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Formation of multinuclear complexes: new developments from cyclam derivatives

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Abstract

Although tetraaza macrocyclic complexes have been known for several decades, most investigations have centered on mononuclear systems. More recently, however, elaboration of the macrocyclic rings has permitted an entry into bi- and higher nuclearity. In this review, the synthesis of N–N-bridged, C–C-bonded and C-spiro-binucleating ligands and metal complexes is described. Attention is paid to the structure of the complexes and its effects on the reactivity and redox behaviour in each system. In some instances, oxidation of the ligand framework results in delocalised metal complexes where, depending on the metal ion, either a delocalised organic based radical or a mixed valence oxidation state is observed. Among newer developments is the self-assembly of cyclam units around a metal template leading to supramolecular systems.

Keywords: Macrocycle; Binucleating; Redox reactivity; Mixed valence; Supramolecular chemistry

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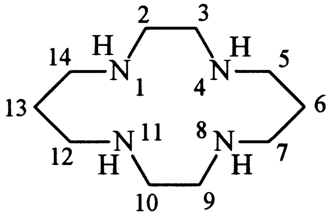
1. Introduction

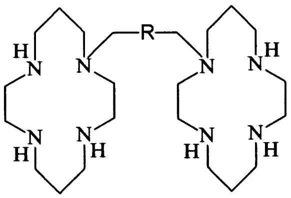
Since the observation of Curtis [1] of the high acid stability of the condensation products of acetone with $[Ni(en)_3]^{2+}$, the chemistry of macrocyclic transition metal complexes has seen unprecedented growth and the trend continues even today. Of the ligands, the saturated 14-membered macrocycle cyclam (1,4,8,11-tetraazatetradecane) (**1**) has been used more extensively than any other cyclic systems for the complexation of transition metal ions.



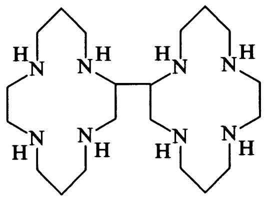
1, Cyclam

Being saturated, robust and one of the most innocent ligands, cyclam does not undermine the metal based chemistry of the complexed ion. Although the cyclam cavity is considered more suitable for first row transition metal ions, second and third row ions have also been studied, where, in some instances, less common oxidation states have been identified [2,3]. Several reviews and articles have been published that cover the various aspects of cyclam complexes [4,5] and its derivatives, including an extensive analysis of crystallographic studies [6]. The latter review primarily deals with an analysis of all nickel(II) complexes of 14-membered tetraazamacrocycles in the Cambridge data base. Significant progress has been made in the synthesis of cyclam-based binucleating ligands and structural and physical studies of the corresponding homo- and heterobinuclear complexes. More recently, aspects of tris-cyclam derivatives and some themes involving supramolecular chemistry have been reported. This review covers strategies for synthesis of ligands and their complexes, structure and spectroscopy, reactivity and electrochemistry which have been published over the past 20 years or so. Although the free ligands have been obtained in many cases, only the metal complexes have been described in some instances, where a metal ion template synthesis was used or due to the chemical instability of the free ligands.

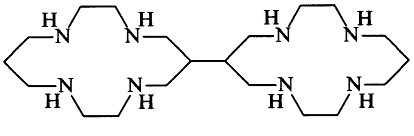
Two macrocyclic ligands can be linked through a variety of bridges involving donor atoms (mainly nitrogen), or directly through a C–C bond linking the carbon framework of each tetraaza macrocycle, and many of these bis(macrocycles) (**2**–**5**) based on cyclam have been studied. Depending upon the mode of connection and the nature of the bridging group, two aspects of their structures influence the chemistry of these systems. They are (i) the inter-metal ion distance and (ii) the relative orientation of the macrocyclic rings with respect to each other. Electrostatic and steric effects also play a role, which is controlled by these structural factors.



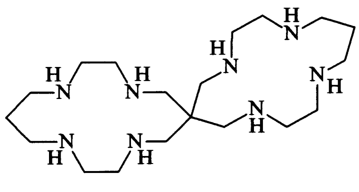
2, N,N'-bis(cyclam)



3, 2,2'-bi(cyclam)



4, 6,6'-bi(cyclam)

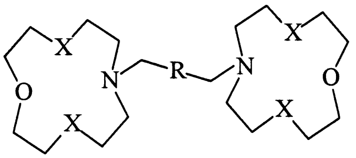


5, 6,6'-C-spirobi(cyclam)

2. N,N′-bridged bis(macrocycles)

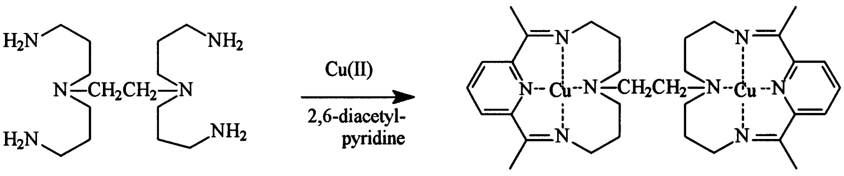
2.1. Synthesis

Two macrocycles, with at least one secondary nitrogen in each structure, can be connected easily through a suitable bridging ligand to form a N,N′-bridged bis(macrocycle).



6 R = p$CH_2C_6H_4CH_2$, X = S
7 R = CH_2CH_2, X = O
8 R = $CH_2CH_2CH_2$, X = O

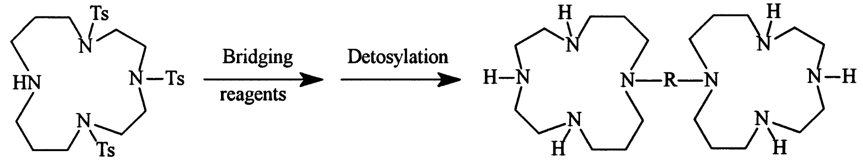
One of the first bis(macrocycle)s (**6**) that was reported by Osborn et al. [7] involve NS_2O donor sets. Similar bis(macrocycle)s, **7** and **8** with NO_3 donor sets, were subsequently reported by Calverley and Dale [8]. In these cases, there is only one secondary nitrogen that can react with the bridging group. Hence, their preparation was relatively straight forward. An example that involves a tetraaza macrocycle (**10**) in which there is only tertiary nitrogen has been reported by Murase et al. [9].



9

$[Cu_2(\mathbf{10})]^{4+}$

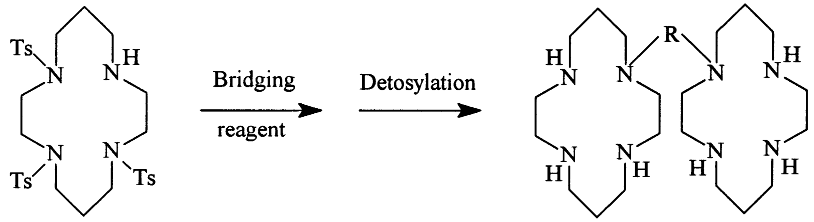
Here, the necessity for selective protection was avoided by forming the bridged open chain ligand **9**, prior to cyclisation, which was then promoted via a metal ion template. Later, the same intermediate was used by this group [10] in a Richman–Atkins [11] type synthesis to form the saturated N,N′-bridged bis(isocyclam) **12** (isocyclam = 1,4,7,11-tetraazacyclo-tetradecane). In the same year, Kaden et al. [12] used tri-protected isocyclam (**11**) to form a series of N,N′-bridged bis(isocyclam)s **12**–**14**. In a similar manner, Fabbrizzi and co-workers [13], by reacting 1,4,8-tritosylcyclam (**15**) with suitable bridging agents, followed by detosylation, prepared a series of N,N′-bridged bis(cyclam)s (**16**–**20**).



11

12 R = p-$CH_2C_6H_4CH_2$
13 R = CH_2CH_2
14 R = $COCH_2CH_2CO$

Since then, various methods have been developed to prepare selectively protected cyclam derivatives [14,15].

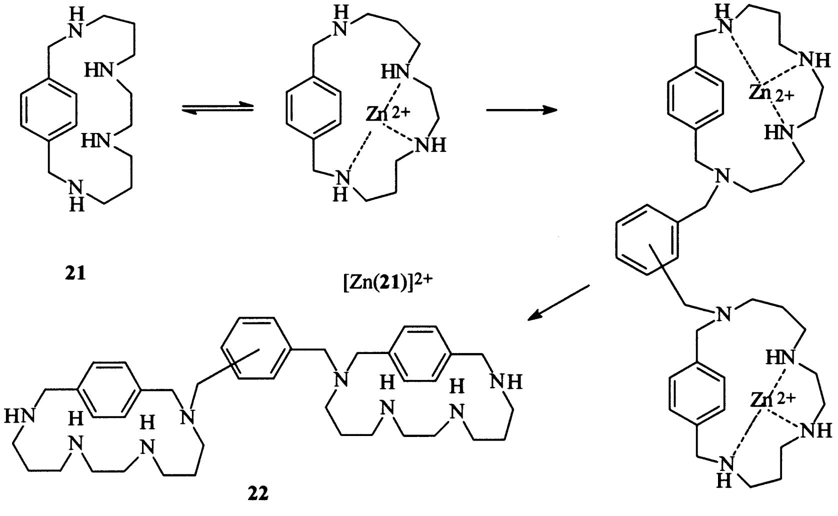


15 1,4,8-tritosylcyclam

16 R = CH_2CH_2
17 R = $CH_2CH_2CH_2$
18 R = $CH_2CH_2CH_2CH_2$
19 R = m-$CH_2C_6H_4CH_2$
20 R = p-$CH_2C_6H_4CH_2$

A wide variety of N,N′-bridged tetraazamacrocycles with various phenylenebis-(methylene) [16] and pyridylbis(methylene) [17] and other heteroaromatic spacers have been prepared by similar methods and have been studied in the context of their ability to inhibit the HIV virus types. Additionally, other macrocyclic complexes have been identified as potential agents for HIV investigation [18]. However, considering the objective of this review they are not dealt with in detail here.

