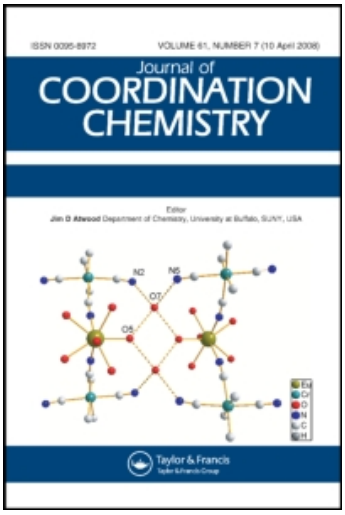

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Synthetic *N*-substituted metal aza-macrocyclic complexes: properties and applications

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Synthetic *N*-substituted metal aza-macrocyclic complexes: Properties and applications

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Recent contributions to the chemistry of macrocyclic metal complexes and ligands are reviewed. The compounds reviewed have the following structural features: aza-macrocycles having 1,10-phenanthroline and 2,2′-bipyridine groups and pendants arms; highly aromatic aza-macrocycles with phthalocyanine and porphyrin units incorporating pendant arms; aliphatic aza-macrocycles with pendant arms and/or polynucleating aza-macrocycles. Several of their chemical properties are critically reviewed but the emphasis is on structural and synthetic details.

1. Introduction

The family of complexes with aza-macrocyclic ligands has remained a focus of scientific attention for many decades [1,2]. To some extent the interest in macrocyclic complexes stems from the chemical properties that the macrocyclic ligands bring to the complexes. One of these properties is the enhanced thermochemical and kinetic stability of the complexes with regard to their dissociation; that is a lesser lability and larger association constants than the homologous open-cycle macrocyclic complexes. No less significant is the stabilization of unusual oxidation states of the transition metal ion by coordination to a macrocyclic ligand. Such unusual oxidation states become accessible in thermal redox reactions and many complexes are able to function as catalysts of various chemical reactions. For example, applications of the macrocyclic complexes to the catalyzed reduction of H_2O to H_2 and CO_2 to CO has brought

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additional attention to the chemistry of the macrocyclic complexes [3,4]. In the same sense, small variations in the ligand structure allow tuning of the electronic properties of the metal ion, making the macrocyclic complexes ubiquitous reactants. Such changes in the electronic properties of the complex are manifested, for example, as changes in the metal ion redox potentials and in the UV–vis and ESR spectra, when small variations are introduced in the structure of the ligand. Additional interest in the macrocyclic complexes arises from their role as models for the prosthetic groups of enzymes and building blocks of supramolecular structures. Because of the numerous areas of chemistry where aza-macrocyclic complexes have found a niche, the preparation of new macrocyclic ligands with ever more elaborate structures is also a vital area of research. In this article, we review the chemistry of transition metal complexes and ligands with the following structural features:

- Aza-macrocycles having 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) groups.
- Aza-macrocycles having 2,2′-bipyridine groups and pendant arms.
- Highly aromatic aza-macrocycles with phthalocyanine- and porphyrin-based incorporating pendant arms.
- Aliphatic aza-macrocycles incorporating pendant arms and polynucleating aza-macrocycles.

2. Aza-macrocycles having 1,10-phenanthroline and 2,2′-bipyridine groups

Several preparations of the ligand hexaazaphenH_2 (**I** in figure 1) have been reported [5–9]. The starting material is 1,10-phenanthroline (1,10-phen) in the first preparation by Ogawa *et al*. [6,7]. The preparation (scheme 1) requires eight successive reactions and the isolation of seven intermediate products. Reflux of 2,9-dichloro-1,10-phen and 2,9-diamine-1,10-phen in nitrobenzene produces the hexaazaphenH_2 ligand with a yield of 94%. A second protocol for the preparation of the ligand is based on the direct condensation of 2,9-diamine-1,10-phen and 1,10-phen at 290–330°C [8].

The hexaazabipyH_2 (**II** in figure 1) ligand homologous of hexaazaphenH_2 has been synthesized by a modification of Ogawa's preparation [9]. Because of the intrinsic reactivity of the 2,2′-bipy ring, the preparation of hexaazabipyH_2 requires four steps (scheme 2).

Complexes of hexaazaphenH_2 can be prepared by a template synthesis or by the direct coordination of a transition metal ion to hexaazaphenH_2. In the template synthesis, a solution of 2,9-diamine-1,10-phen, 2,9-dichloro-1,10-phen and a salt of the transition metal ion in nitrobenzene are heated to 170°C. The same complex is obtained when a hot solution of $Ni(OAc)_2 \cdot 6H_2O$ in benzyl alcohol is added to a refluxing solution of the hexaazaphenH_2 ligand in nitrobenzene. However, no additional details of the preparation have been reported. A considerable number of spectroscopic studies have been dedicated to the elucidation of the structure of the hexaazabipyH_2 and hexaazaphenH_2 structures and the structure of the metallocomplexes [7]. The ligands exist in various tautomeric forms. Amino and imine varieties of the ligands can be produced by the displacement of protons from the bridging nitrogen atoms to the internal nitrogen atoms (equations (1) and (2)).

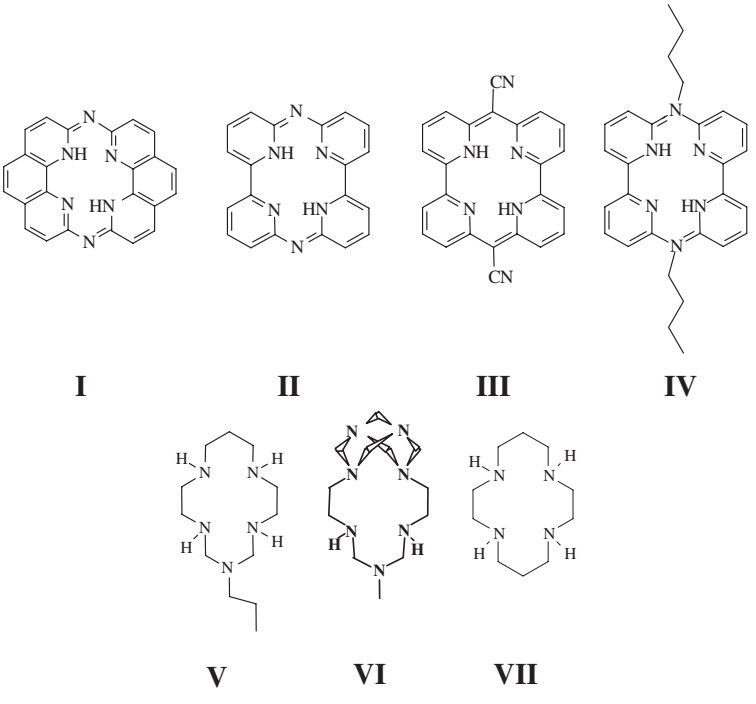
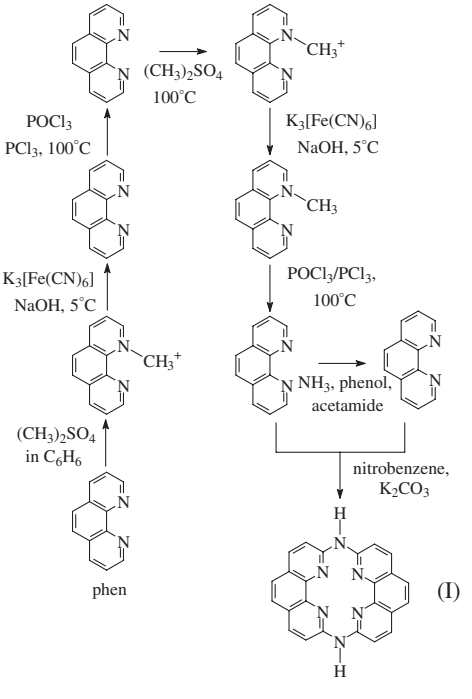
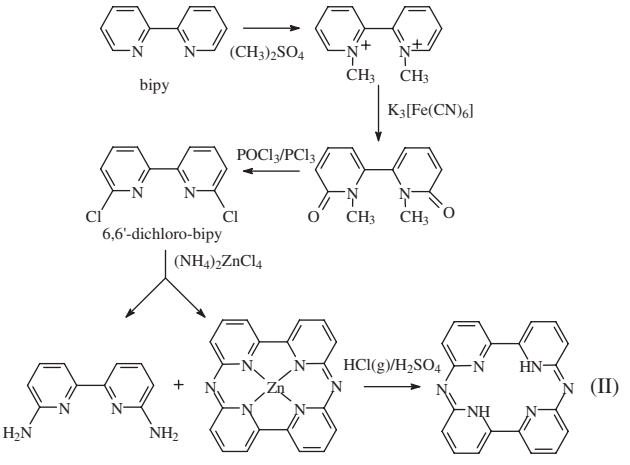


