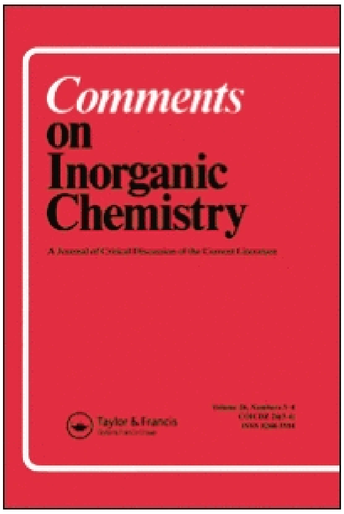

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Pseudo-Encapsulation: Open Prison Ligands for Metal Ions

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Pseudo-Encapsulation: Open Prison Ligands for Metal Ions

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Rapid growth in the range of polydentate ligands prepared in recent decades has produced firstly macromonocyclic systems and subsequently macropolycyclic encapsulating ligands. Intermediate between these can be identified a set of topologically distinctive ligands whose collective grouping is based on their capacity to satisfy fully the coordination demands of metals ions and bind sets of three adjacent donors to polyhedral faces. This family of ligands offer pseudo-encapsulation of metal ions; whereas a macrobicycle may act as a "cage" or "prison" for a metal ion by trapping it in the cavity, the ligands described here present themselves as "open prisons" because of their less complete framework. The concept and types of pseudo-encapsulating ligands extant is examined here for saturated hexaamines which act as sexidentate ligands and commonly form octahedral complexes. Examples of the various topologies assigned as pseudo-encapsulating hexaamine ligands are described. In particular, the differing shape-directed coordination chemistry of *syn*- and *anti*-diammac (6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine) is examined in some detail. The latter isomer is a sterically efficient ligand which forms complexes with "compressed" coordination spheres and extreme physical properties, whereas the former isomer displays no such effects.

Key Words: *polydentate amine ligands, macrocyclic ligands, pendant-arm macro-*

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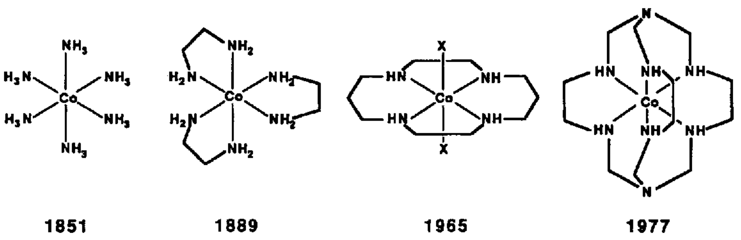
cycles, macrobicyclic ligands, hexaamine complexes, metal ion encapsulation and pseudo-encapsulation

INTRODUCTION

It is possible to map the progress of chemistry by identifying key compounds, since development of related compounds has opened up new areas of research endeavor. An obvious example is the synthesis of the first crown ether by Pedersen, which subsequently led to the development of a vast range of macropolycyclic polyethers and investigations of their chemistry.[1,2] In coordination chemistry specifically, progress can be related to the development of new classes of chelating ligands. Such a progression can be made in the development of saturated polyamine ligands and their complexes, where one can step from the first complexes with ammonia to the first simple chelating diamines, to the macromonocyclic polyamines, and then to the macrobicyclic polyamines (see, for example, Scheme 1).[3-6] Encapsulation of metal ions attained with the macromonocyclic polyamines, as exemplified by the now classical molecule cyclam (1,4,8,11-tetraazacyclotetradecane, **1**) was limited by its "two-dimensional" character, since encircling a metal ion with a ring of donors frequently did not saturate the coordination sphere and left the metal ion "exposed" above and below the macromonocyclic plane, with additional ligands frequently bound in these sites.[7] Saturated quadridentate macromonocycles such as cyclam can adopt "folded" in addition to "flat" geometries for binding metal ions, but the metal ion still demands additional donors to complete its coordination sphere.



SCHEME 1

Following the reporting and study of macromonocyclic polyamines, the subsequent and not too distant temporal development of the hexaamine macrobicyclic ligands such as sar (3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane, **2**) by Sargeson and co-workers addressed both shortcomings of the macromonocycle at once.[8,9] The ligands efficiently encapsulate metal ions in a "three-dimensional" manner, and they present six donor atoms to metal ions, effectively saturating the coordination sphere of many metal ions. Exploitation of these compounds which are relatively simple molecular "cages" is still not complete, but their rapid development following on from and even in parallel with the continuing development of macromonocycles has served to condemn what appears a less dramatic development of another family of ligands to undeserved relative historical obscurity.

One obvious step in meeting the shortcomings of the macromonocycle is to consider the addition of (at least) two pendant arms carrying additional potential donor atoms to the basic macromonocycle framework,[10] rather than a complete extra "strap" with additional donors as is added in the macrobicycles. These arms can be added to a macromonocyclic framework at a choice of either ring nitrogen heteroatoms or carbon atoms. They can serve to meet the demands of a metal ion for additional donors to saturate its coordination sphere without recourse to other additional ligands, and the "extended" molecules can be expected to "encapsulate" metal ions with reasonable efficiency. These "pendant arm" macromonocycles may not appear as elegant or efficient captors of metal ions as the macrobicycles, so it is perhaps inappropriate to define them as encapsulating ligands. We would prefer to call them pseudo-encapsulating ligands. They present, because of the presence in the polydentate ligand of some "simple" chelate arms, greater opportunities for partial or complete "unwrapping" from metal ions than is the case with the macrobicyclic ligands, and this may be in some circumstances a virtue. Whereas the macrobicycle can be described as a "cage" or "prison" for metal ions, the pseudo-encapsulating ligand is more in tune with these enlightened times, as we can define it as an "open prison" ligand.

The concept of a pseudo-encapsulating ligand can be applied more generally than simply to the case of pendant arm macromonocycles. There are a range of molecules we can categorize in this family, as exemplified by the potentially sexidentate species shown in schematic form in Fig. 1 along with examples of "cage" ligands, to confirm the relationship between the species. Examples of most but not all of these sub-groups have been reported, though relatively few have been studied extensively. What is common to all is the possession of at least one set of three adjacent linked donors which bind to an octahedral face when complexed. Overall,

