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Review

Polyamine-based anion receptors: Extraction and structural studies

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Dedicated to Professor Peter Mühl, Dresden on the occasion of his 75th birthday.

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Abstract

In the discussion that follows some of the more recent progress in the area of anion binding by synthetic polyamine receptors is presented, with emphasis given to work undertaken by the authors' groups. A continuing theme in these studies has been the relationship between receptor structure and its anion extraction properties.

Systematic solvent extraction and structural studies for halide and perrhenate complexes with polyamines of tripodal, macrocyclic and macrobicyclic architecture that contain both aromatic moieties and four to eight amine functions have been performed in order to derive relevant structure-binding/extractability relationships. The results demonstrate that the binding and extraction behaviour of the polyamines towards halides and perrhenate is a complex function of their structural features, degree of protonation and lipophilic properties. The extraction is characterized by the preferred formation of mono- and diprotonated amine species in the organic phase. X-ray structure studies of iodide and perrhenate complexes with open-chain tetraamino derivatives and octaamino cryptands in different protonation states lead to the conclusion that in the first case only limited chelation of the anion occurs and in the second only highly protonated species are able to encapsulate the anion. The structural patterns observed are strongly influenced by the presence of water molecules in the crystals.

Keywords: Anion receptors; Polyamines; Extraction; X-ray structures

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1. Introduction

Anion recognition, binding and transport is now a major field of supramolecular chemistry reflecting its relevance to biochemical systems, medicine and pharmacy, analysis, catalysis, recycling and environmental processes. In particular, anion coordination chemistry has developed into an independent research area focussed on the structure and binding modes of anions [1–6]. Over the years manifold receptor architectures for anions have been synthesized and a considerable number have now been involved in structural and transport studies. The goals of these studies have been to understand specific binding behaviour, to derive structure–function relationships and, last but not least, to find useful applications. In contrast to the binding mode of cations which usually involves strong coordinate bonds, anion binding is significantly weaker. For example, it is often associated with multiple hydrogen bond interactions acting in concert with electrostatic interactions, sometimes also with additional π-interactions. Here the most important factor determining the stability of anion complex species is the presence of strong ionic attractions which may frequently account for ∼80% of the stability of such complexes [7]. As a consequence, the design of anion receptors with the required binding strength and selectivity is a subtle task involving the careful positioning of the necessary binding sites in a suitable molecular framework or platform. Due to the predominantly weak interactions involved in anion complexation, the selected medium (water or an organic solvent) will also play a decisive role in influencing complexation behaviour and especially the aqueous-organic phase transfer in such anion extraction systems.

There is a continuing interest in the binding properties of polyaza compounds since these ambivalent ligands are able to interact with both metal cations [8,9] and anions [10–13]. Both types of binding behaviour are strongly influenced by structural factors that include ligand architecture and rigidity as well as by the number and basicity of the nitrogens present; the behaviour in solution is also pH dependent.

Protonated amine and quaternary ammonium functions incorporated in a suitable ligand topology make attractive receptors for anions mainly based on achieving a balanced combination of electrostatic and hydrogen bonding interactions with the anion of interest. This is illustrated by the many synthetic systems now reported as well as by numerous examples found in nature [10–13]. Representative synthetic examples are shown in Fig. 1 while natural systems include the use of protonated linear polyamines with different numbers and spacing of the amine functions as important regulators of cell growth and differentiation through a strong but reversible interaction with the phosphate moieties of DNA [14] and the existence of polyamine-containing spider toxins that are potent inhibitors of glutamate receptors [15].

Our interests have included both the design and synthesis of new anion binding systems incorporating amine functions as well as their application to both health-related and environmental areas [16–20]. For each of these uses a number of special receptor requirements has needed to be fulfilled, with appropriately balanced lipophilicity being of crucial importance.

It also needs to be noted that a further area of related research involves the construction of anion directed supramolecular coor-

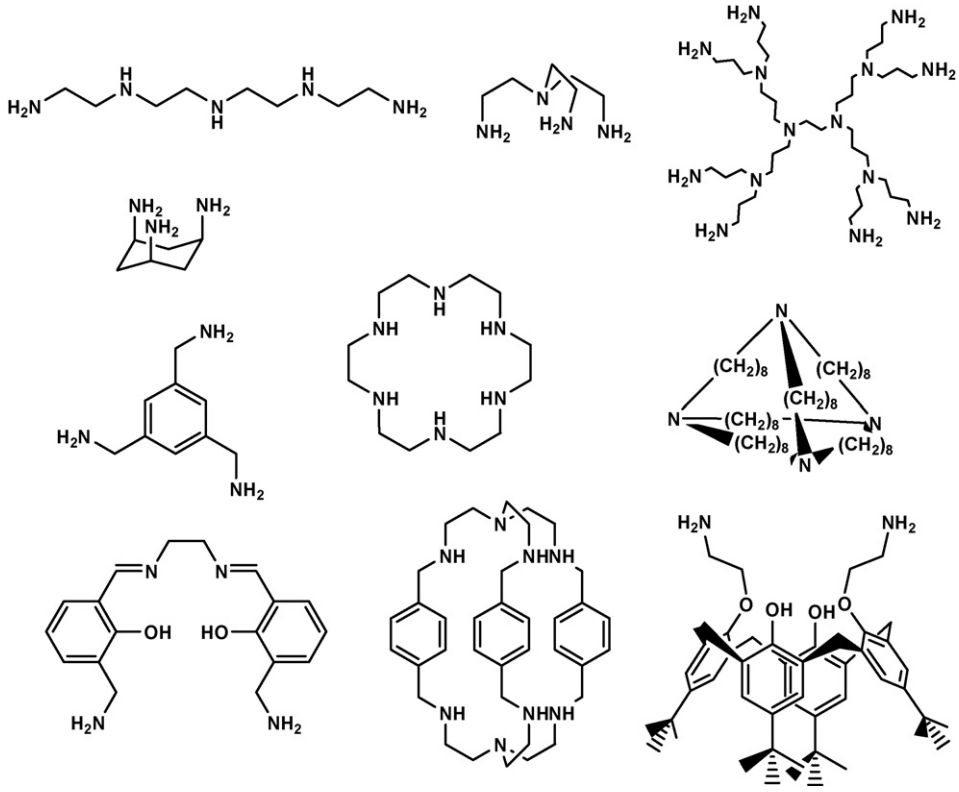


Fig. 1. Representative ligand types with amine functionalities.

dination frameworks which are of increasing interest for the development of new nanosized materials [21–24].

2. Anion extraction

2.1. General considerations

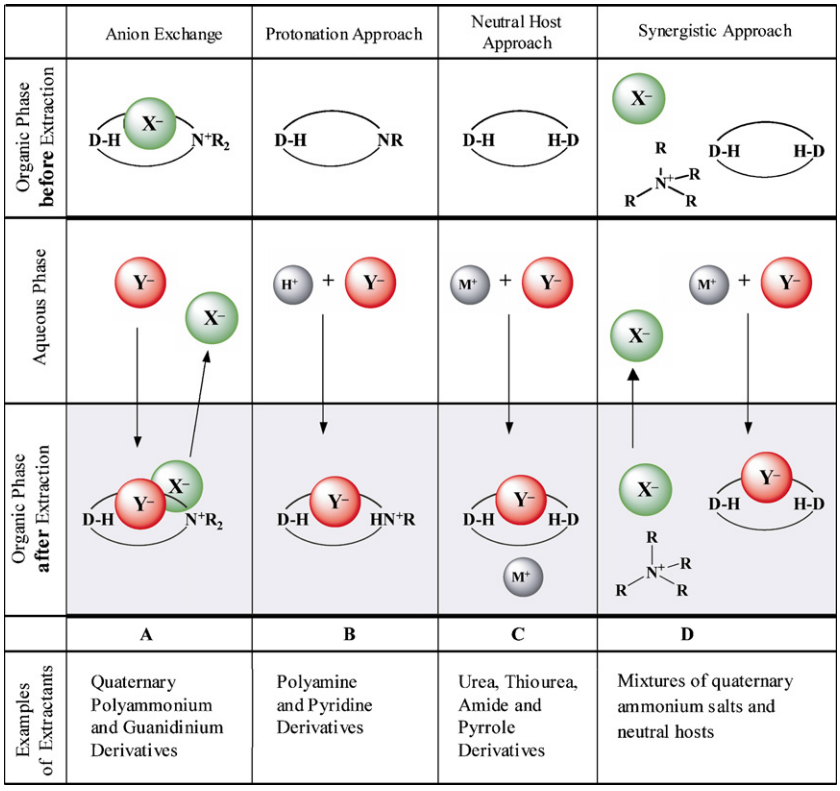
A continuing theme in our investigations, as well as in those of other groups [25–29] has been the application of supramolecular principles to the two-phase solvent extraction of anions in an attempt to increase both extraction efficiency and selectivity for particular anions. In this context it is noted that industrial anion extraction processes are currently largely based on non-specific ion-pair formation processes (involving hydrophobic amines and quaternary ammonium salts) [30].

Compared with the diversity of cation extraction systems so far reported [30], the scope for designing and synthesising new anion systems is more restricted. This is a consequence of the intrinsic nature of anions which are generally larger than cations (and have a resulting lower charge density) and may often be associated with high hydration, with particular anions also showing acid–base properties (resulting in changes in speciation) [31].

