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COMPLEXES OF TRIDENTATE AND PENTADENTATE MACROCYCLIC LIGANDS

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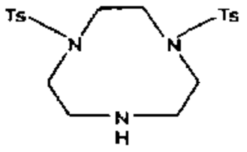
A. INTRODUCTION

Rangoon, Burma, and Calcutta, India, are somewhat unlikely places to begin a review of the chemistry of tridentate and pentadentate macrocyclic complexes. However, in 1937 Peacock and Gwan reported from Rangoon the preparation of the first triaza macrocyclic compound 1,4-ditosyl-1,4,7-triazacyclononane, **1**, [1]. This was not the first report of a tridentate macrocycle, however, as Ray, working in Calcutta, 17 years earlier had reported the preparation of 1,4,7-trithiacyclononane, **2**, [2] although subsequent workers have failed to repeat this synthesis. Pentadentate macrocyclic molecules did not make their appearance until 1964 [3]. In a review of ligand synthesis published in this journal in 1972, Black and Hartshorn [4] cited just two examples of tridentate and two pentadentate macrocyclic ligands. As this review will show, the number of examples known has expanded considerably since that time and ligands of this type have developed from laboratory curiosities into molecules which show considerable potential for practical development. There have been many reviews [5–18] and books [19–22] published on the preparation and chemistry of macrocyclic ligands and their complexes. These works, particularly when dealing with transition metal complexes, have emphasized the chemistry of tetradentate macrocycles. This is the first comprehensive review to concentrate on the chemistry of both tridentate and pentadentate macrocycles, although reviews in Japanese on tridentate macrocycles have been published [23–25]. As this review was about to be submitted, an excellent review by Chaudhuri and Wieghardt on the chemistry of [9]aneN$_3$, **3**, and 1,4,7-trimethyl-1,4,7-triazacyclononane, **4**, and their metal complexes appeared [26].



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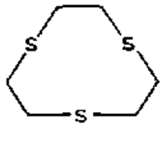

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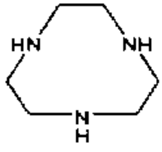

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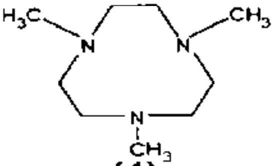

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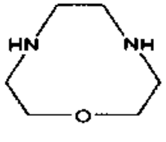

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There are many similarities between the chemistry of tridentate and pentadentate macrocyclic complexes and the chemistry of tetradentate macrocyclic complexes but there are also important differences. All three types of macrocycles show the enhanced stability of the metal complexes of these ligands compared with straight-chain ligands, the so-called "macrocyclic effect" [27]. Even when bound to labile metals, tetradentate macrocycles are generally inert to substitution of the macrocycle, the ligand dissociating only slowly in acid solution. Tridentate macrocycles are usually also inert in this way but pentadentate macrocycles are much more labile. Most tridentate macrocycles coordinate to metal ions so that they occupy three facial sites on the coordination sphere of a metal whereas tetradentate ligands usually occupy four planar coordination sites. Bridged dimeric complexes are common with tridentate macrocycles but such species are rarely formed with tetradentate macrocycles. Pentadentate macrocycles may adopt a variety of coordination modes; one important class of pentaaza macrocycles coordinates in a planar fashion so that pentagonal bipyramidal complexes are formed (cf. Section D(i) (b)).

Because of the extent of this area of coordination chemistry, we have tried to concentrate exclusively on the tridentate and pentadentate macrocycles and will make comparisons with tetradentate macrocycles only when absolutely necessary. Discussion is restricted to ligands containing nitrogen, oxygen, sulphur, phosphorus and arsenic donor atoms. Ligands containing only oxygen donor atoms (the crown ethers form the majority of such ligands) have been excluded from this review. Excellent reviews have been published on the chemistry of the crown ethers [20,28,29].

Whereas many complexes of interest to this review are prepared by template methods, the major advances in the chemistry of these complexes have followed the development over the last 15 years of efficient methods of macrocyclic synthesis. Section B therefore deals with the preparation of the macrocyclic ligands. Section C considers complexes formed by tridentate macrocycles and Section D considers complexes of pentadentate macrocycles. Section E is concerned with some of the properties of macrocyclic complexes which are common to both classes of ligands and to other macrocycles. Section E also includes a discussion of complexes of macrocyclic ligands which contain pendent arms, a rapidly developing area of interest. We have chosen to include in that discussion those macrocycles which are tridentate or pentadentate within the macrocyclic ring; coordination of the pendent-arm donor groups means that the denticity of the ligand is higher. It could be argued that the ligands to include in this review are those with a total denticity of three and five. Tridentate molecules of that type are not known and tetradentate macrocycles with one pendent arm have been reviewed recently [30,31].

The nomenclature of macrocyclic ligands is a difficult topic in a review of this kind as the systematic names of the ligands are extremely cumbersome. A number of different shorthand nomenclatures have been proposed for particular types of ligands but even these can become unwieldy with substituted ligands. We shall largely avoid the issue by using the system proposed initially by Busch [32]. We shall use this system only for the simple macrocycles and shall use numbered structural formulae for the more complex examples and shall refer to such ligands by their numbers. Using

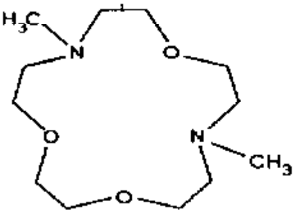
Busch's system, 1,4,7-trithiacyclononane, **2**, is [9]aneS_3, 1,4,7-triazacyclononane, **3**, is [9]aneN_3, 1,4,7-trimethyl-1,4,7-triazacyclononane, **4**, will be called Me_3[9]aneN_3 and 1-oxa-4,7-diazacyclononane, **5**, is called [9]aneN_2O. This review is intended to be comprehensive within the above boundaries and includes work published up to the end of 1986. A few references are made to papers published in 1987. If we have by oversight omitted contributions from some laboratories, we offer apologies to the workers concerned and to our readers.

B. LIGAND PREPARATION

This section concentrates on the preparation of all-nitrogen, all-phosphorus, all-arsenic and all-sulphur donor macrocycles and ligands containing a mixture of these atoms. Excellent reviews of the preparation of aza macrocycles by non-template methods have been published [8,15,22,28,29, 33–35] and the review by Gokel et al. [8] and book by Gokel and Korzeniowski [20] are particularly recommended. Macrocycles containing pyridine, furan and thiophene rings have been discussed in detail by Newkome et al. [10,36]. Template methods of macrocycle preparation have been the subject of a number of reviews [37,38]. Mixed aza–oxa macrocycles, the precursors of the cryptates and cryptands have also been the subject of numerous studies [39–42] and reviews [8,12,35,43,44] and so will not be considered except in passing. With few exceptions, all of which involve sulphur, tridentate and pentadentate macrocycles containing oxygen and donor atoms other than nitrogen have not been reported. These exceptions are included in Section B (iii). Discussion of the preparation of the ligands by template reactions will be deferred until the metal complexes are considered because such methods usually produce the metal complex and not the free ligand.

(i) Nitrogen-containing macrocycles

The most generally useful method for the preparation of polyaza macrocyclic ligands and mixed aza–oxa and aza–thia macrocycles was developed by Richman and Atkins [45–47] following the earlier work of Koyama and Yoshino [48]. This method involves the condensation of two halves of the target molecule in a dipolar aprotic solvent, usually dimethylformamide (DMF). One precursor is a salt of a sulphonamide and the other precursor may contain a number of terminal leaving groups such as chloride, bromide or hydroxide but usually sulphonate esters are used. If terminal dihalides are used, high dilution techniques are required for the cyclization [48,49] and there is greater difficulty with the work-up and lower overall yield. Macrocycle formation frequently requires high dilution techniques, and various types of apparatus have been described which simplify and automate the technique [39,50–54]. Two recent reports have described the preparation in good yield of $Ts_3[9]aneN_3$ (Ts = tosyl) and the diazaoxa macrocycle $Me_2[15]aneN_2O_3$, **6**, by different modifications of the Richman–Atkins procedure. Iwata and Kuzuhara have prepared $[9]aneN_3$ by an intramolecular condensation of a molecule containing both sulphonamide and sulphonate groups [55]. $Me_2[15]aneN_2O_3$ was prepared on a solid support of alumina coated with alkali metal fluorides [56]. The reaction is carried out without nitrogen protection. Both methods show considerable promise for future development.



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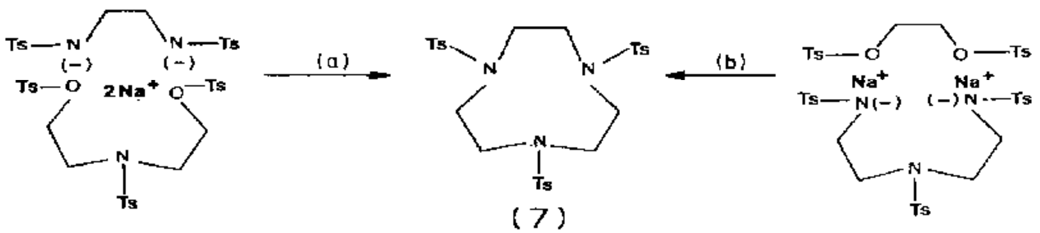
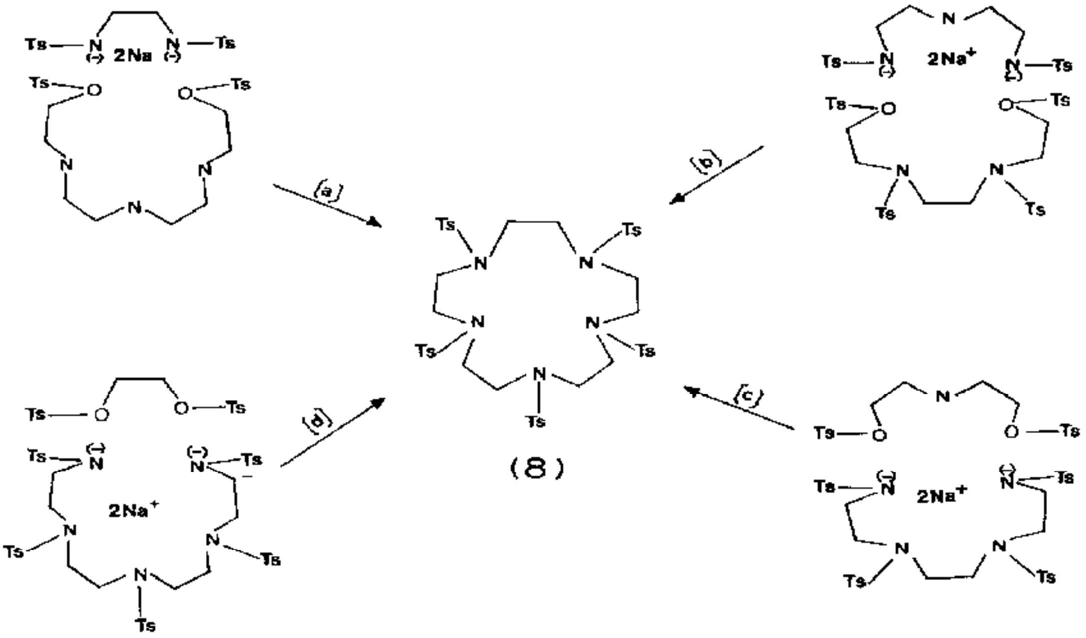
In the Richman–Atkins procedure, sulphonamide ester leaving groups do not require the high dilution technique; indeed, saturated solutions of the reagents appear to give the best yields, probably because the rate of cyclization is increased at higher concentrations and hydrolysis of the sodium salts by trace moisture is less important. This method has been used to produce a wide variety of triaza [48,57], pentaaza [58,59], $[9]aneN_2O$ [60] and $[9]aneN_2S$ macrocycles [61,62] as well as tetraaza, hexaaza, heptaaza and octaaza macrocycles [46,63–65].



Scheme 1.

Usually more than one coupling scheme to produce the same target molecule is possible (see Schemes 1 and 2). Both methods for the production of $Ts_3[9]aneN_3$, **7**, (Scheme 1) have been investigated by Searle and Geue [66] who have shown that lower yields and more intractable byproducts

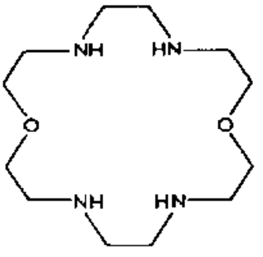


Scheme 2.

result from pathway (a). These lower yields must be due to the inhibition of the initial substitution step, but whether the inhibition is due to less favourable steric factors or to a greater sensitivity to traces of water is not clear. Two of the methods in Scheme 2 (paths (a) and (b)) have been shown to proceed with similar yields of [15]aneN_5, **8**, [67].

The use of precursors of similar length has been suggested as one requirement for high yields in the cyclization step [46]. It is unlikely, however, that both ends of the target molecule couple simultaneously, and once one end has coupled, usually the same intermediate is produced so that no difference in yield is expected from that point onwards. It seems likely therefore that differences in factors such as the relative stability, solubility and sensitivity to water of the different tosylates and sulphonamide salts are the significant factors controlling yield. The choice of preparative method usually depends on the availability and ease of preparation of the precursor diols, amine diols and polyamines. The required amines and diols are usually commercially available, and are tosylated by well-known efficient procedures [48,68–73]. Of the amine diols which have been used, diethanolamine is commercially available and other amine diols are readily synthesized [74]. Two methods for the tosylation of amine diols are in common use; in our experience the use of dichloromethane as solvent and triethylamine as base [59,75,76] is preferable to the use of pyridine in both roles [66,73]. The latter method frequently gives variable yields and intractable oily products.