One of the unusual modes of protecting nitrogens that has been reported [19] recently involves the polyaza[n]paracyclophane (**21**). Since only three of the four nitrogens are involved in coordination at any given instance, complexation to the Zn^{2+} ion is used to suppress the involvement of three adjacent amines. Thus, the uncoordinated amine in $[Zn(\mathbf{21})]^{2+}$ is used to bridge two cyclophane units to form the N,N′-bridged tetraaza ligand (**22**).



21

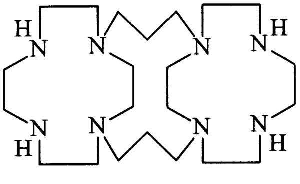
$[Zn(\mathbf{21})]^{2+}$

22

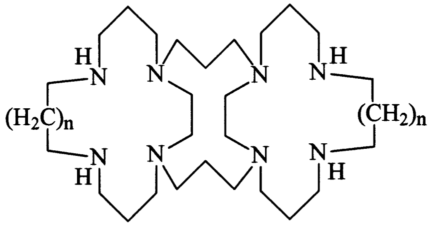
$[Zn_2(\mathbf{22})]^{4+}$

2.2. Cyclam-based tricyclic ligands

Recently, a series of condensed macrocyclic rings (**23**–**25**) (tcoa-13, tcoa-14 and tcoa-15) based on cyclam have been prepared in which all the four nitrogens of cyclam are used.



23 tcoa-13



24a tcoa-14, n = 2
24b tcoa-15, n = 3

These ligands resemble doubly N,N′-bridged macrocycles in their behaviour, forming only binuclear complexes using the terminal rings since the middle cyclam ring now with four tertiary nitrogens not involved in binding a metal ion. Murase et al. [20] first prepared ligand **23**, in which two13-membered rings are fused to a cyclam. This ligand referred to as tcoa-13 forms binuclear complexes and the bis-Cu(II) and Co(III) complexes have been prepared and structurally characterized. Subsequently, toca-14 and tcoa-15 have also been synthesized [21] and their Cu(II) complexes prepared. The outer cyclam rings in this series of macrocycles were constructed on the four pendant arms of N,N′,N‴,N⁗-tetraderivatized cyclams by a double Richman–Atkins cyclisation. Thus, selective protection techniques were not essential for the preparation of these ligands.

2.3. Structural studies of complexes of N,N′-bridged bis(macrocycles)

Only a few N,N-bridged macrocyclic complexes have been structurally characterized. In the structure of $[(NO_2)Cu(\mathbf{6})Cu(NO_2)]^{2+}$ [22], each copper ion adopts a six-coordinate geometry with four donors from each macrocycle and the nitrite attached in a bidentate manner. The structures of the Ni(II) complexes of N,N′-bridged isocyclams $[Ni_2(\mathbf{12})](ClO_4)_4$ and $[Ni_2(\mathbf{13})](ClO_4)_4$ have been determined [12]. In both cases, the Ni(II) centers adopt square-planar geometry with an average Ni–N distance of 1.942 Å. The bond lengths between Ni and the bridging nitrogens are slightly longer than the other Ni–N distances. In these complexes, the *anti* conformation is adopted, where the Ni(II) ions are separated from each other by the greatest distances possible. The internuclear distances were 11.56 and 7.05 Å, respectively, for the complexes $[Ni_2(\mathbf{12})](ClO_4)_4$ and $[Ni_2(\mathbf{13})](ClO_4)_4$.

2.4. Structural studies of complexes of cyclam-based tricyclic ligands

The crystal structures have been reported for the binuclear complexes $[Cu_2(TsO)_2(tcoa\text{-}13)](ClO_4)_2{\cdot}4H_2O$ and $[Co_2CO_3(tcoa\text{-}13)](ClO_4)_2{\cdot}3H_2O$ [20]. In these systems, the 13-membered rings being smaller, force the metal ions slightly out of the macrocyclic plane (0.34 Å). This factor, in combination with the nature of counter ions, appears to determine whether the complexes crystallize in a chair or boat conformation. The tosylate salt crystallizes in chair form with the tosylate ions coordinated to the Cu(II) ions in an *anti*-mode fashion. This feature dramatically increases the interionic distances to 6.876(3) Å, compared with an interionic distance of 4.198(1) Å in the case of the Co(II) complex, where the carbonate ion bridges the Co(II) ions in a bidentate manner. In this cobalt structure all five-membered chelate rings adopt an envelope form, which is thermodynamically less favourable than the *gauche* conformation. The crystal structure of $[Cu_2Cl_2(tcoa\text{-}14)]Cl_2{\cdot}2H_2O$ [21], the doubly N,N-bridged system, has been reported. In this structure, the two terminal cyclam units that have complexed Cu(II) ions are oriented facially with an inter-metal ion distance of 5.16 Å.

2.5. Reactivity of N,N′-bridged macrocyclic complexes

N,N′-bridged bis-macrocyclic complexes were originally prepared to demonstrate cooperative binding of substrates, and to show the nature of inter-metal ion interactions in some metallo-enzymes that have two metal ions. For example, the binuclear Cu(II) complex of ligand **6** in the ‘ear-muff’ conformation has been shown [22] to bind reversibly CO and O_2 and switch between Cu(I) and Cu(II) oxidation states. In this ligand, the macrocyclic cavity being small for Cu(II), the metal ion resides out of the macrocyclic plane and this facilitates a change in coordination geometry between square pyramidal and tetrahedral for the Cu(II) and Cu(I) states, respectively. Molecular modelling indicates the inter-metal ion distance can vary between 3.5 and 5.0 Å, which provides the required conformational flexibility for the reversible binding of substrates. Similarly, ligand **7** has been shown to bind Na^+ more efficiently, most likely through a 'sandwich'-type folding of the bis(macrocycle).

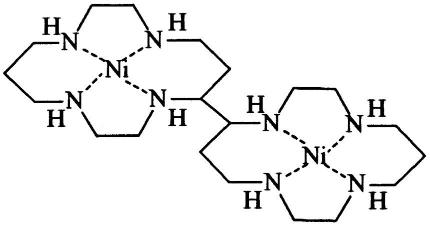
Since the length of the bridging groups controls the inter-metal ion distances in these complexes, they have been considered to be the ideal models to demonstrate the distance dependence of electrostatic and magnetic interactions in binuclear complexes. Kaden and co-workers [12] studied the $Ni^{2+/3+}$ redox couple of complexes $[Ni_2(\mathbf{12})](ClO_4)_4$ and $[Ni_2(\mathbf{13})](ClO_4)_4$ and compared them with the monomeric species $[Ni(isocyclam)]^{2+/3+}$. Due to the large distance (11.56 Å) between the Ni(II) ions in the $[Ni_2(\mathbf{12})]^{4+}$ cation, the individual Ni(II) centers behaved like independent complexes exhibiting a single redox wave. However, in $[Ni_2(\mathbf{13})](ClO_4)_4$ the inter-metal ion distance is only 7.05 Å and a strong electrostatic repulsion was experienced. As a result, this complex showed two distinct redox waves at 1.226 and 1.326 V. The $Ni^{2+/3+}$ couple for the monomeric $[Ni(isocyclam)]^{2+}$ cation showed a single wave at 1.096 V (vs. NHE). Similar observations were also reported by Fabbrizzi and co-workers [13] in the series of bis-Ni(II) and Cu(II) complexes of ligands **16**–**20**. In this case, both the $Cu^{2+/3+}$ (in 70% $HClO_4$) and the $Ni^{2+/3+}$ (in CH_3CN) couples were studied. Using the approach of Richardson and Taube [23], the separation of redox potentials for the successive one electron transfers was obtained and the individual redox potentials were calculated. The electrostatic contribution to the free energy change for the comproportion reaction was estimated and compared with inter-metal ion distances to demonstrate the role of electrostatic effects in binuclear macrocyclic complexes. Interestingly, these effects were more pronounced for the $Cu^{2+/3+}$ couples when compared with the $Ni^{2+/3+}$ couples. This is due to the adoption of square planarity by the copper in both oxidation states, whereas in the case of nickel the Ni(III) ion displays an octahedral geometry, thereby partially neutralizing the charge. Thus, the effect of electrostatic repulsion was greater in the copper complexes.

The effect of distance dependence has also been demonstrated [10,12] by studying the EPR spectroscopy of the bis Cu(II) cations $[Cu_2(\mathbf{12})]^{4+}$ and $[Cu_2(\mathbf{13})]^{4+}$. Complexes with shortest inter-metal ion distances displayed an interaction between the Cu(II) ions showing a distinct seven line spectrum with $A_{\parallel}$ values exactly half that of the mononuclear complex.

