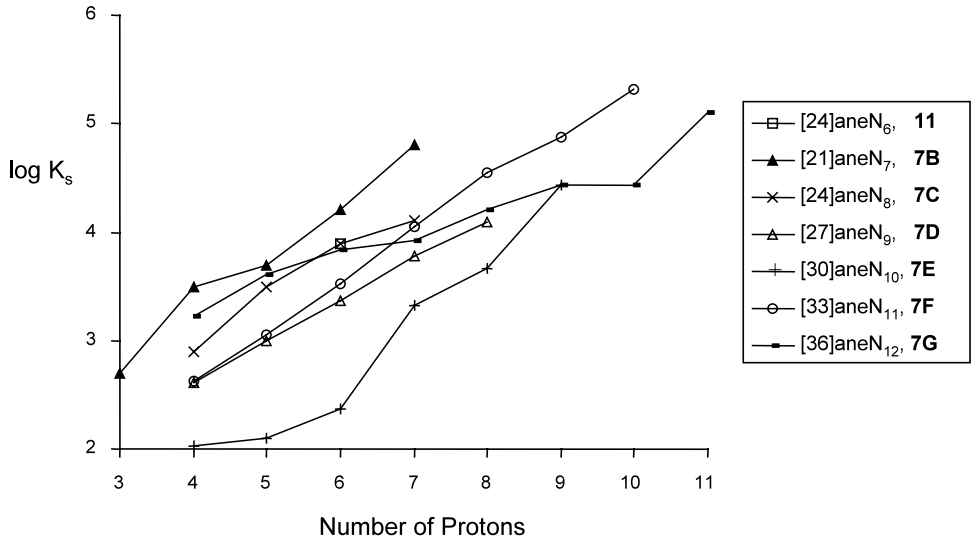


Fig. 8. Binding of $[Co(CN)_6]^{3-}$ with selected aza macrocycles in aqueous solution: **11**, in 0.1 M NMe_4Cl [28]; **7B**–**7G**, in 0.15 M $NClO_4$ [55,57,59].

as on the receptor. At very high degrees of protonation, binding in some of the larger macrocycles (**7F** and **G**, [33]aneN$_{11}$ and [36]aneN$_{12}$) exceeds that of the smaller receptors.

Square planar anionic complexes also bind with the azamacrocycles, and binding constants for $Pt(CN)_4^{2-}$ are shown in Fig. 9 for **7B**–**7F**. While the binding constants are all relatively the same for the most part, there is a steep rise in binding with degree of protonation for the largest macrocycle examined, **7F**, [33]aneN$_{11}$ [55].

Structural findings often indicate layered structures with protonated polyammonium macrocycles alternating with the metallate anions. In this case the metal anion complex lies between the macrocyclic receptors as seen for the hexacyanometallate complex of the decaprotonated **7E**, H_{10}[30]aneN$_{10}^{10+}$ with $Co(CN)_6^{3-}$, (Fig. 10A) [54,55,58]. While an inclusion complex was observed for a $PdCl_4^{2-}$ complex with decaprotonated **7E** (Fig. 10B) [60], the crystal structure of the $Pt(CN)_4^{2-}$ complex with the same macrocycle has a layered structure with metal anion complexes between the receptors (Fig. 10C) [55]. Multiple hydrogen bonding interactions are important in all of these structures, inclusion and layered.

Binding of redox active anionic metal complexes influences the electrochemical behavior, in that the redox couple is normally shifted to more positive potentials in the presence of the polyammonium receptors. Larger macrocycles show greater shifts

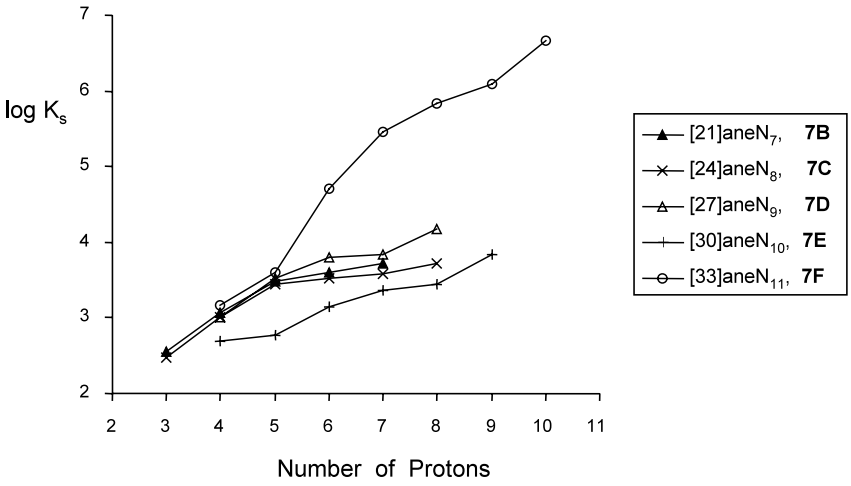


Fig. 9. Binding of $[Pt(CN)_6]^{3-}$ with selected aza macrocycles in aqueous solution in 0.15 M $NaClO_4$ [59].

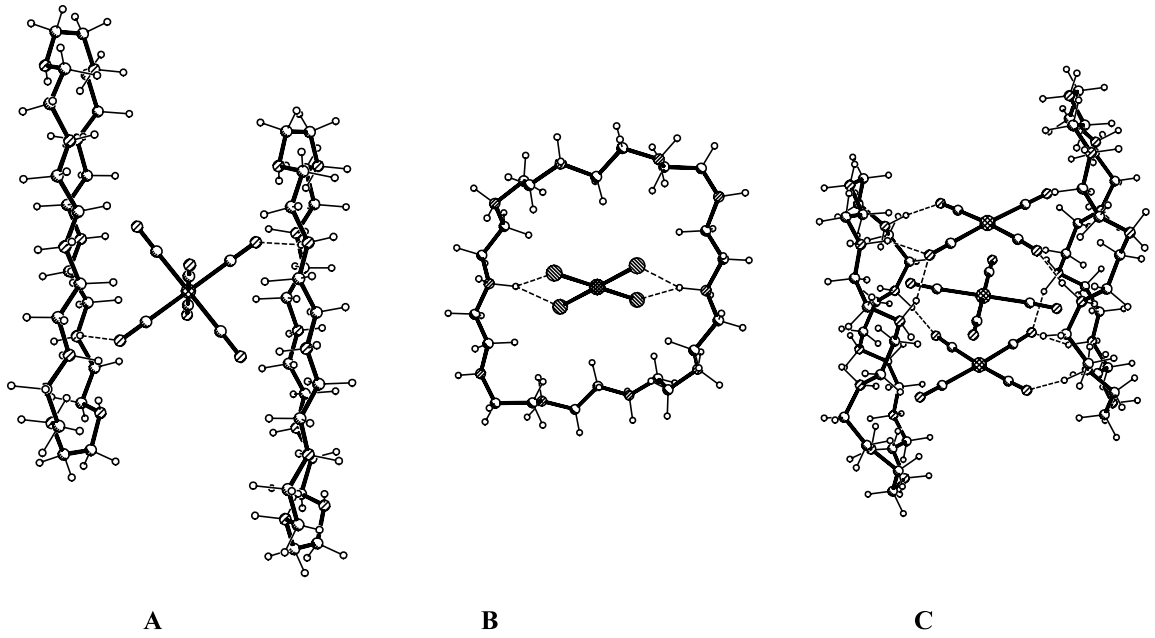


Fig. 10. Structures of metallate anions with the hexaprotonated [30]aneN$_{10}$. (A) $Co(CN)_6^{3-}$ [54,55,58]; (B) $PdCl_4^{2-}$ [60]; (C) $Pt(CN)_4^{2-}$ [55].