Preparation of salts of the sulphonamides is straightforward; either sodium ethoxide, sodium hydride, potassium *t*-butoxide, caesium carbonate or potassium phthalimide may be used [63,66,68,75,77–81]. These salts may be isolated but are moisture sensitive and are usually used immediately. The base used may influence the nature of the product obtained. Biernat and Luboch [79] have reported that the preparation of [18]aneN_4O_2, **9**, may be accomplished using K_2CO_3 as the base, whereas if Na_2CO_3 is used [9]aneN_2O, **5**, is obtained. However, Rasshofer et al. report [80] that there is little difference in yield when Na^+ and K^+ salts are used for the directed preparation of [9]aneN_2O. Caesium salts have been used in preparations where the hydrocarbon chain components are long [63,81] and they are also useful for the synthesis of sulphur-containing macrocycles [78,82]. It was originally suggested that ion pairing effects of the Cs^+ ions were important but it has recently been shown that it is the lack of such ion pairs which results in higher yields of the macrocycles [81,83].



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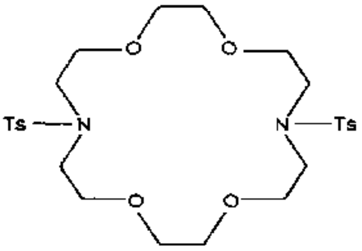
Maximizing the yields of the cyclization reactions appears to be critically dependent on the exclusion of water from the reaction mixture. Careful drying of the solvent and protection of the reaction mixture from atmospheric moisture generally increases cyclization yields.

Products other than the desired macrocycle have been found in the reaction mixture [45,66,84–87]. In addition to straight-chain amines produced by coupling of three or more precursor molecules, macrocycles produced by 2 + 2 coupling of the precursors have been isolated [66,84–86]. The products obtained apparently depend on the mode of coupling. In Scheme 1, reaction (a) is reported to lead to significant amounts of side products whereas reaction (b) gives no side products [64,84]. With methyl-substituted amines and diols the desired triaza macrocyclic products are obtained in small yield, and linear amines are the major products of the reaction [61,87].

Removal of the protecting tosyl groups to produce the ligand requires fairly drastic conditions and can lead to major inefficiencies in the preparation. Acid hydrolysis can be achieved with 97% sulphuric acid followed by treatment with base. This is probably the most widely used detosylation procedure [46,68,75,88–90] but it does not always give reasonable yields [91] and work-up of the resulting solution is difficult. Reductive cleavage of the tosyl group with HBr in acetic acid is the most frequently used alternative method of tosyl removal [48,59,71,87,92,93]. Phenol is sometimes added to the reaction mixture as a bromine scavenger but its presence is not essential. In our experience this method works best (a) when performed with 45% HBr in acetic acid (the lower strength 33% acid is far less satisfactory) and (b) when carried out in sealed tubes at 120 °C. This procedure requires shorter reaction times and a much smaller excess of HBr can be used [59,92]. Other workers have successfully used the reagent under reflux [48,71,94,95] and at room temperature [96–98] but reaction times are longer.

Both the above methods can have disadvantages such as variable yields, incomplete reactions, prolonged reaction times, difficulty of work-up, and occasionally neither method works. Alternative reducing agents that have been used to remove tosyl groups from amines are listed below; not all have been applied to macrocyclic amines and they may not always work [79,91]. For example, sodium naphthalenide in 1,2-dimethoxyethane has been used to detosylate **10** in 76% yield [99] and has been used successfully with linear amines [100] but it did not work either with a tetraazadioxa macrocycle [79] or with pentaaza macrocycles [67]. Electrochemical reductions have been successful [101–103] but seem best suited for small amounts of material. Other reducing agents which have been or could be tried include sodium in liquid ammonia [104,105], sodium in isoamyl alcohol [91,106,107], potassium t-butoxide in tetrahydrofuran (THF) [108], sodium amalgam in Na_2HPO_4-buffered methanol solution [81], lithium in propylamine [109], lithium aluminium hydride [93,110], sodium dihydro-bis(2-methoxy)aluminate [93,111] and alkali metals in hexamethylphosphorustriamide [112].



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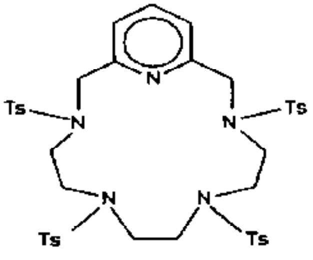
Isolation of the amine or amine salts from the reaction mixture is straightforward although somewhat tedious as solvent extraction, solvent removal and distillation, sublimation or fractional crystallization may all be required [46,59,95]. Chromatographic and electrophoresis methods for determining macrocyclic purity have been described [113–115]. For triaza macrocycles, Searle and Geue [66] have suggested an ion exchange procedure which is simple and achieves good separation of the desired macrocycle from byproducts of the cyclization. Ion exchange may also be used to prepare the free amine from the salts of pentaaza macrocycles [59,66,116].



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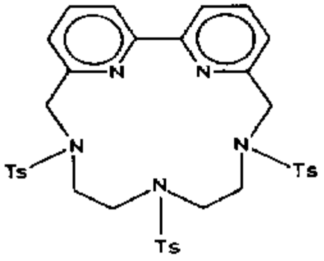

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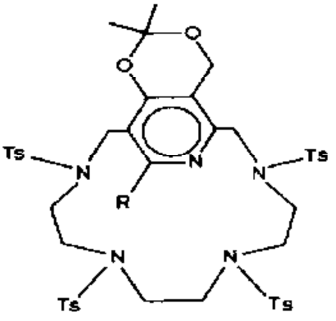

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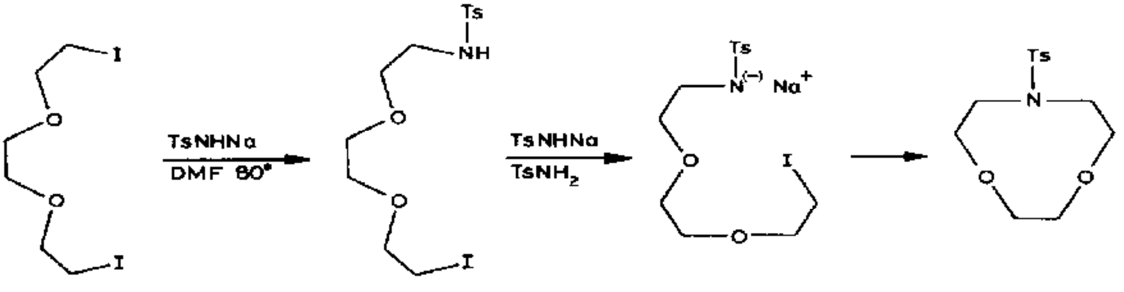
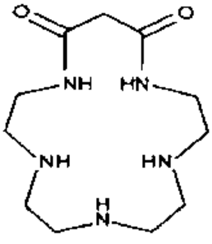
Pentaaza macrocycles **11**, **12** and **13** containing pyridine rings have been synthesized by the Richman–Atkins procedure [117–119]. A modification of the Richman–Atkins method has been used to synthesize mixed-donor macrocycles [120]. This synthesis, outlined in Scheme 3, has the advantage that the reaction proceeds in one pot but the disadvantage that significant amounts of byproducts are formed. Yields have not been optimized, however, and the general approach shows promise.



Scheme 3.

Other methods for the preparation of pentaaza macrocycles have been developed by Kimura and coworkers [121–123] on the basis of an original report by Tabushi and coworkers [124]. This method was originally used to prepare mixed aza–oxa and aza–thia donor macrocycles and uses neither high dilution techniques nor nitrogen protection [123]. Macrocycle production involves refluxing the dimethyl esters of dicarboxylic acids with the polyamine tetraethylenepentamine to produce a variety of ligands which are described in detail in Section D(i) (b), e.g. **14** and **15** [121]. This method has



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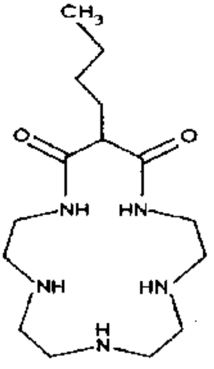

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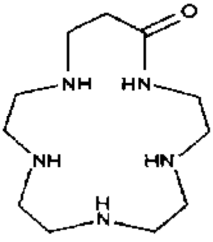

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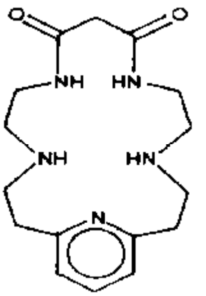

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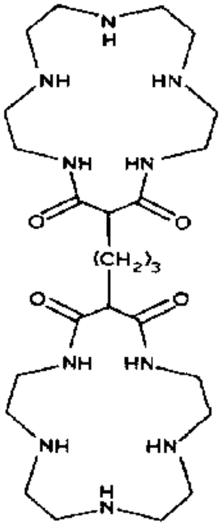

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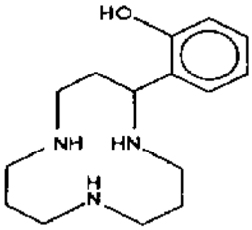
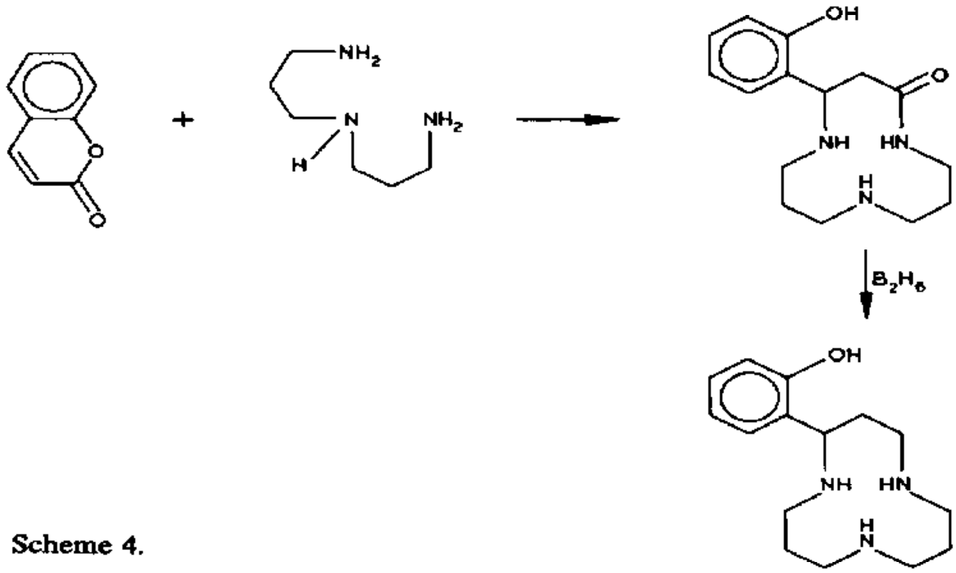


(19)

been extended by Kimura et al. to produce the ligand **16** from methyl acrylate and tetren [121], ligand **17** from 2,6-bis(1,4-diazapentyl)pyridine and dimethylmalonate [121], and ligand **18**, although preparative details have not been reported for **18** [125]. Kimura et al. have used this type of synthesis (Scheme 4) to prepare **19**, a derivative of [12]aneN_3 bearing a pendent phenol group [126].

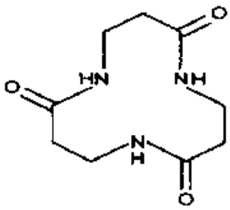
Other triaza macrocycles, **20** and **21**, have been prepared by the condensation of acrolein and ammonia [127] or by methacrylamide polymerization [128]. However, no details of any metal complexes of these molecules have appeared.

Recently, interest has been shown in developing the synthesis of selectively protected macrocycles in order to functionalize the macrocycle at a later synthetic step [77,108,129–134] and this area has been reviewed with an



Scheme 4.

emphasis on tetraaza macrocycles [30,31,135]. The ditosylate of [9]aneN_3, **1**, is readily prepared from [9]aneN_3 [129] and has been used to prepare the bis macrocycles **22** and **23**. Another route to the preparation of the ditosylate of [9]aneN_3 has been described by Martin et al. [108] and the same paper describes 4-benzoyl-1,7-bistosyl derivatives of [9]aneN_3, 1,4,7-[11]aneN_3 and 1,4,7-[13]aneN_3.