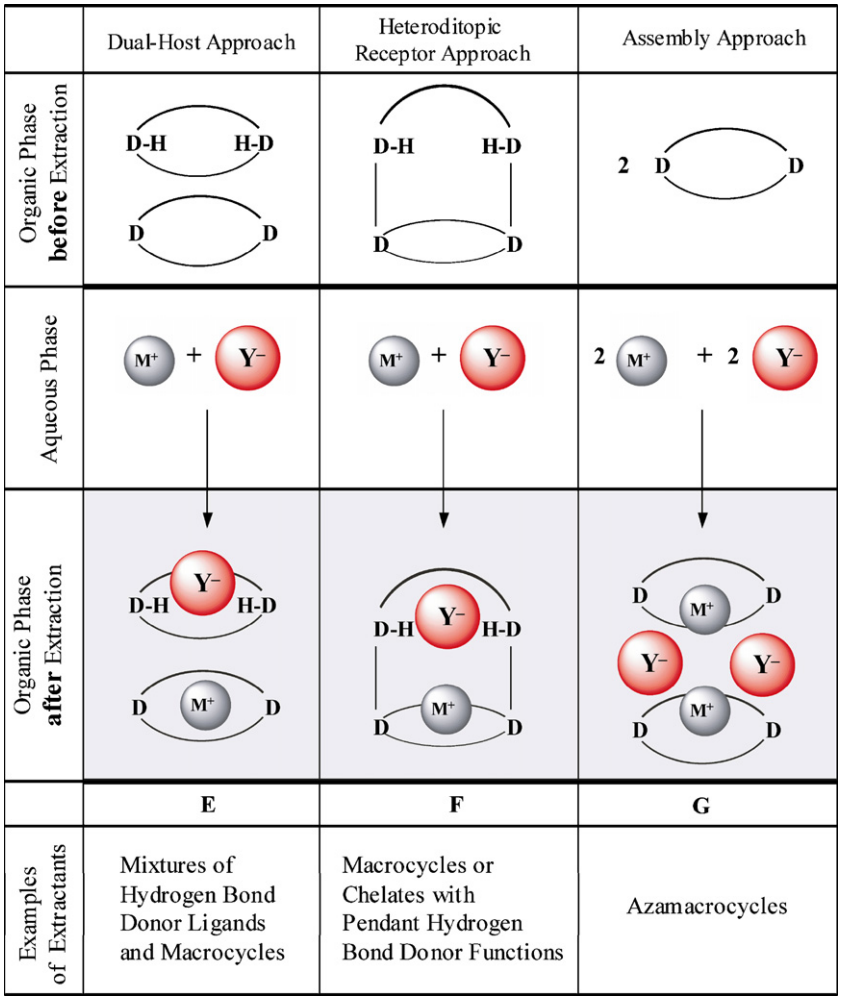
Many factors need to be considered in the design of an extraction reagent. For example, apart from both high lipophilicity and chemical stability, an extractant should give rise to rapid complexation and decomplexation rates and ideally show selectivity for the substrate of interest. Suitable solubility characteristics for use in the chosen two-phase system is also necessary. While these are common requirements with respect to the extractant, a number of different approaches may be possible in terms of the overall extraction process.

Four strategies (A–D) for achieving the supramolecular extraction of an anion Y^- are summarised schematically in Scheme 1.

In each case the supramolecular receptors typically contain multi-binding sites consisting of hydrogen bond donors (including protonated amines) as well as quaternary ammonium functions incorporated in a framework which may, to a lesser or greater degree, show steric complementary to the anion of interest. In all cases considerations of charge neutralisation are important if efficient phase transfer is to take place. The approaches represented by strategies A and B are related in that both involve the presence of positive sites (a quaternary ammonium group or a protonated amine) on the respective receptors that interact electrostaticly with a bound anion and hence contribute to overall charge neutralisation; however, they differ in that A involves an ion exchange step while B incorporates a protonation step. In the case of C, an uncharged host receptor is employed incorporating anion complexing units (typically urea, thiourea, amide, or pyrrole groups). This approach inevitably requires co-transport of a counterion together with the negatively charged supramolecular complex into the organic phase and an efficient extraction will depend strongly on the lipophilicity of this counterion. In contrast, for the synergistic approach D, where the neutral host is combined with a quaternary ammonium salt $R_4N^+X^-$ (providing a hydrophobic cation in the organic phase), the anion extraction is accompanied by counter-transport



Scheme 1. Strategies A–D for achieving anion extraction.



Scheme 2. Strategies E–G for achieving simultaneous extraction of an anion and a cation.

of the corresponding anion X^-. This last example D is a modification of C involving synergistic effects that are generated through the introduction of a second extractant in the organic phase.

Scheme 2 shows three further approaches leading to the simultaneous extraction of both an anion and a cation. Systems E and F each contain dual receptor sites for such an uptake and thus are useful for the extraction of a metal salt MY. They differ in that for E both receptors are separate entities while in F they are combined in a single molecular unit. While the synthesis of the single components employed for E may often be more facile than the combined system F, the latter may show advantages in use since both entropic factors and (potentially) enhanced ion pairing interactions may act to increase cation and anion uptake in this case. Furthermore, specific self-organisation processes involving defined metal binding sites may favour effective anion phase transfer based on assembly formation of the single components as shown in the approach illustrated by G.

The relative behaviour of different anions in two-phase transfer systems has long been known to reflect the Hofmeister bias which ranks the various anions in order of their 'natural' lipophilicity [32–34]. For example, with trioctylamine as extractant the order for extraction of $SO_4^{2-} < PO_4^{3-} < S_2O_3^{2-} < F^- \ll Cl^- < NO_3^- < Br^- \ll I^-$ [35] corresponds well with the Hofmeister order. With regard to this, a continuing theme in anion receptor research has been directed at effectively modifying the hydrophilicity/hydrophobicity balance of bound anions with respect to their phase transfer behaviour such that the Hofmeister order is circumvented [25–29].

2.2. Polyamine extractants

The advances in anion binding chemistry mentioned previously for polyamine systems clearly continue to offer considerable scope for the development of new efficient (and selective) anion extraction reagents. Indeed, a significant number of synthetic anion receptors based on protonated polyamine or quaternary ammonium groups incorporated in, for example, open-chain, macrocyclic, cryptand, calixarene, steroid and dendritic backbones have already received attention [10–13,25–29,36–41].

In the discussion that follows some of the more recent developments in the area of anion binding by synthetic polyamine receptors are highlighted, with emphasis given to work undertaken by the authors' groups. In these latter studies a continuing theme has been the relationship between receptor structure and

its anion extraction properties. For ease of presentation, representative anion binding systems are discussed in turn based on their structural type.

3. Anion binding and extraction studies

3.1. Open-chain receptors based on tris(2-aminoethyl)amine (tren)

Several tripodal protonated tren derivatives substituted with aromatic moieties have been investigated as extractants for pertechnetate and perrhenate ions [18], as well as for chloride, bromide and iodide ions [20], using the extraction system NaX ($X^- = Cl^-, Br^-, I^-, TcO_4^-, ReO_4^-$) – buffer – H_2O/polyamine – $CHCl_3$. Lipophilicity data for these polyamine ligands had previously been obtained using water/1-octanol distribution measurements at different pH values [18,20]. The extraction of chloride and bromide at pH 5.5 was found to be low (≤8%), whereas the extraction of iodide, pertechnetate and perrhenate is generally higher. The favoured extraction of the later over chloride and bromide undoubtedly reflects the differences in their free hydration enthalpies (−338 kJ/mol for Cl^-, −314 kJ/mol for Br^-, but −282 kJ/mol for I^-, −245 kJ/mol for TcO_4^- and −240 kJ/mol for ReO_4^-) [31] influencing phase transfer, but the extent to which other factors, for example, the size of the anion (radii: $Cl^- = 1.72$ Å; $Br^- = 1.88$ Å; $I^- = 2.10$ Å; $TcO_4^- = 2.52$ Å; $ReO_4^- = 2.60$ Å) [31] also play a role is difficult to say (Fig. 2).

The highest iodide extraction is observed for the polyamines **2** (84%) and **5** (82%) as well as for the quaternary ammonium compound [$\mathbf{4}^+ \cdot Br^-$] (86%). The very large differences in percentage extraction between **1**, **2** and **3** likely reflect the relative influences of two important factors affecting extraction behaviour: (i) the lipophilicity of the system and (ii) the protonation behaviour of the extractant. In agreement with the first, the more lipophilic compound **2** shows enhanced extraction of iodide over that observed for **1**. In the case of **3**, factor (ii) may dominate the observed behaviour since iodide extraction is strongly increased with decreasing pH – from 12% at pH 5.5 to 93% at pH 2.1 – indicating that the optimum protonation of this amine derivative for effective extraction had not been reached at pH 5.5. Nevertheless, the partitioning of these two factors is difficult, because