3. C–C bonded bi(macrocycles)

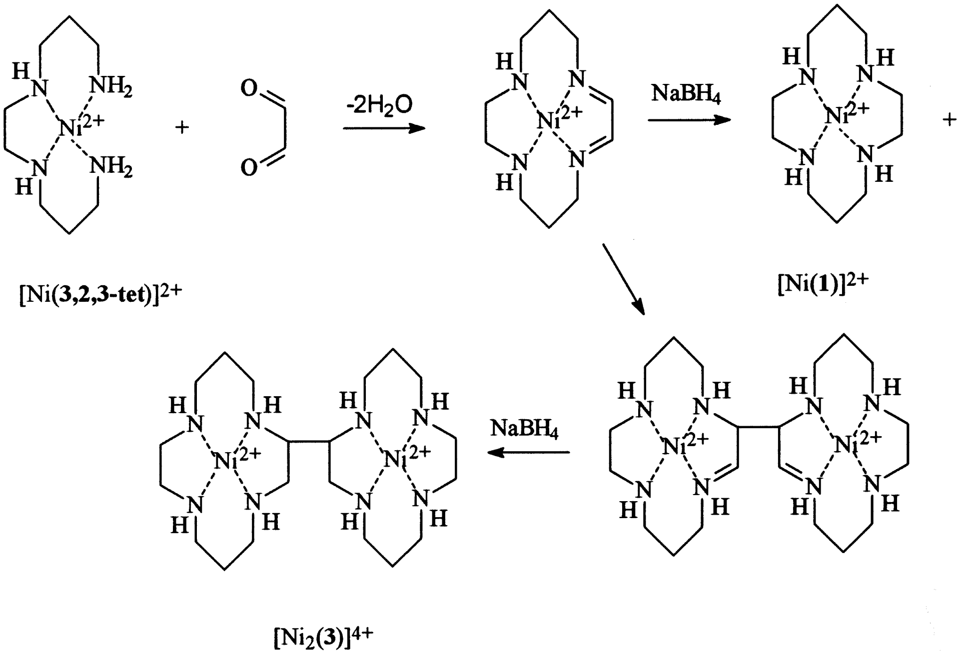
3.1. Synthesis

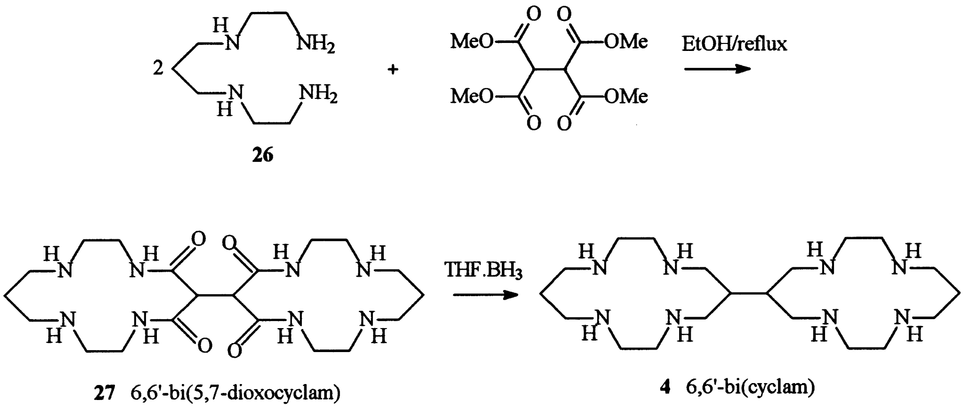
Three isomeric C–C-bridged bis(cyclam)s are possible, 2,2′-bis(cyclam) (**3**), 5,5′-bis(cyclam) (**25**), and 6,6′-bis(cyclam) (**4**).



25 5,5'-bi(cyclam)

Of these, only the 2,2′-bis(cyclam) and the 6,6′-bis(cyclam) are known. The bis-Ni(II) complex, $[Ni_2(\mathbf{3})]^{4+}$, of the C(2)–C(2′) linked cyclam was first reported as a by-product formed during the synthesis of $[Ni(II)(cyclam)]^{2+}$ [24] from the reaction of $[Ni(3,2,3\text{-tet})]^{2+}$, 1,5,8,12-tetraazdodecane with glyoxal, followed by $NaBH_4$ reduction.



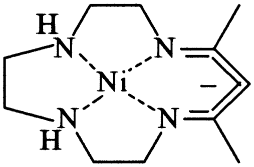


The synthesis of 6,6′-bi(cyclam) (**4**) was reported by Fabbrizzi et al. [25] using the cyclisation method of Tabushi et al. [26]. Complexation of Cu(II) and Ni(II) complexes of both 6,6′-bi(5,7-dioxocyclam) (**27**) [27] and 6,6′-bi(cyclam) [25] have been studied. Two complexes are formed sequentially in the reaction of ligand **27** with Cu(II) ions, where, in a step-wise fashion two protons are liberated per Cu(II) ion. The homobinuclear complexes $[M_2(\mathbf{4})](ClO_4)_4$ (M = Ni(II) and Cu(II)) and the heterobinuclear complex $[CuNi(\mathbf{4})](ClO_4)_4$ have been reported. Mochizuki et al. [28] have reported selective preparation of the mononuclear species $[Ni(\mathbf{4})]^{2+}$ and $[Co(CN)_2(\mathbf{4})]$, with the second macrocycle unoccupied. This permits the selective preparation of several heterobinuclear complexes, and $[NiCo(\mathbf{4})]^{4+}$ and $[CuCo(\mathbf{4})]^{4+}$ have been described.

3.2. Structural studies of C–C bonded bi(macrocyclic) complexes.

The crystal structure of the $[Ni_2(\mathbf{3})]$ complex of 2,2′-bi(cyclam) has been reported [24]. The macrocycles are linked through the C(2) carbons via an equatorial–equatorial bond. The Ni–N distances (1.95(1) Å) are typical of a square-planar system where the cyclam rings adopt the usual *trans*-III conformation.

A number of metal complexes of unsaturated C=C linked bi(macrocycles) that show delocalisation have been prepared vide infra (Section 3.3) by oxidative coupling of the corresponding monomeric species, such as $[Ni(28)]^+$, and have been characterized structurally.



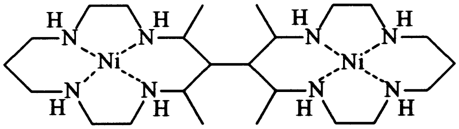
$[Ni(\mathbf{28})]^+$

Analogous complexes have also been obtained by chemical oxidation of complexes of saturated macrocyclic ligands such as cyclam. These are also described, together with the reactivity of C=C linked macrocycles.

3.3. Chemistry and spectroscopy of saturated bi(cyclam) complexes

The cyclic voltammetry of both the binuclear cations $[Ni_2(\mathbf{3})]^{4+}$ and $[Ni_2(\mathbf{4})]^{4+}$ in CH_3CN show two one electron waves ($\Delta E_p = 75$ mV) corresponding to the successive oxidation of the Ni(II) centers [24,29]. Fabbrizzi et al. have studied the electrochemistry of homo- and heterobinuclear complexes of **6**,**6**′-bi(cyclam) in detail and have demonstrated the role of electrostatic interaction in these complexes. In a comparative study [30] of the Ni(II) complexes of cyclam and 6,6′-bi(cyclam), it has been shown that the binuclear cation $[Ni_2(\mathbf{4})]^{4+}$ is a better electrocatalyst than the $[Ni(cyclam)]^{2+}$ cation for reduction of water to hydrogen.

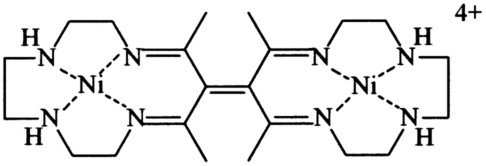
However, it did not show any greater efficiency in the reduction of CO_2 to CO. The cyclic voltammogram [27] of the binuclear Cu(II) complex of **27** also exhibited two redox waves corresponding to the successive oxidation of the Cu(II) centers.



$[Ni_2(29)]^{4+}$

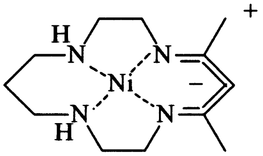
Also, a strong dipole–dipole ($D_{\parallel} = 126$ G) coupling was observed between the Cu(II) centers in this complex [31]. Mochizuki [32] has investigated the use of the binuclear cation $[Ni_2(\mathbf{29})]^{4+}$ in the photochemical conversion of CO_2 to CO using $[Ru(bpy)_3]^{2+}$ as photosensitizer and ascorbic acid as the sacrificial donor. It has been shown that with triflate as the counter-ion, the selectivity for reduction of CO_2 to CO was markedly increased over generation of H_2 from H_2O.

3.4. Redox reactivity and structural studies of bi(macrocycles) and formation of delocalised systems



30

A feature of the complexes of bis(cyclam) and other similar macrocyclic ligands is the possibility of oxidation of the bridge to introduce a segment of delocalisation between the metal centers, as shown above. The first reported example [33] of an unsaturated system involved the coupling in situ of the iodide salt of the diamagnetic 13-membered complex 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) ion $[Ni(\mathbf{28})]^{+}$. In cold acidic solution, the reaction likely involves initially the oxidation of the anionic fragment and coupling with a second moiety. This process is then followed by an oxidation of the C–C bond to yield **30**.



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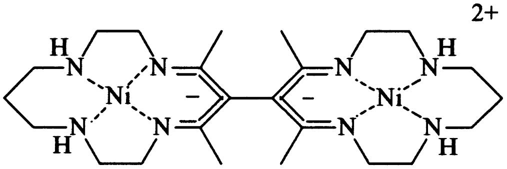
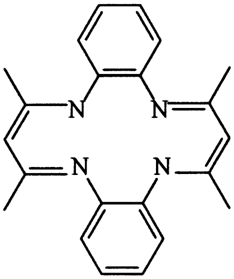


31a

It is of interest that owing to the steric crowding between the methyl groups, the bridging C atoms are displaced by about 0.55 Å from the almost planar arrays of the diimine segments. Further investigations on the corresponding 14-membered ring complex ions [M(**31**)]$^{n+}$ (**31** = 11,13-dienato-12,14-dimethyl-1,4,8,11-tetraaza-cyclotetradecane) showed that a redox wave in the 400–800 mV range versus NHE was largely independent of the metal center and attributable to one electron oxidation of the ligands [34,35].



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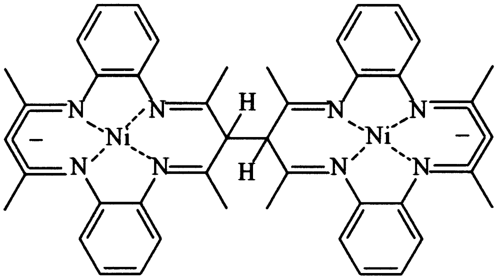
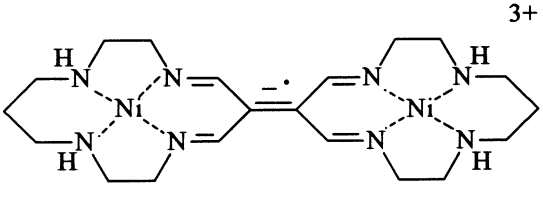


33

The radical which formed coupled rapidly (**31a**) and the resulting dimeric β-diimine species again could be readily dehydrogenated. Similar chemistry was observed with ligand **32** [36,37], where electrochemical oxidation of the Ni(II) complex resulted in the formation of a dimeric complex **33** with the hydrogenated bridge intact. The NMR spectrum of **33** showed that interactions between the methyl groups and the *o*-phenylene protons led to several isomeric forms, including a saddle shaped structure.