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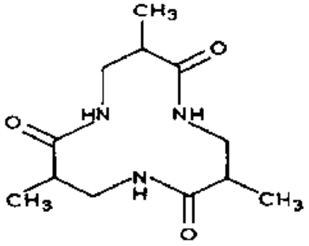

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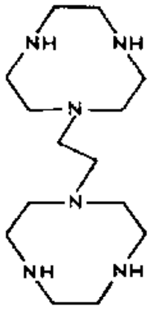

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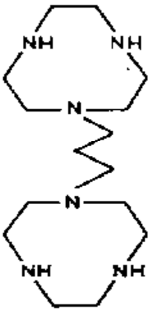

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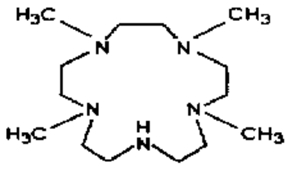

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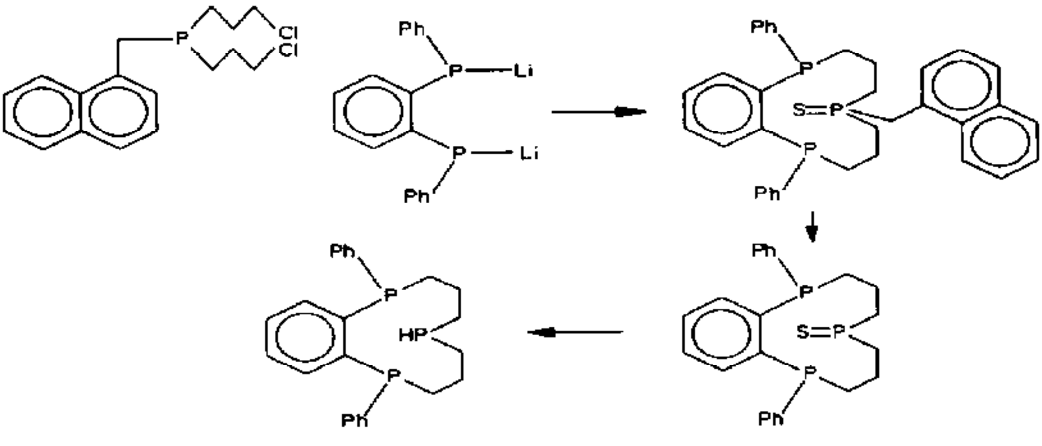
[15]aneN_5 has been selectively protected by cyclizing the tosyl derivative of triethylenetetramine with the mesylate of diethanolamine. Removal of the tosyl groups with sulphuric acid yields the monomesylate; methylation of the N–H groups using formaldehyde and removal of the mesyl group via reductive cleavage gave **24** [132]. Recent reports [96,136] on the selective protection of amines suggest some of the ways in which future advances in this area might be made.

(ii) Phosphorus- and arsenic-containing macrocycles

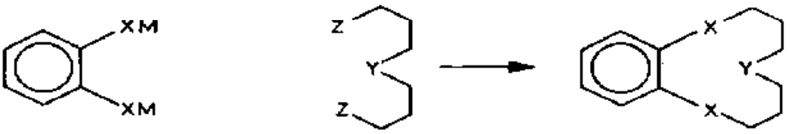
Macrocyclic ligands containing phosphorus donor atoms were first reported in 1975 [137] and an arsenic-containing macrocycle was reported in 1980 [138]. Whereas a considerable number of different tridentate macrocycles containing both phosphorus and arsenic are now known, largely owing to the efforts of Kyba and coworkers [139–141], only two pentadentate macrocycles containing phosphorus as a donor atom in the ring have been reported [142] and these were prepared via a template reaction described in Section D (i) (d). Very recently, mixed aza–phospha and oxa–phospha macrocycles have been prepared [143] but these macrocycles contain more than five donor atoms. There are many problems with the preparation of macrocyclic ligands containing phosphorus and arsenic owing to their sensitivity to air, the difficulty of obtaining the precursor molecules and the lack of suitable protective groups for these elements. A report describing the use of the 1-naphthylmethyl moiety as a protective group for the secondary phosphino group is therefore of great interest (Scheme 5) [144]. The preparation of phosphorus- and arsenic-containing macrocycles is, however, likely to continue to require elegant and elaborate synthetic



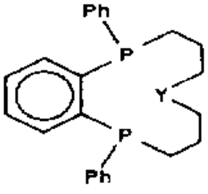
Scheme 5.

efforts to form the precursors and the use of high dilution techniques to assemble the macrocycle.

Kyba and coworkers have described [54,55,138–141,144–149] the preparation of approximately 20 different macrocycles of the type **25**–**27** using a variety of preparative methods outlined in Schemes 5 and 6. Full details of the nature of these ligands are given in Section C (iii). Crystal structures of three of these macrocycles have been determined [139]. Molecules of the type **25** and **26** may exist in a number of different isomeric forms depending on the nature of the group Y. If Y = PPh or AsPh, there are three isomeric forms, two *meso* isomers and one DL pair. If Y = O or S, two isomers exist, one *meso* and one DL pair. If Y = N–R, then there are in principle three isomers but rapid inversion about the nitrogen results in only two forms which can be isolated. The only isomers isolated with **25** and **26** have the phenyl and methyl groups in a *cis* relationship to the benzene ring, but with the ligand **27** a mixture of *cis* and *trans* isomers was obtained. With **26** (Y = PPh or AsPh) two isomers have been isolated [138–140] and have been identified as the *meso-cis* and *meso-trans* forms of the ligand. *Meso-trans* forms of the molecules are not able to act as tridentate ligands (they are bidentate) but the *meso-cis* forms are tridentates although they may not always act as such. Compound **27** has only been observed to act as a bidentate ligand [138] and both **25** and **26** with Y = NPh are bidentate [149].



Scheme 6.



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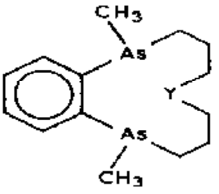

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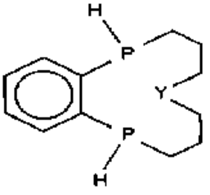

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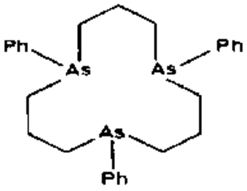
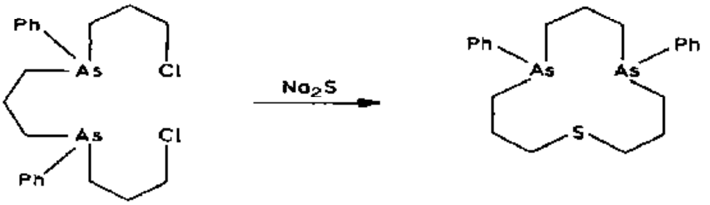


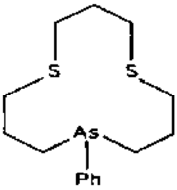
(28)

Kauffmann and Ennen [150,151] have prepared $Ph_3[12]aneAs_3$, **28**, containing three arsenic donors, and it has been shown to be a mixture of two isomers which could not be separated. A thiadiarseno macrocycle **29** has been prepared [152] via the following reaction:



(29)

A similar high dilution reaction has been used to produce the molecule **30** in 31% yield [152,153].



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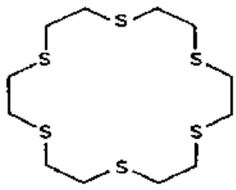
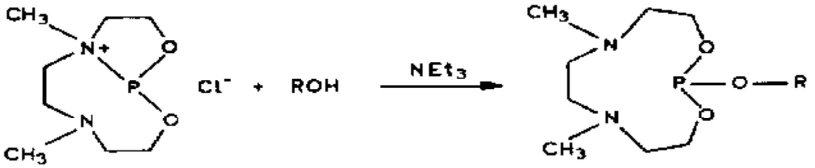


(32)

N_2P macrocycles, **31**, have been prepared by the reaction



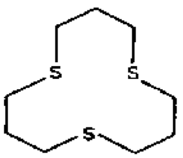
(31)

R = Me, Et, sec-Bu,
(S)-(−)-2-methyl-butyl
and menthyl

and Rh(I) complexes with these ligands have been prepared [154].

(iii) Sulphur-containing macrocycles

Synthesis of macrocyclic sulphides has been the subject of considerable interest and challenge to synthetic organic chemists and a number of reviews have appeared [155,156]. Ray [2] was the first to report the synthesis of [9]aneS_3 but subsequent workers failed to reproduce the reported results and instead, the [18]aneS_6, **32**, macrocycle was obtained [157,158]. In 1970 Rosen and Busch [159] reported the preparation of [12]aneS_3, **33**, in 3% yield using the reaction between a deprotonated dithiol and a dihalide. Very careful work was subsequently undertaken by Ochrymowycz and coworkers in attempts to prepare a wide variety of macrocyclic thioethers by the same type of reaction used by Busch [157,160]. The yields were originally unsatisfactory ([9]aneS_3 was obtained in only 0.04% yield). Subsequent preparations using quaternary ammonium salts instead of sodium salts of the thiols resulted in yields of 4.4% and 2.4% for [9]aneS_3 [161,162]. [18]aneS_6 was isolated from the same reaction mixture in 32% yield [161]. Use of caesium carbonate as base results in a 21% yield of [9]aneS_3 [163,164]. A template reaction between the coordinated deprotonated thiol and 1,2-dibromoethane has been reported to give [9]aneS_3 in 60% yield [165,166].



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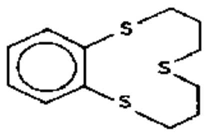

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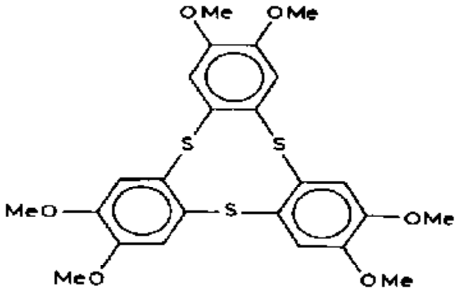


(35)

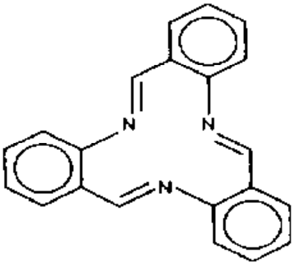
Kyba et al. [139] have reported the preparation and crystal structure of the molecule **34** but to date no complexes of this ligand have been reported. Molecule **35** is prepared by the reaction between the dithiol, bis(2-mercapto-4,5-dimethoxyphenyl)sulphide and the dibromide, 1,2-dibromo-4,5-dimethoxybenzol in the presence of Cu_2O [167]. This molecule exists in a solvent- and temperature-dependent equilibrium of two conformations, a saddle conformation isolated from benzene [168] and the crown conformation isolated from chloroform [169]. The crystal structure of the saddle form of the molecule has been reported [168].

Mixed sulphur–nitrogen macrocycles have been prepared by methods already discussed [62,78,122,123]. Mixed sulphur–oxygen macrocycles may be prepared by reactions either between oligoethylenedichlorides and dimercaptans or sodium sulphide in base [170,171] or between oligoethyleneglycol derivatives and the sodium salt of dithioethene [170–172]. Substituted sulphur macrocycles have been prepared via a bromoalkoxylation reaction of olefins [174]. Buter and Kellogg [82,175] have reported that the yields of thiaoxo macrocycles are significantly improved by the use of caesium carbonate to deprotonate the thiol. Corfield et al. have used the $CsCO_3$ method to prepare [15]aneS_5 in a much improved yield of 52% [176]. The preparation of these molecules has been reviewed [28,155] and more recently summarized [82,174] and will not be discussed further.

C. TRIDENTATE MACROCYCLIC COMPLEXES

(i) Complexes of [X]aneN$_3$ ligands

[9]aneN$_3$, **3**, its *N*-trimethyl derivative Me$_3$[9]aneN$_3$, **4**, and the ligand tribenzo[*b*, *f*, *j*][1,5,9]triazacyclododecane, **36**, are the ligands which form the most commonly studied triaza macrocyclic complexes. Complexes of [9]aneN$_3$ and Me$_3$[9]aneN$_3$ have recently been reviewed by Chaudhuri and Wieghardt [26], and Section C (i) (a) and in particular Section C (i) (b) have been abbreviated as a consequence of the publication of that review. Chaudhuri and Wieghardt have described the chemistry of these complexes in more detail than is attempted here. The ligands **3**, **4** and **36** are similar in that coordination to a metal results in three facial positions of an octahedron being occupied by the ligand. Properties of these complexes have features in common, for example, most are very resistant to acid attack, being stable in concentrated acid. Complexes of **36**, which is formed by a template reaction, are considered in Section C (ii), and complexes of the other two ligands are discussed below. The crystal structure of the monoprotonated form of Me$_3$[9]aneN$_3$ has been reported and the acid–base properties of the ligand, particularly the high pK_1 value, have been explained in terms of the hydrogen bonding observed in the crystal structure [177].



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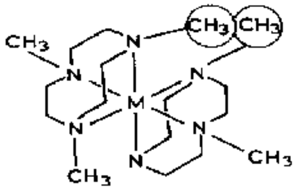

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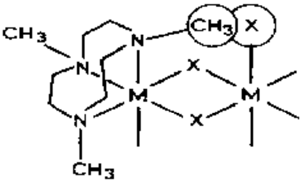
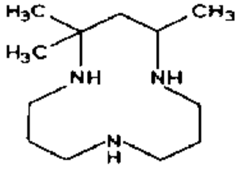


(38)

[9]aneN$_3$ and Me$_3$[9]aneN$_3$ differ in that metal ions are able to coordinate only one Me$_3$[9]aneN$_3$ ligand, and binuclear complexes in which two octahedra share an edge are not observed. This is because the methyl groups interfere with the steric demands of other ligands attached to the same or the other metal atom as shown in **37** and **38**. Binuclear complexes in which two octahedra share a face or a corner are possible for Me$_3$[9]aneN$_3$ and such complexes are common. Therefore [9]aneN$_3$ and Me$_3$[9]aneN$_3$ may form different complexes under the same experimental conditions and the properties of complexes with the same formulation can differ considerably. For example, both ligands form a Co(III) tris(μ-hydroxy)-bridged complex, $\{Co_2L_2(\mu\text{-}OH)_3\}^{3+}$. The [9]aneN$_3$ complex reacts rapidly with acid to give a

bis(μ-hydroxy)-bridged species $\{L(H_2O)Co(\mu\text{-}OH)_2Co(H_2O)L\}^{4+}$ [178]. Me$_3$[9]aneN$_3$ is unable to form bis(μ-hydroxy)-bridged complexes and so the tris(μ-hydroxy)-bridged complex does not react rapidly with acid [179].