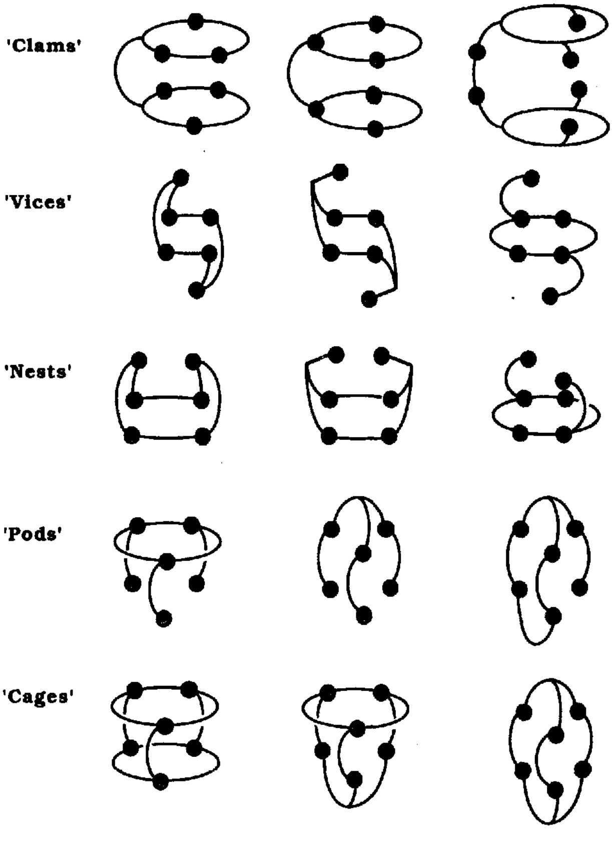
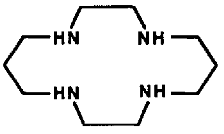


FIGURE 1 Schematic drawings of some pseudo-encapsulating and potentially sexidentate ligands, classified into topologically distinct sub-groups. Potential donors are represented by the hatched circles. (The encapsulating "cage" molecules are included at the base of the figure for comparison.)

the types of polydentate ligand which we classify as pseudo-encapsulating ligands is extensive, being defined by shape rather than donor type. In general, *a pseudo-encapsulating ligand is one capable of saturating the coordination sphere of a metal ion while binding a set (or sets) of three adjacent donors to a polyhedral face (or faces).* However, this discussion will subsequently be restricted to one sub-group which has attracted a good deal of recent attention, namely fully saturated molecules with only six nitrogen donors, which can then be compared with the saturated hexaaza macrobicycles and simpler chelating ligands. An overview of the chemistry of selected examples will serve to demonstrate the character of this family.

Perhaps the "parent" pseudo-encapsulating ligand in this family can be assigned as the branched hexaamine **3**, complexes of which were reported by Schwarzenbach in the 1950's and 1960's,[11] around the period when macromonocyclic complexes were first being examined. This acyclic molecule can be viewed as an acyclic "clam" (see below), since each set of three amine donors made up of one tertiary amine and its two primary amine "pendants" can bind to an octahedral face in forming sexidentate complexes (and are linked by a carbon chain), as defined in a later crystal structure analysis.[12] It is a satisfying "parenting" to assign, given both the important role played by Schwarzenbach in the development of coordination chemistry and the then logical temporal location of the initial development of pseudo-encapsulating ligands ahead of encapsulating ligands.



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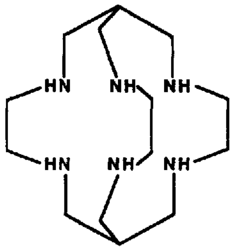

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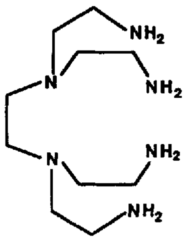

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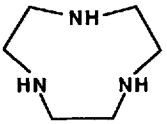
Despite the capacity of the macrobicyclic hexaamines to enforce coordination to metal ions to the point of stabilizing a range of unusual oxidation states, and to prohibit rapid dissociation, it is notable that a great deal of this behavior is carried by more simple bis(triamine) metal complexes. The best studied examples of this are the bis(tacn) (tacn = 1,4,7-triazacyclononane, **4**) complexes, examined in depth by Wieghardt and co-workers.[13] A range of octahedral bis(tacn) metal complexes displays good stability in several oxidation states. Further, the related triamine tach (tach = cyclohexane-1,3,5-triamine, **5**) displays both good thermodynamic and kinetic stability with metal ions such as Ni(II) when compared with a simple chelate such as pn (pn = propane-1,3-diamine) despite the comparable chelation mode, the former binding via six-membered chelate rings like the latter.[14] The first aquation step for simple bidentate chelates from Ni(diamine)$_3^{2+}$ is ca. 100-fold faster than the first step for Ni(tach)$_2^{2+}$ [10]; also, log β for Ni(tach)$_2^{2+}$ is 18.9, much higher than log β for Ni(pn)$_3^{2+}$ (pn = propane-1,3-diamine) of 12.9. Cleavage of Ni(tach)(OH$_2$)$_3^{2+}$ in aqueous acid is nearly 10^5-fold slower than cleavage of the analogous dien (3-azapentane-1,5-diamine) complex. Both tach and tacn donor sets must occupy octahedral faces, with the three donors predisposed in an appropriate triangular arrangement. The first step in dissociation requires not only detachment of one nitrogen donor but also may involve geometrical rearrangement of the backbone (e.g., tach may undergo rearrangement from a chair to a boat geometry to displace the departing donor sufficiently from the initial coordination site).[15] Nevertheless, the displaced donor must still remain reasonably close to the metal ion as a result of the presence of the other pair of chelated donors in the ligand. Consequently, ligands of higher denticity which demand facial coordination of adjacent donors during complexation carry an enhanced capacity to stabilize metal ions in both a thermodynamic and kinetic sense.



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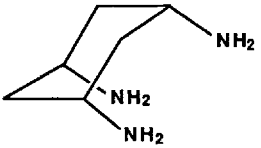

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The pseudo-encapsulating hexaamines discussed here are examples of a range of molecules where the overall ligand shape or topology plays a significant role in determining the way in which ligand and metal ion interact. Some possible variations in shapes of potentially sexidentate pseudo-encapsulating ligands are exemplified in Fig. 1, with trivial but descriptive sub-class names assigned. The topology may contribute strongly to complexation selectivity, giving rise to "toposelectivity," as defined by Lehn, who has assigned topology in terms of a sum of connectivity, cyclic order and dimensionality.[16] The toposelectivity of two geometric isomers of a hexaamine which fall into different sub-classes is addressed later as an example, but initially examples of members of sub-classes are discussed.

TABLE I

Formation constants of polyamines with selected metal ions.[a]

Ligand[b] (Ionic Radius)	Mn(II) (0.80)	Co(II) (0.72)	Ni(II) (0.69)	Cu(II) (0.72)	Zn(II) (0.74)	Cd(II) (0.97)	Hg(II) (1.10)	Pb(II) (1.20)
$(en)_3$	5.8	14.1	18.4	–	13.0	12.3	–	–
$(tach)_2$	–	–	18.9	15.5	–	–	–	–
$(tacn)_2$	9.4	23.9	25.4	27.4	20.5	17.9	21.4	15.4
(dtne)	15.0	18.5	21.5	–	20.0	18.5	–	–
(**3**)	9.3	15.6	19.1	22.1	16.1	16.1	29.6	–
linaneN_6[c]	–	–	–	21.6	14.0	15.3	–	–
[18]aneN_6	–	18.9	19.6	24.4	18.7	18.8	29.1	14.1
$(N{-}Me)_4$[18]aneN_6	–	13.1	16.2	20.5	13.3	16.8	–	–
sen	8.6	18.0	–	26.2	17.0	13.4	–	9.2
syn-diammac	–	–	–	–	16.1	12.1	12.2[d]	11.8
anti-diammac	6.2	–	–	–	15.0	10.6	10.5[d]	10.8

[a] Values are log K_1 for hexaamines, log β_2 for triamines, log β_3 for diamines; temperature (normally 25°C) and electrolyte conditions may not be identical for all determinations.