Chemical oxidation of part of the ligand in nickel(II) cyclam was achieved by reaction with hydrogen peroxide [38]. The mechanism is considered to involve the formation of a Ni(III) hydroxo species (consistent with the initial green coloration of the solution) and a hydroxyl radical. The latter abstracts a hydrogen atom from a ring nitrogen. Subsequent further oxidation yields the diimine in situ and, after coupling and dehydrogenation, the conjugated dimer **34** is formed. The absence of adjacent methyl groups now permits delocalisation in a planar unit, as seen in the structure of this compound (see Fig. 1). Both nickel(II) centers can be oxidized by NO^+ in MeCN, the EPR spectrum being consistent with tetragonally distorted low-spin d^7 ions with no evidence of any metal–metal interaction. Reduction (1e) in anaerobic conditions with a variety of reagents, including Zn dust, gave a bright green product (**34a**), which exhibited a pronounced band at 724 nm. The species was stable in argon, but in air the purple, diamagnetic species was rapidly restored. The EPR spectrum (see Fig. 2) of the reduced ion showed only a symmetric peak at $g = 2.007$, characteristic of an organic radical. No nitrogen coupling was observed, and, similarly, no metal–metal coupling as evidenced by any modification of the spectrum when ^{61}Ni was used.



34a (= [34]$^{-\bullet}$)

The EPR signal may be compared with that of reduced tetracyanoethylene [TCNE$^{\bullet-}$], consistent with a high degree of electron delocalization within the conjugated molecular plane. Further reduction led to a dimeric species with a quasi-aromatic ring structure [38].

The identical ligand system was characterized at the same time with iron(II) as the metal ion [39]. In this case, reaction of cyclam with a dioxygenated acetonitrile solution containing Fe(II) perchlorate resulted in the formation of a purple solution.

Removal of iron oxides permitted the extraction of bright green crystals of **35**. Of interest is the observation of an intense absorption band at 874 nm, similar to that observed above for the reduced nickel complex. Also, if no dioxygen is present, the reaction stops at the purple colored stage. As in the case of the nickel complex, the tetraimino ethylene segment and the iron(II) center are co-planar. Also, the iron–imine–nitrogen distances are the shortest (1.88, 1.90 Å) known in systems of this type. Exceptionally short bonds have also been identified in the Ni(II)–N$_{im}$ system described above. However, distinct differences between the systems arise in comparing electrochemical reductions [40,41]. Whereas in the [Ni(II)]$_2$ system two

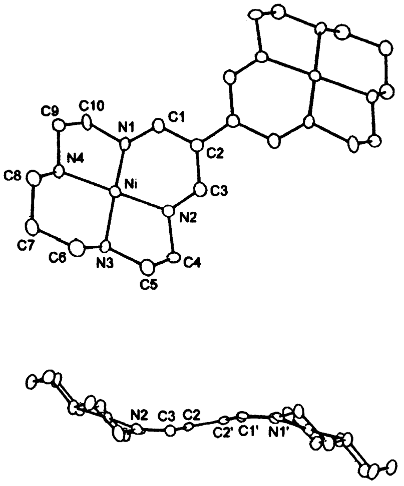
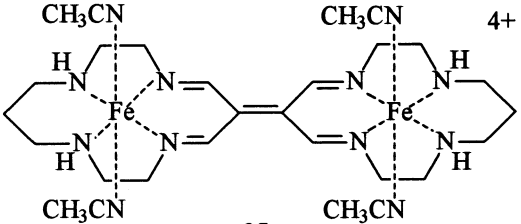


Fig. 1. ORTEP diagram (top) of the cation **34**. Planar view (below) (25% thermal ellipsoids).



35

well identified one electron waves are observed in aqueous media and MeCN, a similar effect in the Fe(II) case is seen only in acetonitrile. Also, there is a significant difference in the first and second reduction potentials of the diiron and dinickel species. This is attributed to a large energy separation between the first and second lowest unoccupied molecular orbitals in the case of the iron complex, where there may be an electrostatic impediment to the introduction of a second electron to a partially filled orbital. On the other hand, if the first and second unoccupied orbitals were closer in energy in the square-planar nickel(II) complex, the added electron can be accommodated in an unoccupied orbital of similar energy. The fact that there is clear evidence for strong coupling between the two iron(II) centres, which is not observed in the nickel(II) system, may contribute to these effects. Of interest is the lack of any sequential oxidation in the case of the dinickel ion, whereas the iron system gives rise to the delocalized mixed valence complex in the first step, and a second oxidation process about 500 mV more anodic. This leads to an estimate of at least 10^{11} for the comproportionation constant corresponding to the equilibrium:

$$[\mathrm{Fe(II)/Fe(II)}] + [\mathrm{Fe(III)/Fe(III)}] = 2[\mathrm{Fe(II)/Fe(III)}]$$

The corresponding ruthenium complex has also been prepared and exhibits properties similar to those of the iron system [42]. Unlike the nickel(II) systems, which are

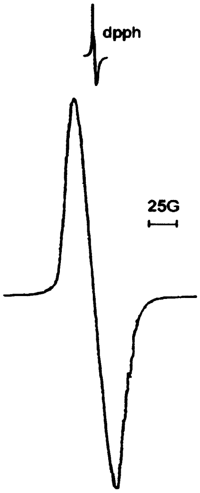


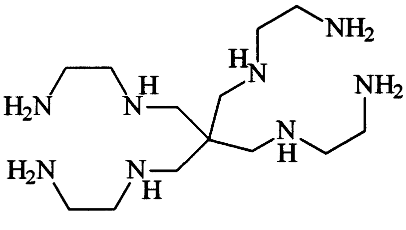
Fig. 2. EPR spectrum of the cation **34a**.

diamagnetic and show no intervalence behavior, the octahedral Ru(II) and Fe(II) ions exhibit two oxidation waves consistent with three accessible metal-based oxidation states. For the isovalent (Fe(II)/Fe(II)) ion, in the addition to the 874 nm band, there are features at 240 and 340 nm. One electron oxidation to the formally (II)/(III) state results in a loss of the 874 nm band, a shift of the 340, and new features at approximately 500 and 970 nm, the latter being assigned to an intervalence transition best described as valence delocalized. X-ray photoelectron spectroscopic measurements on the Ru(II)/(III) species [42] and Mössbauer spectroscopy of the Fe analogue [41], provide support for this state, together with a very large comproportionation constant ($\approx 10^{11}$) for the iron species. In a recent study [43], additional studies have been made on the Ru(II)/Ru(III) ion. Electroabsorption spectroscopy measures the absolute difference in dipole moment between a ground electronic state and a specific excited level. In a system of the type under consideration, where there is little net movement of charge predicted, a small value of the absolute change in μ is anticipated. In the Ru_2 form of **35**, essentially no change was observed, consistent with a complete delocalization of charge and very strong coupling between the metal centers. A three-center molecular orbital model has been assigned to account for the electron delocalization, in which the intervalence transfer is formulated as a bonding to a non-bonding transition, whereas the nominal metal–ligand charge transfer excitation is described as a two center non-bonding to a three-center anti-bonding promotion. There are relatively few examples of this type of almost complete delocalization, and modification of cyclam ligands to incorporate macrobicyclic metal derivatives will be a further source of systems with which to test such theories.

4. 6,6′-C-Spirobi(macrocycles)

4.1. Synthesis

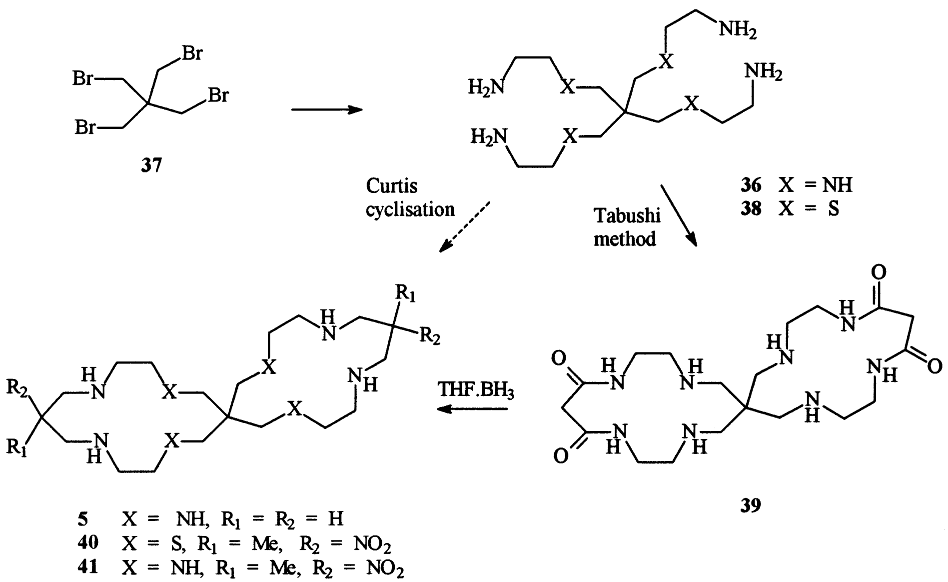
Multi-loop crown ether ligands based on pentaerythritol were first reported by Weber [44]. The objective was to study selective complexation of alkali, alkaline earth cations and also heavy metal ions.



36 tabm

A synthetic strategy based on specific protection–deprotection of pentaerythritol was used to prepare these ligands. These multi-loop crown ether ligands range from simple bis [18]-crown to tri- and tetra-(macrocycles) with various sizes of rings and donor atom combinations. Although Philip [45] first prepared and reported the open chain ligand, tabm (**36**), derived from pentaerythritol, azamacrocyclic ligands based on the pentaerythrityl moiety were unknown until the publication of the structure of the binuclear Ni(II) complex of 6,6′-C-spirobi(cyclam) [46].