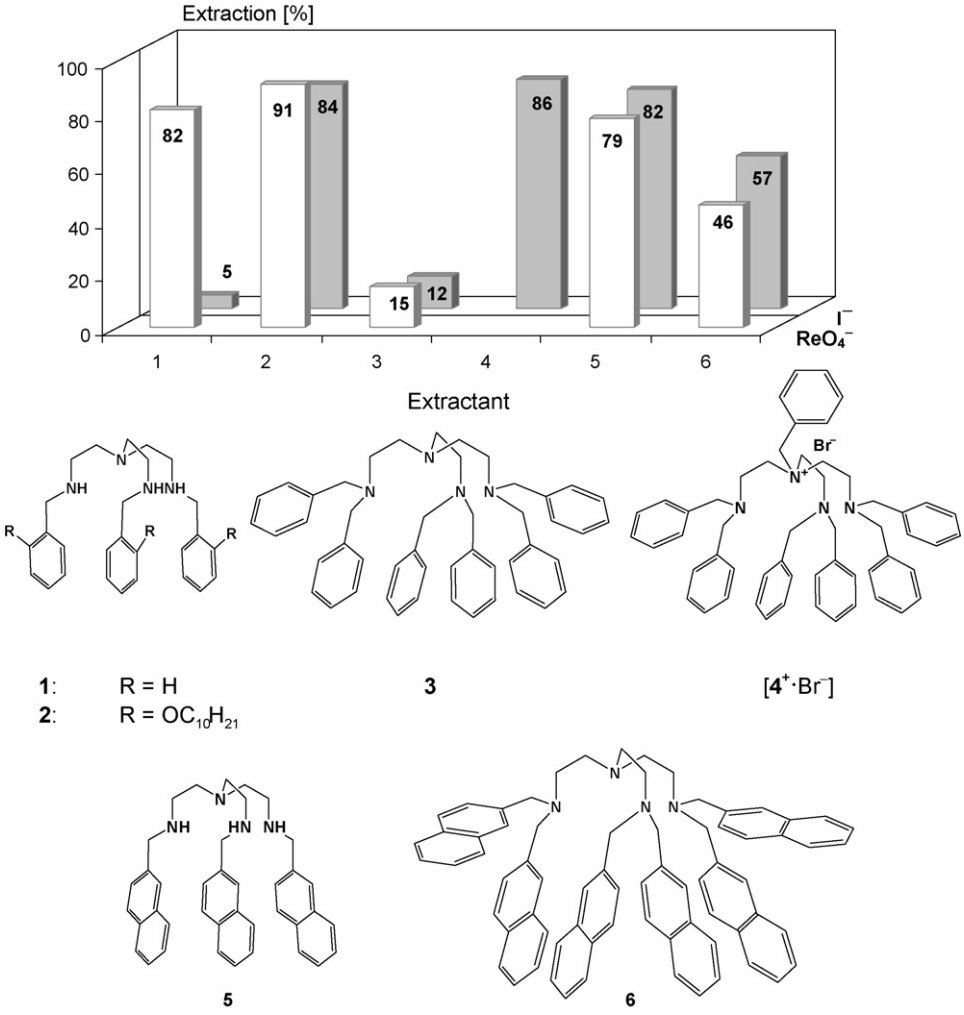


Fig. 2. Perrhenate and iodide extraction (%) by the protonated tripodal polyamine derivatives **1**–**3**, **5** and **6** as well as by the quaternary ammonium compound [$\mathbf{4}^+ \cdot Br^-$] [18,20]; [Na(I, ReO_4)] = 1×10^{-4} M; [ligand] = 1×10^{-3} M/$CHCl_3$; pH 5.5 (MES/NaOH buffer).

lipophilicity drops strongly with increasing protonation, as was confirmed by the octanol-water distribution measurements mentioned earlier. It is noted that, as expected, iodide extraction by the lipophilic quaternary ammonium compound [$\mathbf{4}^{+}\cdot Br^{-}$] is both quite high and pH-independent.

Somewhat similar extraction behaviour to that found for iodide has also been observed for the extraction of the tetrahedral perrhenate anion with these ligands; even so, the high extraction efficiency of **1** towards ReO_4^- in comparison with I^- is remarkable. Obviously the pronounced lipophilicity of perrhenate compensates well for the hydrophilicity of the ligand in this case. Generally, a 1:1 composition of the extracted anion complexes was found to dominate; although in some loading experiments a 1:2 ratio (ligand to anion) has also been detected. These results lead to the conclusion that only mono- or diprotonated amine species are responsible for anion phase transfer in these systems [20].

Interestingly, protonation constants in methanol-water were found to differ only slightly between ligands incorporating secondary and tertiary amines; namely, **1**, **5** and **3**, **6**, respectively [19,20]. Overall, the results suggest that the protonation behaviour of the lipophilic ligands in the two-phase (water/chloroform) extraction system, and hence also their speciation, differs significantly from that occurring in the above single phase (methanol–water mixture) system [19,20,42].

While, clearly, appropriate caution needs be exercised when interpreting solution behaviour in terms of solid-state structures, nevertheless the availability of solid-state information may aid in the understanding of solution behaviour in particular instances.

Crystal structures of anion complexes of protonated tren with various anions, halides, sulfate and phosphate, have been reported, with the protonated ligands adopting chelating arrangements in most instances [40,41,43,44]. For example, in the chloride complex of triprotonated tren, one chloride is bound to a trigonal arrangement of N^+H donors to form a trigonal pyramid; interestingly, the exposed face of this chloride interacts with a number of CH_2 groups forming $CH\cdots C1^-$ hydrogen bonds [41]. In this latter study the structure of the above complex was determined as part of an extensive comparative study in which the X-ray structures of nineteen hydrogen bonded products formed from reaction of diethylenetriamine, *N*-(2-aminoethyl)propane-1,3-diamine, triethylenetetramine, *N*,*N*′-bis(3-aminopropyl)-ethylenediamine and tren with hydrochloric, hydrobromic or hydroiodic acid were determined. It was concluded that the coordination environments adopted by the hydrogen bonded halides are largely imposed by the conformation and the available protonation sites on the host, the host:guest ratio, the existence of any hydrogen bonds between the protonated hosts as well as by the size and electronegativity of the complexed halide. In this context it is noted that the spherical halides are species that are able to participate in a wide range of hydrogen bonded networks, with the structure of the latter being largely influenced by the properties of the poly-protonated amine species involved.

Structural details of a tren molybdate hydrate complex are shown in Fig. 3. The hydrogen-bonded species, $[4(trenH_3)^{3+}\cdot 6(MoO_4)^{2-}\cdot 6H_2O]$, forms a 3D network of

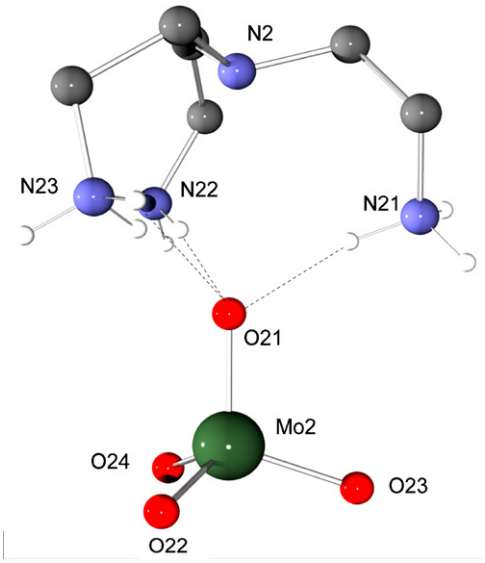


Fig. 3. Structure of the $[(trenH_3)^{3+}\cdot(MoO_4)^{2-}]^+$ cation in the compound $[4(trenH_3)^{3+}\cdot 6(MoO_4)^{2-}\cdot 6H_2O]$ [43].

cations, anions and water molecules in which all hydrogen-bond donors are used [43]. Four of the tetrahedral anions have one molybdate oxygen atom hydrogen bonded to three protonated amine groups of a tripodal cationic ligand in an unusual structural motif. A similar structure was also discussed for the binding of perchlorate by protonated tren [44].

In contrast to the numerous anion complex structures with protonated tren, only four complexes of its tribenzylated derivative **1** have been described until now [19,20,45].

The structure of a mixed perrhenate/chloride complex of the tetraprotonated compound **1** is shown in Fig. 4. A solution of the tetraprotonated tris[2-(benzylamino)-ethyl]amine cation $[2(\mathbf{1}\cdot H_4)^{4+}$, also containing perrhenate and chloride anions, crystallizes in a 1:1:3 ratio, with the lattice structure assem-

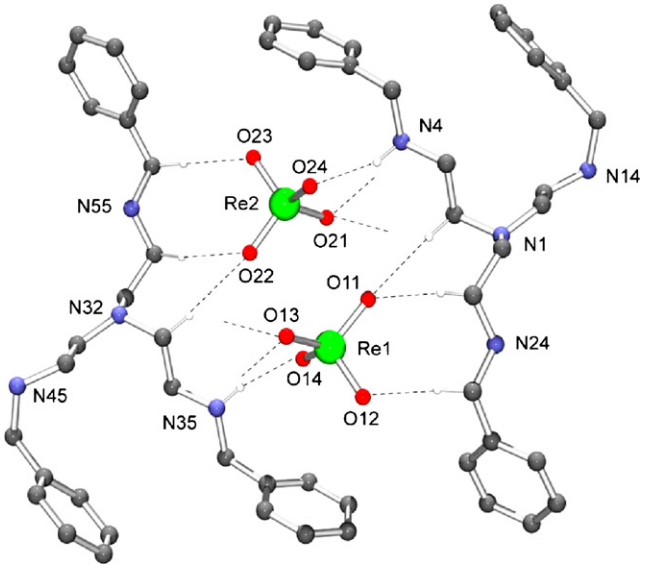


Fig. 4. Structural motif of the complex $[(\mathbf{1}\cdot H_4)^{4+}\cdot(ReO_4)^-\cdot 3(Cl)^-]_n$ showing the perrhenate binding [19].

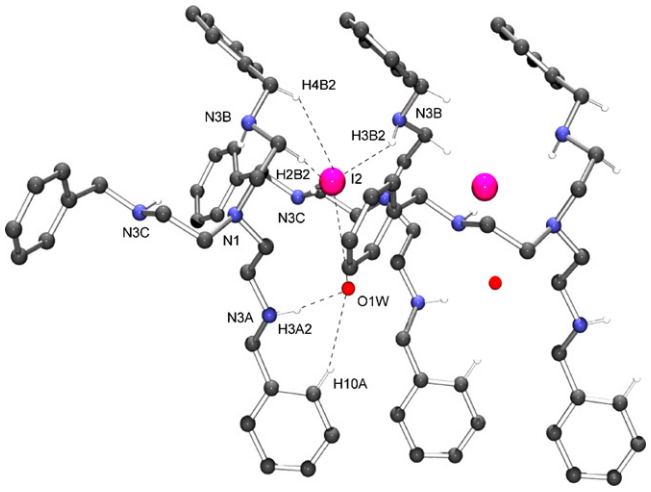


Fig. 5. Structure detail of the compound $[(\mathbf{1}\cdot H_3)^{3+}\cdot 3(I)^-\cdot H_2O]$ showing iodide and water binding [20].

bled from linked sandwich-like 'dimeric' units of composition $[2(\mathbf{1}\cdot H4)^{4+}\cdot 2(ReO_4)^-\cdot 6(Cl)^-]$ [19]. The X-ray structure adopted may, at least in part, be attributed to the cationic ligand exhibiting different (concerted) binding patterns for the two anion types present. The sandwich-like structure incorporates strong $N^+H\cdots O(Re)$ and weak $CH\cdots O(Re)$ hydrogen bonds involving the large tetrahedral perrhenate, with the bonds serving to optimize the distances between the positively charged ammonium ions. The smaller spherical chloride anions assist in the formation of a 2D network by participating in $N^+H\cdots Cl^-$ and $CH\cdots Cl^-$ hydrogen bonds while additional aromatic edge-to-face $CH\cdots\pi$ interactions between aromatic substituents on different layers result in the observed 3D assembly.