[29,57,61,62]. Table 3 shows a comparison of potential shifts $\Delta E^{\circ\prime}$ for different anionic metal complexes and for receptors of varying ring size and spacers between amines. The receptors chosen are **7A**, **7C**, **11** and **12**. $E^{\circ\prime}$ is defined in Eq. (1) as the formal potential of the $A^{m-}/A^{(m+n)-}$ couple:

$$E = E^{\circ\prime} + RT/nF\{\ln[A^{m-}]/[A^{(m+n)-}]\} \quad (1)$$

The experiments for **7A** and **C** were in 0.1 M KCl at pH 5.5, while those for **11** and **12** were in 0.15 M $NaClO_4$ and calculated for the tetraprotonated form of the receptor. Despite the different conditions, receptors of the same size, **11** ([24]aneN$_8$) and **7A** ([24]aneN$_6$), showed similar potential shifts. It would also appear that the controlling factor is not the transition metal complex, since both the ruthenium and iron complexes show the same $\Delta E^{\circ\prime}$ for both **11** and **12**. *N*-Methylation tends to decrease the potential shift.

The presence of second sphere coordination influences the photochemical properties of hexacyanometallates [63–65]. It is well-established that $Co(CN)_6^{3-}$ exhibits a primary photochemical reaction of photoaquation (Eq. (2)):

$$Co(CN)_6^{3-} + H_2O \rightarrow Co(CN)_5(H_2O)^{2-} + CN^- \quad (2)$$

The reaction occurs from excitation of the metal d–d $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption at 312 nm and the $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption at 260 nm. The reactive excited state is considered to be the lowest triplet state, $^3T_{1g}$. The quantum yield is 0.30 [66], and is thought to involve

Table 3
Formal electrode potentials, $E^{\circ\prime}$, and potential differences, $\Delta E^{\circ\prime}$, for metal anion complexes and corresponding polyammonium second-sphere complexes in aqueous solutions

Receptor	Metallate	$E^{\circ\prime}$	$\Delta E^{\circ\prime}$	Receptor	Metallate	$E^{\circ\prime}$	$\Delta E^{\circ\prime}$
–	$Fe(CN)_6^{4-}$	190	–	–	$Ru(CN)_6^{4-}$	705	–
7A [18]aneN$_6$ [a]	$Fe(CN)_6^{4-}$	275	85				
7C [24]aneN$_8$ [a]	$Fe(CN)_6^{4-}$	330	140				
11 [24]aneN$_6$ [b]	$Fe(CN)_6^{4-}$	320	130	**11** [24]aneN$_6$ [b]	$Ru(CN)_6^{4-}$	835	130
12 [32]aneN$_8$ [b]	$Fe(CN)_6^{4-}$	355	165	**12** [32]aneN$_8$ [b]	$Ru(CN)_6^{4-}$	865	165

[a] In 0.1 M KCl at pH 5.5 [29,57].
[b] In 0.15 M $NaClO_4$ [62,63].

CN^- photodissociation that originates from the triplet state. When second sphere complexation with the polyammonium receptors exists, the cobalt complex does not show any changes in the absorption spectrum [63]. Although photoaquation still occurs when the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption is excited, the quantum yield is diminished as seen in Fig. 11 [63–65,67]. This behavior has been attributed to the influence of the macrocycle in shielding the dissociation of the cyanide groups, presumably by hydrogen bonding interactions.

On the other hand the anation reaction of $Co(CN)_5(H_2O)^{2-}$ (i.e. replacement of water by bromide) (Eq. (3)) is accelerated upon addition of **12**, [32]aneN$_8$. This observation suggests that the water is more labile in the second sphere complex and may not be associated with the macrocycle via hydrogen bonding [65].

$$Co(CN)_5(H_2O)^{2-} + Br^- \rightarrow Co(CN)_5(Br)^{3-} + H_2O \quad (3)$$

The chromium(III) analog, $Cr(CN)_6^{3-}$, also undergoes photoaquation with similar effects in the presence of polyammonium macrocycles [68].

Photophysical properties are also effected by second sphere interactions, as illustrated for $Ru(bpy)(CN)_4^{2-}$ [65,69]. The physical properties of this complex are solvent dependent, and vary significantly from H_2O to CH_3CN. For example, in H_2O, the metal to ligand charge transfer transition occurs at higher energies because of hydrogen bonding interactions. The presence of **12**, [32]aneN$_8$, tends to increase the emission quantum yield as well as the lifetime. The effect is especially pronounced in CH_3CN, where hydrogen bonding effects with the solvent are not an interfering factor.

4. Bicyclic ammonium receptors

The bicyclic polyammonium receptors are also known as azacryptands because of their structural similarity with the early ether-derived cryptands of Lehn and coworkers [70]. In their polyprotonated states, these bicyclic amine-based receptors bind more strongly to anions, even monoanions, compared to monocycles, often by two or more orders of magnitude.

4.1. Halides and pseudohalides

The katapinands, **17**, are diaza bicyclic receptors named from the Greek word καταπιϖω meaning to swallow-up [1]. In the series of varying chain lengths, the

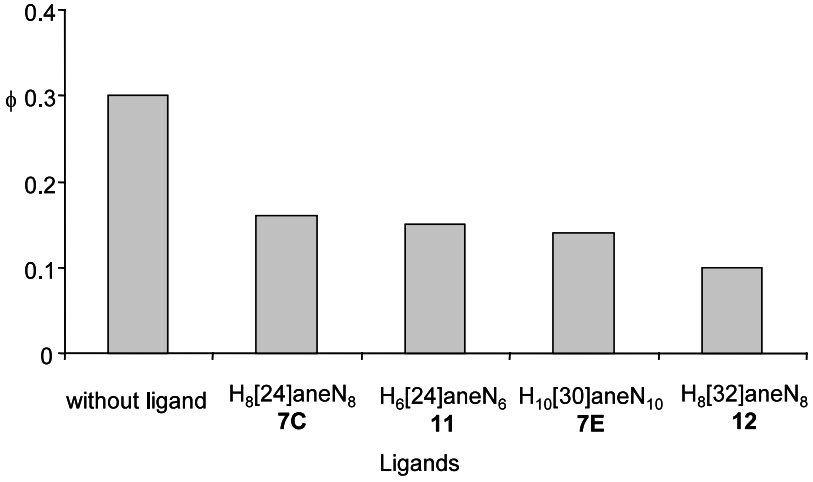
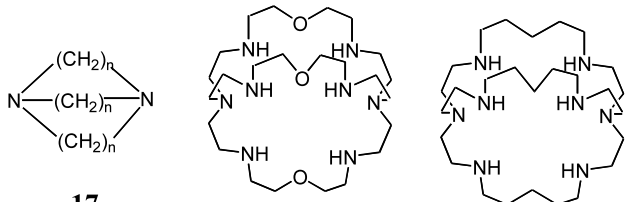


Fig. 11. Representation of the quantum yield (ϕ) for the photoaquation of polyammonium macrocycle complexes of $[Co(CN)_6]^{3-}$ in aqueous 0.1 M $NaClO_4$, using an excitation wavelength of 313 nm [63–65,67].

highest affinity was observed for the binding of chloride ion with **17** ($n = 10$), a not exceptional $K > 10$. Although initial studies indicating encapsulation of a halide inside the cavity using NMR techniques were reported in 1968, the confirming crystal structure did not appear until 1974 [71].



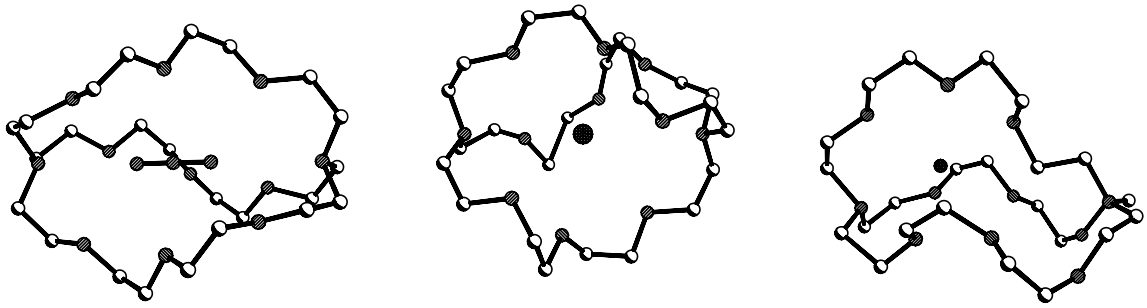
17 **18** **19**

The field expanded with the introduction of the linear bis-tren azacryptand **18** [72,73], which was found to be exceptionally complementary for encapsulating the linear azide ion (Fig. 12A), with an aqueous stability constant of $\log K_s = 4.3$. Crystallographic studies also indicated halide inclusion within the cavity. Chloride and bromide (Fig. 12B) are centrally located. In the fluoride structure a single fluoride sits off-center, closer to one of the tren units (Fig. 12C) [73], although it had been speculated that bifluoride could be encapsulated as well.