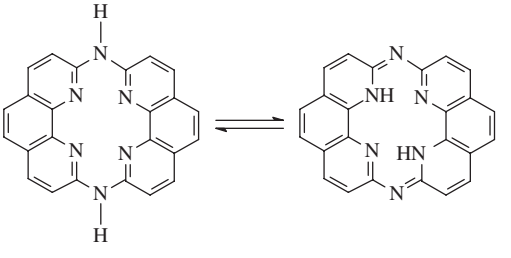
Figure 1. Macrocyclic ligands most commonly referred to in this work.



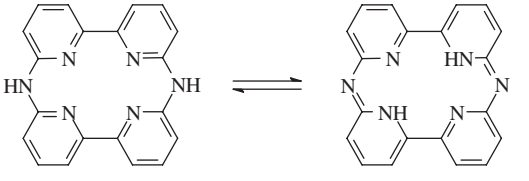
Scheme 1



Scheme 2



amino form imino form (1)



amino form imino form (2)

The IR spectrum of hexaazaphenH_2 in KBr exhibits a broad absorption band at 2780 cm^{-1} and those bands corresponding to the N–H stretching are missing. This experimental observation suggested that the imine was the prevailing form of the ligand. The imine form appears to be stabilized by strong intramolecular hydrogen bonds. Although the UV–vis spectra of the ligands have been published, there are no assignments of the absorption bands [8,9]. It has been concluded, however, that there is less electronic delocalization is the amino bridge of the dichlorhydrate of hexaazaphenH_2 than in the imine bridge [10]. A hypsochromic shift of the absorptions is a consequence of the differences in the electronic delocalization in the amino and imine bridges. Absorption bands in the visible region of the hexaazabipyH_2 spectrum in CH_3Cl are attributed to the imine form of the ligand. By contrast, solutions of

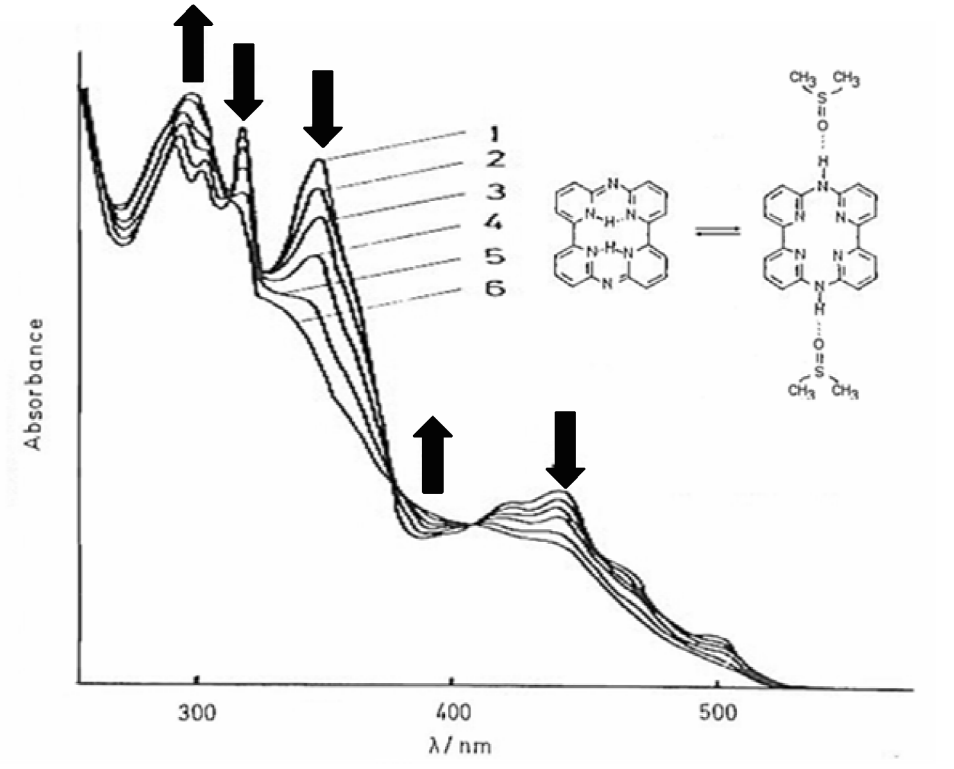


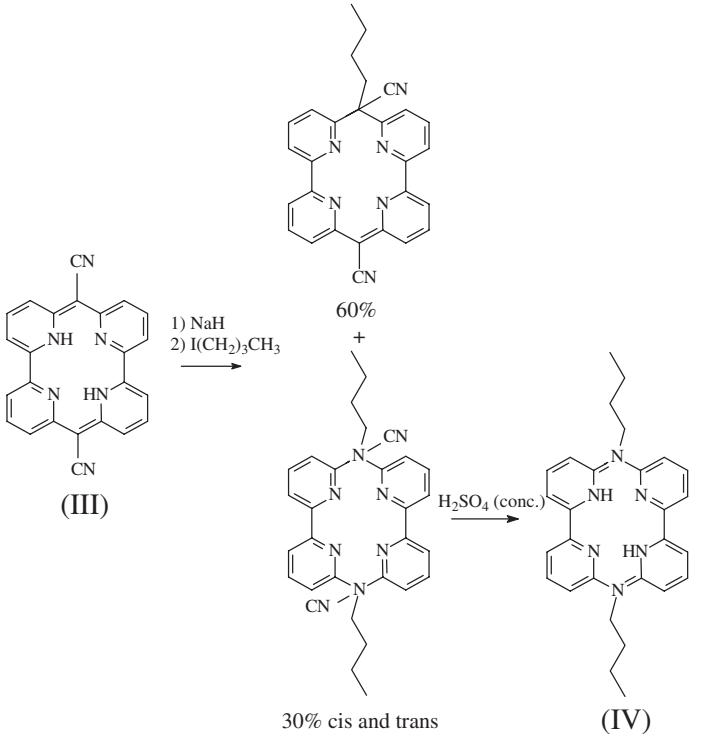
Figure 2. UV–vis spectra of the AzaBipi ligand in $CHCl_3$ solutions containing variable concentrations of DMSO. The ligand concentration is 2.8×10^{-1} mol L^{-1} and the spectra correspond to six successive additions of ~ 0.196 mol L^{-1} DMSO, i.e. from desde [DMSO] = 0 to ~ 0.98 mol L^{-1}. The arrows show the direction of the absorbance changes. Reproduced with permission from Ref. [9].

hexaazabipyH_2 in CH_3CN, where the amino form prevails, absorb only in the UV. Addition of DMSO to a solution of hexaazabipyH_2 in CH_3Cl displaces the tautomeric equilibrium towards the amino form and decreases the absorption bands between 400 and 550 nm (figure 2) [10].