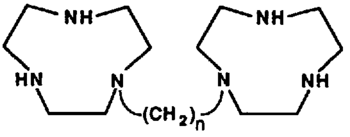
[b] Trivial names correspond as follows: en = ethane-1,2-diamine; tach = **5**; tacn = **4**; dtne = **6**; [18]aneN_6 = **8**; sen = **12**; *syn*-diammac = **11**; *anti*-diammac = **10**.

[c] LinaneN_6 = linear hexaamine "formed" by "snipping" [18]aneN_6 at a C–C bond.

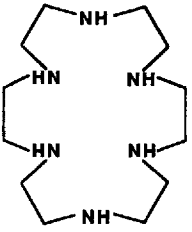
[d] In KCl electrolyte; value for *anti*-diammac in KNO_3 electrolyte is 21.4, and other values cited for Hg(II) measured in the absence of Cl .

"Clam" Ligands

A logical extrapolation from the bis(tacn) system involves the linking of two tacn molecules by a chain of methylenes, which can in principle join either nitrogen or carbon atoms of the two residues. The resultant ligands may bind metal ions with each "lid" of the clam shell occupying an octahedral face. Despite the extensive study of bis(tacn) complexes, very little attention has been focussed on these potentially sexidentate analogues. The syntheses and some complexes of **6** and **7** with ethane and propane chains linking nitrogen centers have appeared.[17,18] The X-ray crystal structure of **6** as a sexidentate ligand bound to Fe(III) has been reported.[19] The complex exhibits a distorted trigonal prismatic geometry with an average Fe–N bond distance of 2.00_4 Å, just slightly longer than that found in the bis(tacn) analogue. However, the ligands have limited preorganization for complexation by a single metal ion, and are ambivalent enough to alternatively bind two metal ions by adopting a bridging mode where each ring binds facially to different metal ions. Large molar extinction coefficients for monomer octahedral complexes of **6** compared with **7** have been assigned to a trigonal twist distortion in the former, relieved in the latter by the presence of a longer bridge.[13] Differing steric demands may account in part for differences in stability constants between **6** and bis(tacn) metal complexes (Table I); Co(II) and Ni(II) are preferred by the latter, with stability enhanced for the former with the larger Mn(II) and Cd(II) ions. The influence of the length of the linking bridge has been established even from this limited study. Whether the presence of two linking chains rather than a single chain would influence properties much as a result of possibly greater rigidity has not been examined to date. Adding three linking chains would generate a polycyclic "cage" molecule with presumably a particularly rigid framework.



6 (n = 2)
7 (n = 3)



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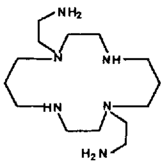
"Vice" Ligands

Another mode of pseudo-encapsulation involves four donors of a ligand encircling the metal ion in an approximate plane while additional donors occupy sites above and below this plane. The metal ion is effectively trapped in a vice, with the mode of coordination normally yielding octahedral or distorted octahedral geometries. This geometry is available to a simple macromonocyclic ligand with six donors, e.g., [18]aneN_6 (**8**), which has been observed to bind metal ions as large as Hg(II) in this arrangement. The "vice" geometry for a macromonocycle described in schematic form in Fig. 1 has been identified as a preferred geometry for **8** when bound to ions of up to 2.2 Å radius from molecular mechanics analysis, and the crystal structure of the complex of the Hg(II) ion in this arrangement has been recently reported.[20] The complex adopts a distorted trigonal prismatic shape with a twist angle of 23° (compared with 0° for trigonal prismatic and 60° for octahedral), and the Hg–N average distance of 2.44(2) Å is similar to distances in other mixed-donor aliphatic HgN_2S_4 and heterocyclic HgN_6 structures. Apart from this observed structure in which sets of three adjacent nitrogen donors occupy a *fac* (D_{3d}) arrangement, an alternate geometry in which the two sets of three adjacent donors occupy *mer* (D_2) geometry is known,[21] and both have been characterized for Co(III) complexes by X-ray crystal structure analyses.[22,23] It is notable that the linear hexaamine ligand which can be viewed as formed effectively by "snipping" open **8** at a C–C bond also adopts the same *fac* geometry at least as its Cd(II) complex.[24] Of course, a greater range of geometries is available to the linear molecule, but when two opposite nitrogens in **8** are replaced by pyridine groups which also incorporate the two originally adjacent methylenes into the pyridine rings, the resultant more rigid ligand can only adopt the *fac* arrangement.[25] With Zn(II), a structure analogous to the Hg(II) complex of **8** has been defined, but to accommodate large metal ions with higher coordination numbers the ligand can revert to its largest cavity size with an approximately planar arrangement of all donors. Despite the extra rigidity introduced with the pyridine groups, metal ion binding constants are generally higher than with **8**. However, with the tetra-N-methylated [18]aneN_6, stability constants generally are lower than those observed with [18]aneN_6,[26] presumably as a result of steric influences introduced by the N-methyl groups.

From the discussion above, it is clear that a macromonocycle is not predisposed to the "vice" geometry, and that alternative binding modes may be observed or preferred with a single metal ion. With larger rings, incorporation of two metal ions in the cavity may be observed, each associated with sets of donors at extreme ends of the cyclic molecule. Even with the relatively small macrocycle **8**, two square planar Pd(II) ions can be incorporated, each binding three nitrogen donors along with an additional chloride ion.[27] The [24]aneN_6 analogue of [18]aneN_6 (where an additional methylene has been inserted in chains between each pair of amines) is another example where two metal ions, in this case Cu(II), are incorporated in the cavity.[28]

Other molecules may be more directed to the "vice" shape. For example, for the putative **9**, where two aminoalkane arms are attached at ring nitrogens, a "vice" geometry where one binds above and one below the macrocycle plane can result. Although **9** does not seem to have been described, synthesis of the analogue with $-CH_2-COOH$ arms rather than $-CH_2-CH_2-NH_2$ arms has appeared and a complex with the "vice" shape characterized by an X-ray crystal structure.[29] The partially N-alkylated molecule **9** is a member of a wide range of fully and partially N-alkylated macrocyclic polyamines where all or some of the pendants carry additional potential donor groups. Molecules with amine, pyridyl and carboxylate groups terminating the pendant arms are among those described.[10,30] Some of these present too many donors for sexidentate coordination, but are in principle efficient pseudo-encapsulating ligands for metal ions demanding higher coordination numbers, such as lanthanide ions.