A related receptor, **19**, with $-(CH_2)_5-$ spacers between the two tren units was also examined for anion binding [74]. As in many of the early reports on anions, this paper was a composite, including both metal ion binding (**19** in the neutral form), anion binding (protonated **19**) as well as mixed metal ion/anion and cascade complexes. Evidence for bifluoride incorporation was presented from potentiometric studies, which indicated $\log K_{[H_6L\cdot F_2H]/[H_6L][F_2H]} = 6.4$ and 5.2 for **18** and **19**, respectively.

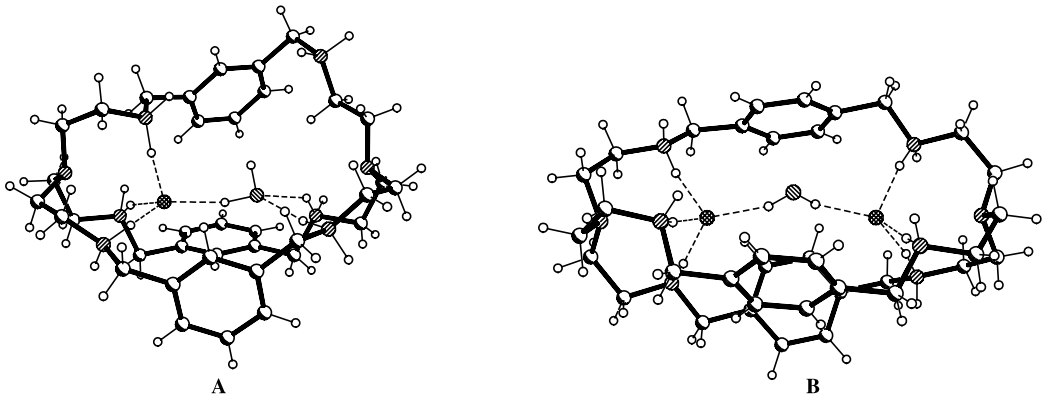
More recently, **10A**, an azacryptand derived from the Schiff base synthetic strategy (Fig. 3, Route B) was found to bind both fluoride and water in the cavity [24,75]. The structure also contained two bifluorides, but outside of the cavity, along with six molecules of water and 1.5 SiF_6^{2-} counterions (Fig. 13A). Bifluorides and water were also found in addition to fluorides in the structure of the monocyclic analog, **9A** [24]. A slightly larger cavity derived from a *p*-xylyl spacer, **10B**, allows not only two fluorides to be bound inside the cavity, but also a water molecule bridge, in a type of cascade complex [76] (Fig. 13B). The latter motif is reminiscent of the ditopic metal ion cascade complexes observed for these ligands [77].

The accessibility of ^{19}F-NMR spectroscopy makes fluoride an ideal guest for examining its interaction with



A **B** **C**

Fig. 12. Crystal structures of $H_6\mathbf{18}^{6+}$ with (A) azide (B) bromide, and (C) fluoride [73].



A **B**

Fig. 13. Fluoride structures with the hexaprotonated $H_6\mathbf{10A}^{6+}$ [75] and $H_6\mathbf{10B}^{6+}$ [76].

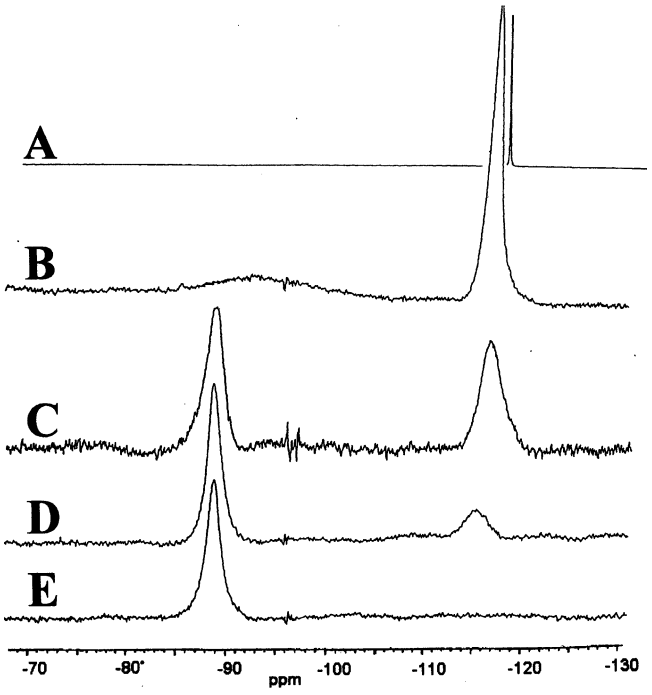
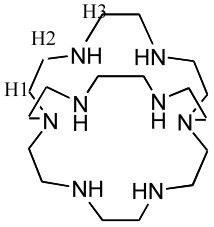


Fig. 14. ^{19}F-NMR of **10A** with F^- as a function of pH [75]: (A) pH 10.5; (B) 9.0; (C) 8.0; (D) 7.0; (E) 6.5.

the host in solution. In a pH study of fluoride binding with **10A** using a 1:1 **10A**:F^- ratio in a DMSO/H_2O solution at −25 °C, a clear dependence of binding as a function of pH (and hence degree of protonation of **10A**) was observed (Fig. 14) [24,75]. A sharp signal for free (solvated) fluoride is seen at −117 ppm at pD 10, where the azacryptand is predominantly neutral. As the pH is lowered, protonation begins to occur and this signal broadens along with the appearance of a new signal at −89 ppm, assigned to internally bound fluoride. (pK_as for **10A** are 9.59, 9.38, 8.80, 7.48, 6.77, and 6.29 [24].) Eventually the signal for free fluoride is totally replaced by the new signal (pD 6.5), indicating encapsulated fluoride. The NMR findings correlate well with potentiometric studies of binding. The latter experiments show only minimal binding at pH 10, but a sharp rise beginning at pH 8 and culminating at pH 6, at which point the macrocycle is essentially hexaprotonated [24].

The 'octaazacryptand,' **20**, designed for its small cavity, binds fluoride with exceptionally high affinity and selectivity, log $K = 8.8$ and log $K_F/K_{Cl} = 7.6$ at pH 5.9 [78–80]. The high binding constant is attributed to a perfect match of cryptand cavity and fluoride size, and it was speculated that the cavity was too small to admit other anions.



20

More recent crystallographic studies indicated that encapsulation of chloride ion [81] could also occur (Fig. 15). Subsequent NMR studies were performed to examine the pH dependence of the ^{1}H chemical shifts for 1:1 complexes of fluoride and chloride with the hexatosylate salt of **20** as compared to the spectra of the hexatosylate salt of **20** alone (the bulky ion presumed not to bind). Results indicated differences in the chemical shift for fluoride throughout the pH range, while the chemical shifts for the chloride and tosylate salts were virtually identical from pD 5.5 to 2.5. Surprisingly, however, below pD 2.5 the chemical shifts for chloride change, paralleling those observed for fluoride. These observations are in keeping with chloride encapsulation upon addition of the sixth proton to **20** [81].

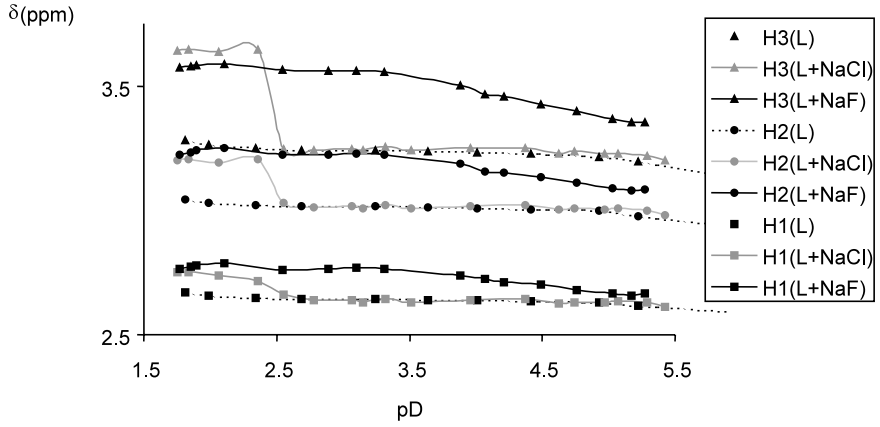


Fig. 15. Aqueous pH titrations showing chemical shifts of the three independent protons in **20** for 1:1 adducts of chloride and fluoride with the hexatosylate salt of **20** (L), compared to the hexatosylate salt alone (L) [81].