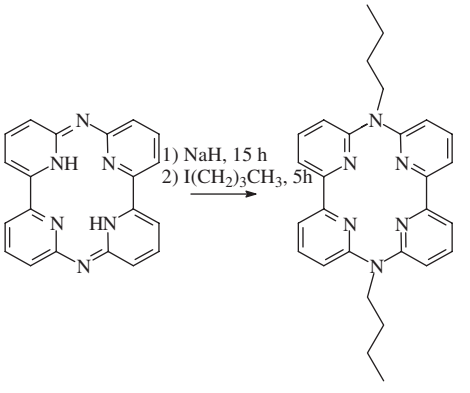
A different interpretation has emerged from a theoretical study of the electronic structures of hexaazabipyH_2, Ni^{II}(hexaazabipy) and Zn^{II}(hexaazabipy) by semiempirical Hartree–Fock methods including the effects of protic and aprotic media [11]. These calculations suggest that the set of bands in the visible spectral region are due to optical transitions of a dimeric species. The macrocyclic dimers are stabilized by intermolecular π–π interactions and a UV–vis spectrum calculated for a dimer with two parallel molecules agrees very well with the experimental observation, that is the computed spectrum shows all the absorption bands between 400 and 500 nm.

3. Aza-macrocycles having 2,2′-bipyridine groups and pendant arms

It has been demonstrated that the bridging nitrogen atoms of hexaazabipyH_2 and related macrocycles can be alkylated (equation (3)) [9].



Scheme 3



(3)

In this general procedure, a macrocycle is first treated with NaH and the product is alkylated with alkylhalides. The product of the alkylation of hexaazabipyH_2 with butyliodide, i.e. hexaazabipy(butyl)$_2$, has almost the same UV–vis spectrum in CH_3Cl solution of hexaazabipyH_2. Resonances at 0.98, 1.49, 1.82 and 3.99 ppm in the ^{1}H NMR spectrum of the alkylated product in CD_3Cl were assigned to protons of the $>NCH_2CH_2CH_2CH_3$ pendant.

Methine bridges of a relative of the hexaazabipyH_2 macrocyle were alkylated with the same protocol described earlier (scheme 3) [12]. The reaction of (CN)$_2$tetraazabipyH_2 (**III** in figure 1) with butyliodide produces the mono- and dialkylated derivatives

and treatment of the dialkylated ligand with concentrated sulfuric acid induces the elimination of the cyano group yielding the tetraazabipy(butyl)$_2$ (**IV** in figure 1). The dicyanodibutyl product exhibits a *cis–trans* isomerism and crystals of the *trans* isomer have been obtained by crystallization from a chloroform–ether–hexane mixed solvent [13]. While most of the bond distances calculated from the X-ray structure of the *trans* isomer have the expected values, the C–C distance between the pyridine (py) groups of each 2,2′-bipy group corresponds to a bond order between 1 and 2. This fractionary bond order results from an angular orientation of the pyridine rings, whose planes form a dihedral angle of 61.5°. Additional structural features are the cyano groups remaining in the molecular plane of the macrocycle and the butyl pendants in positions perpendicular to the molecular plane. There are marked differences between the UV–vis spectrum of the *cis* and *trans* isomers. The spectrum of the *trans* isomer exhibits a single band, $\lambda_{max} = 266$ nm, while the spectrum of the *cis* isomer exhibits two bands, $\lambda_{max} = 250$ and 280 nm. A difference in the double-bond character of the C–C bonds bridging the pyridine groups, that is the double-bond character is larger in the *cis* than in the *trans* isomer, accounts for the disparity in the spectra of the isomers.

There have been no reports concerned with the preparation of transition metal complexes of the tetraaza and hexaaza ligands addressed in this section. However, interactions of the ligands with Li^+ ions have been investigated. The addition of LiCl to a solution of (CN)$_2$tetraazabipy(butyl)$_2$ in CH_2Cl_2 bleaches the red color of the solution. The spectral changes occur with clean isosbestic points and they are attributed to the coordination of Li^+ ions to the macrocycle. Differences in the spectra of the ligand with and without coordinated Li^+ have been attributed to a disruption of the electronic delocalization in the latter species (figure 3). The coordination of the Li^+ ions to the *cis* and *trans* isomers of the macrocycle (equation (4)) has been confirmed by the disappearance of N–H resonances of the inner protons in the ^{1}H NMR spectrum when LiCl is added to the solution of (CN)$_2$tetraazabipy(butyl)$_2$.

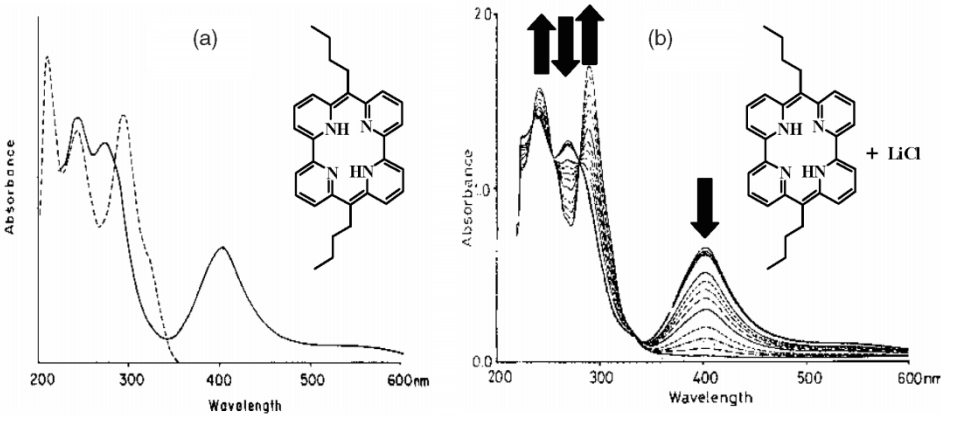
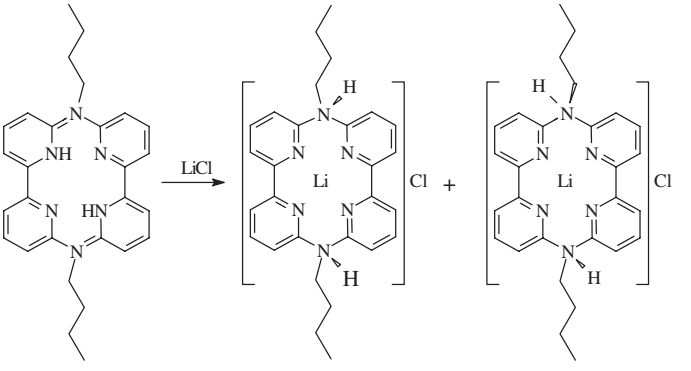
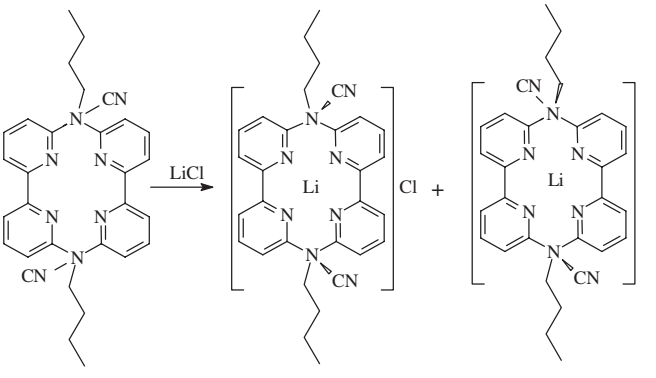


Figure 3. UV–vis spectra of the tetraazabipy(butyl)$_2$ (**IV** in figure 1), in (a) CH_2Cl_2, —, or MeOH, -----; (b), in CH_2Cl_2 solutions containing LiCl. The arrows show the direction of the absorbance changes. Reproduced with permission from Ref. [12].