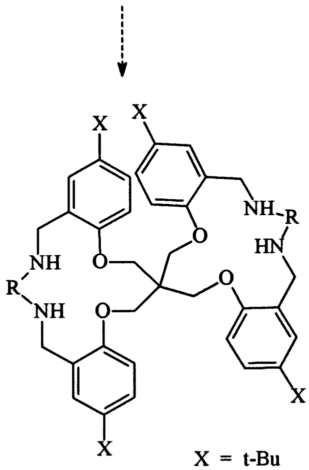
There are unique features of the macrocyclic ligands derived from pentaerythritol. In these ligands: (i) the two macrocyclic units are oriented nearly orthogonal to each other and (ii) due to the tetrahedral geometry of the spiro carbon, the rings are also tilted towards each other. They are also conformationally rigid compared with their crown ether analogues, which are highly flexible and as a result can sandwich an alkali metal ion [47]. Thus, in the binuclear complexes of 6,6′-C-spirobi(cyclam), the metal ions are poised not to be in the same plane. This unique feature prevents spin pairing of adjacent paramagnetic metal ions and has been suggested as a strategy for constructing magnetic [48] and electronic materials [49] and also in the stablization of bi-stable oxidation states [50].



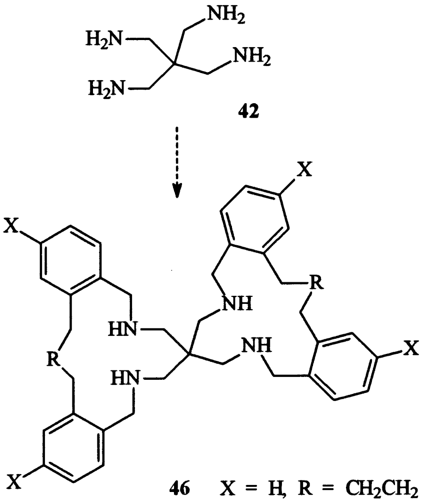
The general approach to the synthesis of a series of 14-membered macrocyclic ligands with bis-N_4, bis-N_2S_2 and bis-O_2N_2 donors from pentaerythrityl tetrabromide **37** has been shown below. An excess of a bidentate ligand $NH_2CH_2CH_2NH_2$ or $Na^+(NH_2CH_2CH_2S^-)$ is reacted with **37** to form the intermediate open chain ligands **36** and **38**, respectively. These open chain ligands are cyclised using various methods. In the case of 6,6′-C-spirobi(cyclam) (**5**) [51], the open chain intermediate (**36**) was cyclised by refluxing with diethyl malonate to form 6,6′-C-spirobi(5,7-dioxocyclam) H_4(**39**) according to the method of Tabushi [26]. This intermediate H_4(**39**) was subsequently reduced with $THF{\cdot}BH_3$ to form 6,6′-C-spirobi(cyclam) (**5**). The ligand H_4(**39**) and the perchlorate salt of **5**, $[H_4(\mathbf{5})](ClO_4)_4$, complexes M(II) (M = Cu or Ni) ions in a step-wise fashion, first forming the mononuclear species

$[M(H_2(\mathbf{39}))]^{2+}$ and $[M(H_2(\mathbf{5}))]^{4+}$, and subsequently the binuclear species $[M_2(\mathbf{39})]$ and $[M_2(\mathbf{5})]^{4+}$ (M = Cu(II) or Ni(II)) [50].

37



X = t-Bu
43 R = CH_2CH_2
44 R = $CH_2CH_2CH_2$
45 R = $CH_2CH_2NHCH_2CH_2$



42

46 X = H, R = CH_2CH_2
47 X = t-Bu, R = $CH_2CH_2CH_2$

The mononuclear species $[M(H_2(\mathbf{5}))]^{4+}$ (M = Cu(II) and Ni(II)) have been isolated and characterized. This provides ways to selectively prepare heterobinuclear complexes. Use has been made [52,53] of the Cu(II) ion templated reaction in the presence of formaldehyde and nitromethane to cyclize the open chain amines **36** and **38** (5,5-bis(4-amino-2-thiabutyl)-3,7-nonane-1,9-diamine. This method yields the Cu(II) complexes $[Cu_2(\mathbf{40})]X_4$ and $[Cu_2(\mathbf{41})]X_4$ ($X = NO_3^-$) directly. Recently, Lindoy and co-workers [54] have reported a series of spirobi(macrocycles) with mixed O,N-donors. Ligands of this type were synthesised by reacting **37** with *o*-hydroxy aromatic aldehydes and the resulting tetraaldehydes were cyclised with diamines to form tetraimines, which were reduced with $NaBH_4$ to the corresponding saturated macrocycles **43**, **44** and **45**. In the case of ligands **46** and **47**, pentaerythrityl tetraamine was reacted with polyether dialdehydes to form tetraimines and these were reduced further. Using these strategies, the position of the O and N donors were reversed [31]. There appear to be no reports available to date on the complexes of these ligands.

4.2. Structural studies of ligands

Although most saturated ligands are high melting solids, they are generally highly hygroscopic and to date there are no structural data available. However, 6,6′-C-spirobi(5,7-dioxocyclam) (**39**) and the tetra-hydroperchlorate salt of 6,6′-C-spirobi-(cyclam) $[H_4(\mathbf{5})](ClO_4)_4$ have been structurally characterised [55]. An ORTEP diagram of **39** is shown in Fig. 3 with an illustration of *trans*-II configuration.

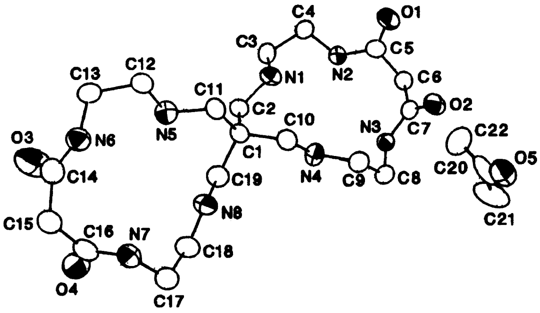


Fig. 3. ORTEP diagram of the ligand **39**·CH_3COCH_3 (30% thermal ellipsoids).

In the structure of **39**, all the four amide groups (N–C=O) are planar as expected. However, owing to the tetrahedral nature of the methylene groups bridging these amides, the N–C=O groups are not coplanar with the macrocyclic plane defined by the four N-donors. As a result, the oxygen atoms of the carbonyl groups project away from the macrocyclic plane in a nearly perpendicular direction. Another important aspect is that all the nitrogen hydrogens were found experimentally and refined. Of interest is that they adopt the less common *trans*-II configuration with respect to cyclam rings, i.e. three of the four hydrogens project away from the macrocyclic plane and on the side opposite to the amide oxygens, as shown in the above diagram. The average C–C, C–N and C=O distances are 1.530(7), 1.396(7) and 1.220(7) Å, respectively. The average amide bond angle N–C=O is 123.4(5)°. The average C(O)–N–C bond angle is 123.3(5)°, much larger than the CH_2–N–CH_2

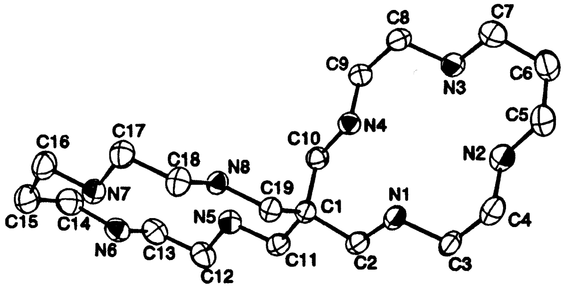
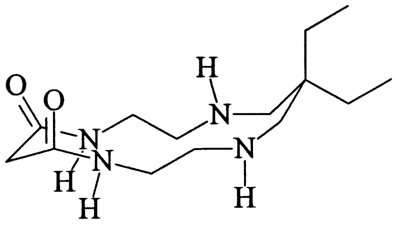


Fig. 4. ORTEP diagram of the cation $[H_4(\mathbf{5})]^{4+}$ (30% thermal ellipsoids).



trans-II

bond angle of 111.5(4)°, suggesting significant delocalisation of the nitrogen lone pair over the N–C=O bond.

An ORTEP diagram of the cation $[H_4(\mathbf{5})]^{4+}$ is shown in Fig. 4. The structural features of the individual cyclam rings is very similar [55] to that of the cyclam cation found in $[H_2(\mathbf{1})](ClO_4)_4$ [56]. The perchlorate anions are located above and below the plane of the macrocycle showing H-bonding interactions. The overall conformation of the cyclam rings is very similar to that found in the structure of its complexes described later in this section. The bond lengths and angles are typical of such distances found in similar salts. The important aspect to note is that diprotonation of the macrocyclic ring and complexation by a divalent cation does not appear to affect the structural aspects significantly.

4.3. Structural studies of C-spiro complexes

A number of C-spirobi(cyclam) complexes have been characterised by X-ray crystallography. Crystal structures $[M_2(\mathbf{5})](ClO_4)_4$ (M = Ni(II) and Cu(II)) have been elucidated [46,50]. The structural parameters for the bis-Ni(II) and the bis-Cu(II) complexes were identical. Both complexes exhibited square-planar geometry with the metal ions in the plane of the macrocycle. The perchlorate counter-ions were located about 3.5 Å above and below the plane of the macrocyclic rings. The Ni–N and Cu–N distances are typical, 1.940(7) and 2.020(5) Å, respectively, and similar to distances found for many mononuclear complexes and the macrocyclic ring adopted the *trans*-III configuration. The average inter-metal ion distances in these complexes varied in the narrow range 6.4–6.6 Å depending upon the coordination geometry.