The structure of a corresponding iodide complex with the triprotonated cation $(\mathbf{1}\cdot H_3)^{3+}$ is shown in Fig. 5 [20]. In this complex the iodide ion is bound by two strong charge-assisted $N^+H\cdots I^-$ hydrogen bonds between two ligand molecules and a further two weak $CH\cdots I^-$ bonds with one of the ligands. It is interesting to note that a water molecule, which is fixed by this last ligand using both a $N^+H\cdots O_{(w)}$ and a $CH\cdots O_{(w)}$ hydrogen bond, also gives an additional weak interaction with the iodide anion. This latter structural detail provides an example of what appears to be an important influence affecting the hydrophilicity–lipophilicity balance for such complexes; namely, the effect of both the bound anion and water molecules on the above balance. Thus, for example, the quite different extraction behaviour of ligand **1** towards perrhenate and iodide (see Fig. 2) might largely reflect such an influence. Another structural feature, namely the pronounced spreading of the three podand arms of the protonated ligand **1** is present in both the above systems, reflecting the significant repulsion of the protonated arms and thus leading to a reduced chelating tendency of this tripodal system. Such a tendency was also confirmed in the results of DFT structure calculations [19].

An NMR titration study indicated that the triprotonated ligand **1** also binds $H_2PO_4^-$ and HSO_4^- more strongly than NO_3^-. The X-ray structure of $[(\mathbf{1}\cdot H_3)^{3+}\cdot 3(H_2PO_4)^-\cdot H_3PO_4]$ shows that four phosphate ions are associated with the protonated ligand and these were assigned as three $H_2PO_4^-$ entities. The structure of the related bromide complex, $[(\mathbf{1}\cdot H_3)^{3+}\cdot 3(Br)^-]$, differs slightly even though the tripodal amine unit remains triprotonated and quasi-planar. In this case C_{2v}-like symmetry is present, with two of the ligand's arms pointed in a similar direction with a bromide ion lying between them. The two remaining bromides are positioned 'outside' of the tren arms [45].

Structure-related tripodal Schiff base ligands also possess some potential for anion extraction although their chemical stability is rather limited. For example, the monoprotonated trisbiphenyl substituted Schiff base **7** extracts iodide or perrhenate to a small extent (2–5% at pH 7.4). The structure of a corresponding tetrafluoroborate complex $[(\mathbf{7}\cdot H)^+\cdot(BF_4)^-]$ is shown in Fig. 6. In part, reflecting the presence of three strong

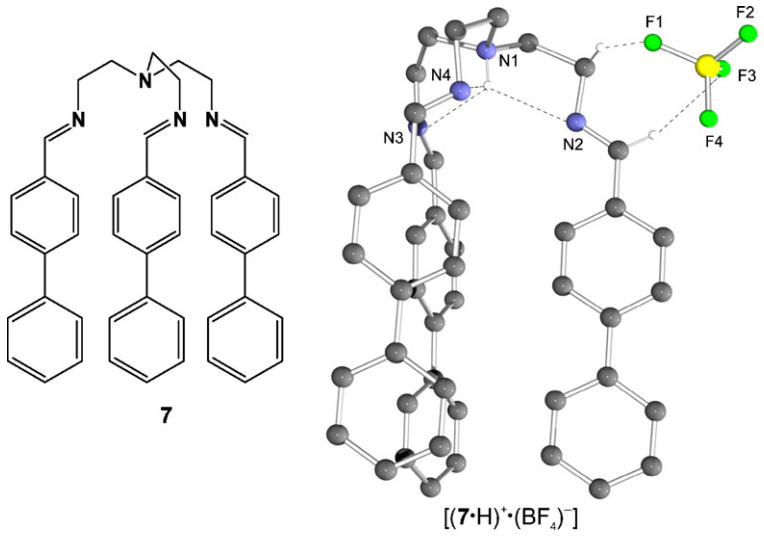


Fig. 6. Structure of the monoprotonated Schiff base tetrafluoroborate complex $[(\mathbf{7}\cdot H)^+\cdot(BF_4)^-]$ showing three strong hydrogen bonds between amine and imine functions of the ligand together with only two weak $CH\cdots FB$ hydrogen bonds between an outside located BF_4^- and $(\mathbf{7}\cdot H)^+$.

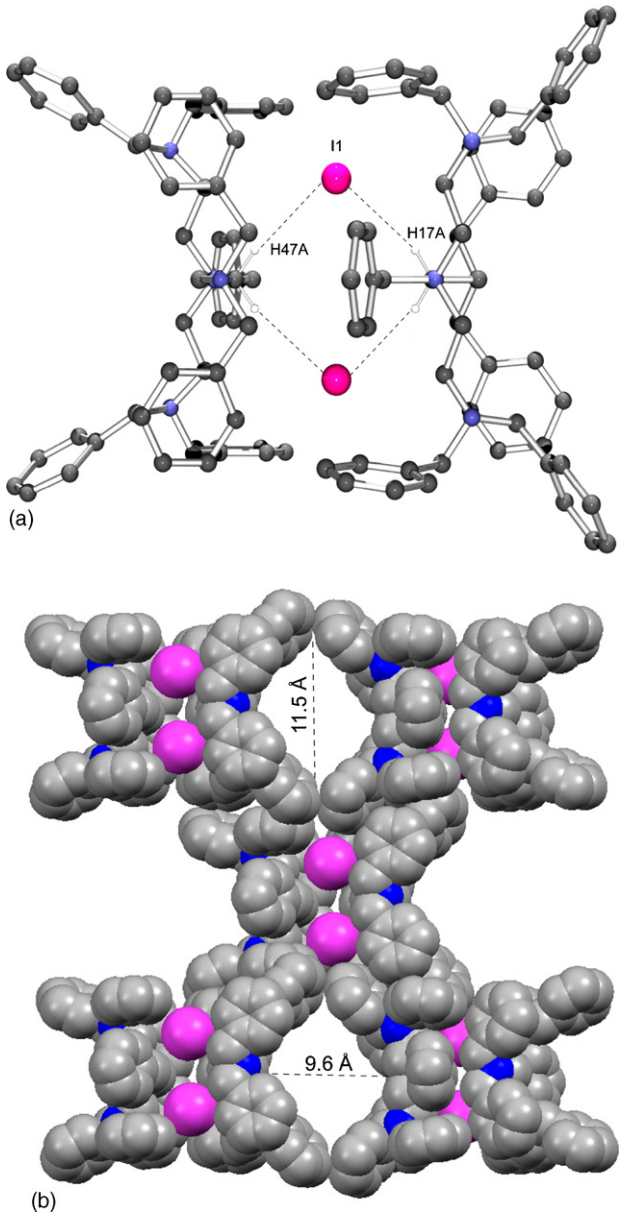


Fig. 7. Structural details of the dimeric unit of the iodide complex [$\mathbf{4}^{+}\cdot I^{-}$] (a) and of the corresponding nanoporous self-assembled framework (b) [20].

intramolecular $N^{+}H\cdots N{=}C$ hydrogen bonds, only weak binding of the BF_4^{-} anion via two $CH\cdots FB$ hydrogen bonds is present.

An interesting result arising from the crystallisation process of iodide with the quaternary ammonium cation ($\mathbf{4}^{+}$) is the formation of the anion-directed framework shown in Fig. 7 [20]. The structure consists of a dimeric arrangement formed from two [$\mathbf{4}^{+}\cdot I^{-}$] units which are stabilized mainly by electrostatic interactions between the iodides and the quaternary ammonium cations. Further stabilisation results from two weak $CH\cdots I^{-}$ hydrogen bonds involving each iodide as well as from additional π–π interactions between aromatic moieties (Fig. 7a). In this way the self-assembly process leads to a nanosized hydrophobic pore pattern which was shown to include organic solvent molecules such as methanol or acetonitrile (Fig. 7b). TGA measurements show that the release of the solvent molecules begins only at temperatures above 80 °C.

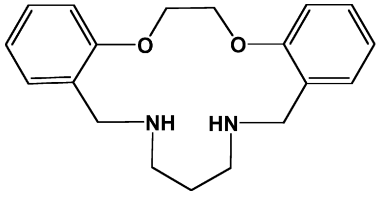
3.2. Macrocycles

A large number of macrocyclic polyamine-based receptors for anions has now been investigated both in solution and the solid state [12,13,46–62]; however, the number of such systems employed for anion solvent extraction has been relatively limited.

One extraction study has centred on the series of structurally related N_4O_2-donor macrocycles **8**–**13** (Fig. 8). Generally similar halide extraction properties to those found for the open-chain derivatives **1**–**6** discussed in Section 3.1 were observed for these systems [20]. Namely, in all cases only very minor extraction of chloride or bromide occurred while much greater iodide extraction was observed for **9**–**12**; however, iodide extraction by **8** and **13** was also poor. On the one hand this latter behaviour again appears to reflect the low lipophilicity of the unsubstituted ligand **8** while, on the other, the significantly different protonation behaviour of **13** (which contains only tertiary amines) in the organic phase is likely important in this case; the extraction of iodide by **13** becomes significantly higher at lower pH (and this also correlates well with the behaviour of ligand **3**). Despite proposing different protonation behaviour for **13** in the organic phase, it nevertheless needs to be noted that the protonation constants in 95% methanol for this tertiary amine system do not differ greatly from those for **8**, **10** and **11** containing secondary amines [63].