Table 4
Potentiometric determination of protonation constants of **18** with a variety of electrolytes [82]

pK_a	NaTMBS [a]	$KClO_4$	KCl	KNO_3
pK_1	9.92	9.89	9.89	9.93
pK_2	9.26	9.23	9.17	9.31
pK_3	8.22	8.29	8.26	8.55
pK_4	7.53	7.65	7.89	7.91
pK_5	6.68	6.64	7.28	7.32
pK_6	6.05	6.01	6.60	6.63

[a] TMBS = Trimethylbenzenesulfonate.

4.2. Oxo anions

In a classic paper early in the beginning era of anion coordination, Lehn and co-workers examined the protonation constants of **18** with a variety of electrolytes, including the commonly employed KCl and KNO_3 [82]. In this widely cited treatise, the authors explained the importance of competitive anion binding affecting protonation constant determination. The results are shown in Table 4. Trimethylbenzene sulfonate (TMBS) was chosen for its bulk and perceived innocence in binding. The similarities between the pK_as of the perchlorate and TMBS were taken to mean that neither electrolyte was competing for binding, and thus did not affect the pK_a measurements significantly. On the other hand, in the presence of chloride and nitrate, higher pK_as were observed, particularly as more acidic conditions were reached. Binding studies indicated that binding was occurring, with $\log K_s = 2.26$ for chloride and 2.93 for nitrate for the hexaprotonated **18** (using perchlorate as supporting electrolyte). The authors postulated internal binding for nitrate with a proposed structure (Fig. 16A).

It was not until 1998, however, that an encapsulated nitrate was observed crystallographically in an azacryptand, in this instance for **10A** [22,83]. The C_3 symmetry of the receptor is perfectly suited to the D_{3h} geometry of nitrate, such that the cavity contains two nitrates, perfectly aligned in an eclipsed conformation (Fig. 16B). More recently we have isolated several nitrate complexes with the hexaprotonated **10C**, some of which show a single nitrate in the cavity (Fig. 16C) [84]. The complex shown is the pentatosylate mononitrate salt of **10C**.

The very first crystallographic verification of internal binding of an oxo anion, however, was reported for a perchlorate encapsulated in the furan cryptand **10B** [85]. Likewise, host **10A** has been found to be a versatile receptor for tetrahedral species, encapsulating thiosulfate and chromate [86], as well as perchlorate [87] (Fig. 17). Of the tetrahedral species, hydrogen bonding

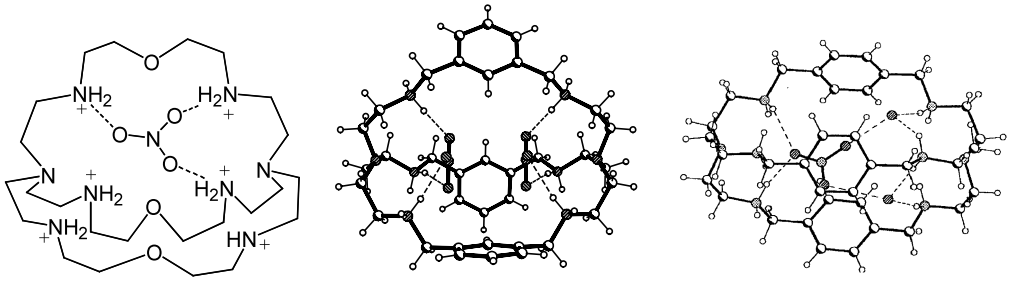


Fig. 16. (A) Proposed mode of binding of nitrate with H_6**18**$^{6+}$ [82]. (B) Ditopic nitrate complex with H_6**10A**$^{6+}$ [22,83] (C) Monotopic complex of nitrate with H_6**10C**$^{6+}$ [84].

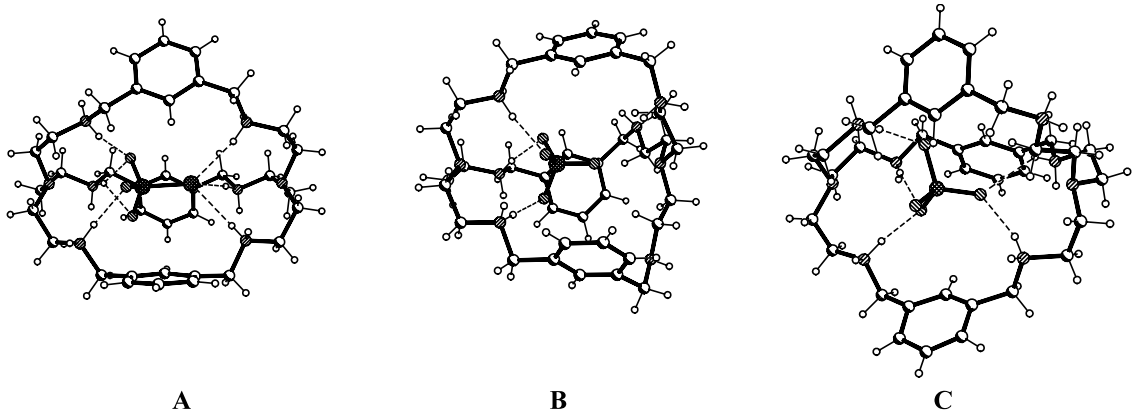


Fig. 17. Crystal structures of encapsulated tetrahedral oxo anions with $H_6$10A^{6+}: (A) thiosulfate [86]; (B) perchlorate [87]; and (C) chromate [86].

interactions appear to be maximized in the thiosulfate structure, probably due to the longer S–S bond, which can extend farther along the cavity. The apical sulfur is bound by three protonated amines on one side of the bicycle, while each of the three oxygens are held by the other side in a fashion similar to that observed for the nitrate complex of **10A** (Fig. 16B). The other tetrahedral molecules, chromate and perchlorate, do not appear to be as perfectly accommodated (Fig. 17B and C). In these structures at least one oxygen is not hydrogen bonded with the receptor, but instead often with nearby water molecules. We have also observed internal binding of sulfate with **10A**, but the structure, which contains considerable disorder, is still being unraveled [88]. A similar situation of non-ideal topology was observed for the perchlorate complex with **10B** [85]. Most of these structures contain significant disorder in the azacryptand and/or the counterions and solvent, and thus present challenges to the chemist and crystallographer.

It is unfortunate that there are no comprehensive studies of systematic binding of a variety of anions with a series of these interesting and readily available aza cryptands. However, in the binding studies that have been reported, there are no *major* selectivity successes observed for the binding of oxo anions, with the exception perhaps that dinegative species are bound more strongly than mononegative anions [22,83,86,87].

4.3. Organic anions

Aza cryptands also bind nucleotides [34]; however, they are not effective hydrolysis catalysts. These findings are perhaps a reflection of increased crowding (and possibly lack of an appropriate lone pair) that may hinder phosphoramidate formation. As noted earlier (Fig. 5) [33], such an intermediate appears to be a key pathway in dephosphorylation in polyaza monocycles.

Despite the increased steric congestion in the bicycles, they can, however, engulf dicarboxylates as seen in the crystal structure of terephthalate with **21** [89] (Fig. 18).