Many triaza macrocyclic ligands with ring sizes greater than nine have been prepared and complexes of these ligands are also considered in this section. As the macrocyclic ring size is increased, the steric demands of the macrocycle may determine the type of complex formed. Co([12]aneN$_3$)$_2^{3+}$ complexes have not been isolated and this has been attributed to steric effects similar to those observed with Ni([9]aneN$_3$)$_2^{3+}$ [48,180]. If the size of the macrocyclic ring is greater than 12, the macrocycle may block one of the remaining coordination sites and five-coordinate complexes become common [57,181–183]. A similar effect is observed with complexes of the ligands Me$_3$[12]aneN$_3$, **39**, Me$_3$[12]eneN$_3$, **40** and Me$_4$[12]eneN$_3$, **41**, where a methyl group blocks one coordination site [184–186]. Triaza macrocycles with ring sizes smaller than 13 usually coordinate metal ions in a facial manner. If the macrocyclic ring is larger than 15, the nitrogen atoms are able to occupy three of the coordination sites of a square-planar complex, and such complexes have been observed with Pt(II) [187].



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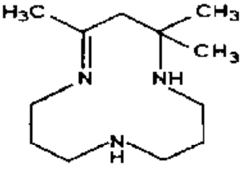

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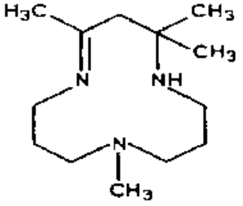
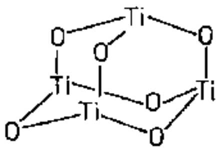


(41)

(a) First-row transition metal complexes

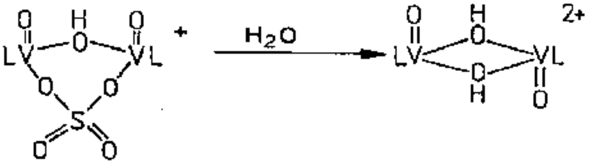
Titanium. Only one complex of titanium with a triaza macrocycle has been prepared, a Ti(IV) complex of [9]aneN$_3$, $Ti_4L_4O_6^{4+}$, with an adamantane-like structure, **42** [188]. Four titanium atoms occupy the corners of a regular tetrahedron and are linked by μ-oxo bridges located above the centre of six edges of the tetrahedron. Each titanium has a distorted octahedral geometry



(42)

with three facially coordinated nitrogen atoms from the amine and three μ-oxo groups. This same structure has been found in In(III) and Mn(IV) complexes [189].

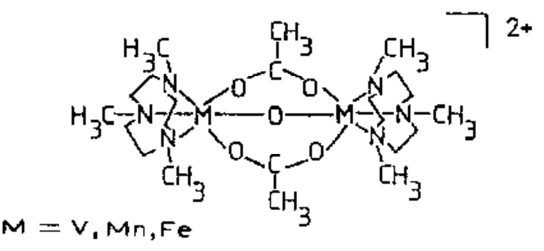
Vanadium. Reaction of $VOSO_4 \cdot 5H_2O$ with [9]aneN_3 in aqueous solution leads to the formation of a (μ-sulphato)(μ-hydroxo)V^{IV} dimer, **43**, which upon recrystallization releases sulphate and forms the bis(μ-hydroxo)-bridged species **44**. A monomeric VO[9]aneN_3(NCS)$_2$ complex has also been isolated



(43) (44)

[190]. Complex **44** has a *trans* disposition of oxo groups and is similar to an Mo(V) oxo-bridged dimer discussed in Section C (i) (b). The bis hydroxo dimer has a temperature-dependent magnetic moment which indicates antiferromagnetic coupling of the metal centres [190]. Exchange interactions in the dimer have been investigated using electron spin resonance (ESR) spectra of powders, frozen solutions and single crystals and contributions of dipole–dipole and exchange interactions to the zero-field splitting parameters have been calculated [191].

V(III) complexes of Me$_3$[9]aneN_3 have been reported [192]. The preparation of monomeric $LVCl_3 \cdot$ DMF under anaerobic conditions and its subsequent reaction in air with excess acetate gives a (μ-oxo)bis(μ-acetato)-bridged dimer, **45**. Magnetic moments of this complex indicate the absence of



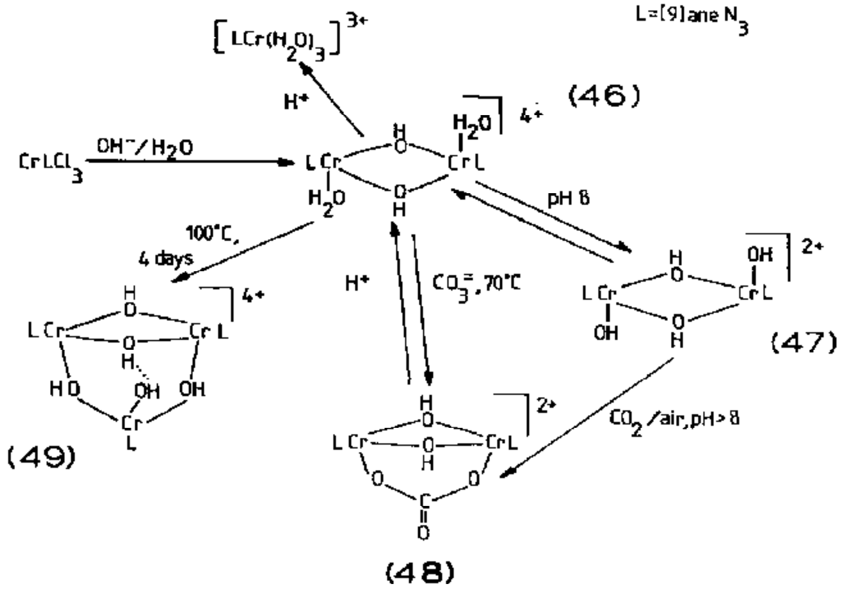
(45)

coupling between the metal centres. Structures of the corresponding Mn(III) [193] and Fe(III) [194] complexes are similar and the crystallographic data for all three complexes have been compared [192].

Chromium. Products formed by reaction of Cr(III) with [9]aneN_3, [12]aneN_3 and Me$_3$[9]aneN_3 are dominated by a propensity of the complexes to form hydroxo bridges. This property is shared by Co(III) and Rh(III), and many of the reactions to be outlined here are common to all three elements.

Pedersen's method for the synthesis of Cr(III) amine complexes [195] has been used to prepare $Cr([9]aneN_3)_2^{3+}$ [196] and $Cr[9]aneN_3(H_2O)_3^{3+}$ [197]. Reaction of $[9]aneN_3$ or $[12]aneN_3$ with $Cr(CO)_6$ leads to the formation of $Cr[X]aneN_3(CO)_3$ in good yield [198,199]. These complexes are stable to moisture and air and react with dilute nitric acid to give nitrosylcarbonyl compounds $Cr[X]aneN_3(CO)_2(NO)^+$. Similar reactions have been observed with molybdenum and tungsten and these are discussed in Section C (i) (b).

$Cr[9]aneN_3(H_2O)_3^{3+}$ is the precursor of a wide variety of dimeric bridged species (Scheme 7). Complex **46** has *trans* stereochemistry [197]; in solution



Scheme 7.

(pH > 8) it is deprotonated in a two-step reaction forming the *trans* hydroxo species, **47**. The intermediate is presumed to be a *trans*-aqua hydroxo complex but it has not been isolated. Cation **46** reacts with carbonate or more slowly with air to form a μ-carbonato complex **48**. Kinetic studies of the acid-catalysed decarboxylation of **48** [200] have shown that the reaction is reversible and that monomeric $Cr[9]aneN_3(H_2O)_3^{3+}$ forms. An analogous Rh(III) complex reacts in an identical manner and kinetic data for both complexes have been compared [200]. A *cis*-aqua-di-μ-hydroxy species has been prepared using a modification of the procedure described above. Values of the equilibrium constants for the two-step deprotonation reaction of the two isomers have been measured and the presence of a transient monohydroxy-bridged species suggested [201]. Attempts to prepare dimeric tri-μ-hydroxo-bridged Cr(III) species analogous to known Co(III) and Rh(III) complexes gave a trimeric Cr(III) species **49**. This complex contains four μ-hydroxo linkages and one terminal coordinated hydroxide which is involved in intramolecular hydrogen bonding to a bridging hydroxo group [197]. With [12]aneN_3, the tri-μ-hydroxy dimer, [12]aneN_3Cr(μ-OH)$_3$-Cr[12]aneN_3^{3+}, has been prepared and the crystal structure of the bromide salt determined. Reaction of this dimer with hydroxide ion to give $L_2Cr_2(OH)_2(\mu\text{-}OH)_2^{2+}$ is rapid and the mechanism of the reaction has been discussed [198].

Me_3[9]aneN_3 reacts with Cr(III) in methanol to give $CrLCl_3$ which in the presence of hydroxide ion forms a tri-μ-hydroxo dimer [179]. The Cr–Cr distance (264.2 pm) in this complex is the shortest known for a dinuclear chromium complex.

Spin-exchange interactions between the chromium atoms in the tri-μ-hydroxy dimer have been the subject of several magnetic and spectroscopic studies. Magnetic susceptibility and ESR powder spectra [202] give comparable values for the spin-exchange coupling constant $2J$ and the magnetic moment is temperature dependent, indicating an antiferromagnetically coupled system. The large J values have been compared with the values obtained for μ-hydroxo and di-μ-hydroxo complexes and molecular orbital theory has been used to explain the J values in terms of superexchange interactions through the three OH bridges. Single-crystal ESR studies [203] have provided information on the contribution of the various spin states to the spin Hamiltonian and on the energy and geometry of the dimer in each spin state. Estimates from ESR spectra of the energy separation between excited states gave values comparable with those obtained from high resolution Zeeman absorption spectra and magnetic circular dichroism (CD) measurements [204]. Exchange coupling constants calculated from the splitting of the energy levels are in very good agreement with the magnetic susceptibility results.

Phosphorescence decay of the Cr([9]aneN_3)$_2^{3+}$ ion has been studied in both N-protonated and N-deuterated complexes in an extension of previous work on Cr(III) amine complexes [205].

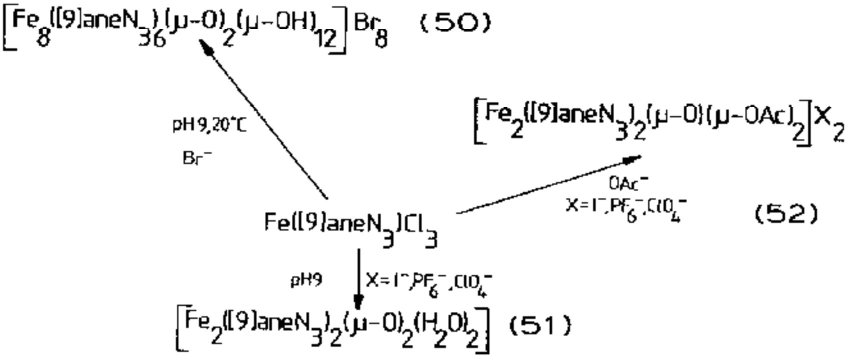
Manganese. Complexes of [9]aneN_3 and Me_3[9]aneN_3 have been prepared with Mn(II) [196,206], Mn(III) [193,206], mixed-valence Mn(III)–Mn(IV) dimers [206] and Mn(IV) [189]. Aqueous solutions of Mn([9]aneN_3)$_2^{2+}$ are relatively stable although they are air sensitive [196]. Cyclic voltammograms of this complex show a highly irreversible oxidation peak at 25 ° C, and only at 3 ° C and at fast scan rates is the corresponding reduction peak observed. Only one Mn(II) complex of Me_3[9]aneN_3 has been isolated; it is dimeric with one μ-hydroxo and two μ-acetato groups [206].

Reaction of [9]aneN_3 and Me_3[9]aneN_3 with Mn(III) acetate at pH 4–5 results in the isolation of the previously mentioned (μ-oxo)bis(μ-acetato) dimers, **45** [193,206]. Magnetic susceptibility measurements show no temperature dependence, indicating that there is no spin–spin coupling between the Mn(III) centres. This is in contrast with other Mn(III) μ-oxo- and μ-acetato-bridged dimers which show strong spin–spin coupling [207–209]. Cyclic voltammograms of these complexes show quasi-reversible one-electron oxidations to mixed-valence Mn(III)–Mn(IV) dimers which are unstable in solution. Irreversible two-electron reductions to monomeric Mn(II) complexes occur at more negative potentials. Subsequent work has shown that the Mn(III) complexes can be oxidized chemically and the crystal structure of a mixed-valence complex has been determined [206].

Reaction of the dimeric Mn(III) complexes with azide or thiocyanate leads to the isolation of $MnLX_3$ complexes (L = [9]aneN_3 or Me_3[9]aneN_3) [210]. The crystal structure of Mn[9]ane$N_3(N_3)_3$ has revealed a tetragonally distorted octahedral polyhedron in which the Mn–N bond distances vary from 191 to 226 pm. Solutions of Mn(III) acetate and Me_3[9]aneN_3 react with ammonium sulphide forming an Mn(II) complex which contains the bidentate S_4^{2-} anion [210].

An Mn(IV) complex formed with [9]aneN_3 in alkaline solution is a tetrameric cluster, **42**, with the oxo-bridged adamantane core described earlier [189]. This complex which is stable in neutral and alkaline solutions has been proposed as a model for the water oxidizing centre in photosynthesis [211]. Magnetic susceptibility measurements are consistent with the spin-only value for Mn(IV) centres. Electrochemical oxidation of Me_3[9]aneN_3Mn^{III} to an Mn(IV) species has been accomplished but this complex is not very stable [206].