The results for the pH dependence of **12** (Fig. 9) are in accordance with complex protonation equilibria being present for this system since high iodide extraction was found to occur over the broad pH range 2–6 (but falls off significantly at lower and higher pH values) [20].

As noted already, water molecules are not infrequently associated with ligand-bound anions in solid-state structures and such behaviour has been postulated to occur in solution for particular phase transfer systems [20]. A further example of such behaviour in the solid state occurs in the case of the anion complex of diprotonated **11** which binds a $PF_2O_2^{-}$ anion in its cavity together with a connecting 'internal' water molecule to yield a cationic cluster unit of type $[(\mathbf{11}\cdot H_2)^{2+}\cdot(PF_2O_2)^{-}\cdot H_2O)]^{+}$ [63] (Fig. 10).



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Reaction of the mixed N_2O_2-donor macrocycle **14** and the sodium salts given by NaX (X = picrate, ClO_4^{-}, BF_4^{-}, PF_6^{-}, SCN^{-} and BPh_4^{-}) in methanol yields crystalline ion-pair products in each case incorporating the protonated macrocycle as the cation, with the respective anions as the counterion [64]. The

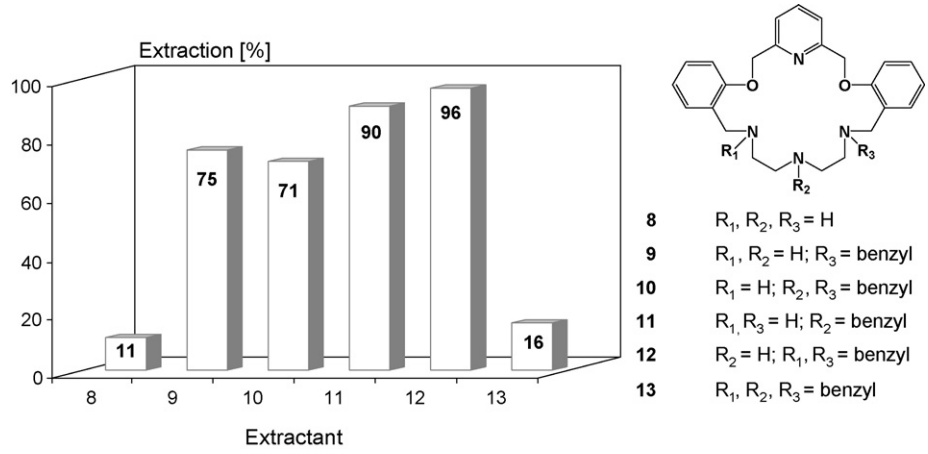


Fig. 8. Iodide extraction (%) by protonated N_4O_2-donor macrocycles **8**–**13** [20]; [NaI] = 1×10^{-4} M; [ligand] = 1×10^{-3} M/$CHCl_3$; pH 5.5 (MES/NaOH buffer).

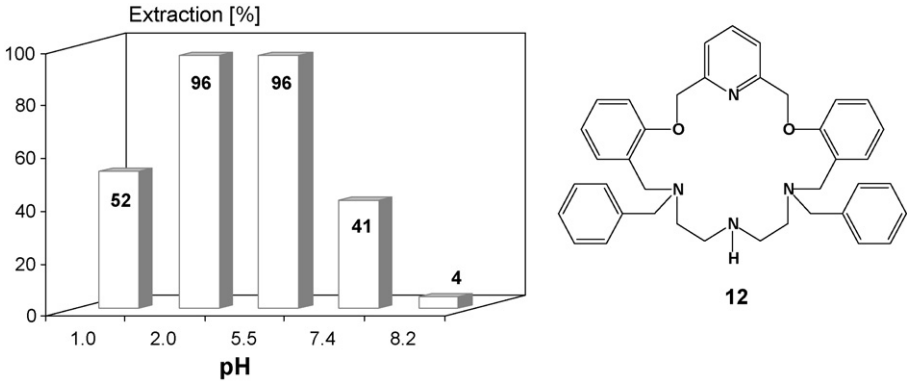


Fig. 9. pH Dependence of iodide extraction (%) by the protonated N_4O_2-donor macrocycle **12** [20]; [NaI] = 1×10^{-4} M; [ligand] = 1×10^{-3} M/$CHCl_3$; pH 1.0 [HCl] = 1×10^{-1} M; pH 2.0 with [HCl] = 1×10^{-2} M; pH 5.5–8.2 (MES/NaOH, HEPES/NaOH buffers).

results confirm that the affinity of **14** for protons is greater than for the sodium ion and that the mode of ligand protonation as well as the hydrogen bonded network that forms is highly dependent on the properties of the available anion (and, in particular, its size, shape and polarizability). Also, the choice of solvent was shown in one instance to influence whether inter- or intraligand protonation occurs. As expected, the positioning of a proton either inside or outside of the molecular cavity results, as might be predicted, in very different hydrogen bond networks forming in the respective protonated macrocyclic arrays. The proton-to-

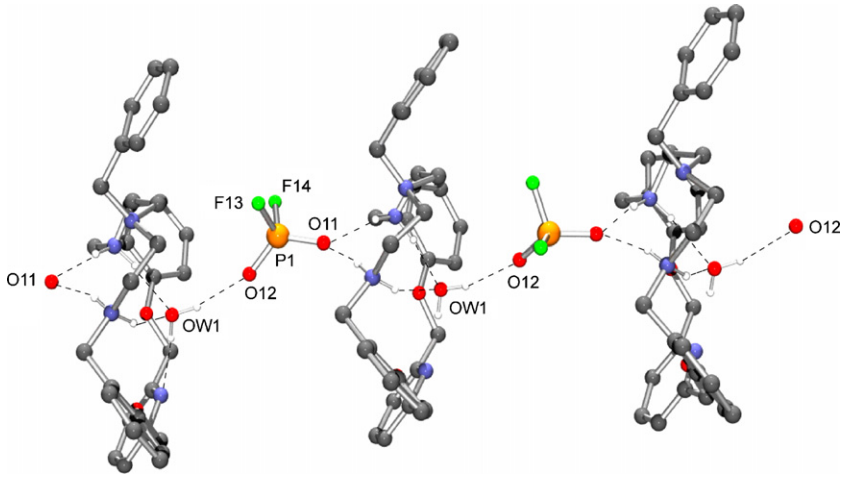
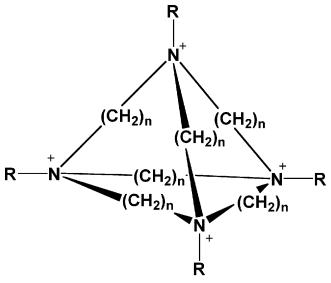


Fig. 10. Part of the structure of the complex $[(\mathbf{11}\cdot H_2)^{2+}\cdot(PF_2O_2)^-\cdot(H_2O)]^+\cdot(PF_6)^-$ showing the hydrogen bonding motif bridging between ligand, anion and water [63].

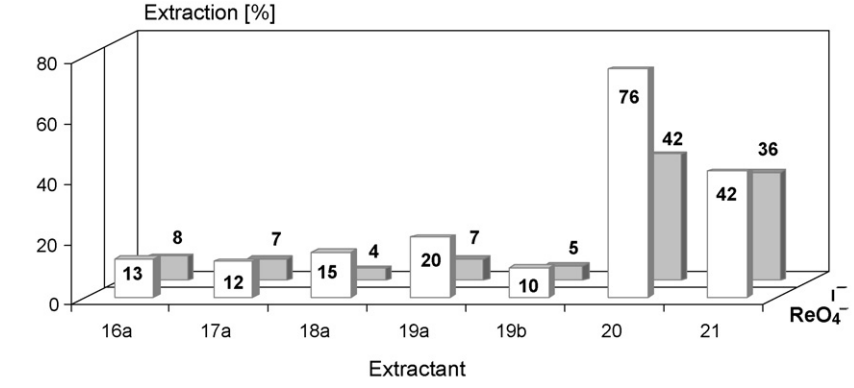
ligand ratios were found to be 1:2 for the perchlorate, tetrafluoroborate, hexafluorophosphate and thiocyanate salts and 1:3 for the picrate salt. The corresponding ratio for the tetraphenylborate salt was 2:3. Overall the study serves to confirm that the structure adopted by 'simple' host–guest systems of the present type is highly dependent on subtle changes of both the conditions employed and the nature of the host–guest components themselves. That is, from the above as well as from a range of other studies it is clear that the weak interactions involved in anion binding are quite sensitive to small changes in the experimental conditions as well as to structure variations in the acceptor-anion system under investigation.