Inversion at one tertiary nitrogen center in N-pendant macrocycles such as **9** prior to complexation permits the alternate "nest" geometry discussed below. However, with alternatively C-pendant analogues such as *anti*-diammac (**10**), the disposition of the pendants is fixed so the ligand is preorganized as a sexidentate ligand for the "vice" geometry. Coordination of **10** introduces a pair of linked and strained five-membered chelate rings involving each primary amine "cap." Where a carboxylate pendant replaces the primary amine, less strained six-membered chelate rings form,[31] and six-membered rings could also be achieved by introducing an additional methylene between the primary amine and the tertiary ring carbon. The direct fusing of the primary amine pendant to the ring has important consequences for complexes of **10** discussed in detail later.



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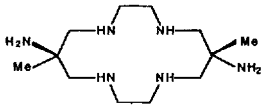

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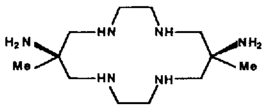

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"Nest" Ligands

An alternative to disposition of additional donors on opposite sides of a central plane is the location of donors on the same side. This has an immediate outcome on metal coordination for ligands based on a macromonocycle, since to bind both of the additional pendant donors the metal ion cannot adopt a geometry in which it lies centrally in the macrocyclic plane, since then only one pendant donor can bind axially. For all six to coordinate, it is necessary for the metal ion to sit above the four coplanar donors, held in a "nest" with the two pendants coordinated above the metal ion, or at least it requires macrocycle folding. This "nest" shape is fairly flexible and undemanding in its geometry with saturated molecules, with distortions accommodated in part by twisting towards trigonal prismatic geometry with molecules such as *syn*-diammac (**11**). Higher coordination numbers may be preferred by some metal ions, when the ligand fails to satisfy the donor demands of the metal ion; additional unidentate donors occupy sites above the approximate center of the "nest," accommodated by some "folding back" of the two facial caps to open up the nest. Such structures have been observed with Cd(II) and Pb(II) complexes of **11**,[32,33] for example, whereas with smaller metal ions such as Cr(III) a distorted octahedral geometry with a "folded" macrocycle is found.[34]

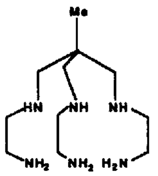
"Pod" Ligands

The previous examples have two pairs of three adjacent donors occupying octahedral faces. An alternative is to present one pair of three adjacent donors to the metal ion, with three chelating arms branching off from this "anchor" group. These tripods may be inherently less efficient ligands. Each simple chelate arm is less restricted in its potential dissociation reactions and such reactions may prove more facile. Several examples of this simple type exist. For example, sen (5-(4′-amino-2′-azabutyl)-5-methyl-3,7-diazanonan-1,9-diamine, **12**) has been known for some time,[35] and forms complexes with a wide range of metal ions.[36] A crystal structure of the Ni(II) complex of sen has been described recently, the metal accommodated in a slightly trigonally distorted octahedral environment (twist angle 51.5°); the average Ni–N distance is 2.11_4 Å, but the Ni–N(primary) distances are ca. 0.15 Å longer than the Ni–N(secondary) distances, consistent with the structural rigidity of the "cap" unit of the molecule which incorporates the secondary amines.[37] The analogue with longer 3-aminopropyl rather than 2-aminoethyl arms is also known,[38] as is the aza-capped analogue where the tertiary carbon of the cap and its attendant methyl group is replaced by a tertiary nitrogen.[39,40] The aza-capped molecule is formed as one product in a condensation reaction between $Ni(en)_3^{2+}$, formaldehyde and ammonia.

Structural studies of pod ligands based on tacn reported to date generally have aromatic nitrogen donors on the arms. For example, tacn with three 2-pyridylmethyl arms has been characterized as Fe(III), Mn(II), Ni(II) and Pd(II) complexes, with all but the latter adopting trigonally distorted octahedral structures, the latter having a distorted square-based pyramidal geometry with one arm uncoordinated.[41,42] More elaborate molecules with three 2,2′-bipyridyl arms have been described.[43] Where three $-CH_2-COO^-$ or $-CH_2-CH_2-S^-$ arms are present, distorted octahedral complexes of Al(III) and In(III), respectively, have been reported,[44] among others. Simple hexaamines have been described, nevertheless. Addition of three 2-aminoethyl arms to tacn yields taetacn (**13**),[45] and the analogue with an additional methylene in each arm (taptacn) has also been described recently,[46,47] the X-ray crystal structures of both the Co(III) and Ni(II) complexes being reported. The Co(III) complex of taptacn is robust, but the coordinated primary amines dissociate fairly readily from the Ni(II) complex, although oxidation to the sexidentate Ni(III) complex is reversible in aprotic solvents, the Ni(III) complex having been characterized as a low-spin system with axial symmetry from electron spin resonance spectroscopy.[46] The Co(III) complex has a structure which appears to be a composite of the structures of $Co(pn)_3^{3+}$ and half of $Co(tacn)_2^{3+}$, with slight elongation of the Co–N bonds (average 2.00_8 Å) and a very small trigonal distortion from octahedral geometry. The trigonal twist in the Ni(II) structure where M–N bond distances are longer is greater than in the Co(III) structure, but is still small. The mean Ni–N distance of 2.14_0 Å is comparable to that observed in $Ni(pn)_3^{2+}$.

Molecules incorporating a spiro-carbon such as **14** carry four chelating arms, but can bind in a pod with a dangling chelate arm which may "capture" another metal ion. Alternatively, they can bind two metals ions with two pairs of arms, particularly with metal ions seeking four coordination.[48] Where four donors form part of a macromonocycle with two additional donors in a pendant arm, "flexibility" of the pods will be reduced slightly. Some examples of this type have appeared recently, e.g., **15** results from a metal-directed condensation reaction which yields a *spiro*-bis(macrocycle) as an additional product.[48] Other *spiro*-bis(cyclam) complexes have also been reported,[49] but these molecules do not have the opportunity to perform as octahedral pseudo-encapsulating ligands as a result of their topology, since the two macrocycles are required to lie on opposite sides of the *spiro* carbon with their donor planes approximately at right angles. Molecules such as **15** again introduce an ambivalence discussed with **14** above, and despite the drawing of the molecule as effectively a sexidentate with a dangling arm, binding of two metal ions, each with four donors, is likely. Where only a single pendant arm carrying two potential donors is attached to a macromonocyclic tetraamine, as in cyclam with one N-(2,2′-bipyridinylmethyl) arm,[49,50] only six donors are available, but ambivalence between four coordination and six coordination remains and the former permits the pendant arm to chelate an additional metal ion in the same way that six coordination of **14** or **15** permits the additional pendant arm to bind another metal ion.

Both **12** and **13** can be viewed as "half-capped" cages, and both have undergone metal-directed reactions as their Co(III) complexes with formaldehyde and carbon acids which close off the "open" octahedral face to form "cage" complexes.[45,51,52] Likewise, the aza-capped analogue of **12**,[48] and also **14**,[53] can be converted to a macrobicyclic ligand, the latter carrying a pendant with additional potential donors. These reactions define the close topological relationship between "pod" and "cage" ligands.