Iron. Fe(III) and Fe(II) complexes of [9]aneN_3 and Me_3[9]aneN_3 exist in several different forms, the simplest of which is Fe[9]aneN_3Cl_3 [212]. Reac-



Scheme 8.

tion of Fe[9]aneN_3Cl_3 with $NaNO_2$ in HCl solution gives Fe[9]aneN_3-(NO)$(NO_2)_2^+$ which contains low spin iron. It is possible to reduce this complex electrochemically in acetonitrile solution but the neutral species has not been isolated [213]. Hydrolysis of Fe[9]aneN_3Cl_3 gives rise to a variety of products depending on the reaction conditions [212,214] (cf. Scheme 8).

Product **50** is an octameric cation in which six iron atoms have one bound [9]aneN_3 and the other two iron atoms are surrounded by six oxygen atoms in a distorted octahedral arrangement (Fig. 1). Seven bromide ions are bound to the cation [212]. Products **51** and **52** are formed in the absence or presence of acetate respectively. Dimeric (μ-oxo)bis(μ-acetato) complexes of both [9]aneN_3 and Me_3[9]aneN_3 are of interest as model compounds for the iron centres in the oxygen-transport protein hemerythrin [215–217]. The active site of this protein has been identified as a (μ-oxo)bis(μ-carboxylato)diiron(III) moiety, in which one of the iron atoms is octahedral

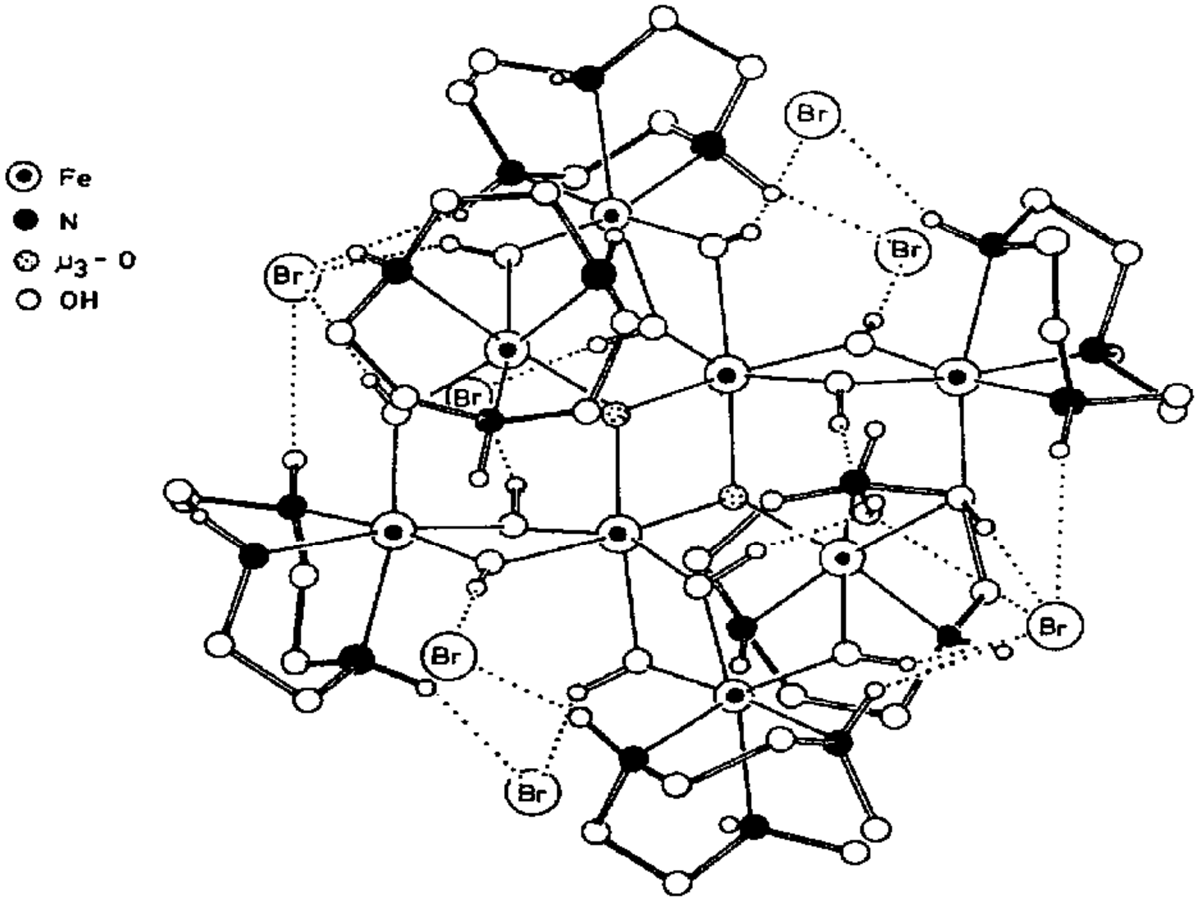


Fig. 1. Structure of the $\{Fe_8([9]aneN_3)_6(\mu\text{-}O)_2(\mu\text{-}OH)_{12}Br_7\}^+$ cation, **50**. Reproduced with permission from ref. 212.

and the other is trigonal bipyramidal. Histidine completes the coordination sphere of the iron atoms [217]. The crystal structure of $Fe_2([9]aneN_3)_2(\mu\text{-}OAc)_2(\mu\text{-}O)^{2+}$ has been determined and the spectral and magnetic properties have been compared with those of the isolated protein [215]. Extended X-ray absorption fine structure (EXAFS) spectra of this complex have shown that the binuclear complex does not have as great a similarity to the spectrum of azidomethemerythrin as other model complexes [218]. Reactivities of both complexes towards azide and thiocyanate anions have been shown to be quite different from that of hemerythrin [219]. Azide and thiocyanate anions react with $[9]aneN_3$, replacing the labile carboxylate bridges with two anions (retaining the oxo bridge), and then with excess of the anion the dimeric species breaks down to a monomeric $FeLX_3$ complex. With $Me_3[9]aneN_3$, monomer formation occurs in one step [219]. The protein molecule reacts with only one azide or thiocyanate ion to retain the $Fe_2(\mu\text{-}O)(\mu\text{-}carboxylate)_2$ structural unit, where the anion binds to one iron(III) centre.

Bis($[9]aneN_3$) complexes of Fe(II) and Fe(III) have been prepared and their visible spectra and electrochemical behaviour determined [196]. Subsequently, the crystal structures of both the Fe(II) and Fe(III) complexes have been reported [220]. Marsh [221] has redetermined the structure of the Fe(III) complex because the incorrect lattice type and Laue symmetry had been used in the earlier investigation. Both complexes are octahedral but exhibit trigonal distortion similar to that observed in the $Ni([9]aneN_3)_2^{2+}$ complex [222].

An Fe(II) complex of $Me_3[9]aneN_3$, $FeL_2(\mu\text{-}OH)(\mu\text{-}OAc)_2$, has been prepared by reaction of $Me_3[9]aneN_3$ with $Fe(ClO_4)_2$ in the presence of acetate ions [194]. This compound has been proposed as a model for the active site of the protein deoxyhemerythrin. Magnetic properties and spectral parameters are quite similar. If this reaction is carried out in the presence of NCS^-, NCO^- or N_3^-, complexes of the composition $[\{FeLX_2\}_2]$ are obtained [214]. The crystal structure of the thiocyanato complex has been determined and the Fe(II) shown to be six-coordinate with one terminal and two bridging thiocyanate groups. Reaction of these complexes with NO gives monomeric $FeL(NO)X_2$ complexes ($X = NCS^-$ or N_3^-) and the structure of $FeMe_3[9]aneN_3(N_3)_2(NO)$ has been determined [213]. In this complex, iron has a distorted octahedral geometry; the Fe–NO moiety is bent and the Fe–N distance is short (173.8 pm). These are the only known iron nitrosyl complexes with a quartet ground state.

Cobalt. Co(III) complexes were the first complexes of $[X]aneN_3$ ligands to be reported. $Co([9]aneN_3)_2^{3+}$, $Co([10]aneN_3)_2^{3+}$ and $Co[11]aneN_3BrCl_2$, were obtained by mixing aqueous solutions of $CoCl_2$ with $[X]aneN_3 \cdot 3HBr$ and

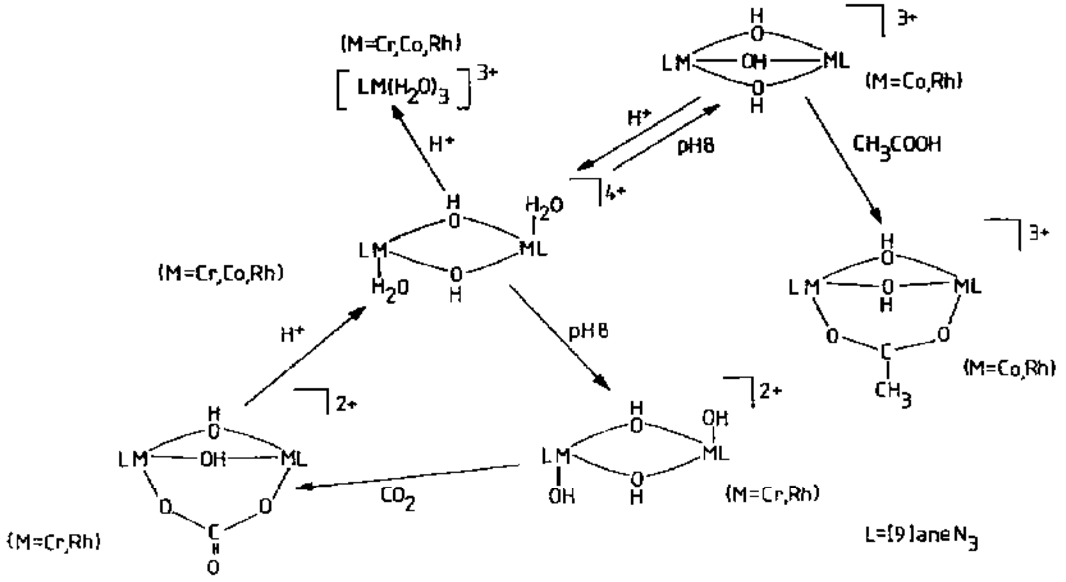
NaOH and oxidizing with air. With [12]aneN_3 the formation of the bis complex was observed in solution but solid complexes could not be isolated. This failure was attributed to steric factors [48]. Geometric isomers of Co([10]aneN_3)$_2^{3+}$ are possible owing to different dispositions (*cis* and *trans*) of the six-membered chelate rings and the *cis* complex is optically active [84,85]. *Cis* and *trans* isomers have been separated and shown to occur in equilibrium in a *trans*:*cis* ratio of 96:4. Force field calculations on the isomers of Co([10]aneN_3)$_2^{3+}$ have been performed and the energy difference between the *trans* and *cis* isomers was calculated to be 9.3 kJ mol^{-1}; the experimental value is 8 kJ mol^{-1} [223].

Co([9]aneN_3)$_2^{2+}$ has been prepared by the Pedersen method [196] and by reduction of Co([9]aneN_3)$_2^{3+}$ with zinc [224]. In Co–N_6 complexes there is an increase in Co–N bond length in going from oxidation state III to II, accompanied by an increase in strain energy of the coordinated amine which results in greater stability of the III oxidation state over that of the II state. Differences in the Co–N bond lengths in the Co(Me[9]aneN_3)$_2^{3+}$ and Co([9]aneN_3)$_2^{2+}$ complexes are small (18 pm compared with a normal value of 25 pm) [224,225]. Thöm et al. [226] have attributed this small difference to H–H non-bonded repulsions (inter- and intra-ligand) which prevent the Co^{3+}–N bond from attaining the strain-free value of 192.5 pm.

Redox potentials of the Co(II)/Co(III) couple for the bis complexes have been determined [196]. Co([9]aneN_3)$_2^{2+/3+}$ complexes are of interest in kinetic studies of redox reactions because both oxidation states are inert to substitution. Rate constants for the reaction between {(*R*)-2-Me[9]aneN_3}{[9]aneN_3}Co^{2+} and {(*S*)-2-Me[9]aneN_3}{[9]aneN_3}Co^{3+} have been measured [224] and these rate constants have been assumed for the self-exchange reaction of the Co([9]aneN_3)$_2^{2+/3+}$ complexes. Deviations from the predicted behaviour in cross reactions between Co([9]aneN_3)$_2^{2+}$ and Co(phen)$_3^{3-}$ (phen = 1,10-phenanthroline) have been investigated [227]. Co([9]aneN_3)$_2^{2+}$ has also been used in electron transfer studies with inorganic redox partners [224,227–229], in the reduction of parsley ferrodoxin and horse heart cytochrome c [229], methemerythrin [230–232].

Co[9]aneN_3(H_2O)$_3^{3+}$ reacts with tripolyphosphate in aqueous solution to form Co[9]aneN_3($P_3O_{10}H_2$)$^{2-}$ and the crystal structure of this complex has been determined. Hydrolysis of the tridentate tripolyphosphate ion is faster than the hydrolysis of uncoordinated tripolyphosphate by a factor of 10^6 [233].