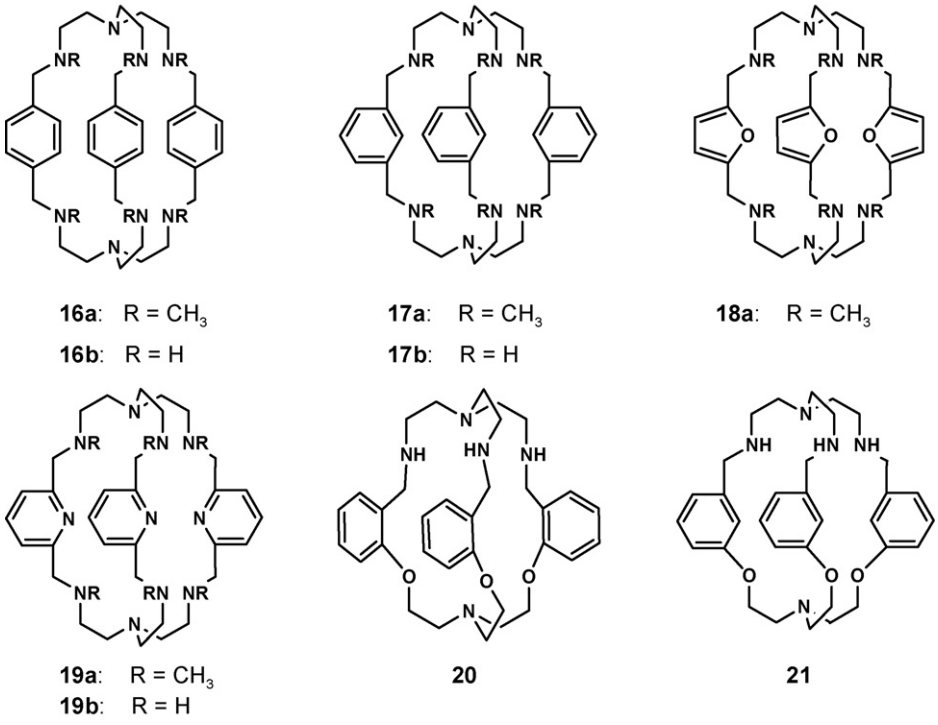
3.3. Cryptands

In early studies it was observed that the extraction behaviour of tetrahedral tetraammonium receptors of type **15** (incorporating either 6 or 8 methylene linking groups between four quaternary nitrogen centres) towards anions is rather poor. This is largely a consequence of the low solubilities of these tetrapositively charged species in organic solvents [17]. The extraction order of $I^- > Br^- > Cl^-$ found for these anions again mirrors their hydration free energies, with the strongly hydrated oxoanions sulfate and hydrogen phosphate also showing only weak interaction.



15: R = H, CH_3; n = 6, 8





16a: R = CH_3
16b: R = H

17a: R = CH_3
17b: R = H

18a: R = CH_3

19a: R = CH_3
19b: R = H

20

21

Fig. 11. Perrhenate and iodide extraction (%) by protonated aminocryptands **16a–21** [16,18,20]; [Na(I, ReO_4)] = 1×10^{-4} M; [ligand] = 1×10^{-3} M/$CHCl_3$; pH 7.4 (HEPES/NaOH buffer).

An investigation of the halide (Cl^-, Br^-, I^-), pertechnetate and perrhenate extraction by a number of protonated cryptand derivatives has been carried out under comparable conditions to those employed for the tripodal and macrocyclic polyamine derivatives discussed above [16,18,20].

The results for iodide [20] and perrhenate [16,18] extraction by seven amino cryptands **16a–21** are summarized in Fig. 11. It is clearly evident that the octaamino cryptands **16a–19b** allow only limited extraction towards both perrhenate and iodide. In all cases the perrhenate extraction is slightly higher, reflecting the relative lipophilicity differences between these anions. Under the same conditions, only **20** and **21** show useful extraction efficiencies, but these are lower than observed for their open-chain analogue **2**. For each of **16a–21** the data presented were obtained within the optimum extraction pH range of 7–8 determined for these amino cryptands. The observed differences in extraction efficiency very likely reflect the presence of additional protonation equilibria in the case of the octaamino derivatives **16a–19b** [18] relative to the pentaamino species **20** and **21** [65], with all of the former being more highly protonated under the conditions employed, resulting in reduced lipophilicity for these systems.

In accord with the above (and as expected), cryptands **17** and **19** were each shown to exhibit six protonation steps [18] while the corresponding tren derivative, **1**, showed four [19]. For comparison, the dibenzylated macrocyclic ligand **11**, a very efficient iodide extractant from the ligand series **8–13**, exhibited only two under the conditions employed for the measurement [63]. This fact is illustrated in Fig. 12 which shows the pH dependence of the protonation behaviour for ligands **1**, **13** and **19b** [18,19,63].

At least with respect to the extraction of both perrhenate and iodide ions into an organic phase, the above results are in keeping with extraction efficiency being enhanced when ligands incorporating a lower number of protonated amine groups are employed. Undoubtedly this is due to the presence of higher lipophilicities for the resulting complexes. Indeed, this is also in agreement with the exclusive extraction of 1:1 and 1:2 (ligand to anion) species also found in case of the functionalised tren derivatives (see Section 3.1).

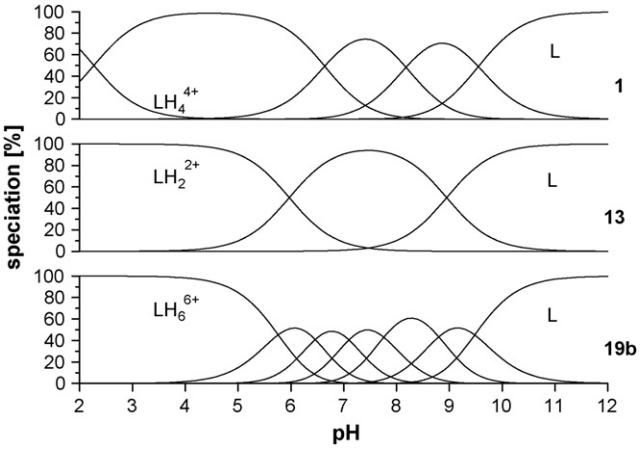


Fig. 12. Calculated distribution curves of protonated polyamine species for **1**, **13** and **19b** as a function of pH using the pK_a values of **1** and **13** in methanol/water [19,63] and of **19b** in water [18].

Amino cryptands of different structure generally form both inclusion and *exo*-cavity complexes with a large number of different anions, for example, with the spherical halides but also with various tetrahedral anions. Such products are stabilised in many cases by the presence of linking water molecules [10,11,37,38].

During our anion binding studies three different iodide complexes of the unsubstituted hexaprotonated ligand **16b** (R = H) were isolated from the same solution, with the respective structures differing significantly in terms of the number of bound water molecules present [20]. Such formation of different anion complex structures during crystallisation very likely reflects the complexity of the species present in solution which, as we have discussed already, may be greatly influenced by a number of factors. The isolated products were of composition: $[(\mathbf{16b}{\cdot}H_6{}^{6+}{\cdot}(I)^-]^{5+}{\cdot}4(I)^-{\cdot}(I_3)^-{\cdot}0.5H_2O$, $[(\mathbf{16b}{\cdot}H_6)^{6+}{\cdot}(I)^-]^{5+}{\cdot}3(I)^-{\cdot}2(I_3)^-{\cdot}4H_2O$ and $[(\mathbf{16b}{\cdot}H_6)^{6+}{\cdot}(I)^-]^{5+}{\cdot}2(I)^-{\cdot}3(I_3)^-{\cdot}6H_2O$. Two X-ray structures are shown in Fig. 13.

The structures clearly illustrate the effect that water content may have on the structure adopted. In the nearly water-free product (Fig. 13a), the encapsulated iodide is not stabilised in the centre of the cage. Instead, two half-occupied iodide positions were identified off-set from the centre to wards each 'end' of the cage. Each 'half-occupied' iodide is associated with three strong $N^+H\cdots I^-$ hydrogen bonds that fall in the range 2.54–3.05 Å. Further weak $CH\cdots I^-$ hydrogen bonds ($C\cdots I^-$ 3.8–4.4 Å) to the three aromatic groups complete the coordination sphere of each iodide. The calculated (PM3) energy barrier of 6 kcal/mol for the interchange between the iodide positions in the cage is small and therefore "hopping" between the two positions seem a reasonable interpretation of the observed result. The formation of triiodide ion during crystallisation is evidently a consequence of air oxidation, as previously reported for other systems [52]. The *exo*-cavity anions I^- and $I_3{}^-$ are weakly bound by $CH\cdots I^-$ or $CH\cdots I_3{}^-$ interactions.

In contrast to the above structure, the other two complexes of hexa-protonated **16b** have an iodide ion located almost centrally in the cage. In the case of the structure illustrated in Fig. 13b, this is likely due to the influence of the two water molecules that also occupy the cryptand's cavity. The included iodide ion is bound to five secondary amine nitrogen atoms of **16b** via water-mediated strong hydrogen-bonds, with $I^-\cdots O_{(w)}$ and $O_{(w)}\cdots N^+$ distances falling in the range 3.43–3.57 and 2.81–3.01 Å, respectively. Additional weak interactions with the three aromatic units $CH\cdots I^-$ ($C\cdots I^-$ 4.2–4.4 Å) complete the iodide coordination sphere. As in the previous case, the *exo*-cavity iodides and triiodides interact only weakly with the ligand via $CH\cdots I^-$ or $CH\cdots I_3{}^-$ hydrogen bonds.

The structures of anion complexes of mono- or diprotonated cryptands that have been determined so far [16,20] reveal

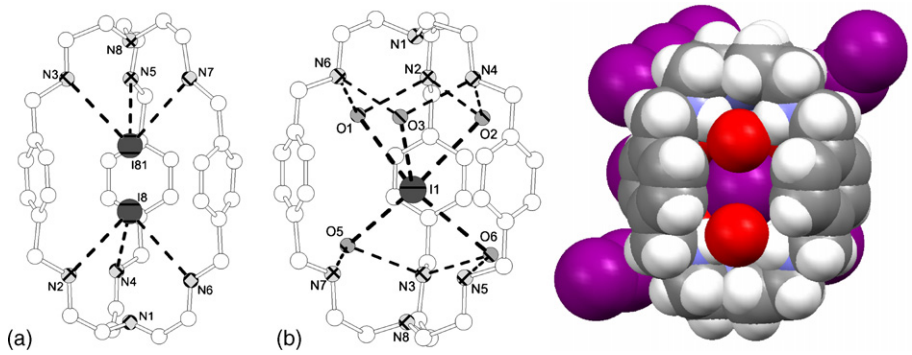


Fig. 13. Hydrogen bonding modes of the encapsulated iodide in crystals of (a) $[(\mathbf{16b}\cdot H_6)^{6+}\cdot(I)^-]^{5+}\cdot 4(I)^-\cdot(I_3)^-\cdot 0.5H_2O$ and (b) $[(\mathbf{16b}\cdot H_6)^{6+}\cdot(I)^-]^{+}\cdot 2(I)^-\cdot 3(I_3)^-\cdot 6H_2O$ [20].