Structural characterization of the mono-nuclear species $[Ni(H_2(\mathbf{5})]\ (ClO_4)_4$ and also the heterobinuclear complex $[NiCu(\mathbf{5})](ClO_4)_4$ have been attempted [57]. In both instances, scrambling of the metal ion sites was observed. In the former case, the unoccupied macrocyclic ring and the Ni(II) containing macrocycle were randomly distributed, and in the latter both the Cu(II) and Ni(II) were square-planar and also distributed randomly. Also, in both systems, owing to the high thermal motion of the perchlorate ions, the structures were not fully resolvable. The conformations of the macrocycles in these complexes are very similar to that of the $[H_4(\mathbf{5})]^{4+}$ all being isomorphic.

Also, a μ-chlorobridged bis-Cu(II) one dimensional polymer of 6,6′-C-spirobi(cyclam) has been characterised structurally [58]. In this polymer, $\{[Cu_2(\mathbf{5})(\mu\text{-}Cl)](ClO_4)_3\cdot EtOH\}_n$, the Cu(II) ions adopt a square-pyramidal geometry through bridging to a chloride ion and are located 0.15 Å above the macrocyclic plane defined by the four donors. The zigzag propagation of this polymeric chain results from the ligand structure. The average Cu–N distance is 2.01 Å and the Cu–Cl distance is 2.627(2) Å. There are two types of inter-metal ion distances. The chloride bridged Cu(II) ions are 5.25 Å apart and the distance between non-chloride bridged Cu(II) ions within a macrocyclic unit is 6.41 Å. Those Cu(II) ions that are chloro-bridged are facially oriented, while those at 6.41 Å are nearly orthogonal (86.9°).

Although structures of Cu(II) complexes of open chain precursors, tabm and 5,5-bis(4-amino-2-thiabutyl)-3,7-nonane1-1,9-diamine, have been reported, no structural reports are available for the complexes of **40** and **41**. However, the inter-metal ion distances in these complexes have been estimated [59,60] by studying the dipolar coupling constants from their EPR spectra since dipolar interactions are related directly to internuclear distances. From these studies, distances of 6.4 ± 0.1 for the N_4 and 7.1 ± 0.2 Å for the N_2S_2 donor systems have been estimated, which are reasonable in comparison to their open chain analogues.

4.4. Redox reactivity of C-spirobi(cyclam) complexes

The redox process involving the Ni(II) centers in the binuclear cation $[Ni_2(6,6'\text{-C-spirobi(cyclam)}]^{4+}$ has been investigated extensively in various solvents by different electrochemical (cyclic and differential pulse voltammetry, polarography and coulometry), as well as stopped flow techniques [61]. The $Ni^{2+/3+}$ redox couple showed a strong dependence on the nature of the counter ions as well as on solvent. In aqueous acidic perchlorate medium, a single wave was observed for the two electron oxidation process. While the value ΔE_p was 58 mV, this wave was not reversible due to complications from homogeneous reactions. However, in the presence of chloride or sulfate ions, the reversibility of this couple dramatically improved with a drastic decrease in the ΔE_p value to 28 mV. In the absence of coordinating anions, the successive redox potentials were separated only by a statistically average value of 36 mV, as expected for complexes with similar redox sites. However, in the presence of coordinating anions, electrostatic interactions were significantly diminished and a single step two electron process became dominant.

Cyclic voltammogram of $[Ni_2(\mathbf{5})]^{4+}$ in CH_3CN showed two reversible waves for the successive one electron oxidation with a ΔE_p value of 100 mV (0.735 V for the Ni(II)–Ni(II)/Ni(II)–Ni(III) couple and 0.835 V for the Ni(II)–Ni(III)/Ni(III)–Ni(III) couple) estimated from differential pulse polarogram [61]. Although this observation demonstrated the existence of significant electrostatic repulsion between the metal centers in these types of complexes and the intermediacy of a mixed-valent species, the difference in successive redox potentials was not significantly great (for $\Delta E_p = 100$, the estimated comproportionation constant, K_c was only 49) to isolate the mixed-valent Ni(II)–Ni(III) species.

Despite the lack of isolability of the mixed-valent Ni(II)–Ni(III) species, the transient UV–vis spectrum was derived using stopped flow techniques in acetonitrile. In this procedure, the Ni(II)–Ni(III) species was generated in situ by mixing equimolar quantities of the more stable isovalent Ni(III)–Ni(III) species and the outer sphere reductant $[Ni(II)([9]aneN_3)_2]^{2+}$ ($Ni^{2+/3+} = 0.525$ V). A dramatic change in the UV–vis spectrum was observed with the generation of the mixed valent species with characteristic features at 296 and 380 nm. This species decomposed within a second during which time the gradual disappearance of the spectrum can be monitored. By studying the kinetics of this process at different wavelengths in the range 320–450 nm, a fast formation step, followed by a slightly slower decomposition step was identified. These steps were assigned to the formation of the mixed-valent species and its disproportionation to the isovalent species.

$$\mathrm{Ni(III)–Ni(III)} + [\mathrm{Ni(II)([9]aneN_3)_2}]^{2+} \rightleftarrows \mathrm{Ni(II)–Ni(III)} + [\mathrm{Ni(III)([9]aneN_3)_2}]^{3+}$$

$$2\mathrm{Ni(II)–Ni(III)} \rightleftarrows \mathrm{Ni(III)–Ni(III)} + \mathrm{Ni(II)–Ni(II)}$$

The rate constants for these steps were found to be $(40.7 \pm 3.4) \times 10^6$ M^{-1} s^{-1} and $(13.4 \pm 0.9) \times 10^6$ M^{-1} s^{-1}, respectively. For the purpose of comparison, the reduction of the bis-Ni(III) complex of **4**, 6,6′-bi(cyclam), was also studied. The high solubility of this complex permitted this study to be conducted under pseudo first-order conditions and the second order rate constants for similar steps were found to be $(5.06 \pm 0.86) \times 10^4$ M^{-1} s^{-1} and $(0.75 \pm 0.2) \times 10^4$ M^{-1} s^{-1}, respectively. These studies indicated that the rate of disproportionation for the C–C-linked mixed valent complex was at least seven times slower than that for the C-spiro species. Again, this is consistent with the inter-metal ion distances in these complexes. A much shorter distance of 6.4–6.6 Å in the 6,6′-C-spirobi(cyclam) species accelerates the disproprotionation of the mixed-valent species compared with the C–C-linked 6,6′-bi(cyclam) in which the estimated inter-metal ion distance was 8.4 Å. This can be attributed to significantly diminished electrostatic repulsions in the latter case, as has been demonstrated in their electrochemistry.

A subtle steric effect was also displayed by the binuclear nickel complex of 6,6′-C-spirobi(cyclam). Since both Ni(II) and Ni(III) cations tend to adopt octahedral geometry, simultaneous formation of bis-octahedral species was shown to induce such effects. In particular, this is magnified during the formation of the bis Ni(III) species when both Ni(III) centers prefer only octahedral geometry. This is apparent when the EPR spectra of the Ni(III) species of cyclam and 6,6′-C-spirobi-(cyclam) are compared (Fig. 5). In chloride medium, the Ni(III) species of cyclam shows the presence of an axially symmetric species with hyperfine splitting in the $g_{\parallel}$ feature. However, for the bis-Ni(III) species of 6,6′-C-spirobi(cyclam), three features are displayed which show no resemblance (see Fig. 5) to those expected for an axial complex. Interestingly, over a long period of time (weeks), a slow transformation to an axially symmetric species was observed. This has be attributed to the conformational rigidity of the macrocyclic framework and slow kinetics of substitution.

Electrochemistry of $[\mathrm{Cu_2}(\mathbf{5})]^{4+}$ and $[\mathrm{NiCu}(\mathbf{5})]^{4+}$ has been investigated in acetonitrile medium [50]. In the case of $[\mathrm{Cu_2}(\mathbf{5})]^{4+}$, a reversible wave for the Cu(II)–Cu(II)/Cu(II)–Cu(III) ($E_{1/2} = 1.120$ V) couple was observed, followed by an irreversible wave for the Cu(II)–Cu(III)/Cu(III)–Cu(III) ($E_{1/2} = 1.430$ V) couple. Similarly, a reversible wave for the Cu(II)–Ni(II)/Cu(II)–Ni(III) ($E_{1/2} = 0.750$ V) couple and an irreversible wave for the Cu(II)–Ni(III)/Cu(III)–Ni(III) were observed. The large separation between these successive one electron waves permitted the preparation of the mixed valent species $[\mathrm{Cu^{II}–Cu^{III}}(\mathbf{5})]^{5+}$ and $[\mathrm{Ni^{III}–Cu^{II}}(\mathbf{5})]^{5+}$, which have been characterized by spectroscopy. One of the notable features is the large decrease in

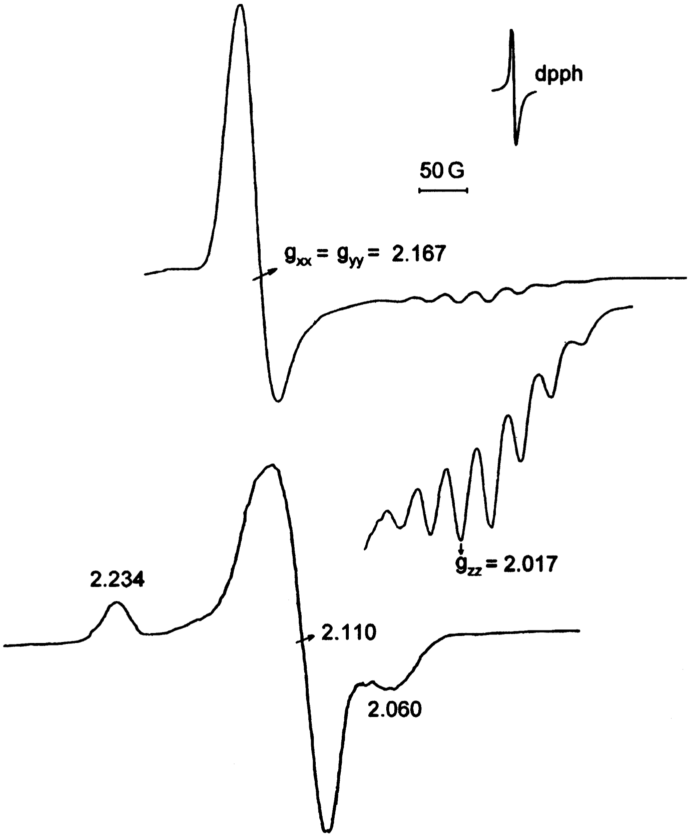
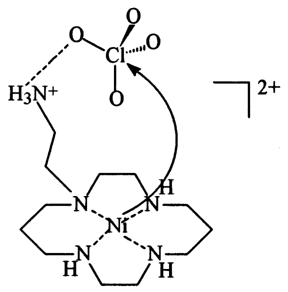


Fig. 5. EPR spectra of (top) $[Ni(Cl)_2(\mathbf{1})]^+$ and (below) bis-Ni(III) complex of **5** in 1.0 M chloride medium.