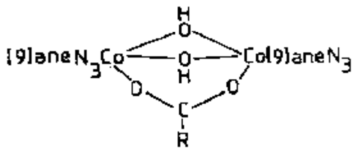
Reactions of Co[9]aneN_3^{3+} complexes to form dimeric species are similar to those of Cr(III), except that the reaction of Co[9]aneN_3Cl_3 with hydroxide ions leads to the formation of a tri-μ-hydroxy-bridged dimer which was not observed with Cr(III) (Scheme 9) [178,196]. A symmetrical di-μ-OH-μ-acetato complex can be formed by reaction of the tris(μ-hydroxy) dimer with



Scheme 9.

complex can be formed by reaction of the tris(μ-hydroxy) dimer with acetate. Rates of formation of the *trans*-aqua-di-μ-hydroxy complex from the tris(μ-hydroxy) dimer in acid media have been measured and the crystal structure of this latter complex determined [178]. A tri-μ-hydroxy dimer of $Me_3[9]aneN_3$ has been prepared [179] and as discussed above, hydroxo-bridge cleavage does not occur in acid solution.

Interesting variations on the di-μ-hydroxo-μ-acetato species are complexes of type **53** with a variety of bridging groups; $Ru(NH_3)_5$(nicotinate) or $Ru(NH_3)_5$(isonicotinate) [234], pyrazine carboxylate [235], *p*-nitrobenzoate [235], pyridine-4-carboxylate [236] and pyridine-2,4,6-tricarboxylate [236].



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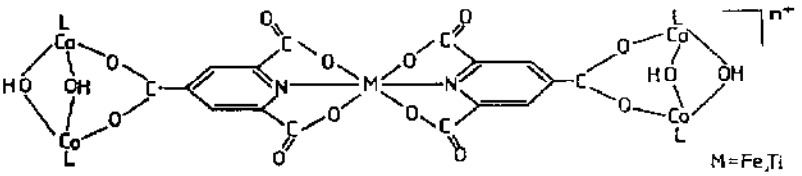

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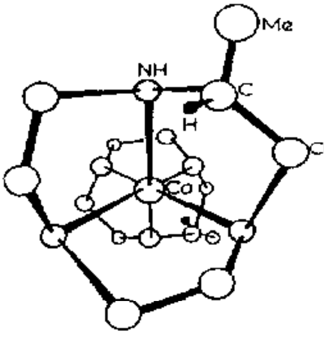
These complexes have been used to study intramolecular electron transfer reactions. Rates of reaction with outer-sphere reducing agents $Fe(dipic)_2^{2-}$ and $Ti(dipic)_2^-$ (dipic = pyridine-2,6-dicarboxylate) were also measured. Reaction of $Fe(H_2O)_6^{2+}$ or $Ti(H_2O)_6^{3+}$ with an excess of the cobalt complex forms a 2 : 1 intermediate, **54**, which is followed by intramolecular electron transfer. It is found that no intramolecular electron transfer occurs with iron (it is observed with titanium) but when three ammonia molecules are bound instead of $[9]aneN_3$, intramolecular electron transfer does occur. This behaviour, and similar observations with the Ru–nicotinate complexes [234], are examples of how non-bridging ligands influence electron transfer rates, probably due in this instance to changes in the redox potential of the Co(III) centre [236].

Crystals of $Co([9]aneN_3)_2Cl_3 \cdot 5H_2O$ spontaneously resolve on crystallization from HCl solution and the single-crystal CD spectrum has been measured [237]. Measurements have also been made of the single-crystal CD spectrum of the complex $Co((R)\text{-}2\text{-}Me[9]aneN_3)_2^{3+}$ which has been investigated by Mason and coworkers [238,239] and Nonoyama [240] and the crystal structure of the $Co((R)\text{-}2\text{-}Me[9]aneN_3)_2I_3 \cdot 5H_2O$ salt has been determined [225]. Two modes of coordination are possible for this ligand (**55** and **56**); the ligands have different configurations of the coordinated nitrogen atoms and a total of nine geometric isomers are possible for the bis complex. Nonoyama has separated the complex into five components, some of which contain more than one isomer, so that all nine isomers have been observed [240]. Three geometric isomers with the common bis(1*S*, 2*R*, 4*R*, 7*S*) configuration were present in the crystal subject to structural analysis [225]. All the chelate rings have the λ conformation and this complex has been found to exhibit a very large ring conformation *d*-electron optical activity [238].



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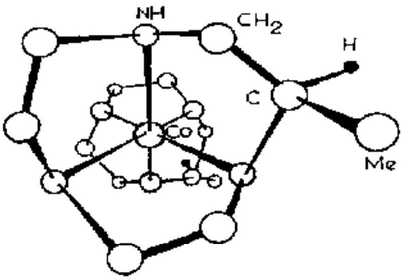

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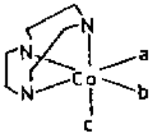
Many mixed-ligand Co(III) complexes containing $[9]aneN_3$, $[10]aneN_3$, $[12]aneN_3$ or $(R)\text{-}2\text{-}Me[9]aneN_3$ have been prepared and characterized.

Other ligands present in the coordination sphere of the Co(III) may be either monodentate, bidentate or tridentate. With monodentate ligands, complexes of the type Co[X]aneN_3(a)$_3$ [241–244] and Co[X]aneN_3(a)(b)(c)$^{n+}$ (a, b and c are monodentates) [245,246] have been prepared. Complexes of the type Co[X]aneN_3(a)(b)(c)$^{n+}$ have a chiral arrangement of donor atoms around the cobalt (**57** and **58**) and isomeric forms of a wide variety of such complexes have been partly resolved using column chromatography techniques [245,246]. Comparison of the CD spectra of these complexes with the spectra of Co$(NH_3)_3$(a)(b)(c) complexes [247] suggests that the chiral arrangement of donor atoms and not the conformation of the chelate rings is the main source of *d*-electron optical activity in these complexes.

As mentioned above, there are two modes of coordination of the 2-Me[9]aneN_3 ligand, and isomers of Co((*R*)-2-Me[9]aneN_3)$(NH_3)_3^{3+}$ have been separated [242]. CD spectra of these complexes are unusually weak. If it is assumed that the CD spectrum arises mainly from chelate-ring conformations, then the intensity of the effect suggests that the methyl-substituted chelate ring is, to a first approximation, fixed in the λ conformation and the other chelate rings of the macrocycle are flexible.



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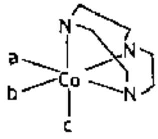

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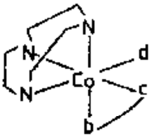

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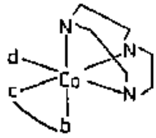

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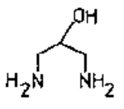
Co[X]aneN_3(BC)(D) complexes, where [X]aneN_3 = [9]aneN_3, [12]aneN_3 or (*R*)-2-Me[9]aneN_3, BC = glycine (gly), valine or *β*-alanine, and D is a monodentate ligand, may exist as enantiomers **59** and **60**, and such complexes have been resolved [241,248]. X-ray structural determinations have established that (−)589-Co[9]aneN_3(gly)$(NH_3)^{2+}$ [249] and (−)589-Co[9]aneN_3(*β*-alanine)$(NH_3)^{2+}$ [241] have opposite absolute configurations. A total of 12 diastereoisomers are possible for 2-Me[9]aneN_3 complexes of this type and column chromatography has been used to separate the prepared complexes into three fractions. Various sources of optical activity in the complexes have been considered and the conclusion drawn was that the chiral arrangement of donor atoms can account for the observed effects.

Mixed-ligand complexes containing triaza macrocycles and tridentate ligands have been studied by a number of groups. Co[9]aneN$_3$dpt^{3+} (dpt = 1,8-diamino-4-azaheptane) is of interest because dpt is forced to coordinate facially whereas it prefers a meridonal mode of coordination [250]. Two isomers of Co[9]aneN$_3$((*R*)-2-Me[9]aneN$_3$)$^{3+}$ have surprisingly intense CD spectra. The only sources of optical activity in complexes of this type are the chiral carbon atom and the conformation of the chelate rings. As the CD spectra are quite different from the spectrum of Co(NH$_3$)$_3$((*R*)-2-Me[9]aneN$_3$)$^{3+}$, it was concluded that interligand interactions have made the conformations of the chelate rings rigid [240,242].

Nonoyama and Sakai have prepared mixed-ligand complexes of (*R*)-2-Me[9]aneN$_3$ and 1,1,1-tris(aminomethyl)ethane, and separated two isomeric forms [242]. CD spectra of these isomers indicate conformational flexibility in the 1,2-diaminoethane portion of the macrocycle. A mixed-ligand complex of Co[9]aneN$_3$ with 1,2,3-triamino-2-methylpropane has been prepared [251]. Potentially tridentate amino alcohols **61** and **62** have been used to



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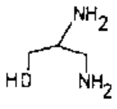

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form mixed-ligand complexes with Co[9]aneN$_3^{3+}$. Complexes are formed in which **61** and **62** act as either tridentate or bidentate ligands. Base hydrolysis reactions of the complexes with bidentate ligands were investigated but the dangling hydroxyl group did not become coordinated [243].

A Co(II) mixed-ligand complex of CoMe$_3$[9]aneN$_3^{2+}$ and *N*-hexadecyliminodiacetate has been prepared by Rix and Williams [252] and the chemical shifts of the protons of the hexadecyl moiety have been measured. It was suggested that this complex could have value as a probe of distances from interfaces into organic layers such as biological membranes. Thiocyanato-bridged Co(II) dimers with [9]aneN$_3$ and larger ring triamines have been prepared [183]. With macrocyclic ring sizes smaller than 13, six-coordinate dimers with di-μ-thiocyanato bridges form, whereas with larger triamines five-coordinate monomeric complexes form. Five-coordinate Co(II) complexes of **39** and **40** have been prepared [184,186]. A dimeric di-μ-hydroxy Co(III) complex which contains octahedral Co(III) has also been prepared [184].

Nickel. Monocomplexes and bis complexes of [9]aneN$_3$ with Ni(II) have been synthesized [57,253]. Bis complexes with 2-methyl-[9]aneN$_3$ have been prepared and the CD spectra recorded [240]. Formation constants of these complexes will be discussed in Section E (i). Analysis of the electronic spectrum of $Ni([9]aneN_3)_2^{2+}$ indicates a strong ligand field around the Ni(II) and the Racah parameters suggest a distorted octahedral structure [253]. Crystal structure analysis of $Ni([9]aneN_3)_2^{2+}$ [222] confirmed a trigonally distorted octahedron. $Ni([10]aneN_3)_2^{2+}$ has also been structurally characterized [254]. This complex has the *trans* arrangement of six-membered rings and a slight trigonal distortion. A crystal-field analysis of the spectrum of $Ni([9]aneN_3)_2^{2+}$ has been carried out using a trigonally distorted octahedral model, and the large D_q value was attributed to the trigonal distortion [255]. Thöm et al. have pointed out that the distortion in $Ni(en)_3^{2+}$ is greater than in $Ni([9]aneN_3)_2^{2+}$ but a smaller D_q value is observed; therefore trigonal distortion is not able to explain the D_q values [226]. The origin of the large D_q values is discussed in Section E (i). A band in the electronic spectrum, originally attributed to the splitting of the energy state $^3A_{2g} \rightarrow {}^3T_{2g}$ owing to the trigonal distortion [255], has been reassigned as being due to a mixing of the $^1E_{1g}$ and $^3T_{2g}$ excited states [256].

Monocomplexes of Ni(II) with triaza macrocycles of varying ring size have been prepared and bridged dimeric species are common. For macrocycles with a ring size of 12 or less, six-coordinate Ni(II) complexes with two bridging and one terminal thiocyanate anions are isolated [182]. With larger ring sizes five-coordinate monomeric complexes are formed. Similar behaviour has been mentioned above for the Co(II) thiocyanato complexes [183]. Chloro-bridged dimers have been isolated with $[9]aneN_3$ and $[10]aneN_3$ and the nickel in these complexes is probably five-coordinate [182].

Azide-bridged complexes with $Me_3[9]aneN_3$ and $[12]aneN_3$ have been described [257]. $Ni_2(Me_3[9]aneN_3)_2(\mu\text{-}N_3)_3(ClO_4)$ has been isolated by reacting a methanol solution of $Ni(ClO_4)_2$ with triethylorthoformate followed by the addition of $Me_3[9]aneN_3$ and NaN_3. In the absence of perchlorate anion, $L_2Ni_2(\mu\text{-}N_3)_2(N_3)_2$ is formed. $[12]aneN_3$ gave a similar complex. Structures of both types of complex have been determined, and in $Ni_2(Me_3[9]aneN_3)_2(\mu\text{-}N_3)_3(ClO_4)$ the azide groups are coordinated end-to-end. Steric requirements of the $Me_3[9]aneN_3$ ligand force the nickel into a distorted octahedral environment. $Ni_2([12]aneN_3)_2(\mu\text{-}N_3)_2(N_3)_2$ also has end-to-end bridging azides. The eight-membered $Ni_2(\mu\text{-}N_3)_2$ ring is approximately planar and the azide bridges are asymmetric but in this complex Ni(II) is nearly octahedral. Variable-temperature magnetic susceptibility measurements have shown the nickel ions to be strongly antiferromagnetically coupled, the larger coupling being observed in the di-μ-azido dimers [257].

$Ni([9]aneN_3)_2^{3+}$ has been the subject of a number of studies. Preparation of this complex is achieved by a variety of methods including oxidation with peroxydisulphate [196], Co^{3+} [258], $NOBF_4$ or controlled potential electrolysis [68]. A reduction potential of 0.95 V (vs. normal hydrogen electrode

(NHE)) has been measured using cyclic voltammetry [196,259] and thermodynamic parameters for the oxidation reaction have been determined [260]. Solvent stabilization of the trivalent state has been observed [68]; the trivalent state is more stable in dimethylsulphoxide (DMSO) than in DMF.