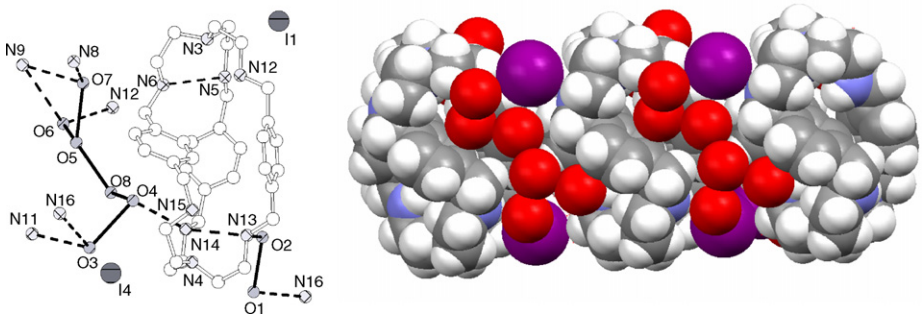


Fig. 14. Structure of the *exo*-cavity iodide complex $[\mathbf{16b}\cdot H_2]^{2+}\cdot 2(I)^-\cdot 8H_2O$ showing the formation of dimeric and hexameric water clusters [20].

the importance of positive charge repulsion on the conformations adopted by the protonated structures. For example, in contrast to the hexaprotonated species, the diprotonated ligand **16b** (R = H) shows a flat arrangement of its iodide complex $[\mathbf{16b}\cdot H_2]^{2+}\cdot 2(I)^-\cdot 8H_2O$ (see Fig. 14). This ligand conformation is stabilised by two intramolecular hydrogen bonds in each tren (capping) fragment, restricting the space for encapsulation, with anion binding thus occurring outside the cavity. A characteristic feature of this iodide complex is the presence of discrete hexameric and dimeric water clusters incorporating short hydrogen bonds $O_{(w)}\cdots O_{(w)}$ (2.64–2.85 Å) and $N\cdots O_{(w)}$ (2.69–3.05 Å), leading to an extended hydrogen bond network connecting the ligand molecules in all three directions. The *exo*-cavity iodide ions show only very weak interactions with secondary amine functions ($N\cdots I^-$ 3.5–4.3 Å).

X-ray analysis of a single crystal of the complex $[(\mathbf{17b}\cdot H_6)^{6+}\cdot(ReO_4)^-]^{5+}\cdot 5(ReO_4)^-\cdot 5H_2O$ (Fig. 15) [18] showed that it does not differ greatly from the structure of the perchlorate analogue reported earlier [67]. One anion is included in the cavity being held by a similar mix of direct $N^+H\cdots O(Re)$ and indirect (water-mediated) hydrogen bonds to that in the perchlorate analogue; however, unlike the perchlorate structure, N^+H donors from both ends of the cryptand are involved in direct H-bonding to the anion. There are also hydrogen bonds directed to anions outside of the cryptand cavity.

In contrast, in $[(\mathbf{19b}\cdot H_6)]^{6+}\cdot 6(ReO_4)^-\cdot[\mathbf{19b}\cdot H_6]^{6+}\cdot 4(ReO4)^-\cdot 2(ClO_4)^-\cdot 3H_2O$ neither of the oxoanions ReO_4^- and ClO_4^- are encapsulated within the cavity of the pyridine-containing cage **19b** (R = H), the latter acts as a cleft rather than a cavity-binder. Each of the three anions, two perrhenate and a perchlorate, occupy the three clefts formed by each

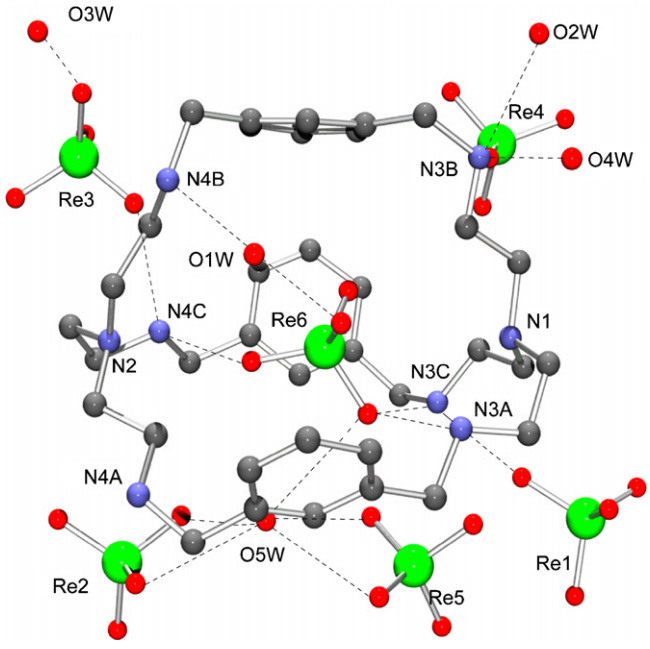


Fig. 15. Molecular structure of the perrhenate complex $[(\mathbf{17b}\cdot H_6)^{6+}\cdot(ReO_4)^-]^{5+}\cdot 5(ReO_4)^-\cdot 5H_2O$ [18].

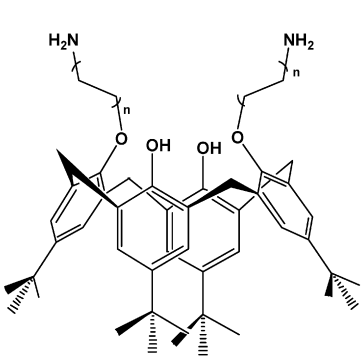
cryptand cation [18]. However, such a 1:3 structure (ligand to anion) does not appear to form in solution since NMR titration data yielded a good fit for a 1:1 model. A further NMR study performed at pH 3 indicated that complexation of perrhenate is stronger than occurs for perchlorate or nitrate.

It is noted that up to the present no inclusion complexes of the pentaamino cryptands **20** and **21** appear to have been isolated. Both the penta-protonated and the mono- or diprotonated cations bind ClO_4^- and ReO_4^- only in an *exo*-cavity arrangement [16,65,66].

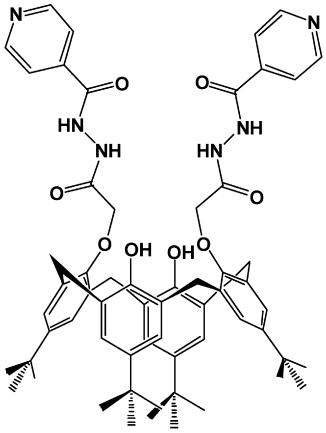
In summary, relative to the tripodal and macrocyclic ligands discussed above, octaamino cryptands show significantly poorer extraction of halide, pertechnetate or perrhenate anions as a consequence of the formation of highly protonated species with pronounced hydrophilicity over a broad pH range. Since it is established that inclusion complexes only form when such polyamino cages are extensively protonated, it may be concluded that inclusion complexes are of little significance in aqueous/organic phase transfer processes for systems of the present type.

3.4. Calixarenes

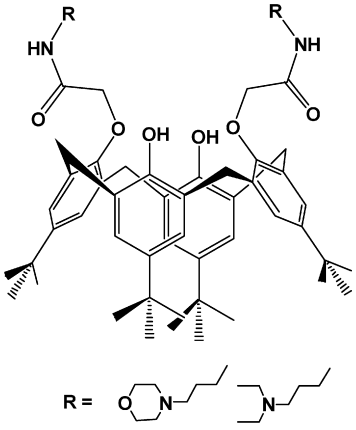
A number of anion receptors based on calixarene frameworks have now been investigated [12,68,69], but only in some cases have they been used in solvent extraction studies. These latter include calixarene derivatives incorporating aminoalkyl (**22**) [70,71], pyridyl (**23**) groups [72] and quaternary ammonium groups (**24**). Such species in their protonated state have been demonstrated to be very good extractants for selected oxoanions. For example, derivatives of type **22** have been shown to readily extract chromium(VI) as $HCrO_4^-$ or $HCr_2O_7^-$ from acidic aqueous solution into a chloroform phase [71].



22a: n = 1
22b: n = 2



23

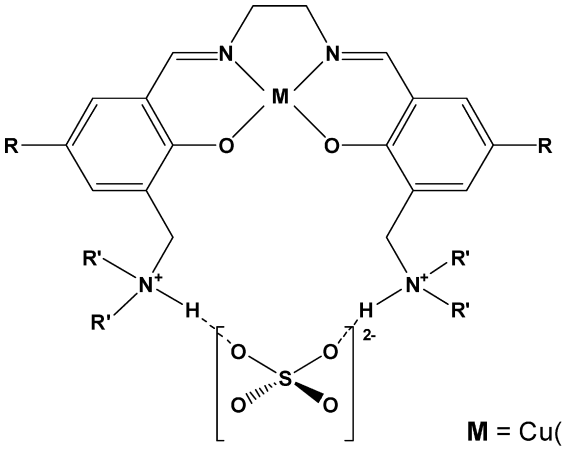


24a **24b**

The order of decreasing extraction of $S_2O_3^{2-} > SeO_4^{2-} \cong SO_4^{2-} > HCrO_4^- > NO_3^-$ for **22b** at pH 2.6 clearly favours divalent anions over monovalent ones and hence yields anti-Hofmeister behaviour [70]. The observed behaviour in this case is likely a reflection of the conditions employed having a marked influence on the speciation present in the respective anion systems [71]. The introduction of pyridine units to the calixarene platform (ligand **23**) also leads to interesting chromate extraction behaviour for the acidic pH range <2. In contrast, the methylation of the pyridine nitrogens in **23** leads to a significant decrease in the degree of phase transfer which points to the importance of hydrogen bond formation for the dichromate binding (in addition to the electrostatic interaction) [72]. There is an improvement in the extraction properties towards Cr(VI) on protonation of different amine functions in calix[4]arene diamide derivatives of type **24a**,**b**. Reflecting the different basicities of the amine substituents, **24a** yields moderate extraction at pH <2 and **24b** gives high extraction in the pH region between 2.5 and 3.5. In comparison, the extraction abilities of the related amine-free systems are very low [73].