Table 5
Binding of quaternized receptors with halides in water

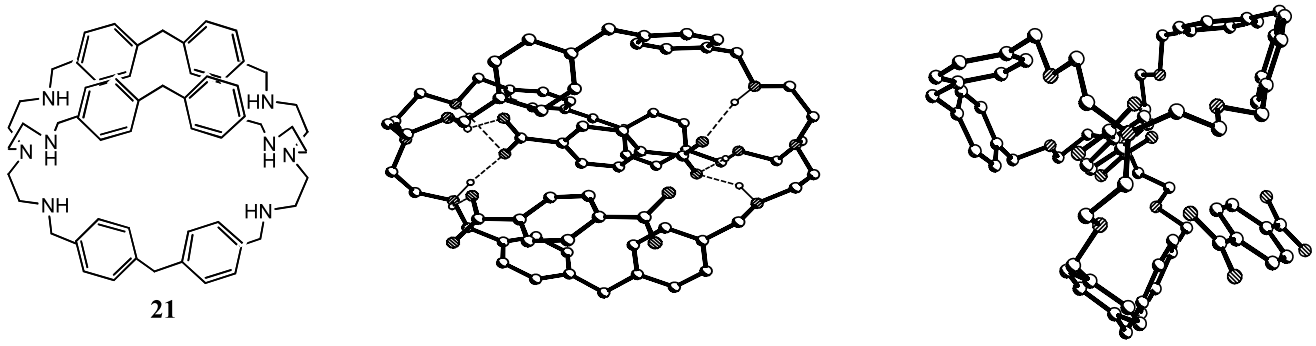
Receptor	Cl^-	Br^-	I^-
22 [a]	> 4.0	< 1.0	< 1.0
23 [a]	> 4.5	1.55	< 1.0
24 [b,c]	1.0	1.8	n.o.
25A [b,d]	1.3	2.45	2.2
25B [b,e]	< 0.5	2.45	2.4
29A [f]	2.43	3.33	3.81

[a] pH 1.5 (KNO_3) [2].
[b] Ref. [3].
[c] KF supporting electrolyte.
[d] KNO_3 supporting electrolyte for Cl^- and Br^-, KF for I^-.
[e] KF supporting electrolyte.
[f] In D_2O, in presence of 0.2 M NaF for the I^- determination [109].

In a related series of receptors, including the well-studied **18** bis-tren, significant affinities for dicarboxylates, and especially oxalate, were observed. For example, the log K_s of **18** with oxalate and malonate are 4.95 and 3.10, respectively [73].

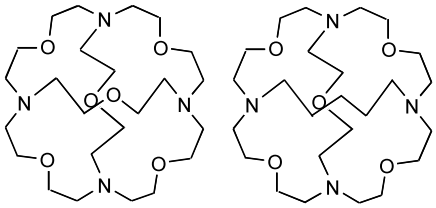
5. Polycyclic ammonium receptors

The macrotricyclic 'soccer ball' ligand, **22**, was first designed as a receptor for alkali metal ions [90], along with a slightly modified host, with the fourth bridge consisting of a simple hydrocarbon chain, **23**. These ligands are also especially well-suited for spherical recognition, incorporating halides internally with high affinities such as for Cl^- (log $K > 4.0$) [2,91] (Table 5). Binding constants are considerably higher than those observed for polyaza cryptands and the katapinands, reflective of the ideal topology for halide binding. Size and shape of the macrocycle play a definite role, as the affinity of **22** for Cl^- over Br^- exceeds 10^3, while NO_3^-, CF_3COO^- and ClO_4^- (the wrong shapes) and iodide (too large) do not form complexes.



21

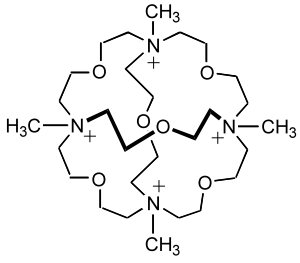
Fig. 18. Views of the crystal structure of terephthalate with H_6**21**$^{6+}$, the structure on the right showing a second terephthalate approaching the cryptand.



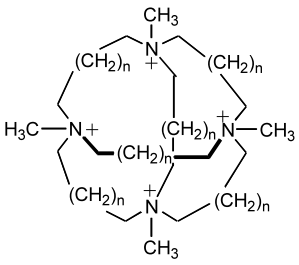
22 23

Theoretical studies have been performed for **22**, and indicate a complex interplay of anion and receptor hydration, dehydration and steric effects, and electrostatic interactions [92]. The shape of the seemingly rigid polycycle changes dramatically upon approach and encapsulation of the halide. When chloride is distant from the macrocycle, the receptor is tetrahedral in shape with the N–H bonds *endo* and the nitrogens about 5.5 Å apart. As the chloride approaches, the receptor contracts, opening a space for the hydrogen atoms of the three ammonium groups closest to the halide. These protons then shift to point toward the halide, drawing it into the cavity.

Shortly after the introduction of the soccer ball ligand, **22**, Schmidtchen synthesized a quaternized analog, **24**, to explore ammonium receptors insensitive to pH [3]. This series has expanded over a wide range of studies illustrating the utility of these systems for anion recognition [93–109]. Binding is clearly weaker than that observed when hydrogen bonding interactions are accessible. The quaternized **25A** and **B** were found to show more flexible binding than **24**, however, forming complexes with I^- in addition to Cl^- and Br^-. All three quaternized hosts (**24**, **25A**, and **25B**) showed selectivity for Br^- over other halides in aqueous solution (Table 5). The higher binding for **25A** and **B** was attributed to the greater flexibility of the hydrocarbon chains.



24

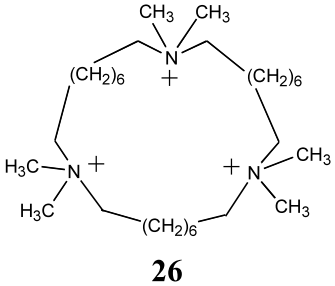


25 **A** n = 4
B n = 6

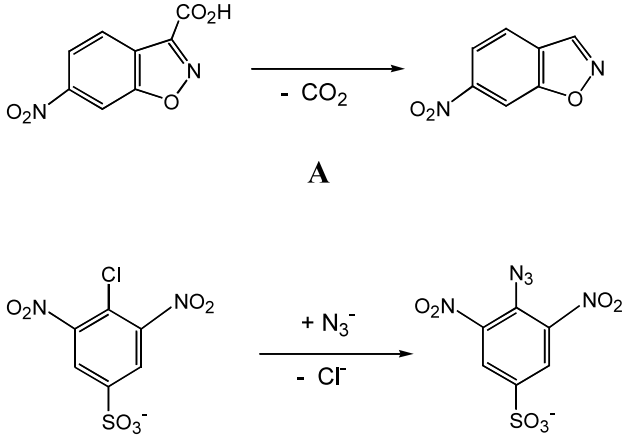
A crystal structure of **25B** with I^- indicated inclusion of the halide in the cavity [93]. By exploiting ^{35}Cl- and ^{19}F-NMR, Ichikawa and Hossain were able to examine the solution environment of the halide and to illustrate inclusion, for chloride in **25B** [107] and for fluoride in **25A** and **B** [108].

In later studies, these quaternized anion receptors were shown to catalyze reactions that have anionic transition states. An example is the decarboxylation of 6-nitrobenzisoxalole-3-carboxylate [104] where $k_{cat}/k_{uncat} = 110$ (Fig. 19A). In another class of reactions, nucleophilic aromatic substitution [96–101], an example is the substitution of chloride with azide in 1-chloro-2,6-dinitro-3-sulfonate ion, where $k_{cat}/k_{uncat} = 1700$ (Fig. 19B). Only the larger receptor, **25B**, is active, while the smaller **25A** inhibits the substitution [99,100]. The monocyclic triaza analog **26**, with $-(CH_2)_8-$ bridges can also catalyze decarboxylation, although to a much lesser extent.

By modifying the quaternary ammonium hosts, dual anion/cation ditopic receptors for zwitterionic guests were synthesized, **27** [103]. When association of the zwitterioinic guests was compared between the ditopic **27** and a monotopic crown ether control **28**, binding was higher for the monotopic system, but the selectivity factor was higher for the ditopic receptor by a factor of



26

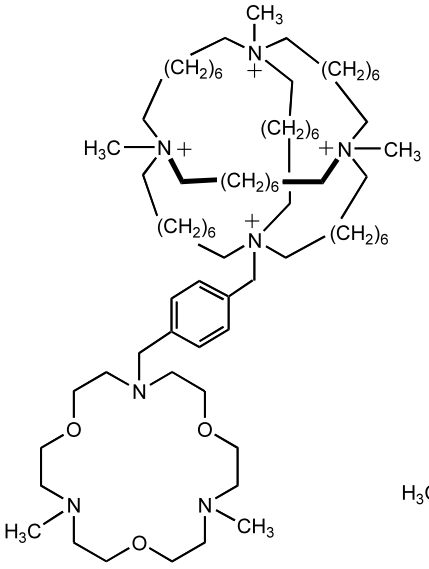


A

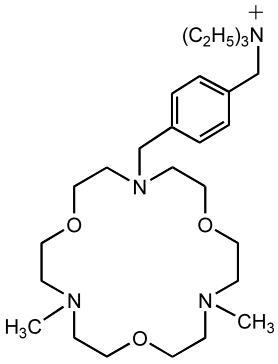
B

Fig. 19. (A) Decarboxylation of 6-nitrobenzisoxalole-3-carboxylate catalyzed by (**25B**) [104]. (B) Nucleophilic aromatic substitution of azide for chloride catalyzed by **25B** [99,100].