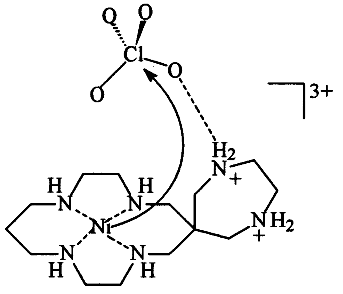
the $A_{\parallel}$ values for Cu(II) in the mixed valent species. For example, compared with 200 G observed for the Cu(II) ion in $[Cu^{II}–Ni^{II}(\mathbf{5})]^{4+}$, a value of only 95 G was observed in the $[Cu^{II}–Ni^{III}(\mathbf{5})]^{5+}$ ion.

4.5. Reduction of perchlorate ion

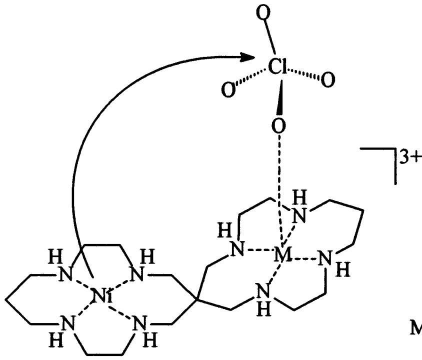
The perchlorate salts of the complexes of **5** (6,6′-C-spirobi(cyclam)) are only sparingly soluble compared with those of **4** (6,6′-bi(cyclam)). However, solutions of such salts were observed to undergo changes consistent with the slow development of Ni(III) species. Although reduction of the perchlorate ion is thermodynamically feasible it is also kinetically stable.



$[Ni(H(\mathbf{48})(ClO_4)]^{2+}$



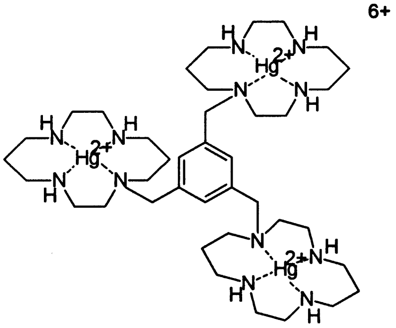
$[Ni(H_2(\mathbf{49})(ClO_4)]^{3+}$



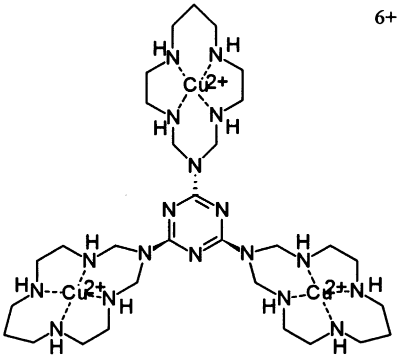
$[Ni(M)(\mathbf{5})(ClO_4)]^{3+}$
M = Cu(II) or Ni(II)

However, as demonstrated by Fabbrizzi [62], when the structural features of a complex facilitate close contacts between a potentially reducing metal ion such as Ni(II) and a perchlorate anion, the perchlorate ion may be reduced. The Ni(II) cation $[Ni(H(\mathbf{48})]^{3+}$ (**48**, scorpiand) in the presence of strong aqueous $HClO_4$ was observed to form Ni(III) species with the evolution of chlorine gas. This was attributed to reduction of perchlorate by the Ni(II) center in the complex. The protonated amino group of the pendant arm has been proposed to bind perchlorate and position it in close proximity to the reducing agent, Ni(II) ion in this case. This process has been observed in the mononuclear Ni(II) species $[Ni(H_2(\mathbf{49})(ClO_4)]^{3+}$, where the overall process results in chloride ion formation and the *trans*-dichloro Ni(III) species $[Ni(H_2(\mathbf{49})Cl_2](Cl)(ClO_4)_2{\cdot}2H_2O$ has been structurally characterized [63]. The binuclear complexes of 6,6′-C-spirobi(cyclam), particularly the heterobinuclear Ni(II)–Cu(II) complex, exhibit similar redox activities under appropriate conditions. Even in the absence of di-oxygen, in the presence of perchlorate ions, H^+ and a coordinating anion, slow formation of Ni(III) species can be observed by EPR techniques. Similar reactions were also observed in the case of $[Ni_2(6,6'\text{-C-spirobi(cyclam)})]^{4+}$ in CH_3NO_2 medium. However, in this case, the process was extremely slow.

A common structural feature found in all these complexes is a strong perchlorate ion binding site (an ammonium group, a Cu(II) or even a Ni(II) ion) in the proximity of a Ni(II) center. The model for this behaviour is considered to be neighbouring group participation, where proximity of a reagent site or a lone pair of electrons enhances intramolecular reactions. Although the final product of reduction is chloride in all cases of 6,6′-C-spirobi(cyclam) complexes, ClO_2 has been detected by EPR as an intermediate during the overall reaction in the formation of the Ni(III) species $[Ni(H_2(\mathbf{49})Cl_2](Cl)(ClO_4)_2{\cdot}2H_2O$. An intriguing feature of these systems is that nickel(II) is the metal ion reductant. In these species, like the peroxide oxidation of nickel(II) cyclam described above, the formation of a nickel(III) center, stabilized by a strong ligand field, may be the important feature in the process. In general, owing to the high redox potentials of the Ni(III) ions in aqueous media, the final products observed are the corresponding Ni(II) complexes.



$[Hg_3(\mathbf{50})]^{6+}$



$[Cu_3(\mathbf{51})]^{6+}$

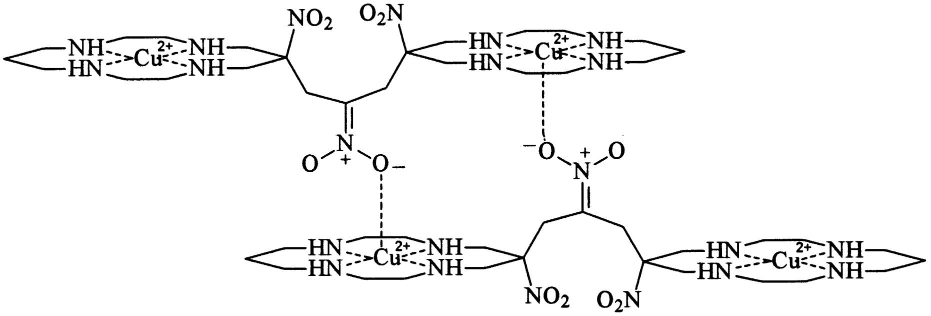
5. Complexes incorporating covalently-bound cyclam units

There are at least two reports presented [64,65] of covalently bound triscyclam ligands. Recently, a tris(cyclam) (**50**) based on 1,3,5-trimethylenebenzene has been prepared and its Hg^{2+} complex has been used as a molecular recognition agent for tris(histidine). A Cu(II) ion directed synthesis of 2,4,6-tris(6-azacyclam)triazine (**51**), together with a crystal structure, has been reported by Bernhardt and Hayes [65]. While all other structural parameters are not unusual, the structure reveals that two of the three macrocyclic units are on the same side of the aromatic triazine ring, while the other is on the opposite side, thus exhibiting a *syn*, *syn*, *anti* conformation with Cu–Cu distances of 7.97, 9.36 and 9.45 Å. Molecular mechanics calculations have indicated that in terms of energy (less than 2 kJ mol^{-1}) this isomer does not differ significantly from the *syn*-, *syn*-, *syn*-isomer. The existence of the former conformation in solution is also evident in the electrochemical behaviour of this complex. Voltammetry studies in CH_3CN have indicated two waves, one at -1.14 V (vs. $Fc^{0/+}$) with 1e characteristics and one at -1.35 V with 2e characteristics, unlike the three waves (or a single wave depending upon the extent of electrostatic interaction) anticipated for the all *syn* conformation. although the EPR spectrum is qualitatively identical to a mononuclear species, investigations are underway to study the nature of magnetic interactions between the copper.

6. Supramolecular chemistry

Cyclam, its derivatives and their complexes are excellent supramolecular synthons [66]. Numerous reports exist in the literature that demonstrate the extensive variety of structures possible with simple cyclam salts [67] and their complexes [68–70]. Recent studies indicate that derivatives of complexes of cyclams are also interesting supramolecular synthons [71].

All of the bi- or bis(macrocycles) described in this review so far are linked covalently either directly through a C–C bond or through a bridging group. Strategically designed macrocycles and their complexes can be assembled on a metal ion template through coordinate bonds. Unlike covalently linked macrocycles, such supramolecular assemblies are interesting in that they can be assembled reversibly and also a variety of metal ion templates can be used.