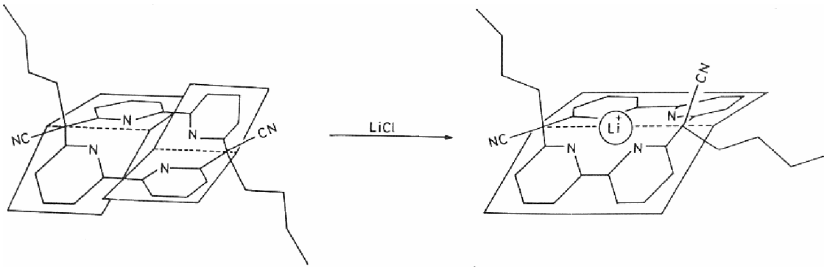
(4)

A similar complexation reaction occurs when LiCl is added to solutions of the dicyanodibutyl product in $CHCl_3$ or CH_3OH (equation (5)).



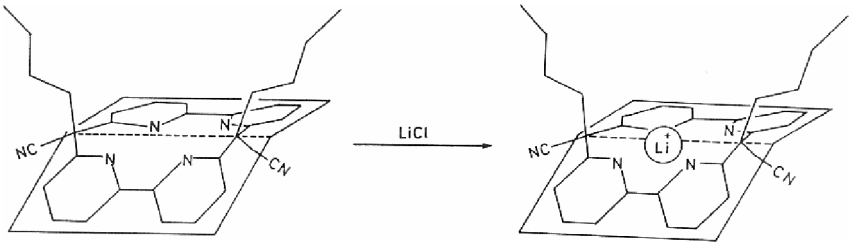
(5)

The UV–vis spectra of the *cis* and *trans* isomers become identical when LiCl is added to their solutions in $CHCl_3$. When the solvent is CH_3OH, no spectral changes are caused by the addition of LiCl. The coordination of Li^+ to the dicyanodibutyl in $CDCl_3$ becomes evident in the ^1H NMR spectrum of the ligand as a lower field displacement of the resonances corresponding to α-CH_2 groups in the butyl pendants closest to the macrocycle. The ^1H NMR spectrum of the *trans* isomer of the dicyanodibutyl complex is markedly dependent on the temperature. A single resonance of the α-CH_2 is split into two signals below 40°C because a pyramidal structure with planar 2,2′-bipy groups is the most stable at low temperatures. Such a structure destroys the equivalence of the α-CH_2 protons (equation (6)).



(6)

Neither the feel ligand nor the *cis* isomer of the Li^+ complex in equation (7) exhibits a temperature-dependent spectrum.



(7)

A monoalkylated ligand, $(CN)_2$tetraazabipyH(dodecyl), with a single dodecyl pendant arm and its Li^+ and Zn^{2+} complexes have been synthesized and characterized by means of their ^1H NMR and UV–vis spectra [14]. The ^1H NMR spectrum of the free ligand exhibits the band profile expected for asymmetric 2,2′-bipy groups. Coordination of the ligand to Zn^{2+} produces a more symmetric conformation of the ligand and the number of resonances in the aromatic region is decreased. The signal of the α-CH_2 at 2.75 ppm is broadened and shifted to 3.18 ppm in the complex. Also the 15 ppm resonance of the internal N–H protons is displaced to 6.7 ppm because coordination of the metal ion induces tautomerization and the displacement of the proton to another position in the ligand. The UV–vis spectrum of the free ligand is the same in CH_2Cl_2, CH_3CN and CH_3OH and only undergoes a small hypsochromic shift with increasing solvent polarity. Coordination of the ligand to Zn^{2+} causes a solvent-dependent change in the intensity and position of the absorption bands. Such a complexation in CH_3OH solutions makes the band at 350 nm disappear and intensifies the band at 378 nm. In CH_2Cl_2, it causes the bands between 430 and 590 nm to be replaced by two new absorption bands at $\lambda_{max} = 303$ and 360 nm. The variations in the absorption spectrum with solvent have been interpreted on the basis of the formation of solvent-specific species. Coordination of the Zn^{2+} to the ligand in CH_3OH induces the dissociation of the internal N–H protons, and orbitals of the methine bridges remain part of the macrocycle's extended π system. By contrast, the inner N–H protons reappear, protonating the methine bridges of the complex formed in CH_2Cl_2. Protonation of the methine bridges disrupts the electronic delocalization and the electronic transitions become more localized in each 2,2′-bipy group.

4. Highly aromatic aza-macrocycles with phthalocyanine and porphyrin-based incorporating pendant arms

Two oligomers containing μ-oxo silicon phthalocyanine (trimers and tetramers) have coplanar silicon phthalocyanine units showing central symmetry along the Si–O–Si axis [15]. There is no significant overlap between the molecular orbitals of different units. In the absorption spectrum of the oligomers, the Q-bands are blue shifted with respect to the position of the band in the spectrum of the monomer. Such a spectral shift is attributed to an excitonic interaction of the transition dipoles producing

a new set of excited states. Because the displacement of the Q-band with respect to the monomer increases with the number of phthalocyanine rings, this is in agreement with the molecular exciton model of a linear polymer. A poly(aniline)-containing pendant Cu-phthalocyanine unit, PAnCuPc, was synthesized by using Cu-phthalocyanine sulfoamyl chloride and poly(aniline) as starting materials [16]. PAnCuPc is soluble in aprotic solvents such as NMP, DMF, DMAc and DMSO, and in solvents with low boiling points such as THF and $CHCl_3$. The UV–vis spectrum of PAnCuPc exhibits very intense bands in the visible and near-IR. Membranes from the condensation of poly(vinyl chloride) (PVC) and zinc-phthalocyanine (ZnPc) were prepared and tested in a SO_4^{2-}- selective electrode [17]. In these preparations, hexadecyltrimethylammonium bromide (HTAB) was used as a cation excluder and dibutyl phthalate (DBP) and benzyl acetate (BA) were used as plasticizing solvent mediators. A membrane having a composition of ZnPc-PVC-HTAB-BA in a ratio of 5 : 32 : 3 : 60 exhibited the best response to SO_4^{2-} and an excellent selectivity for SO_4^{2-} over a large number of common inorganic anions.

The use of metal phthalocyanine in the catalyzed oxidation of sulfur-containing inorganic and organic compounds is an area of current interest in applied chemistry. Cobalt phthalocyanine sulfonate ($CoPc(SO_3Na)_n$) has been used as a catalyst in the steady-state oxidation of H_2S with oxygen at pH = 8 [18]. Soluble salts of Mn^{2+}, $MnSO_4$ and $MnCl_2$ were introduced into the medium of the reaction as cocatalysts. The affinity of Co(II) phthalocyanine toward the oxidation of 2-mercaptoethanol was calculated with a hybrid Hartree–Fock/density functional method [19]. Medium and surface effects on the reactivity, the donor–acceptor intermolecular hardness [20–23] and the electrophilicity index [24] were considered in the calculation. The results demonstrated that the solvent and the surface have a cooperative effect, increasing the reactivity of the adsorbed complex. Other theoretical studies on the oxidation of 2-mercaptoethanol by CoPc have shown that a surface, such as graphite, decreases the activation energy of the process. An increased reactivity of the complex in the oxidation process is also predicted [25]. Detailed theoretical modeling of the charge transfer mechanism of the CoPc-mediated oxidation of 2-mercaptoethanol has also been reported [26]. In addition to finding the best charge transfer descriptors, this work identified the places on the reaction coordinate where the net charge transfer of one electron was produced [26]. In a related context, the electrocatalytic activity of cobalt tetra-aminophthalocyanine (CoTAPc) in the one-electron oxidation of various thiols was also investigated [27]. The electrocatalyzed oxidations of 2-mercaptoethanesulfonic acid, reduced glutathione and L-cysteine were investigated by using adsorbed monomeric CoTAPc and electropolymerized poly-CoTAPc films on a vitreous carbon electrode. Films of different thickness were used for these experiments. The electrocatalytic activity of the poly-CoTAPc films towards the oxidation of the thiols increased slightly with the thickness of the film but it still remained close to the activity of the adsorbed monomeric CoTAPc.