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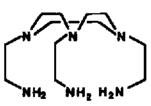

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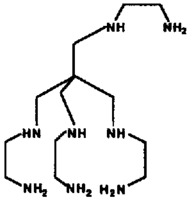

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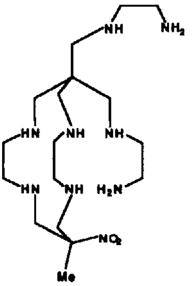

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Formation constants with a range of metal ions have also been examined for the pod ligand **12** and other polyamines discussed above, and are included in Table I. In general, no clear trends develop from the collected data, although some comparisons between ligands are interesting. For example, with first-row metal ions, the "pod" (or "hemi-cage") geometry of **12** is "superior" to the geometry adopted by the acyclic ligand **3**, with stabilities of the complexes of **12** higher in general than those of **3**. However, the larger main group cations Cd(II) and Pb(II) form relatively weak complexes with **12**, probably because the trigonal cap linking the secondary amines limits separation of these donors in pseudo-octahedral geometries, limiting the size of the pseudo-cavity. This view is in line with the conclusion in the structural study of the Ni(II) complex of sen described above, and supports the concept of pseudo-encapsulation and the implication that structural and physical properties may deviate from the norm as a result of pseudo-encapsulation. This is addressed in detail in the specific case study below.

"Cage" Ligands

The encapsulating "cage" ligands can be considered, as mentioned above, as an extension of "pod" ligands, but with both "ends" closed off. One can see the close relationship by comparing the molecules sen (**12**) and sar (**2**). The *cis*-diammac molecule (**11**) can also be considered as a precursor to the cages, since linking of the two pendant primary amines will convert this into a "cage" ligand, albeit with a different cavity framework. The metal-free cages necessary for most complexation studies are accessible by removal of the original templating metal (usually cobalt) from the cages, usually as $CoBr_4^{2-}$ (from refluxing the reduced complex in concentrated HBr under an oxygen-free atmosphere) or $Co(CN)_4^{2-}$ (by a similar reaction with excess cyanide ion).[54] By contrast, the pseudo-encapsulating diammac isomers (**10** and **11**) are conveniently prepared around a Cu(II) template, and can be isolated under less rigorous conditions following zinc reduction in dilute aqueous acid.[55] A detailed description of the hexaamine "cages" is outside the scope of this report, but it is appropriate to draw attention to the relationship to certain pseudo-encapsulating molecules as the final stage of this general discussion of pseudo-encapsulating ligand topologies.

A CASE STUDY: *syn*- AND *anti*-DIAMMAC

The two geometric isomers of the potentially sexidentate polyamines 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine are examples of a "vice" ligand (*anti* or *trans* isomer) and a "nest" ligand (*syn* or *cis* isomer). Both are based on the cyclam macromonocycle with additional primary amine donors fused directly to ring carbon atoms,[55,56] the location of the pair of additional donors relative to the macromonocyclic core defining the ligand class. Interconversion between the two geometric isomers is not possible. The demands of the two ligands when binding to metal ions are distinctly different. Metal ion complexes of sexidentate *anti*-diammac have consistently very short M–N bond lengths in comparison with other hexaamine complexes (Fig. 2).[57–64] Further, d-d electronic maxima lie at higher energy and redox couples are shifted to more negative values than is the case with other hexaamine complexes. With the *syn* isomer, the metal ion "compression" of *anti*-diammac is absent.[34]

Some understanding of this difference comes from molecular mechanics analysis of the two ligands coordinated as sexidentates.[65]

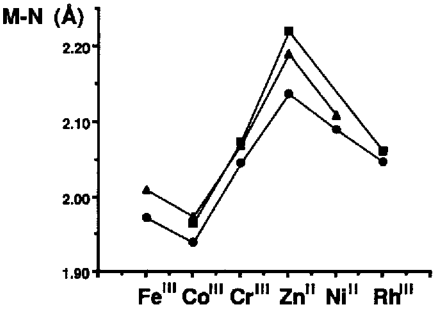


FIGURE 2 Variation of the average metal–nitrogen bond length for a range of metal ion complexes with hexaamine donors. Ligands depicted are $(en)_3$ [▲], *anti*-diammac [●], and diAMsar [■].

Because of the relatively rigid nature of the ligands when coordinated, only three non-degenerate conformations of the complexes of each may exist. With *anti*-diammac, a chiral trans-δδ(λλ) conformer and two centrosymmetric conformers, trans-λδ and trans-δλ, are predicted; with the *syn* isomer, three chiral conformers cis-λλ, cis-λδ and cis-δδ have been described,[65] but not all have been observed. Plots of minimized strain energy for an "idealized" situation of six identical M–N distances versus this distance show a variation in size preference for metal ions with conformer. However, a relatively deep "well" is observed with the conformers of *anti*-diammac with the minimum less than 2.10 Å in all cases, indicative of a capacity to accommodate metal ions with only relatively small ionic radii, whereas the contrasting quite flat "wells" for the conformers of the *syn* isomer have minima ranging out to near 2.50 Å, indicating that larger metal ions can be accommodated adequately. Comparisons of experimental and strain-energy minimized M–N bond lengths and angles for a number of complexes suggest the model employed has some validity. Further, experimental evidence supports the general premise that *anti*-diammac is more demanding than the *syn* isomer in terms of the size of metal ions it can accommodate. An important prediction from the calculations is that *syn*-diammac, unlike *anti*-diammac, will not exhibit short M–N bond lengths and the concomitant somewhat unusual physical properties.

Anti-diammac is a good example of a pseudo-encapsulating "vice" ligand, since its behavior as a ligand contrasts sharply with that of simple chelates and also with that of macrobicyclic "cage" analogues. For determinedly square planar metal ions such as Pd(II) and Pt(II), the ligand accommodates the metal ions in the cyclam core of the ligand with the pendants unbound.[66] An octahedral Pt(IV) complex has been proposed, however.[67] With macrobicyclic substituted sar ligands, there are no stable square-planar complexes reported, although an octahedral Pt(IV) has been encapsulated and characterized.[68] Quinquedentate coordination of *anti*-diammac has been observed with oxovanadium(IV),[69] one pendant "giving way" to the strong oxo group, in contrast to the behavior with sar type ligands, where sexidentate coordination by the hexaamine occurs but with deprotonation of two amine donors and imine character being introduced.[70] With a range of other relatively small metal ions [Fe(III), Co(III), Cr(III), Rh(III), Zn(II), Ni(II)],[57-64] *anti*-diammac acts as a sexidentate ligand, the complexes adopting distorted octahedral geometries and consistently short M–N distances compared with hexaamines in general (Table II). For the smaller ions, typically distances to the axial primary amines are slightly longer than to the equatorial secondary amines, although all are shorter than in "usual" hexaamine complexes. With low-spin d^5 Fe(III) with a $^2T_{2g}$ ground state, operation of a Jahn–Teller effect may account for some elongation. However, similar elongation is observed with Cr(III) which has a $^4A_{2g}$ ground state where no Jahn–Teller effect can apply, and consequently there is another origin for the somewhat elongated bonds to the primary amine donors generally.