2.5 [103].



27

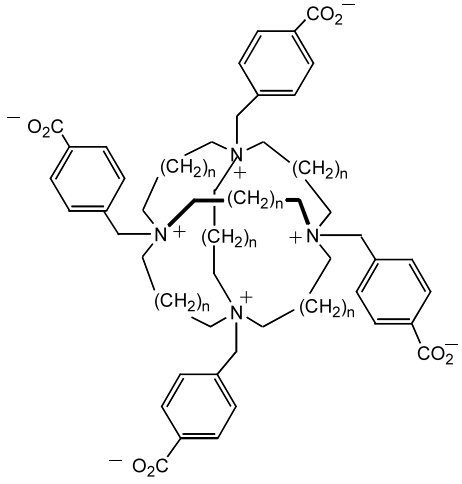


28

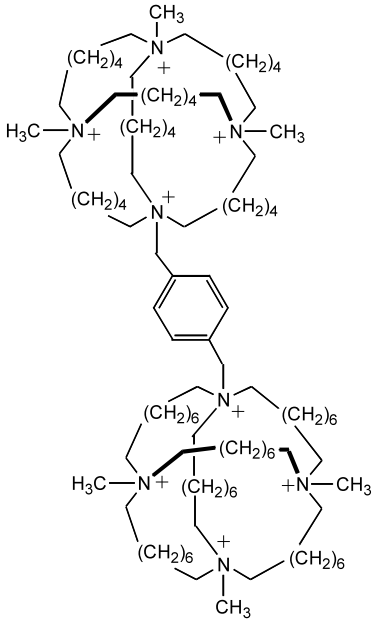
of the negative targets. Binding studies indicated 1:1 host–guest stoichiometries, and the results are shown in Table 5. Because of only small chemical shifts for **29B**, binding constants were only evaluated for **29A**, and showed that the introduction of the negative charges did not appear to detract from anion binding.

By linking two of the quaternary ammonium polycycles together, a ditopic receptor (**30**) was synthesized as a host for dianionic guests [105,106]. A mixed dianion was chosen as the guest and consisted of a carboxylate known to bind with the polycyclic receptor and an *o*-nitrophenolate, which undergoes a bathochromic shift in the visible region when it associates with the polycycle. The results indicated enhanced binding for the ditopic receptor (**30**) over the monotopic control (**25B**). Affinities also increased with an increase in the length of the $-(CH{=}CH)_n-$ chain separating the two anionic units for guests **31**, maximizing at **31C**, with $K_{s30}/K_{s25B} = 11.1$.

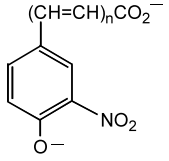
A corollary to the polyaza cryptands that imposes



29 **A** n = 4
B n = 6



30



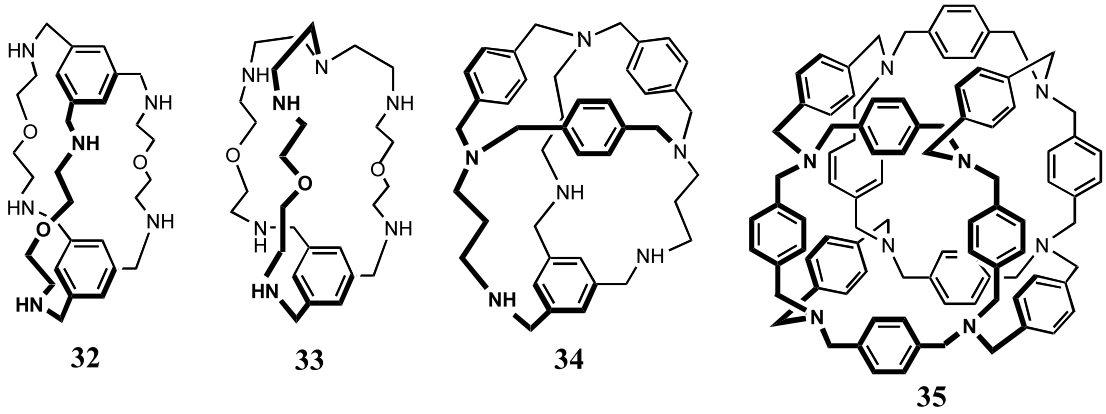
31 **A** n = 0
B n = 1
C n = 2
D n = 3

In a slightly different variation of the zwitterionic idea, Schmidtchen synthesized a zwitterionic receptor using phenylcarboxylates to quaternize the receptors, **29** [109]. The rationale was to obtain a neutral receptor that would obviate the need for the corollary negative counterion. Rigid phenyl groups were used to maximize the distance between the positive and negative ends, and therefore to interfere as little as possible with the binding

more rigidity to the receptor consists of two face-to-face, 1,3,5-trisubstituted benzenes with bridges containing amines, **32**–**34** [110,111]. While these could also be categorized as bicyclic, with the phenyl rings as the bridgehead 'atom', for the purposes of this review they shall be considered as polycyclic. Small anions are bound with relatively high affinity in **32**–**34** and NMR studies indicate 1:1 complex formation. The log K_s

varies from ca. 2.5–4.0 for monoanions such as Cl^-, NO_3^-, and N_3^-, and 5.0–6.5 for dianions such as SO_4^{2-}, $S_2O_6^{2-}$ and $C_2O_4^{2-}$. Crystallographic findings for both the nitrate and tosylate complexes indicated that the anions reside outside of the cavity, at least in the solid state.

A more complex polycyclic azaparacyclophane, an extension of the concept behind **34**, is **35**. Called Kyuphane, this receptor has six faces and is soluble in aqueous media below pH 4 [112]. While the monocyclic analogs are hosts for aromatic guests as well as catalysts for ester hydrolysis [113–115], Kyuphane displays a pH-dependent binding capability as well as size and shape selectivity. The polycyclic **35** binds anionic fluorescent molecules such as 1-anilinonaphthalene-8-sulfonate (ANS) at pH 4, in the tetraprotonated state [112].



6. Conclusion

In the last 30+ years, many explorations into the coordination chemistry of anions have been mounted. A number of these have involved the polyamine systems described in this review. Now, anion coordination chemistry has reached the point of having its own texts, one on supramolecular aspects [116] and the other on analytical determinations [117], a clear sign that anion coordination chemistry has come of age.

Acknowledgements

The authors gratefully acknowledge the Environmental Management Science Program, Offices of Science and Environmental Management, U.S. Department of Energy under Grant DE-FG-96ER62307 for support of the authors' research cited in this review.