Various phthalocyanine complexes with novel electronic properties have been reported recently. Sandwich complexes, lutetium bisphthalocyanines and bisnaphthalocyanines with interesting electronic properties were studied as electron acceptors associated with the electron donor polyvinylcarbazole in single-layer photoconductors [28]. These lanthanide complexes function as electron acceptors and electron donors and they strongly absorb light with frequencies from the near-UV to the near-IR.

A 1,10-phenanthroline-appended metal-free azaphthalocyanine has been prepared with a 10,12-diimine-11H-pyrrolo[3,4-b]dipyrido[3,2-f : 2′,3′-h] quinoxaline precursor [29].

The formation of inclusion complexes between cyclodextrin and various phthalocyanines, that is zinc phthalocyanine, various peripherally substituted zinc phthalocyanines and zinc naphthalocyanine, has been reported [30]. These complexes have 2 : 1 and 4 : 1 (cyclodextrin : phthalocyanine) stoichiometries and their photochemical and photophysical properties have been compared with those of the uncomplexed phthalocyanines. Porphyrins bearing the redox-active phenylenediamine pendant groups and their zinc complexes have been synthesized to afford dimensionally oriented π-conjugated systems. They were characterized both spectroscopically and electrochemically [31,32]. In particular, *p*-*t*-butylcalix[4]arenes bearing four redox-active phenylenediamine pendant groups on the lower rim have been obtained. The interconversion of the oxidation states of the pendant groups has been demonstrated both chemically and electrochemically [32]. Treatment of the zinc porphyrin-bearing four dimensionally oriented phenylenediamine strands with DABCO leads to sandwich complexes where the porphyrin moieties are surrounded by π-conjugated pendant groups [33]. The introduction of four aniline trimer pendant strands at the *meso*-position of the porphyrin scaffold leads to three-dimensionally oriented π-conjugated systems [34]. The ^{1}H NMR and UV-vis spectra revealed that strands of the alpha beta-isomer might be in equilibrium with conformers in which one or more strands lean toward the porphyrin ring.

The synthesis and study of extended chiral and enantiopure multiporphyrinic devices includes a two-dimensional molecular system [35]. This molecular system consists of a star-shaped pentaporphyrin with chiral enantiopure linkers derived from uridine. The core porphyrin show dual electrochemical and photophysical properties [35,36]. To explore new architectures for the self-assembly of multiporphyrin arrays, a one-flask protocol of a shape-persistent cyclic hexameric porphyrin array was developed. Six derivatives bearing diverse pendant groups were prepared on the basis of the protocol. The new arrays contain 6–12 carboxylic acid groups, 12 amidino groups, 6 thiol groups, or 6 thiol groups and 6 carboxylic acid groups in a protected form, i.e. *S*-acetylthio, TMS-ethyl, TMS-ethoxycarbonyl. The arrays have alternating Zn^{II} and free base porphyrin or all Zn^{II} porphyrin [37].

A number of protocols have been devised for the preparation of a series of porphyrin-bearing ester pendant arms [38–40]. The protocols allowed the preparation of products where the number of potential coordinating groups varied from one to four. Structural properties related to the coordination of Bi(III) were investigated. Bismuth forms a stable eight-coordinated complex with the porphyrin ligands. The complex geometry is square antiprismatic and the X-ray structure shows the formation of a dimer assembled through the mutual coordination of a terminal ester group [39].

A series of hanging porphyrin xanthene and dibenzofuran compounds have pendant groups with various proton-donating abilities. The corresponding chloroiron(III) complexes with hanging porphyrin xanthene ligands were found to promote the catalase-like disproportionation of hydrogen peroxide. The results demonstrated that intramolecular protons have a dramatic effect on the catalytic activation of O–O bonds [40]. In a copper(I)-template preparation of the first [2]catenate, electron-donor and -acceptor porphyrin groups were linked without the need of covalent bonds to keep them together. The preparations involved reactions with macrocycles

incorporating 2,9-diphenyl-1,10-phenanthroline residues and pendant porphyrin [41]. In a related compound, a catenate was used as a spacer between two porphyrins [42]. The porphyrins function as an electron donor and acceptor and they were linearly positioned at each side of the catenane core.

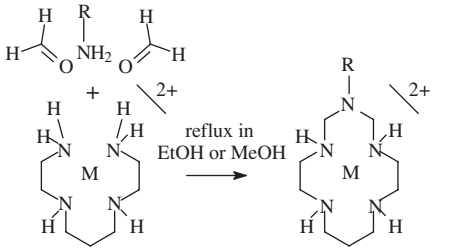
Several literature reports have been concerned with porphyrin complexes of various metals (zinc being the most abundant) bound to polymers. The photophysical behavior of zinc(II) tetraphenylporphyrin (ZnTPP) in a copolymer of 0.1 mol% zinc(II) 5-[4-(6-methacryloyloxyhexanoyloxy)phenyl]-10,15,20-triphenylporphynate (ZnTPP-C-5-MA) and 99.9 mol% cholesteryl-6-methacryloyloxyhexanate (Chol-C-5-MA) has been investigated and compared with that of monomeric ZnTPP-C-5-MA [43]. The absorption maxima of the Soret and Q-bands of monomeric ZnTPP-C-5-MA are solvent dependent, that is the maxima in *n*-hexane are 7.6 nm shorter than those in benzene. By contrast, no such solvent dependence was observed for the polymer-bound ZnTPP. The experimental observations suggest that the ZnTPP chromophores in the copolymer are ''protected'' in the Chol stacks and they become isolated from the bulk solution. A series of highly electron-deficient [5,10,15,20-tetrakis (perfluoroalkyl)porphinato]zinc(II) complexes and their free base analogs were prepared by the condensation of perfluoro-1-(2′-pyrrolyl)-1-alkanol precursors [44]. The procedure used continuous water removal during the reaction to yield the meso perfluorocarbon-substituted porphyrin. Characterization of the compounds in the series was made on the basis of optical spectroscopy, photophysical properties, electrochemistry and X-ray photoelectron spectroscopy. The nature of the porphyrin-pendant *meso*-perfluoroalkyl group has a large effect on the macrocycle's solubility. A pendant zinc porphyrin has also been derivatized, with carboxylic acid or amide groups, to accept the ''hydrogen-bonding'' functionalities and C-60 was functionalized with a ligating group, pyridine, and a second electron donor, the *N*,*N*-dimethylaminophenyl group [45]. The supramolecular triads formed by self-assembly of the functionalized zinc porphyrin and fullerene derivatives were characterized by spectroscopic and electrochemical techniques and were modeled by using *ab initio* computational methods. Evidence was provided for the axial coordination of the pyridine entity to the zinc metal center and hydrogen bonding between the nitrogen of the pyrrolidine ring and the pendant carboxylic acid or amide groups. The addition of cyclodextrin to solutions of self-aggregative sensitizers prevents the aggregation and improves the quantum yields of the photoinduced energy and electron transfers [46]. With the addition of 2,3,6-tri-*O*-methyl-beta-cyclodextrin (TMBCD) to an aqueous solution of poly-ZnP, the inclusion in cyclodextrin isolates the zinc tetraphenyl porphyrin pendant and lengthens the lifetime of the singlet excited state. Novel photosystems consisting of a TTF-linked porphyrin dyad and its zinc complex have redox-active pendants [47]. Based on the absorption spectrum, there is no electronic interaction between the two chromophores in these dyads. However, the fluorescence of the porphyrin pendant is dramatically quenched by an intramolecular electron transfer reaction from the TTF pendant to the porphyrin.