Coordination of the pendant amine "pulls" the adjacent methylenes of the ring towards the metal center and opens the angles at the coordinated secondary amines, while the C–N(pendant)–M angle is small compared with an idealized tetrahedral angle (up to 10° less). To relieve this strain, either the M–N(pendant) bond must be shortened or the N(pendant)–M–N(secondary) angles contracted even more. Because of the form of attachment of the pendants directly to the cyclam ring, elongation of the axial bonds is not permitted without concomitant "sideways" pivoting movement about an imaginary axis joining the two adjacent secondary amine donors, producing substantial distortion from octahedral geometry. As a result, short metal–nitrogen bond lengths

TABLE II

Selected physical properties of some hexaaminemetal complexes.

N_6[a]	M–N_{av}, Å[b]	λ_{max}, nm(ϵ_{max}, $M^{-1}cm^{-1}$)	$E_{1/2}$, V[c]
		M = Cobalt(III)	
$(NH_3)_6$	1.96_1	475(75), 339(46)	−0.06
$(en)_3$	1.96_4	468(75), 340(68)	−0.20
$(tacn)_2$	1.97_4	458(100), 333(89)	−0.41
dtne	–	495(323), 346(230)	−0.01
[18]aneN_6	1.96_7	476, 349	–
(3)	1.98_2	488(224), 345(170)	–
taptacn	2.00_4	497(77), 358(92)	−0.01
syn-diammac	–	459(120), 334(98)	−0.44
anti-diammac	1.93_{7s}, 1.94_{6p}	447(73), 328(76)	−0.57
diAMsar	1.97_4	471(135), 343(108)	−0.44
		M = Chromium(III)	
$(NH_3)_6$	2.06_4	462(44), 346(37)	−0.59
$(en)_3$	2.07_5	457(86), 351(70)	−0.62
$(tacn)_2$	–	439(88), 340(64)	−1.14
dtne	–	481(280), 360(142)	−0.77
(cyclam)$(NH_3)_2$	–	445sh(32), 420(36), 334(50)	–
syn-diammac	2.06_{1s}, 2.06_{1p}	452(128), 350(68)	−1.11
anti-diammac	2.03_{7s}, 2.06_{7p}	427(55), 332(52)	−1.04
diAMsar	2.07_0	456(203), 447(208), 346(109)	−1.11
		M = Iron(III)	
$(en)_3$	–	465, 364	–
$(tacn)_2$	1.99_8	500sh, 430(82), 336(288)	+0.13
dtne	2.00_4	476sh, 457(460), 355(770)	+0.41
anti-diammac	1.95_{8s}, 1.98_{5p}	417(55), 332(140)	−0.13
diAMsar	2.01	438, 366	+0.07
		M = Rhodium(III)	
$(NH_3)_6$	2.06_9	305, 255	−0.76
$(en)_3$	2.06_2	301, 255	0.48
anti-diammac	2.04_{4s}, 2.05_{6p}	289(180), 243(180)	−1.02
diAMsar	–	299, 251	−1.18

TABLE II (*Continued*)

N_6[a]	M–N_{av}, Å[b]	λ_{max}, nm(ϵ_{max}, $M^{-1}cm^{-1}$)	$E_{1/2}$, V[c]
M = Nickel(II)			
$(en)_3$	2.12	545(6.9), 345(9.0)	–
$(tacn)_2$	2.10	870sh, 800(7), 505(5), 308(12)	+0.95
dtne	–	917(31), 848(31), 516(18), 363(16)	+1.10
[18]aneN_6	–	835(19), 530(11), 345(11)	+0.90
syn-diammac	–	883(8.0), 809(9.4), 516(5.4), 490(4.4), 323(6.8)	+0.74
anti-diammac	2.07_{1s}, 2.12_{6p}	870sh(3.8), 798(4.6), 488(5), 318(5.2)	+0.67
sen	2.11	523(7.6), 327(9.8)	+0.92
diAMsar	2.11	800(14.8), 504(9.9), 328(13.2)	+0.90

[a] Trivial names correspond as follows: en = ethane-1,2-diamine; tach = **5**; tacn = **4**; dtne = **6**; taptacn = **13**, with additional methylene in each "arm"; [18]aneN_6 = **8**; sen = **12**; *syn*-diammac = **11**; *anti*-diammac = **10**.

[b] Average of all six M–N distances, except for diammac, where averaged primary (p) and secondary (s) distances are given.

[c] M(III)/(II) couple, versus SHE.

observed are the result of a balance of bond angle and bond length distortions and a minimization of intramolecular strain in the ligand. *Anti*-diammac can be considered a sterically efficient ligand, although it is difficult to say whether the observed M–N bond distances in the series of complexes examined are genuinely compressed or instead elongated to a lesser degree from their ideal strain-free distances compared with other hexaamine complexes. There remains a certain amount of controversy regarding the choice of appropriate strain-free M–N bond lengths in molecular mechanics calculations, but a recent list of strain-free M–N distances[71] can be compared with average M–N distances for complexes of *anti*-diammac. Comparative values {strain-free M–N (Å), observed average M–N (Å)} for Co(III) {1.925, 1.94)}, Fe(III) {1.94, 1.97}, Rh(III) {2.04, 2.05}, Cr(III) {2.05, 2.05}, Ni(II) {2.10, 2.09} and Zn(II) {2.17, 2.14} show that for small metal ions sexidentate complexes of *anti*-diammac display elongated M–N bond lengths compared with the "ideal" values whereas for larger metal ions it appears that bond compression is occurring.

The "compressed" coordination spheres for metal ions bound by *anti*-diammac contrast with the behavior in macrobicyclic sar (and analogue) complexes,[8,69,70,72] where M–N distances may even be greater than those in $M(en)_3^{3+}$ analogues (Table II). The trend in bond lengths with metal ion for the hexaamines *anti*-diammac, tris(en) and diAMsar appears in Fig. 2, and it is apparent that the behavior for *anti*-diammac is a general one. As a consequence of the "compression" of coordination spheres in complexes of *anti*-diammac, physical properties are affected. Electronic maxima are consistently shifted to shorter wavelength. Although the shorter than average M–N distances do contribute to an increase in separation of the metal d-orbitals, this effect may be small in comparison with other factors such as the basicity of the N-donors and particularly the steric relaxation upon excitation. There need not be a correlation between the energy of electronic maxima and the M–N bond length alone, but it is apparent that all of the sexidentate complexes of *anti*-diammac display both the shortest M–N bonds and the highest energy electronic maxima of a large series of hexaamines (Table II). The ligand field strength may be quantified using the empirical relationship $100.f.g = D_q$ (where f is the dimensionless spectrochemical ligand field parameter and g cm^{-1} is the spectrochemical metal ion parameter).[73] The values of f are reasonably constant, averaging 1.37, and with g define this ligand as perhaps the strongest field saturated polyamine ligand extant. Other physical properties may be affected, though the relationship between property and bond compression may be tenuous. As an example, reduction potentials for complexes are generally more negative compared with other hexaamines (Table II). The "compressed" cavity is presumably inappropriate for the generally larger lower oxidation state ions, presumably leading to more negative reduction potentials. Also, the Co(III)/(II) self-exchange rate is ca. 10^8-fold faster than the value for $Co(en)_3^{3+}$, ca. 2×10^4 faster than for $Co(taptacn)^{3+}$, ca. 5×10^3-fold faster than for $Co(tacn)_2^{3+}$, and ca. 100-fold faster than the result for $Co(sar)^{3+}$.[63] The rapid self-exchange rate of the *anti*-diammac complex is consistent with molecular mechanics calculations of bond-length relaxations from Co(III) to Co(II), since the average change predicted is significantly smaller than that predicted for both en and sar complexes. Further, the phosphorescent lifetime for the deuterated Cr(III) complex of *anti*-diammac of 2 μs is notably longer than that estimated for an analogous macrobicyclic hexaamine of less than 10 ns.[62] It is believed that this difference relates to the higher ligand field of *anti*-diammac compared to sar, which leads to a relatively high-lying quartet excited state which would be less easily populated from the ^2E_g excited state should deactivation occur through a mechanism of thermally induced back intersystem crossing.