Redox studies with bis complexes formed by [9]aneN_3, [10]aneN_3 and [11]aneN_3 have shown that increasing macrocyclic ring size makes attainment of the Ni(III) state more difficult [68]. Reducing the metal ion radius and increasing macrocyclic ring size are believed to increase non-bonded repulsive interactions between ligands, and hence the Ni(III) state is less favoured. Structural analysis [180] has shown Ni([9]aneN_3)$_2^{3+}$ to have a tetragonally distorted octahedral geometry with two long axial (212 pm) and four short (197 pm) equatorial bonds. The magnetic moment is normal for low spin Ni(III) [196]. ESR spectra have been analysed in detail and are consistent with the tetragonal distortion observed in the solid [180]. Calculations of g values using data from reflectance spectra and spin–orbit coupling parameters estimated from UV and visible spectra are in good agreement with the experimental ESR values.

Use of Ni([9]aneN_3)$_2^{3+}$ as an outer-sphere electron transfer reagent has been the subject of numerous reports. A self-exchange rate constant for the Ni^{2+}/Ni^{3+} couple (6×10^3 M^{-1} s^{-1}) has been calculated from cross reactions with a series of Fe(II) 1,10-phen and bipy (2,2′-bipyridyl) complexes [258]. A direct determination of this rate (30 M^{-1} s^{-1} at $-4°C$) has been made using ESR measurements of the hyperfine broadening of ^{61}Ni([9]aneN_3)$_2^{3+}$ compared with that of ^{58}Ni([9]aneN_3)$_2^{3+}$ [75]. A self-exchange rate constant for the Ni([10]aneN_3)$_2^{(3+/2+)}$ couple (2×10^4 M^{-1} s^{-1}) has been calculated from the rates of a variety of cross-reactions with inorganic redox reagents [89]. Ni([9]aneN_3)$_2^{3+}$ has been used to study the oxidation of benzene diols and ascorbic acid [259], dimeric rhodium acetato complexes [261], Ni(II) complexes of tetradentate macrocycles [262], $Fe(H_2O)_6^{2+}$, VO^{2+}(aq) [263] and $Ti(H_2O)_6^{3+}$ [264].

Ni(II) complexes of the macrocycle Me_3[12]eneN_3, **40**, are prepared by a template reaction between Ni(dpt)$^{2+}$ and acetone [184,185,265]. The product was initially formulated as a complex of a ligand containing the *N*-isopropylideneamino group [265] but more detailed investigations, including a crystal structure analysis of $NiL(NCS)_2$ [184], have shown that Me_3[12]eneN_3 is formed. Subsequent investigations have shown that using 4-methyl-4-azaheptane-1,7-diamine and acetone, macrocycle Me_4[12]eneN_3, **41**, is formed [186]. Removal of **40** from the metal ion and reduction with borohydride gives Me_3[12]aneN_3, **39**, and nickel complexes of this ligand have been prepared and their hydrolysis behaviour in aqueous solution investigated [185]. Compounds formed by all three ligands are frequently dimeric with di-μ-hydroxo, μ-oxalato, μ-carbonato and other bridging groups.

Crystal structures of NiL$(NCS)_2$ (L = **40**) [184], $\{Cu_2(L)_2(\mu\text{-}CO_3)\}ClO_4$ (L = **41**) [266,267] and the spectroscopic properties of the $Me_3[12]aneN_3$ [185] complexes show that five-coordinate complexes form because the conformation adopted by the triaza macrocycle blocks the sixth coordination site. A six-coordinate Co(III) complex of **40** has been isolated [184] so that this ligand conformation is not always adopted. Martin and Willis have used **40** to isolate Ni(II) and Cu(II) complexes of hexafluorodiacetone alcohol, which chelates as a uninegative ligand [268] and Ni(II) complexes of potentially tridentate ligands containing fluorinated tertiary alkoxy groups [269].

Rates of dissociation of the complexes $Ni[9]aneN_3^{2+}$, $Ni[12]aneN_3^{2+}$ and $NiMe_3[12]aneN_3^{2+}$ in acid solution have been studied [92,270]. These reactions are much slower than reactions of nickel complexes of linear polyamines and also much slower than reactions of the copper complexes of these macrocycles.

Copper. Initial investigations into the chemistry of the triaza macrocyclic complexes of Cu(II) were concerned with the determination of formation constants of the complexes and the nature of the species present in aqueous solution. Results of these investigations are discussed in Section E. Rates of formation of copper complexes have been studied in acetate buffers [271,272] using $[9]aneN_3$, $[10]aneN_3$ and $[12]aneN_3$, and under the experimental conditions used the reactive species are HL^+ and $Cu(OAc)^+$. Rates of these reactions are rapid and there is a strong dependence of rate upon ring size [272]. Rates of dissociation of triaza macrocycles from copper have been studied by a number of groups [92,271,273,274]. Reasonable agreement between the different groups has been obtained when medium effects, which are known to be important in reactions of this type, are taken into account. There are no clear trends in the rate of the reaction with macrocyclic ring size. Methyl substitution of the carbon atoms of the macrocycle decreases the rate of reactions. $CuMe_3[12]aneN_3^{2+}$ reacts very much more slowly than other triaza macrocyclic complexes and this has been shown to be due to an increased enthalpy of activation, reflecting increased steric hindrance to the dissociation process. A general mechanism for the dissociation of polyamine complexes proposed by Margerum et al. [275] has been used to interpret these kinetic results [92,274]. Differences in the rate constants for different macrocyclic ligands are thought to be due to either subtle structural and conformational effects which affect Cu–N bond strengths or the ease with which the nitrogen can rotate away from the copper.

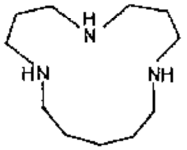
The most remarkable fact about these reactions with the copper complexes is their rate. Acid dissociation reactions of triaza macrocycles with most other metal ions are characterized by the slowness of the reactions.

Rates for the copper complexes are comparable with, but slower than, reactions of linear amines. Activation parameters for the dissociation of Cu(II) and Ni(II) complexes of [9]aneN_3 and [12]aneN_3 have been determined and it was shown that it is a favourable entropy of activation for the Cu(II) complexes which accounts for the rapid reactions [92]. These Cu(II) complexes are thought to be five-coordinate in aqueous solution, so that the rate-determining step, the breakage of the first metal–nitrogen bond, might be accompanied by formation of a bond to a water molecule in the vacant coordination site. Six-coordinate Ni(II) complexes are unable to maintain their coordination number in this fashion.

Monomacrocycle complexes of Cu(II) can be divided into two general types, $CuLX_2$ complexes with X representing a halide and dimeric complexes of the type $Cu_2L_2XY^{2+}$ in which X and Y may be hydroxide, halide or pseudohalide anions [57,87,92,265,267,274]. Two structures of Cu[9]aneN_3X_2 complexes have been determined for X = Cl [276] and X = Br [277]. As expected, the [9]aneN_3 ligand occupies three sites on a triangular face of a square pyramid with the remaining two basal sites filled by halide ions. $Cu-N_{(axial)}$ bonds are short compared with similar bonds in complexes of linear amines, reflecting the constraining nature of the [9]aneN_3 ligand. Bond distances and angles within the macrocyclic ligand are comparable with those in the structure of Ni([9]ane$N_3)_2^{2+}$ [222], suggesting that [9]aneN_3 is imposing the coordination geometry on the copper. The crystal structure of $CuLNO_3^{2+}$ (L = **63**) has shown what changes occur in the geometry around the copper with an increase in macrocyclic ring size [278]. The coordination geometry becomes irregular, the Cu–N bond lengths are inequivalent but axial elongation is not observed and the N–Cu–N bond angles vary from 86° to 139°. Redox potentials and solution spectroscopic properties of this complex have also been examined.

Ligand-exchange reactions of the Cu[9]aneN_3^{2+} and Cu[10]aneN_3^{2+} complexes with ethylenediaminetetraacetic acid (EDTA) and CyDTA have been studied [279]. The proposed mechanism is similar to the mechanism for the ligand-exchange reactions of complexes of linear amines [275]. Displacement of [10]aneN_3 is slower than that of [9]aneN_3 which is thought to be due to greater steric constraints in the intermediate with the [10]aneN_3 complex.

Bis complexes of Cu(II) with [9]aneN_3, 2-methyl[9]aneN_3, [10]aneN_3 and [11]aneN_3 have been prepared [57,240,274,280] but attempts to prepare bis complexes of [12]aneN_3 were unsuccessful [280] as were attempts to prepare such complexes with **63** and **64** [274]. A crystal structure analysis of Cu([9]ane$N_3)_2$[Cu(CN)$_3$] has been completed at 293 and 110 K. Differences in the Cu–N bond lengths and in the thermal parameters of atoms along the Cu–N bond directions were interpreted as indicating the presence of a dynamic Jahn–Teller process in the crystals. ESR investigations over a wide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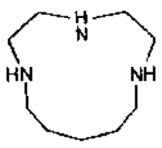
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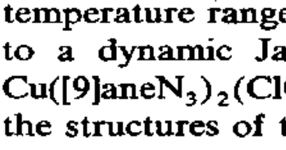
temperature range have also indicated that a transition occurs from a static to a dynamic Jahn–Teller distortion with increasing temperature [281]. $Cu([9]aneN_3)_2(ClO_4)_2 \cdot 2H_2O$ has also been structurally characterized [282]; the structures of the cations in the two complexes are very similar. Electrochemical investigations of the oxidation and reduction of the complex were also reported.

A most unusual example of isomerism occurs with the di-μ-hydroxy-bridged complex with the ligand $Me_3[9]aneN_3$ [283]. Two forms (green and blue) of this complex have been isolated and crystals of the blue form can be grown from aqueous solutions of the green form. Exchange interactions in these two isomers and in the corresponding complex with $[9]aneN_3$ have been studied using single-crystal and powder ESR experiments [191]. The blue isomer has an $S = 0$ ground state whereas the ground state of the green isomer is $S = 1$. It is suggested that the blue isomer is the di-μ-hydroxy-bridged species **65** and the green isomer is the μ-oxo-μ-aqua species **66**.



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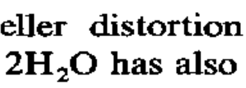
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Differential thermal analysis (DTA) measurements indicate that in the solid state the two forms are not interconvertible and the diffuse reflectance spectra show significant differences. Significant differences in the O–H stretching region of the IR spectrum and in the single-crystal ESR parameters are also observed.

Azide-bridged dimers with the $Me_3[9]aneN_3$ ligand also behave unusually [284]. Two complexes have been isolated using $Cu(ClO_4)_2$ as the source of copper ions, at low perchlorate concentrations an $\{L_2Cu_2(\mu\text{-}N_3)(N_3)_2\}ClO_4$ complex, **67**, is isolated whereas at higher perchlorate concentrations an $\{L_2Cu_2(\mu\text{-}N_3)_2\}(ClO_4)_2$ complex, **68**, is obtained. If $Cu(OAc)_2$ is used as the source of copper ions, then $LCu(N_3)_2$, **69**, is isolated. A product similar to **69**, i.e. **70**, is isolated using $[9]aneN_3$ as the macrocyclic ligand [284]. Crystal structures and magnetic susceptibility measurements have been completed for all these complexes and the structures and bonding details are

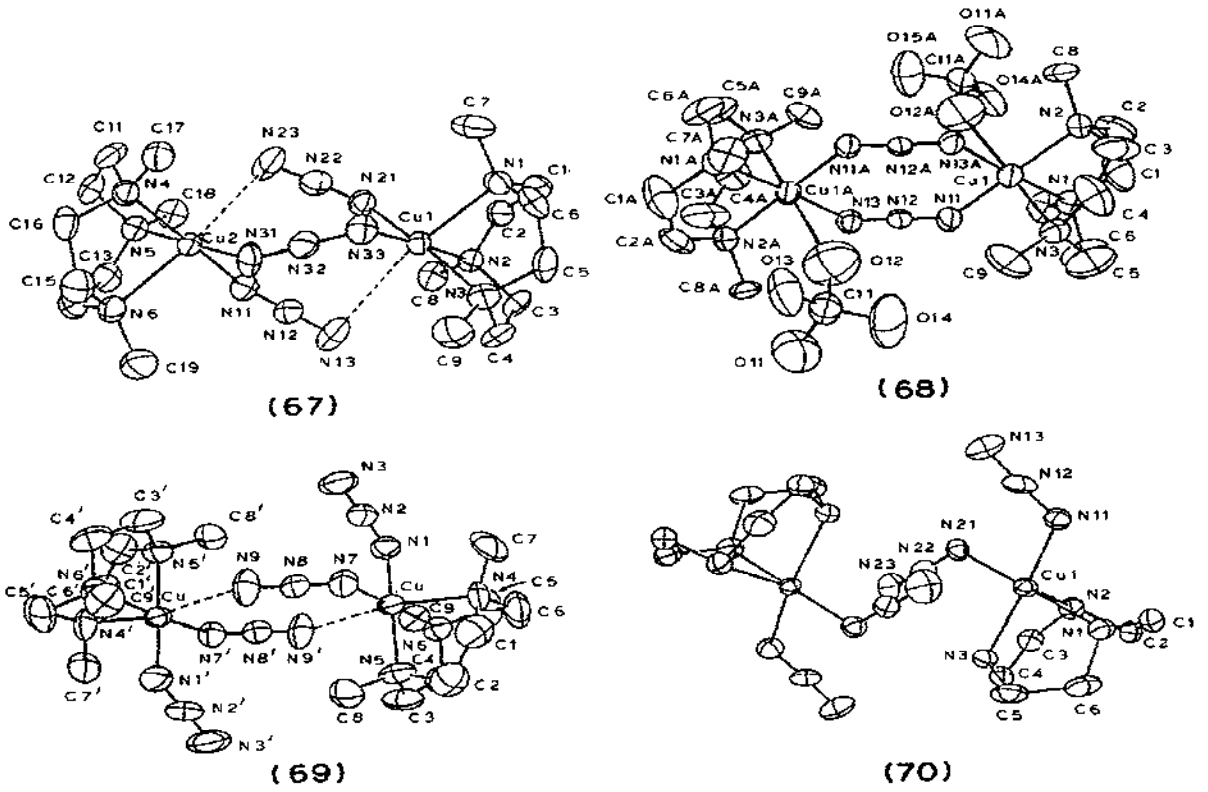


Fig. 2. Structures of azide complexes of CuMe$_3$[9]aneN$_3^{2+}$, **67**, **68** and **69**, and of Cu[9]aneN$_3^{2+}$, **70**. Reproduced with permission from ref. 284.

shown in Fig. 2. Both **67** and **68** are strongly antiferromagnetically coupled ($J < -400$ cm^{-1}) but **69** and **70** show no temperature-dependent magnetism.