A pendant methylviologen, MV^{2+}, has been derivatized into the meso-phenyl groups of iron porphyrins by using an amide bridge in either the *p*- or *m*-position of MV^{2+} [48]. These iron porphyrins were successfully used for the six-electron reduction of nitrobenzene to aniline, a model reaction of the nitrite reductase-catalyzed reduction of nitrite to ammonia. Both *p*- and *m*-MV^{2+}-pendant iron porphyrin give somewhat larger yields

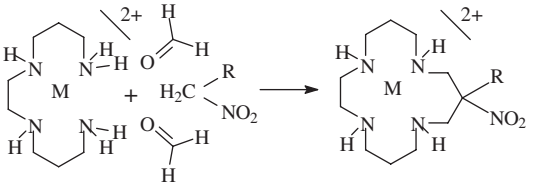
of aniline in the reduction of nitrobenzene and much larger yields of *p*-methoxyaniline in the reduction of *p*-nitroanisole than does normal iron tetraphenylporphyrin. Direct observation of the ferric-porphyrin cation radical as an intermediate in the photoinduced oxidation of ferric- to ferryl-heme tethered to $Ru^{II}(bipy)_3$ in reconstituted myoglobin has been reported [49,50]. The preparation and electrochemical reactions of conjugated dimers of nickel(II) octaethylporphyrin linked by extended *meso*, *meso*-alkynyl bridges, i.e. NiOEP-C-2-X-C-2-NiOEP [where X = (C-2)(*n*), for *n* = 0, 1 or 2; *trans*-CH=CH; 1,4-C_6H_4; 1,3-C_6H_4; 2,5-C_4H_2S] and *trans*-NiOEP-CH=CH-Y-NiOEP [where Y = C-2; *trans*-C-2-CH=CH; *trans*-C-2-CH=CH] have been reported [51]. Each [P-2](0) dimer has been converted to its electrogenerated dianion, and, as far as possible, to the intervening monoanion as well. Novel polymers were prepared with aryl isocyanide bearing porphyrin complexes and a Pd–Pt μ-ethynediyl complex as an initiator [52]. UV–vis absorption spectroscopy provided some evidence that porphyrin groups in the side chains of the polymer are regularly arranged by the helical main chain of poly(isocyanide). A Rothemund synthesis produced 2-aza-3-(2′-pyrrolyl)-5,10,15,20-tetraphenyl-21-carbaporphyrin. An alternative and convenient method for the preparation of the same compound used 2-aza-5,10,15,20-tetraphenyl-21-carbaporphyrin as a starting material [52], and four perylene–porphyrin building blocks for use in Glaser, Sonogashira or Suzuki polymerizations have been synthesized [53]. The building blocks have reactive groups (4-ethynylphenyl, 4-iodophenyl, bromo) at the *trans*(5,15)*meso*-positions of a zinc porphyrin and contain two or four perylene-monoimide chromophores attached at the 3,5-positions of the nonlinking *meso*-aryl rings of the porphyrin. The perylene–porphyrin building blocks were prepared by different routes: (1) a reaction of a diperylene-dipyrromethane with an aldehyde to yield a *trans*-A(2)B(2)-porphyrin, (2) a reaction of a diperylene-aldehyde with a dipyrromethane to yield a *trans*-A(2)B(2)-porphyrin, and (3) reaction of a diperylene-dipyrromethane with a dipyrromethane-dicarbinol to yield a *trans*-AB(2)C-porphyrin or ABCD-porphyrin. The use of perylenes increased the light-harvesting efficiency. This improvement is a particularly important in the green region of the light spectrum where porphyrins are relatively transparent. Another benefit is the greater solubility of the derivatized porphyrins in relation to the underivatized porphyrins. Tetra-4[4′-(2-methylbutoxy)benzoyloxy]phenyl porphyrin has been synthesized and its absorption spectrum in a solid film shows a strong circular dichroism [54]. A phenol pendant-capped porphyrin [55,56] and its iron(III) complex [57] were synthesized and characterized by ^1H and ^{13}C NMR. Modified tetraarylporphyrins, 5-(3,4-dihydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin and 5-(2,3-dihydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin, possessing a single pendant catechol group in one *meso* position, were used as tentative models for the inter-prosthetic group interaction in sulfite oxidase [57], providing a good insight into the coupling of oxo-Mo(V) and Fe(III) centers. A reaction of these novel ligands with LMoO(2+) (L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) followed by the insertion of Fe(III) into the porphyrin produced the bimetallic complexes FeCl(3,4-Mo-TTP) and FeCl(2,3-Mo-TTP) with Mo···Fe distances of 9.4 and 7.3 Å calculated with a theoretical model. Addition of excess *N*-methylimidazole produced the six-coordinate complexes Fe(N-MeIm)(2)(3,4-Mo-TTP)Cl and Fe-(N-MeIm)(2)(2,3-Mo-TTP)Cl with low-spin Fe(III) centers and two axial imidazole ligands.

5. Aliphatic aza-macrocycles incorporating pendant arms and polynucleating aza-macrocycles

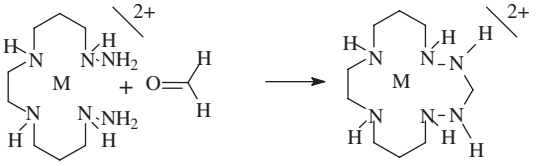
The use of formaldehyde with "locking groups" in a template synthesis has been widely applied to the preparation of macrocycles with various pendant arms. A number of examples are shown in equations (8)–(10) [2,58–60].



(8)



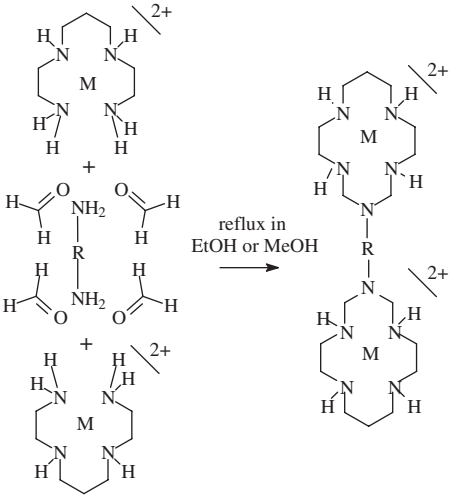
(9)



(10)

In principle, any methyl or methylene group (e.g. CH_3CN, $CH_3CH_2NO_2$), primary amine (e.g. R-NH_2 with R = aliphatic or aromatic group) or amide (e.g. R-CO-NH_2, R-SO_2-NH_2) whose protons are sufficiently acidic can be used as locking groups. Numerous mononuclear transition metal macrocyclic complexes with one or two pendant arms have been prepared by this general procedure. Reactions with aliphatic diamines, from 1,2-ethylenediamine to 1,5-pentylenediamine, have been used for the preparation of dimeric macrocyclic complexes. A complex of Ni^{2+} with

N,*N*′-bis-(2-aminoethyl)-1,3-propanodiamine and the diamine are condensed with formaldehyde in a typical template reaction (equation (11)).