3.5. Heteroditopic extractants

A range of heteroditopic host systems that combine both anion and cation binding sites in the one framework have been reported [27], one category of this type being based on bis-salicylaldimine ($salenH_2$) derivatives incorporating attached amine and/or amide groups (located in either open-chain or macrocycle configurations) [74–76]. An example of each of the latter types is given by **25** and **26** [77,78], respectively. On binding a metal salt such as nickel(II) or copper(II) sulfate, these uncharged ligands undergo a zwitterionic transformation to form an overall neutral assembly which is soluble in non-polar solvents such as chloroform. A comparison of the solid-state structures of copper(II) sulfate and neutral 'copper-only' complexes demonstrated how incorporation of the metal ion into the $salen^{2-}$ unit preorganises the protonated anion binding site for accommodation of the sulfate group [77]. These systems represent very efficient pH-switchable extractants for nickel(II) and copper(II) sulfate of the type illustrated by strategy F in Scheme 2.



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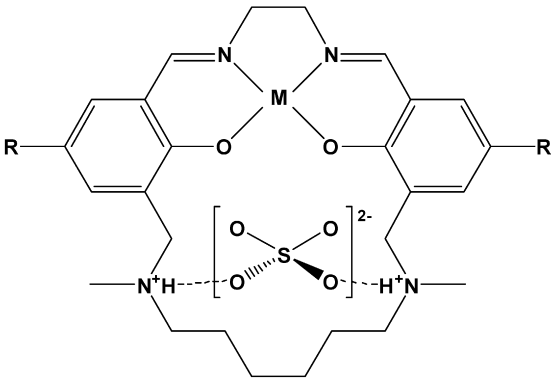
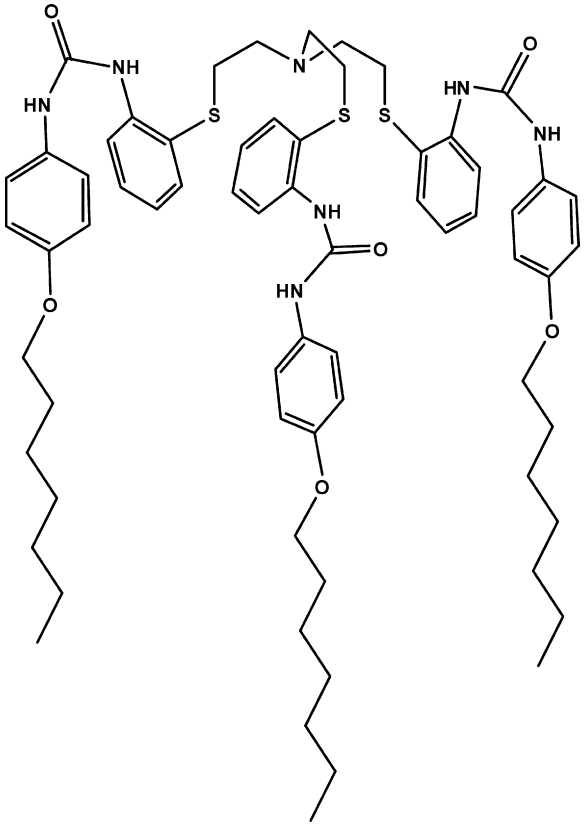


26

X-ray structure determinations of the nickel(II) and copper(II) sulfate complexes of the *tert*-butyl substituted ligand **26** showed that in the solid state the SO_4^{2-} anion does not occupy the cavity enclosed by the hexamethylene strap but rather is bound intermolecularly as a hydrate to tertiary nitrogen atoms on adjacent complexes to form a dimeric hydrogen bonded structure of stoichiometry 2:2:2:2 (ligand:metal:sulfate:water) [78]. However, in solution it was postulated that multi-equilibria associated with different binding modes of the anion occur.

In a further development, a structurally related receptor to **25** incorporating mixed amine/amide anion-binding functions has been demonstrated to give interesting pH dependent Cl^-/SO_4^{2-} selectivity [79].

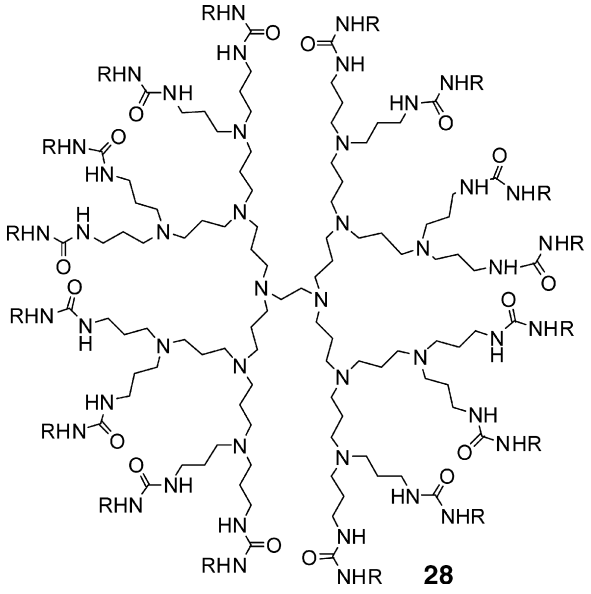


27

Another promising ditopic receptor for the simultaneous binding and extraction of a cation and an anion is given by the multi-functionalized tripodal amine ligand **27** which yields a pronounced anti-Hofmeister tendency with respect to the extraction of silver salts. Using this ligand the extraction of silver together with hydrophilic acetate matches the extraction in presence of the lipophilic picrate [20].

3.6. Dendrimers

Reflecting their unusual topology, dendrimers have been shown to exhibit a diverse range of host-binding behaviour that includes anion binding [80].



28

Readily synthesized lipophilic urea-functionalized dendrimers such as **28** have been reported to show efficient phase transfer (water/chloroform) behaviour towards pertechnetate, perrhenate and ATP anions [81]. Such dendrimers are readily protonated at their 'inner' tertiary amine functions and hence are capable of binding anions. The incorporation of the hydrogen-bond donor entity, urea, is also advantageous in this

regard as this group has also been well documented to act as an anion binder [2–4]. Moreover, the respective products have hydrophobic peripheries which will clearly aid the phase transfer process; in addition, their demonstrated pH dependency allows controlled release of guest anions from the dendrimer host.

Multi-crown dendrimers of four different generations incorporating polyamine functions have been synthesized by grafting 4, 8, 16, and 32 benzo[15]crown-5 moieties on to the periphery of oligoethyleneoxy-modified polypropyleneamine dendrimers (POPAM dendrimers) [82]. The extraction of pertechnetate (present in the aqueous phase as sodium pertechnetate) by these dendrimers has been reported. In this study it was demonstrated that the crown ether units are quite poor in terms of the simultaneous extraction of the sodium cations under the conditions employed. On the other hand, the (protonated) amine nitrogen atoms in the dendrimer core readily bind to and promote phase transfer of the pertechnetate anion. As expected, the extraction efficiency increases with both increasing dendrimer generation and decreasing pH. This observation is in accord with the anion being bound to protonated tertiary amine groups in the interior of the dendrimer.

4. Concluding remarks

As illustrated in the above discussion, various categories of polyamine receptors displaying a wide range of molecular architectures have now been employed for anion binding, both in the solid state and in solution. Such behaviour has been extensively investigated and continues to show considerable potential for the analytical sensing and monitoring as well as for the separation of individual anions, especially in relation to industrial and environmental applications. One general advantage of the polyamine systems consists in their often good synthetic availability and the corresponding possibility for facile structural modification—allowing a ready extension of the present spectrum of anion, cation and ditopic receptors with tailor-made properties in the future.

An understanding of anion binding by synthetic hosts provides an aid for interpreting biochemical anion recognition as well as for gaining insight into natural anion membrane transport processes. In this connection it will be interesting to extend the study to new polyamine host/anion guest systems with defined bound water molecules (or clusters) as models for the water behaviour in biological systems [83–85]. Important studies on enhanced anion complexation by incorporation of water [86] or DMSO [87] into the binding motif are now complete. These open promising possibilities for controlling the binding selectivity by incorporation of solvent molecules. More generally, the results of such studies are of major potential importance for obtaining a wider understanding extraction behaviour, with implications for both the structural and thermodynamic aspects of the extraction process.

Apart from the topics discussed in this review, it is noted that other aspects of anion binding are being actively pursued. These include the chiral recognition of anions [88–90], the use of ligand-bound metal centers especially for cascade coordination [91,92] or for second-sphere coordination [93,94] as well as molecular dynamics simulations of anion complex formation and phase transfer processes [95–97].

Last but not least the construction of anion-directed supramolecular assemblies has become a topic of considerable interest and is of increasing importance for the development of new nanosized materials for use in a range of analytical, environmental, industrial and biochemical/medical applications [98].

Acknowledgements

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