References

[1] C.H. Park, H.E. Simmons, J. Am. Chem. Soc. 90 (1968) 2431.
[2] E. Graf, J.-M. Lehn, J. Am. Chem. Soc. 98 (1976) 6403.
[3] F.P. Schmidtchen, Angew. Chem. Int. Ed. Engl. 16 (1977) 720.
[4] G.J. Quigley, M.M. Teeter, A. Rich, Proc. Natl. Acad. Sci. USA 75 (1978) 64.
[5] I. Labadi, E. Jenei, R. Lahti, H. Lonnberg, Acta Chem. Scand. 45 (1991) 1055.
[6] E. Lahti, H. Lonnberg, Biochem. J. 259 (1989) 55.
[7] W.H. Voige, R.I. Elliott, J. Chem. Ed. 59 (1982) 257.
[8] F. Takusagawa, T.F. Koetzle, Acta Crystallogr. Sect. B 35 (1979) 867.
[9] N.H. Woo, N.C. Seeman, A. Rich, Biopolymers 18 (1979) 539.
[10] N. Gavrushenko, H.L. Carrell, W.C. Stallings, J.P. Glusker, Acta Crystallogr. Sect. B 33 (1977) 3936.
[11] H.-J. Schneider, T. Schiestel, P. Zimmermann, J. Am. Chem. Soc. 114 (1992) 7698.
[12] M.E. Huston, E.U. Akkaya, A.W. Czarnik, J. Am. Chem. Soc. 40 (1989) 8735.
[13] M.T. Albelda, M.A. Bernardo, E. García-España, M.L. Godino-Salido, S.V. Luis, M.J. Melo, F. Pina, C. Soriano, J. Chem. Soc. Perkin Trans. 2 (1999) 2545.
[14] M.A. Bernardo, J.A. Guerrero, E. García-España, S.V. Luis, J.M. Llinares, F. Pina, J.A. Ramírez, C. Soriano, J. Chem. Soc. Perkin Trans. 2 (1996) 2335.
[15] P.D. Beer, E.J. Hayes, Coord. Chem. Rev. (2002) this issue.
[16] Nomenclature for the monocycles will include the ring size in brackets followed by 'ane' for saturated carbon chain, followed by the number(s) of heteroatoms. Hence, [18]aneN_6 is an 18-membered ring with six nitrogens, the amine corollary to the well-known 18-crown-6.
[17] J. Cullinane, R.I. Gelb, T.N. Margulis, L.J. Zompa, J. Am. Chem. Soc. 104 (1982) 3048.
[18] G. Papoyan, K. Gu, J. Wiórkiewicz-Kuczera, K. Kuczera, K. Bowman-James, J. Am. Chem. Soc. 118 (1996) 1354.
[19] S. Boudon, A. Decian, J. Fischer, M.W. Hosseini, J.-M. Lehn, G. Wipff, J. Coord. Chem. 23 (1991) 113.

[20] J. Wiórkiewicz-Kuczera, K. Kuczera, C. Bazzicalupi, A. Bencini, B. Valtancoli, A. Bianchi, K. Bowman-James, New J. Chem. 23 (1999) 1007.
[21] D. Chen, A.E. Martell, Tetrahedron 47 (1991) 6895.
[22] T. Clifford, A. Danby, J.M. Llinares, S. Mason, N.W. Alcock, D. Powell, J.A. Aguilar, E. García-España, K. Bowman-James, Inorg. Chem. 40 (2001) 4710.
[23] D.A. Nation, J. Reibenspies, A.E. Martell, Inorg. Chem. 35 (1996) 4597.
[24] J.A. Aguilar, T. Clifford, A. Danby, J.M. Llinares, S. Mason, E. García-España, K. Bowman-James, Supramol. Chem. 13 (2001) 405.
[25] Q. Lu, R.J. Motekaitis, J.J. Reibenspies, A.E. Martell, Inorg. Chem. 34 (1995) 4958.
[26] Q. Lu, J.H. Reibenspies, R.I. Carroll, A.E. Martell, A. Clearfield, Inorg. Chim. Acta 270 (1998) 207.
[27] C. Bazzicalupi, A. Bencini, A. Bianchi, M. Cecchi, B. Escuder, V. Fusi, E. García-España, C. Giorgi, S.V. Luis, G. Maccagni, V. Marcelino, P. Paoletti, B. Valtancoli, J. Am. Chem. Soc. 121 (1999) 6807.
[28] B. Dietrich, M.W. Hosseini, J.M. Lehn, R.B. Sessions, J. Am. Chem. Soc. 103 (1981) 1282.
[29] E. Kimura, A. Sakonaka, T. Yatsunami, M. Kodama, J. Am. Chem. Soc. 103 (1981) 3041.
[30] A. Bencini, A. Bianchi, M.I. Burguete, P. Dapporto, A. Doménech, E. García-España, S.V. Luis, P. Paoli, J.A. Ramirez, J. Chem. Soc. Perkin Trans. 2 (1994) 569.
[31] E. Kimura, Y. Kuramoto, T. Koike, H. Fujioka, M. Kodama, J. Org. Chem. 55 (1990) 42.
[32] M.W. Hosseini, J.M. Lehn, Helv. Chim. Acta 69 (1986) 587.
[33] E. Kimura, M. Kodama, T. Yatsunami, J. Am. Chem. Soc. 104 (1982) 3182.
[34] M.W. Hosseini, M.P. Mertes, J.-M. Lehn, Helv. Chim. Acta 66 (1983) 2454.
[35] M.W. Hosseini, J.-M. Lehn, L. Maggiora, K.B. Mertes, M.P. Mertes, J. Am. Chem. Soc. 109 (1987) 537.
[36] A. Bencini, A. Bianchi, E. García-España, E.C. Scott, L. Morales, B. Wang, M.P. Mertes, K.B. Mertes, Bioorg. Chem. 20 (1992) 8.
[37] L. Qian, Z. Sun, J. Gao, B. Movassagh, L. Morales, K.B. Mertes, J. Coord. Chem. 23 (1991) 155.
[38] J.A. Aguilar, A.B. Descalzo, P. Díaz, V. Fusi, E. García-España, S.V. Luis, M. Micheloni, J.A. Ramírez, P. Romani, C. Soriano, J. Chem. Soc. Perkin Trans. 2 (2000) 1187.
[39] J.A. Aguilar, E. García-España, J.A. Guerrero, S.V. Luis, J.M. Llinares, J.F. Miravet, J.A. Ramirez, C. Soriano, J. Chem. Soc. Chem. Commun. (1995) 2237.
[40] Q. Lu, A.E. Martell, R.J. Motekaitis, Inorg. Chim. Acta 251 (1996) 365.
[41] A. Bianchi, M. Micheloni, P. Paoletti, Inorg. Chim. Acta 151 (1988) 269.
[42] A. Bencini, A. Bianchi, C. Giorgi, P. Paoletti, B. Valtancoli, V. Fusi, E. García-España, J.M. Llinares, J.A. Ramírez, Inorg. Chem. 35 (1996) 1114.
[43] M.W. Hosseini, J.-M. Lehn, K.C. Jones, K.E. Plute, K.B. Mertes, M.P. Mertes, J. Am. Chem. Soc. 111 (1989) 6330.
[44] M.W. Hosseini, A.J. Blacker, J.-M. Lehn, J. Am. Chem. Soc. 112 (1990) 3896.
[45] F. Fenniri, M.W. Hosseini, J.-M. Lehn, Helv. Chim. Acta 80 (1997) 786.
[46] A. Doménech, E. García-España, J.A. Ramírez, B. Celda, M.C. Martínez, D. Monleón, R. Tejero, A. Bencini, A. Bianchi, J. Chem. Soc. Perkin Trans. 2 (1999) 23.
[47] P.G. Yohannes, M.P. Mertes, K.B. Mertes, J. Am. Chem. Soc. 107 (1985) 8288.
[48] P.G. Yohannes, K.E. Plute, M.P. Mertes, K.B. Mertes, Inorg. Chem. 26 (1987) 1751.
[49] M.W. Hosseini, J.-M. Lehn, J. Chem. Soc. Chem. Commun. (1985) 1155.
[50] M.W. Hosseini, J.-M. Lehn, J. Am. Chem. Soc. 109 (1987) 7047.
[51] Z. Jiang, P. Chalabi, K.B. Mertes, H. Jahansouz, R.H. Himes, M.P. Mertes, Bioorg. Chem. 17 (1989) 313.
[52] H. Jahansouz, Z. Jiang, R.H. Himes, M.P. Mertes, K.B. Mertes, J. Am. Chem. Soc. 111 (1989) 1409.
[53] M.P. Mertes, K.B. Mertes, Acc. Chem. Res. 23 (1990) 413.
[54] A. Bianchi, M. Micheloni, P. Paoletti, Pure Appl. Chem. 60 (1988) 17.
[55] A. Bencini, A. Bianchi, P. Dapporto, E. García-España, M. Micheloni, J.A. Ramirez, P. Paoletti, P. Paoli, Inorg. Chem. 31 (1992) 1902.
[56] E. García-España, M. Micheloni, P. Paoletti, Inorg. Chim. Acta 102 (1985) L9.
[57] J. Aragó, A. Bencini, A. Bianchi, A. Domenech, E. García-España, J. Chem. Soc. Dalton Trans. (1992) 319.
[58] A. Bianchi, E. García-España, S. Mangani, M. Micheloni, P. Orioli, P. Paoletti, J. Chem. Soc. Chem. Commun. (1987) 729.
[59] A. Bencini, A. Bianchi, E. García-España, M. Giust, S. Mangani, M. Micheloni, P. Orioli, P. Paoletti, Inorg. Chem. 26 (1987) 3902.
[60] A. Bencini, A. Bianchi, P. Dapporto, E. García-España, M. Micheloni, P. Paoletti, P. Paoli, J. Chem. Soc. Chem. Commun. (1990) 753.
[61] F. Peter, M. Gross, M.W. Hosseini, J.-M. Lehn, J. Electroanal. Chem. 144 (1983) 279.
[62] F. Peter, M. Gross, M.W. Hosseini, J.-M. Lehn, R.B. Sessions, J. Chem. Soc. Chem. Commun. (1981) 1067.
[63] M.F. Manfrin, L. Moggi, V. Castelvetro, V. Balzani, M.W. Hosseini, J.-M. Lehn, J. Am. Chem. Soc. 107 (1985) 6888.
[64] V. Balzani, N. Sabbatini, Chem. Rev. 86 (1986) 319.
[65] F. Pina, A.J. Parola, Coord. Chem. Rev. 185–186 (1999) 149.
[66] L. Moggi, F. Bolletta, V. Balzani, F.J. Scandola, Inorg. Nucl. Chem. 28 (1966) 2589.
[67] F. Pina, L. Moggi, M.F. Manfrin, V. Balzani, M.W. Hosseini, J.-M. Lehn, Gazz. Chim. Ital. 119 (1989) 65.
[68] J. Sotomayor, A.J. Parola, F. Pina, E. Zinato, P. Riccieri, M.F. Manfrin, L. Moggi, Inorg. Chem. 34 (1995) 6532.
[69] M.A. Rampi, M.T. Indelli, F. Scandola, F. Pina, A.J. Parola, Inorg. Chem. 35 (1996) 3355.
[70] B. Dietrich, J.-M. Lehn, J.P. Sauvage, Tetrahedron Lett. 34 (1969) 2889.
[71] R.A. Bell, G.G. Christoph, F.R. Fonczek, R.E. Marsh, Science 190 (1975) 151.
[72] J.-M. Lehn, E. Sonveaux, A.K. Willard, J. Am. Chem. Soc. 100 (1978) 4914.
[73] B. Dietrich, J. Guilhem, J.-M. Lehn, C. Pascard, E. Sonveaux, Helv. Chim. Acta 67 (1984) 91.
[74] R.J. Motekaitis, A.E. Martell, I. Murase, J.-M. Lehn, M.W. Hosseini, Inorg. Chem. 27 (1988) 3630.
[75] T. Clifford, S. Mason, J.M. Llinares, K. Bowman-James, J. Am. Chem. Soc. 122 (2000) 1814.
[76] M.A. Hossain, J.M. Llinares, S. Mason, P. Morehouse, D. Powell, K. Bowman-James, Angew. Chem. Int. Ed. Engl. 41 (2002) 2335.
[77] J.-M. Lehn, Pure Appl. Chem. 52 (1980) 2441.
[78] B. Dietrich, J.-M. Lehn, J. Guilhem, C. Pascard, Tetrahedron Lett. 30 (1989) 4125.
[79] B. Dietrich, B. Dilworth, J.-M. Lehn, J.-P. Souchez, Helv. Chim. Acta 79 (1996) 569.
[80] S.D. Reilly, G.R.K. Khalsa, D.K. Ford, J.R. Brainard, B.P. Hay, P.H. Smith, Inorg. Chem. 34 (1995) 569.
[81] M.A. Hossain, J.M. Llinares, C. Miller, K. Bowman-James, Chem. Commun. (2000) 2269.
[82] R.J. Motekaitis, A.E. Martell, J.-M. Lehn, E.I. Watanabe, Inorg. Chem. 21 (1982) 4253.