It is clear that the physical properties of complexes of this pseudo-encapsulating ligand are indicative of the special nature of the ligand. Chemical properties and reactivity are also altered substantially; for example, the Fe(III) complex is stable in aqueous solution for extended periods (unlike the ethane-1,2-diamine complex) and is not susceptible to oxidative dehydrogenation reactions at all. Given the strain evident in the "cap" unit when bound as a sexidentate, it is interesting to examine the kinetic stability of the unit. For the inert metal(III) complexes, quinquedentate and quadridentate coordination have been reported in some cases in addition to sexidentate coordination. For Co(III), both latter complexes can be coerced to undergo "lid-on" reactions in basic solution, but the sexidentate complex is remarkably resistant to dissociation, and may be refluxed in strong acid for days without measurable dissociation.[60] This behavior is also found in other complexes such as Rh(III) and Fe(III).[59,61] By contrast, the Cr(III) undergoes relatively facile hydrolysis of one pendant group in acid solution, the group being rapidly recoordinated in base.[62] With the labile metal ions, "lid-on" and "lid-off" reactions are reasonably fast, and markedly more so than with macrobicyclic hexaamines, although removal of labile metal ions such as Cu(II) or Mn(II) from diAMsar or sar does occur in aqueous acid via a four-coordinate intermediate where a complete "strap" of the macrobicycle is dissociated.[72,74]

Interestingly, the pendant group appears to play a role in capturing metal ions. Intermediates with the ligand bound as a unidentate via one pendant amine and as a bidentate via one pendant amine and an adjacent secondary amine have been characterized with Hg(II) by crystal structure analyses,[33] and a Rh(III) complex of an acyclic analogue with the same cap has the whole cap bound as a tridentate ligand and other potential donors dangling unbound.[75] Kinetic studies of complexation reactions with labile metal ions suggest a role for the pendant in the initial capture of metal ions,[76] which in concert with the structural studies is indicative of an active role for the pendant donors in metal ion capture.

The *syn*-diammac isomer presents a stark contrast with the *anti*-diammac isomer, and is a good example of a pseudo-encapsulating "nest" ligand. The molecule can act as a sexidentate ligand, with inert complexes of a number of first-row transition metal ions now described.[34,76] A tendency towards formation of significant amounts of quinquedentate coordinated or square-planar [with Ni(II)] complexes suggests that there is some driving force towards incorporation of the metal ions into the parent macrocyclic cavity coplanar with the secondary amine donors, where at best one pendant may bind. Sexidentate coordination requires the metal to lie out of the macrocyclic plane or at least dictates the macrocycle be folded. For the only X-ray crystal structure of an inert metal ion completed, that of Cr(III), bond distances are not unusual and the intraligand angles reveal little strain in the ligand, in agreement with molecular mechanics predictions.[34] A significant trigonal twist distortion of the *syn*-diammac complex is observed, however, in contrast to the structure of the *anti*-diammac where a significant axial elongation and exceptionally short Cr–N bond lengths are observed.[62] Electronic maxima (d-d transition energies) of complexes of *syn*-diammac, in contrast to the *anti* isomer, are all typical of hexaamine complexes. The more positive metal(III)/(II) redox couples for cobalt and chromium complexes of the *syn* isomer compared with the *anti* isomer are consistent with expectations that the former isomer should prefer the extended M–N bond lengths met upon reduction, whereas the latter isomer opposes an extension of bond lengths and reduction to the divalent state and should generally be more difficult in that case. This description is in line with a study which has shown a correlation between half-wave potentials and steric relaxation upon reduction for a range of hexaaminecobalt(III) complexes.[77]

Whereas *syn*-diammac can accommodate large metal ions such as Cd(II) and Pb(II) in structures of augmented coordination number, there is no firm evidence for sexidentate complexation of metal ions larger than ca. 0.8 Å ionic radius with *anti*-diammac. Although Zn(II) [ionic radius 0.74 Å] has been characterized with sexidentate coordination to *anti*-diammac by an X-ray structure analysis, Cd(II) [0.95 Å] does not appear to bind in the same mode.[63] Stability constants for the 1:1 complex with the larger metal ions are consistently greater with the *syn* isomer than with the *anti* isomer,[33] although the differences are not sufficiently great to support a dramatic variation in coordination mode in solution. Overall, the two isomers *anti*- and *syn*-diammac display quite different physical and structural properties as a result of the mode of coordination ("vice" or "nest") which is dictated by the ligand. One can anticipate like variations with pseudo-encapsulating type generally.

It is also appropriate to compare the diammac isomers with the hexaamine "cage" ligands. The parent sar macrobicycle can be considered as a cyclam macromonocycle with an additional strap on one side carrying two additional donor groups. In this sense, it is more comparable with *syn*- than *anti*-diammac, and indeed the two primary amines in the *syn* isomer may in principle be linked to form a macrobicyclic ligand, a task not feasible with the *anti* isomer. Comparative X-ray crystal structures of complexes of *syn*- and *anti*-diammac and the "cage" ligand diAMsar appear in Fig. 3. The "vice" and "nest" structures of the geometric isomers of diammac are clearly shown, as is the "cage" trapping the metal

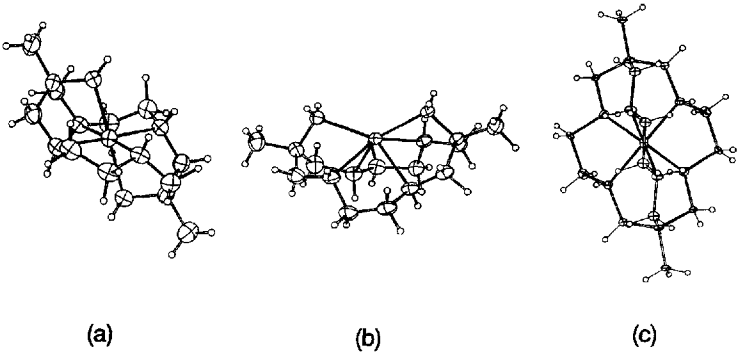
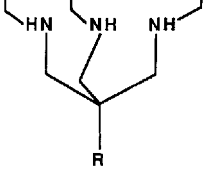