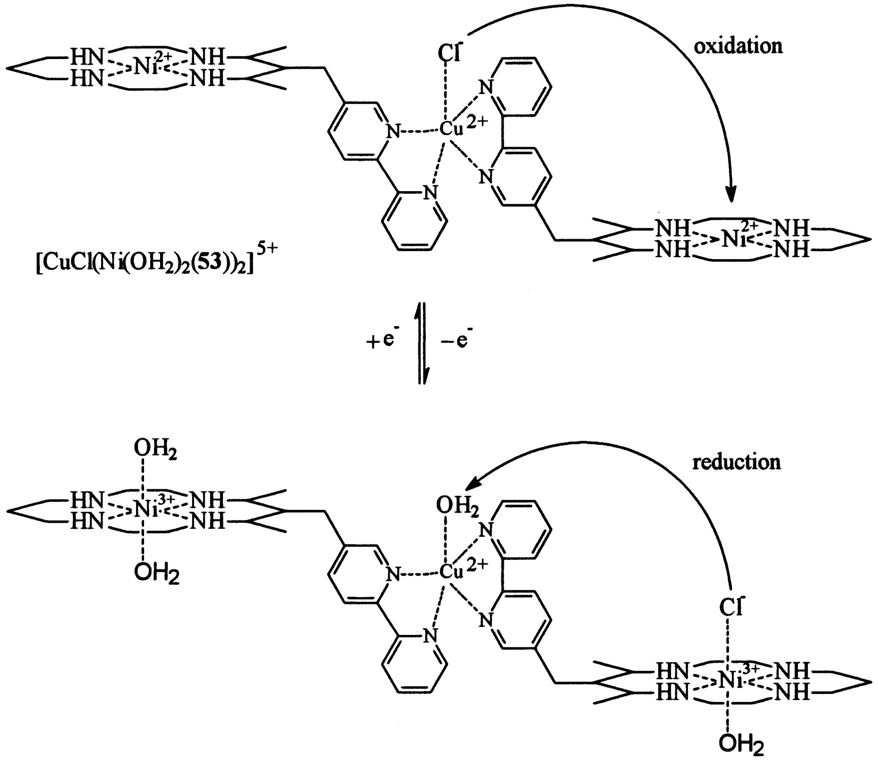


Dimer of $[Cu_2(\mathbf{52})]^{4+}$

This strategy, is particularly interesting for the formation of homo- and heteromultinulcear complexes.

In a remarkable one-pot synthesis, Bernhardt and Jones [72] have formed a binuclear Cu(II) cation $[Cu_2(\mathbf{52})]^{4+}$, in which two cyclam rings are bridged by a $-CH_2C(=NO_2)CH_2-$ group. This complex, which was synthesized by reacting 2,3,2-tet (1,4,8,11-tetraazaundecane), $Cu(II)(NO_3)_2 \cdot 3H_2O$, formaldehyde and $K_2(CH(NO_2)CO_2)$ in aqueous solution spontaneously self-assembles to form a dimeric tetranuclear species in the solid state. The crystal structure of this tetranuclear complex has been determined, the inter-metal ion distance in the dinuclear unit being 11 Å. A model used for simulation of the solution EPR spectrum of this complex indicates that the species exists as discrete dinuclear units in solution and the macrocylic planes are twisted by 80°. This value is 30° more than the twist angle observed in the tetranuclear assembly, suggesting that during the formation of the dimeric tetranuclear species, the solution structure is perturbed. However, the inter-metal ion distances calculated by this model agree with the value observed in structural studies.

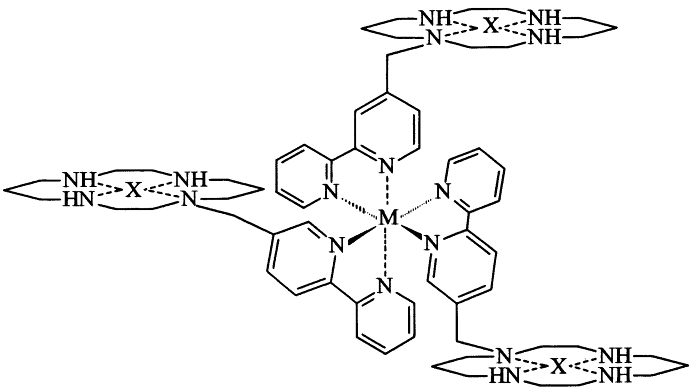
Fabbrizzi et al. [73] have described a 2,2′-dipy substituted in the C(6) position of cyclam analogue **53** that has been assembled on a Cu(II) ion to form a bis(macrocyclic) structure with two Ni(II) and a –[Cu(II)(dipy)$_2$]– bridging unit that shows redox dependent *trans*-location of an anion that is axially coordinated to the metal ions. In the reduced state, the Ni(II) ions are square-planar and the Cu(II) ions are penta-coordinate with an axial anion. As has been shown by electrochemical techniques, upon oxidation to Ni(III), this anion on the Cu(II) axial site is *trans*-located to the Ni(III) sites, which prefers the octahedral geometry. The anions studied include Cl^-, NCS^-, N_3^-, NCO^- and NO_3^-.



$[CuCl(Ni(OH_2)_2(53))_2]^{5+}$

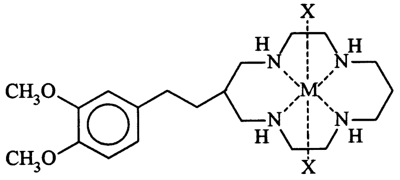
$[Cu(OH_2)(Ni(OH_2)_2(53))(NiCl(OH_2)(53))]^{7+}$

A *N*-(dipy) substituted cyclam (1-(2′,2″-bipyridyl-5′-yl-methyl)-1,4,8,11-tetraazacyclotetradecane) (**54**) and its complexes have been shown to form tris(cyclam) type supramolecular structures templated on Fe(II) or Ru(II) [74]. In this study, the ability of the metal ions to choose binding sites (cyclam or dipy units) preferentially has been exploited to form either mono- or hetero- bi-, tri- and tetranuclear complexes, and their photochemistry has been investigated using laser flash photolysis.

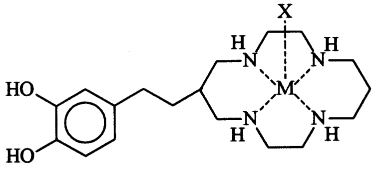


$[M(M'(\mathbf{54}))_3]^{8+}$ M = Ru(II) or Fe(II)
M' = Ni(II), Cu(II), Zn(II)

Recently, a (3,4-dimethoxy phenylethyl) substituted in the C(6) of cyclam [75] has been synthesized using Tabushi's cyclisation method [26], and the corresponding Ni(II) and Cu(II) complexes $[M(\mathbf{55})]X_2$ ($M = Cu(II)$, Ni(II); $X = Cl^-$, Br^-, ClO_4^-) have been studied.



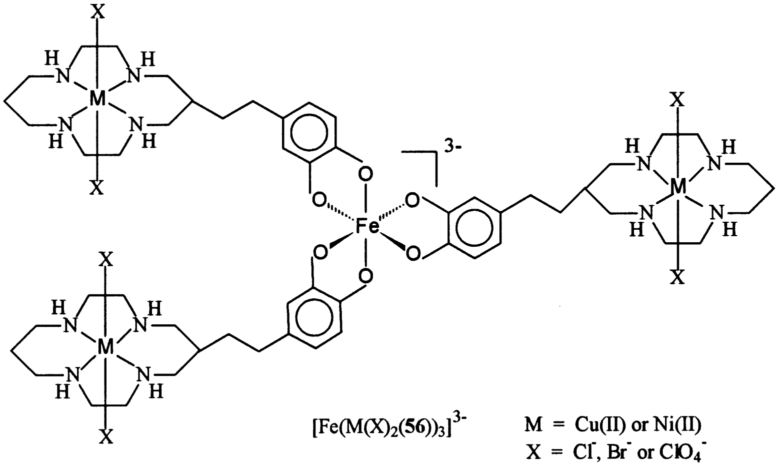
$[M(X)_2(\mathbf{55})]$



$[M(X)(H_2(\mathbf{56}))]^+$

M = Ni(II) or Cu(II)
X = Cl^-, Br^- or ClO_4^-

Also, these metal complexes have been demethylated using BBr_3 and the corresponding catechol appended complexes $[M(H_2(\mathbf{56}))]X_2$ ($M = Cu(II)$, Ni(II); $X = Cl^-$, Br^-, ClO_4^-) have been obtained. The crystal structures of $[Cu(Br)_2(\mathbf{55})]$ and the catecholate complex $[Cu(Br)(H_2(Br\text{-}\mathbf{56}))]Br{\cdot}H_2O$, where $H_2(Br\text{-}\mathbf{56})$ is the bromo derivative of $H_2(\mathbf{56})$, have been determined.



$[Fe(M(X)_2(\mathbf{56}))_3]^{3-}$ M = Cu(II) or Ni(II)

X = Cl^-, Br^- or ClO_4^-

In both complexes, the Cu(II) ion is within the macrocyclic cavity with an average Cu–N distance of 2.01 Å. In $[Cu(Br)_2(\mathbf{55})]$, the Cu(II) is pseudo-octahedral, with Cu–Br(1) = 2.9996(3) and Cu–Br(2) = 2.925(3) Å, whereas in $[Cu(H_2(Br\text{-}\mathbf{56}))Br]Br{\cdot}H_2O$, the Cu(II) is square-pyramidal with a Cu–Br distance of 2.904(2) Å. In $[Cu(Br)_2(\mathbf{55})]$, the ethylene bridge that links cyclam to the aromatic group adopts a *cisoid* conformation. However, in $[Cu(H_2(Br\text{-}\mathbf{56}))Br]Br{\cdot}H_2O$, the ethylene bridge adopts a *transoid* conformation, probably due to the bulky bromine atom on the aromatic ring.

The Fe(III) templated formation of the tris-catecholate species $[Fe(M(Br)_2(\mathbf{56}))_3]^{3-}$ has been studied by UV–vis and EPR spectroscopy. UV–vis bands characteristic of tris-catecholate Fe(III) complexes [76,77] were observed. Also, EPR signals consistent with the FeO_6^{3-} moiety were observed ($g = 4.367$, 4.118, 3.805 and 2.067 (Cu(II)) when M = Cu(II) and $g = 4.396$, 4.114 and 3.828 when M = Ni(II)), suggesting $S = 5/2$ for the Fe(III) ion [76]. Further studies are in progress.

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