(11)

The formation of the macrocyclic complexes can be confirmed by following the disappearance of the bands of the primary amine groups in the IR spectrum of the solid. No ^{1}H NMR spectra of the complexes have been reported because of the presence of high-spin species. A ligand field band, $\lambda_{max} = 450\,nm$ with $\varepsilon = 50\,M^{-1}\,cm^{-1}$, and an intense band, $\lambda_{max} = 210\,nm$ with $\varepsilon = 1.1 \times 10^4\,M^{-1}\,cm^{-1}$, are seen in the UV–vis spectra of the complexes. The metal centers behave independently in the cathodic reduction or anodic oxidation. The cyclic voltammetries of the bisnickel complexes and the reference compound *N*-propyl-[14]aneN_5 (**V** in figure 1) in N_2 saturated solutions exhibit waves at the same potentials [61]. In the bisnickel complexes, each electrochemical process corresponds to a transfer of two electrons, i.e. $\sim -1.4\,V$ *vs.* SCE for Ni(II/I) and $\sim 1.1\,V$ *vs.* SCE for Ni(III/II). The cyclic voltammogram of the bisnickel macrocycles in a 10% H_2O–CH_3CN mixed solvent saturated with CO_2 exhibit a catalytic wave at $\sim -1.7\,V$ *vs.* SCE. The peak current of the catalytic wave of the bisnickel complexes is less than the current recorded with the reference complex. It is argued that steric restrictions allows only one metallic center to interact with the surface of the electrode. The slight increase in the peak current with the length of the bridge is in accordance with this proposition. A separation of the catalytic wave into two suggests that two types of reactive centers are adsorbed in the electrode.

It has been shown that macrocyclic complexes with long pendant arms can be self-assembled to form supramolecular structures (figure 4a). The Ni^{2+} complex formed when R = 1-hexadecyl is used as a locking group in equation (8) [62,63]. Various solvents, such as CH_2Cl_2, hot CH_3CH_2OH and DMF, can be used to solubilize the complex. An interesting supramolecular packing results when a solution of the complex in a warm CH_3CH_2OH–H_2O mixed solvent is treated with $LiClO_4$. Recrystallization of the salt from hot CH_3CH_2OH gave crystals with unique arrangement of hydrophobic layers (figure 4b). The overlap of the hydrophobic arms of the macrocycle prevents

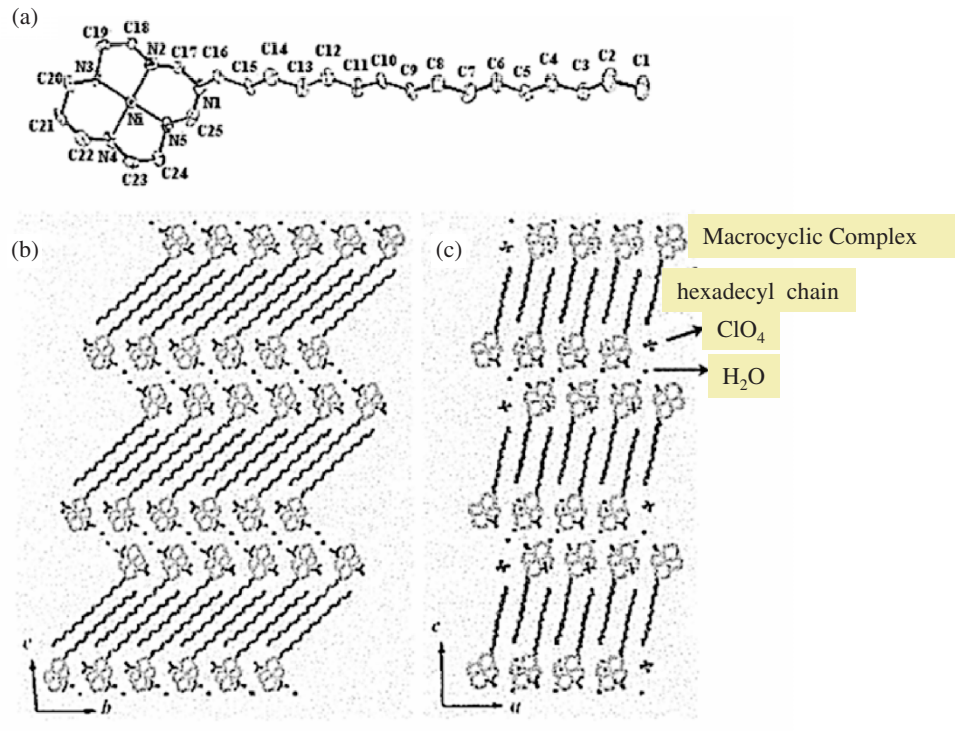


Figure 4. Structures of the Ni(II) complex of *N*-hexadecyl substituted penta-azacyclam. (a) ORTEP diagram with thermal ellipsoids drawn at a 30% probability. Packing seen through the axis *a* (b) or the axis *b* (c). Reproduced with permission from Ref. [62].

the transit of ions and water molecules. Such a transit is, however, allowed at the bilayers of the macrocyclic complexes (figure 4c).

Supramolecular self-assemblies, where the noncovalent π–π and H-bond interactions were judiciously used for an organized stacking of transition metal macrocyclic complexes, have been reported. To form the assemblies, a hexaazamacrocyclic complex with two 4-methylenepyridine arms was treated with organic compounds that were able to coordinate to the metal center (figure 5) [62]. Ethylenediamine, isonicotinate and biq-4,4-dicarboxylate (biq = 2,2′-biquinoline) created three different types of assemblies. They are held together by hydrogen bonds and π–π interactions between py and biq rings. Many features of the assemblies' structure have been assessed by X-ray crystallography. The molecular assemblies based on the complexes of nicotinate and biq-4,4-dicarboxylate are insoluble in all solvents where the supramolecular structure is preserved. In addition, the biq-4,4-dicarboxylate-based structure shows remarkable thermal stability. It relinquishes three H_2O molecules per unit formula at 80°C and can be heated at 250°C without decomposition. In addition to the self-assembled supramolecular arrangements, new preparative protocols have extended the field of macrocyclic ligands into the realm of dendrimers. Triamines have been used as locking groups in a template synthesis to produce a trimeric macrocycle (equation (12)) [63].