FIGURE 3 Views of the X-ray structures of cationic complexes of (a) *anti*-diammac [as the Zn(II) complex]; (b) *syn*-diammac [as the Cd(II) complex]; (c) sar [as the V(IV) complex], respectively, "vice," "nest" and "cage" ligands.

ion in the diAMsar complex. The view of the diAMsar complex also emphasizes the cyclam parentage of this molecule (in common with diammac) and the manner in which the third "strap" involves two secondary amines disposed in the *syn* geometry like the pendants in *syn*-diammac. Like *syn*-diammac, M–L distances in complexes of sar and analogues such as diAMsar (**16**, R = NH_2) are not unusually short; in fact, they tend to be longer than usual with some metal ions (Table II).[70,72] This presumably relates to the cavity size, since reduction of the size of one "cap" in the sar core by rearrangement to absar (**17**) produces a smaller cavity and this is reflected in physical properties.[78] The putative diabsar (**18**) would result from bridging of the two amine pendants in *syn*-diammac with an ethylene chain, so in principle the parent diammac presents a smaller pseudo-encapsulation cavity than diAMsar, although relaxation in the case of the open "nest" of the *syn* isomer is more probable than in diAMsar. The trend in average M–N bond lengths from *anti*-diammac to *syn*-diammac to diAMsar for the Cr(III) complexes [2.04_9 to 2.06_1 to 2.07_0 Å] reflects expectations about "cavity" size. The bond length in diAMsar is intermediate between the average distances in $Cr(NH_3)_6^{3+}$ [2.064 Å] and $Cr(en)_3^{3+}$ [2.075 Å], indicating no special influence of the macrobicyclic ligand on M–N bond distances for this metal ion at least.



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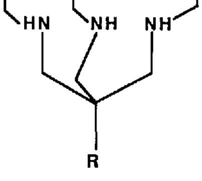

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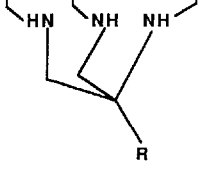

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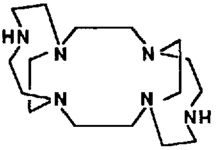
What may be a more important consequence of encapsulation by the "cage" ligands compared with the "vice" or "nest" ligands is the stabilization of unusual oxidation states as a result of greatly diminished dissociation rates. The Co(III) ion in both diammac and diAMsar exhibits quasireversible electrochemistry, but only in the latter is the Co(II) oxidation state complex stable for extended periods and decomposed only by extended treatment with strong acid or cyanide ion. Not all metal ions exhibit stability in a number of oxidation states in the "cage" ligands, however, with even the Cr(II) complex not having any appreciable lifetime. While the "cage" ligands are efficient "prisons" for some metal ions except under extreme conditions, the pseudo-encapsulating molecules are more readily coerced to open their prison doors via "lid off" reactions.

CONCLUSION

The range of pseudo-encapsulating ligands extant considering hexaamines alone is surprisingly extensive, but the "family" has not been defined collectively earlier. They are not by nature large or necessarily elegant molecules within the context of the rapidly expanding field of encapsulating molecules, but the diammac example discussed above illustrates their capacity to direct some interesting chemistry. While the chemistry of the family of ligands has been the subject of what appears to be limited examination, their study has grown almost by stealth to the stage where examples of many of the topologies presented in Fig. 1 are known. Their shape-directed demands may present opportunities for metal ion selection yet unexamined in any detail. Introduction of alternate or mixed donors (N, S and O can be readily involved) extends the range rapidly. The flexibility of some of the molecules (such as [18]aneN_6) which prohibits any pre-disposition towards a particular pseudo-encapsulation shape could be altered by the introduction of "reinforced" character, i.e., additional carbon chains linking appropriate pairs of amines. This type of chemistry has been explored for simple macromonocycles by Hancock and co-workers.[79] Addition of two ethylene chains across pairs of secondary amines in [18]aneN_6 would generate two distinct geometric isomers, **19** and **20**, which are in effect then two tacn rings linked by two rather than one chain (as in **7**). These shape-directed molecules would represent new examples of a vice (**19**) and nest (**20**) ligand, and present a synthetic challenge which has not yet been entertained.

Those molecules discussed above are dominantly "sole parent" ligands, binding one metal ion. However, one can conceive of more complex molecules capable of binding two metal ions simultaneously and satisfying their donor demands. Particularly when additional donors are introduced, this is feasible. To the best of our knowledge, this area remains largely unexamined.



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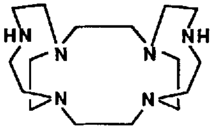

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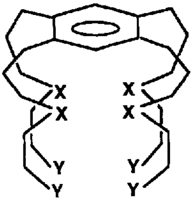

21

The pod and cage ligands described above are based on three chains evolving from a tertiary carbon or nitrogen. For higher coordination numbers, four chain molecules would be of interest. This is inherently already available in a fashion with "face-to-face" tetraamine macromonocycles (in effect, "clams"),[80] but the flexibility and numbers of potential donors of these directs them towards dinucleation. There is the prospect of building relatively small four-armed "pods" from tetra-substituted benzenes such as **21** (X, Y = N, S, O donors; Y donors may possibly be linked further); molecules with short chains from the benzene ring to the first donors may tend to be directed towards dinucleation in the same way that the spiro-carbon molecules such as **14** can bind two metal ions simultaneously. Presumably with longer primary chains from the benzene ring and selection of donors, metal ions demanding higher coordination numbers can be accommodated by the single pseudo-encapsulating ligand. However, as complexity grows, the attractive simplicity of the sexidentate systems is lost.

There still remains for largely saturated polydentate ligands challenges in design, synthesis and complexation studies. Apparently simple molecules such as diammac can present surprising outcomes. We are currently examining saturated analogues of diammac based on cyclohexane-1,2-diamine which introduce chirality and or additional rigidity to the molecules,[81] and consequences in terms of both the number of geometric and optical isomers potentially available and the way they interact with metal ions offer a greater challenge than applied with diammac. Although thermodynamic data for complexation of pseudo-encapsulating ligands is appearing, kinetic studies remain scarce. Possible applications of these molecules is also little explored. The availability of pendant donors on some molecules has been recognized as a logical site for introducing hydrophobicity, for attaching fluorescent or electroactive "antenna" molecules, or for covalent linking to biomolecules or polymers while still retaining a significant set of donors capable of strong metal binding. Such molecules may then have some role in sensing or removing metal ions. The relatively facile and inexpensive syntheses of molecules such as diammac and analogues may add to their potential value in applications, and to their accessibility for study of their coordination chemistry.

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