[83] S. Mason, T. Clifford, L. Seib, K. Kuczera, K. Bowman-James, J. Am. Chem. Soc. 120 (1998) 8899.
[84] N. Alcock, K. Bowman-James, submitted to Cambridge Data Base.
[85] G. Morgan, V. McKee, J. Nelson, J. Chem. Soc. Chem. Commun. (1995) 1649.
[86] B.M. Maubert, J. Nelson, V. McKee, R.M. Town, I. Pál, J. Chem. Soc. Dalton Trans. (2001) 1395.
[87] M.J. Hynes, B. Maubert, V. McKee, R.M. Town, J. Nelson, J. Chem. Soc. Dalton Trans. (2000) 2853.
[88] D. Powell, K. Bowman-James, unpublished results.
[89] J.-M. Lehn, R. Méric, J.-P. Vigneeron, I. Bkouche-Waksman, C. Pascard, J. Chem. Soc. Chem. Commun. (1991) 62.
[90] E. Graf, J.-M. Lehn, J. Am. Chem. Soc. 97 (1975) 5022.
[91] B. Metz, J.M. Rosalky, R. Weiss, J. Chem. Soc. Chem. Commun. 1 (1976) 533.
[92] B. Owenson, R.D. MacElkro, A. Pohorille, J. Am. Chem. Soc. 110 (1988) 6992.
[93] F.P. Schmidtchen, Chem. Ber. 113 (1980) 864.
[94] F.P. Schmidtchen, Chem. Ber. 114 (1981) 597.
[95] F.P. Schmidtchen, J. Chem. Soc. Chem. Commun. (1984) 1115.
[96] F.P. Schmidtchen, Angew. Chem. Int. Ed. Engl. 20 (1981) 466.
[97] F.P. Schmidtchen, J. Mol. Cat. 37 (1986) 141.
[98] F.P. Schmidtchen, Top. Curr. Chem. 132 (1986) 101.
[99] F.P. Schmidtchen, Chem. Ber. 117 (1984) 725.
[100] F.P. Schmidtchen, Chem. Ber. 117 (1984) 1287.
[101] F.P. Schmidtchen, J. Molec. Catal. 38 (1986) 272.
[102] F.P. Schmidtchen, J. Chem. Soc. Perkin Trans. 2 (1986) 135.
[103] F.P. Schmidtchen, J. Org. Chem. 51 (1986) 5161.
[104] F.P. Schmidtchen, Z. Naturforsch. Teil. C 42 (1987) 476.
[105] F.P. Schmidtchen, J. Am. Chem. Soc. 108 (1986) 8249.
[106] F.P. Schmidtchen, Tetrahedron Lett. 27 (1986) 1987.
[107] K. Ichikawa, A. Yamamoto, M.A. Hossain, Chem. Lett. 12 (1993) 2175.
[108] M.A. Hossain, K. Ichikawa, Tetrahedron Lett. 35 (1994) 8393.
[109] K. Worm, F.P. Schmidtchen, Angew. Chem. Int. Ed. Engl. 34 (1995) 65.
[110] D. Heyer, J.-M. Lehn, Tetrahedron Lett. 27 (1986) 5869.
[111] T. Fujita, J.-M. Lehn, Tetrahedron Lett. 29 (1988) 1709.
[112] Y. Murakami, J. Kikuchi, T. Ohno, T. Hirayama, Y. Hisaeda, H. Nishimura, J. Snyder, K.J. Steliou, J. Am. Chem. Soc. 113 (1991) 8229.
[113] H.J. Schneider, R. Kramer, S. Simova, Y. Schneider, J. Am. Chem. Soc. 110 (1988) 6442.
[114] H.J. Schneider, T. Blatter, A. Eliseev, V. Rüdiger, O.A. Raevsky, Pure Appl. Chem. 65 (1993) 2329.
[115] H.J. Schneider, T. Scheistel, P. Zimmermann, J. Am. Chem. Soc. 114 (1992) 7698.
[116] A. Bianchi, E. García-España, K. Bowman-James (Eds.), Supramolecular Chemistry of Anions, Wiley-VCH, New York, 1997.
[117] T.R. Crompton, Determination of Anions, Springer, New York, 1996.