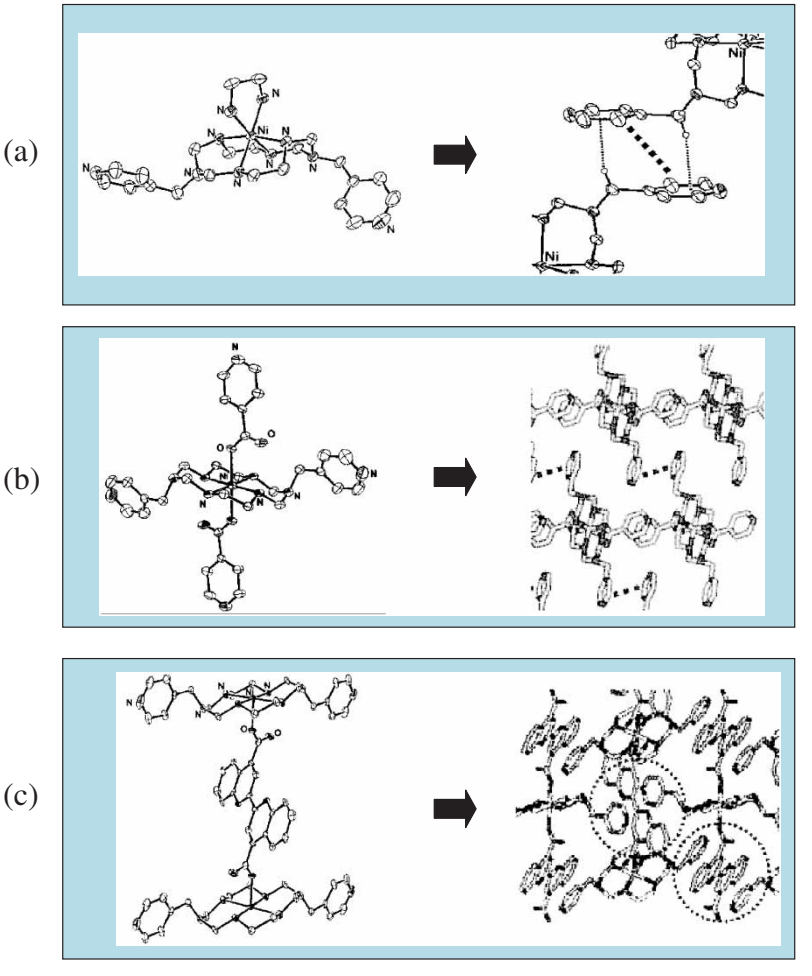
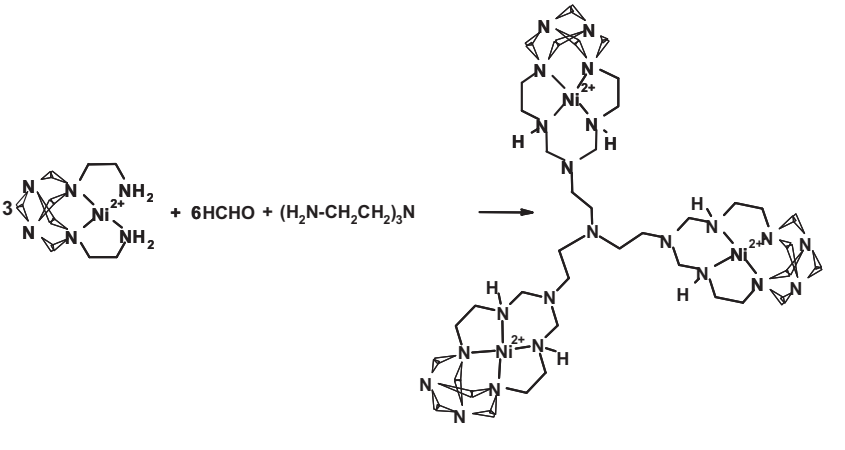
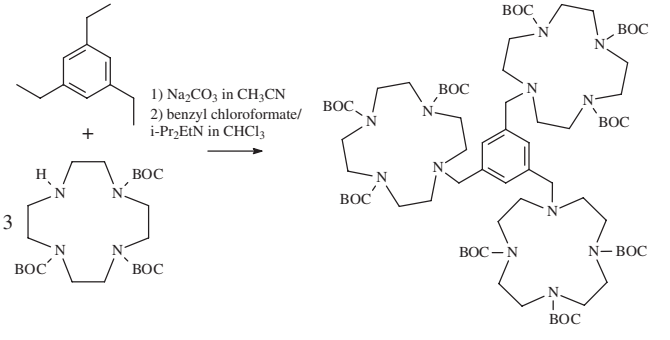


Figure 5. Self-assembled arrangements of the hexaazamacrocyclic complex of Ni(II) and di-*p*-CH_2-py with various axial ligands, L_{ax}. (a) L_{ax} = ethylenediamine, (b) L_{ax} = isonicotinate, (c) L_{ax} = 2,2′-biquinolina-4,4′-dicarboxylate. Adapted from Ref. [63].



(12)

Although the reaction is thermochemically disfavored, the dendrimer is obtained in 50% yield when water is present. The UV–vis spectra in CH_3NO_2 of the dendrimer, $\lambda_{max} = 438\,nm$, $\varepsilon = 83\,M^{-1}\,cm^{-1}$, and **VI** (figure 1), a related monometallic complex with $\lambda_{max} = 439\,nm$ and $\varepsilon = 273\,M^{-1}\,cm^{-1}$, exhibit similar spectral features. No changes in the spectrum of the dendrimer were observed when SCN^-, Cl^-, py, NH_3 or NO_3^- were added to the solution. However, CN^- changed the color of the solution from yellow to pink followed by demetallation of the dendrimer in a few minutes. The electrochemical properties of the dendrimer were investigated in a 9 : 1 CH_3CN–H_2O mixed solvent [60,64]. The Ni(II/I) couple is more positive than the couple in the complex of cyclam (**VII** in figure 1), where the respective reduction potentials are $-1.44\,V$ *vs*. SCE and -1.56 *vs* SCE in N_2 saturated solutions. The cathodic peak of the wave is increased three times when the solution is saturated with CO_2 but it increases about five times in the solution of the cyclam complex. Although the dendrimer is not as good a catalyst as the complex of cyclam, is a better catalyst than **VI**, whose cyclic voltammogram under CO_2 shows a twofold enhancement of the wave at $-1.44\,V$ *vs*. SCE. There is some evidence that there is no adsorption of the dendrimer on the electrode for the reduction of CO_2 to CO and that Co is the only product of the catalyzed reaction. In a different synthetic approach, dendrimers have been obtained by the reaction of a tribromide with a macrocycle having all but one of the reactive amino groups protected with BOC (*tert*-butyloxycarbonyl) (equation (13)) [65].



(13)

Polymeric complexes containing macrocyclic units have been reported recently (figure 6) [66]. Applications of these polymers to the catalysis of chemical reactions and to the construction of supramolecular devices are highly probable. Another type of macrocycle described as ''self-protected'' has also been reported recently (figure 7) [67]. Reactions of these ligands with dielectrophiles produce bimacrocyclic cages. Coordination of Ni^{2+} or Cu^{2+} to the cages can be effected by deprotonating the ligand with a weak base. The resulting complexes are inert to substitution and stabilize the 3+ oxidation state of the metal ions.

Acknowledgments

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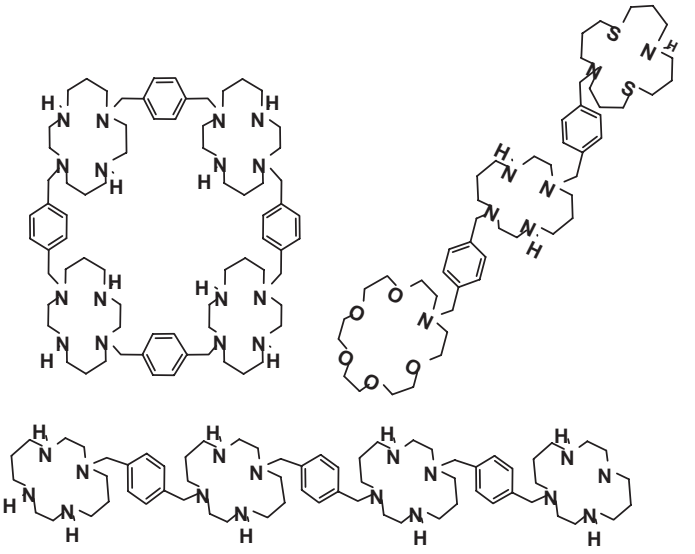

Figure 6. Polymers containing aza-macrocycles for the construction of supramolecular structures.

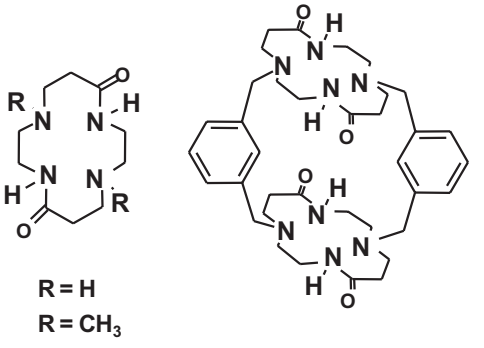

Figure 7. Bimacrocyclic box with *m*-xylyl bonds and monocyclic equivalent.

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