A dimeric complex containing a bidentate bridging hydrogencyanoamido ligand HNCN$^-$ and Me$_3$[9]aneN$_3$ has been isolated [285]. This was prepared by mixing solutions of Cu(II), Me$_3$[9]aneN$_3$ and thiourea, leading to precipitation of a green solid and elemental sulphur. An X-ray analysis of the solid has revealed copper in a pseudo-trigonal-bipyramidal environment with three nitrogen atoms from the macrocycle and two nitrogen atoms from the HNCN$^-$ ligand bridging the copper centres. The copper atoms are antiferromagnetically coupled.

Copper complexes of **39**, **40** and **41** have been prepared [184–186]. An unusual mode of carbonate binding occurs in $\{Cu_2(L)_2(\mu\text{-}CO_3)\}(ClO_4)_2 \cdot HCONMe_2$ (L = **41**). The carbonate ion acts as a bidentate ligand to both copper atoms in the dimeric unit [266,267]. One carbonate oxygen lies along a two-fold axis which relates the halves of the dimer, with this oxygen coordinated to both copper atoms. The other carbonate oxygen atoms are each coordinated to one copper to complete a square pyramidal arrangement about each Cu(II) ion. One of the geminal methyl groups blocks the "vacant" octahedral coordination site. Formation constants of the copper complexes of $Me_3[12]aneN_3$ with both Cu(II) and Zn(II) have been determined and the results obtained for these five-coordinate complexes compared with the results for the six-coordinate complexes of $[12]aneN_3$ [185].

Zinc. All the reported studies of complexes of zinc with triaza macrocycles have been concerned with the determination of the formation constants of the monoligand complexes and the associated thermodynamic parameters [253]. These studies are discussed in Section E (ii). No solid complexes of zinc with any triaza macrocycle have been reported.

(b) Molybdenum and tungsten complexes

Molybdenum. Wieghardt and coworkers have reported extensive studies of molybdenum complexes (oxidation states 0–VI) of $[9]aneN_3$ [199,286–291], $Me_3[9]aneN_3$ [289,292–294] and $[12]aneN_3$ [295] and have summarized the chemistry in an excellent and detailed review [26] so that only a brief outline is given here. Unusual complexes isolated include seven-coordinate species $LMo(CO)_3X^+$ (X = Cl, Br, I) (the structure of $LMo(CO)_3Br$ has been determined) [199], air-stable nitrosylhydride and carbonylhydrides, e.g. $LMo(CO)_2(NO)$ [199], and a wide range of binuclear Mo(III) and Mo(V) complexes [287]. $Me_3[9]aneN_3$ forms a different series of complexes from those formed with $[9]aneN_3$ because of the steric hindrance imposed by the methyl groups discussed earlier [293].

Preparative reactions of these complexes are characterized by a strong product dependence on the exact reaction conditions. Reaction of $Mo[9]aneN_3(CO)_3$ with nitric acid solutions leads to a variety of products depending on the concentration of nitric acid. Low concentrations yield $Mo([9]aneN_3)(CO)_2NO^+$, slightly higher concentrations give $Mo([9]aneN_3)(NO)_2X^+$ ($X = H^-$ or Br^-) or $Mo[9]aneN_3(CN)_3$ and even higher concentrations yield $Mo_2([9]aneN_3)_2O_5^{2+}$ [199]. A feature of these reactions is the remarkable stability of the bonds between the macrocycle and the molybdenum in all oxidation states. Treatment of the complexes with concentrated acid, often for extended periods, does not lead to loss of the macrocycle but to substitution of the other ligands and to oxidation of the metal.

These hydridocarbonyl and hydridonitrosyl complexes of molybdenum are unusual in that they are stable to air and are not sensitive to light or moisture. They act as weak acids in aqueous solutions; $\{Mo([9]aneN_3)$-

$(CO)_3H\}$ has a pK_a of 2.4 and $\{Mo([9]aneN_3)(NO)_2H\}$ has a pK_a of 4.9 [199]. There are strong analogies between the complexes formed by the triaza macrocycles and those of the corresponding complexes of the ligands η^5-cyclopentadienyl and tris(1-pyrazolyl)borate ligands although the latter ligands have a negative charge.

Two interesting examples of isomerism are encountered with these complexes; $\{Mo(Me_3[9]aneN_3)(NO)(OEt)X\}^+$, (X = Cl or Br) has been isolated as blue and green forms [292] and *syn* (yellow) and *anti* (purple) complexes of the $L_2Mo_2O_4^{2+}$ cation ($L = [9]aneN_3$ or $[12]aneN_3$) have also been isolated [290,295]. The exact difference between the two forms of $MoL(NO)(OEt)X^+$ has not been determined, but it has been suggested that they are distortional isomers in which the Mo–OEt bond lengths are different [292]. Similar isomerism has been described with other molybdenum complexes, and for $MoOCl_2(PMe_2Ph)_3$ complexes it has been shown that the Mo=O bond lengths are different [296]. The yellow and purple $([9]aneN_3)_2Mo_2O_4^{2+}$ isomers have very different electronic spectra; the purple isomer has an intense band at about 550 nm which is not observed in the yellow isomer. Yellow *anti* isomers of both $[9]aneN_3$ and $[12]aneN_3$ and a purple *syn* isomer of $[9]aneN_3$ have been characterized by X-ray crystallography [287,290,295] as has the *anti* isomer of the related $\{Mo_2([9]aneN_3)_2O_2(\mu\text{-}S)_2\}^{2+}$ cation [297]. The four-membered Mo_2O_2 ring in the *anti* isomer is planar whereas it is puckered in the *syn* isomer. Mo–Mo bond lengths in the *anti* complexes (258.6(1) for $[12]aneN_3$ and 256.1(1) pm for $[9]aneN_3$) are slightly longer than the bond in the *syn*-$[9]aneN_3$ isomer (255.5(1) pm) [290]. The greater thermodynamic stability of the *syn* isomers is attributed to the fact that puckering the ring results in a small but significant decrease in the non-bonded interactions between the terminal and bridging oxygen atoms [288].

Kinetic studies of the conversion of the *anti* to the *syn* isomer for both the $[9]aneN_3$ and $[12]aneN_3$ complexes have been performed [288,295]. *Anti*-$Mo_2([12]aneN_3)O_4^{2+}$ does not isomerize in acid solution. However, in basic solution conversion to the *syn* isomer is rapid and the following mechanism has been proposed [295]:

$$\textit{anti}\text{-}[L_2Mo_2O_4] + OH^- \overset{K_1}{\rightleftharpoons} [L_2Mo_2O_4OH]$$

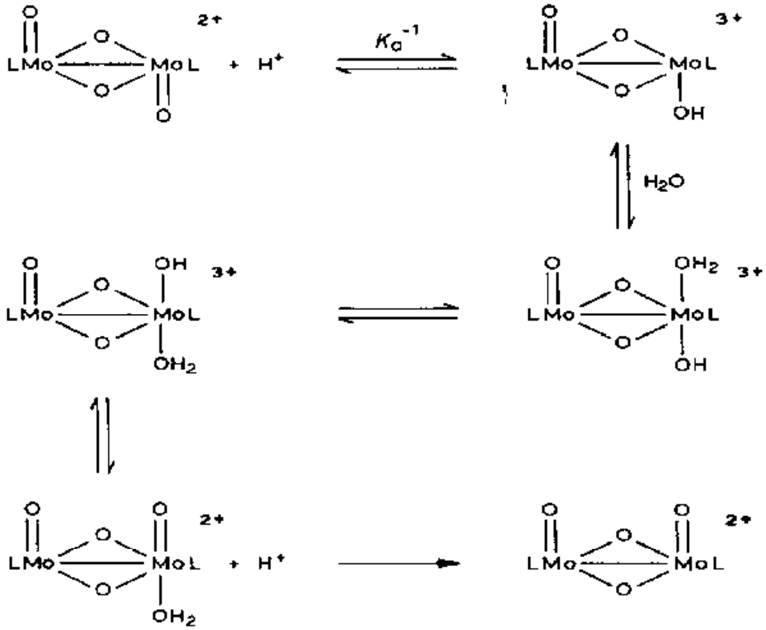
$$[L_2Mo_2O_4OH] \xrightarrow{k_b} \textit{syn}\text{-}[L_2Mo_2O_4]$$

$k = K_1k_b = 0.10\ M^{-1}\ s^{-1}$ at 25 °C. A similar rate constant was obtained for the $[9]aneN_3$ complex ($0.13\ M^{-1}\ s^{-1}$) and in this case values of K_1 ($9\ M^{-1}$) and k_b ($0.015\ s^{-1}$) were derived from the kinetic data. Greater steric demands of the larger macrocycle were suggested as being responsible for the lower value of K_1 which must obtain for the $[12]aneN_3$ complex.

The *anti*-[9]aneN_3 complexes also isomerizes under acidic conditions, the rate dependence on H^+ having the form

$$k_{obs} = k_a/1 + K_a[H^+]^{-1}$$

with $k_a = 2.4 \times 40^{-4}$ M_1^{-1} s^{-1} and $K_a = 2.3$ M at 294 K. The mechanism proposed to explain this dependence is

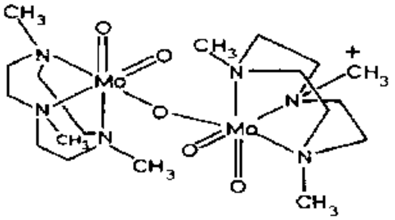


It is difficult to see how this mechanism can explain the inability of the [12]aneN_3 complex to react under acid conditions. Both complexes have very similar structures so that the first protonation step should be the same. A larger macrocycle may make it more difficult for the water to attack the molybdenum in an associative-type reaction but the structures of the complexes do not suggest that this is particularly likely. Perhaps protonation of a nitrogen of the macrocyclic ligands is involved in the reaction, a water molecule taking the place of the nitrogen. Such a reaction could be strongly dependent on the size of the macrocycle and the conformation of the chelate rings. However, the stability of the [9]aneN_3–Mo bonds in strong acid suggests that some other explanation is needed.

Kinetic studies have been performed on the oxidation of $Mo([9]aneN_3)_2$-$(\mu\text{-}OH)_2(H_2O)_2^{2+}$ by perchlorate and nitrate and the substitution reactions of the OH^- ligands by chloride ion [288,291]. These reactions apparently proceed via associative mechanisms, and for the nitrate reduction, direct evidence for the transfer of the oxo group from the nitrate to the molybdenum has been obtained [291].

Electrochemical investigations of a wide range of mononuclear $MoLX_3$

(L = [9]aneN_3 or Me_3[9]aneN_3) complexes in a variety of oxidation states have been reported [289,292–294]. Reduction of the $LMoO_3$ and $L_2Mo_2O_5$ species indicates that there are species in solution which have not yet been isolated as solid complexes. Of particular interest is the mixed-valence Mo(V)–Mo(VI) species thought to be **71** which shows a strong intervalence absorption band and has an ESR spectrum which indicates complete delocalization of the odd electron. Also of interest is the possibility of a trimeric species $L_3Mo_3O_4^{4+}$, **72**, produced by a two-electron reduction of $LMoO_3$ (L = [9]aneN_3). A sulphur analogue of this species, $L_3Mo_3S_4^{4+}$, [297] and the tungsten complex [298] have both been isolated and structurally characterized. In addition to the studies mentioned above the following complexes have been structurally characterized: $Mo_2L_2(OH)_2(\mu\text{-}OH)(\mu\text{-}Br)^+$ [286], $Mo_2L_2(\mu\text{-}OH)_2(\mu\text{-}OAc)^{3+}$ [287] and $MoL'Br_3$ [293] (L = [9]aneN_3 and L′ = Me_3[9]aneN_3).



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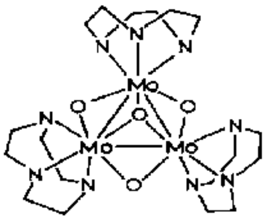


(72)

Tungsten. Tungsten complexes of [9]aneN_3 and Me_3[9]aneN_3 have not been investigated in quite the same detail as the molybdenum complexes but the reactions are similar and similar isomeric forms of the complexes have been isolated [199,292,298,299]. Thus two forms (*syn* and *anti*) of the $L_2W_2O_4^{2+}$ cation have been isolated as have blue and green forms of the WMe_3[9]aneN_3(NO)Br(OEt)$^+$ cation [298]. One example of isomerism observed with the tungsten complexes which has not been observed with the corresponding molybdenum complexes is found with distortional isomers of the WMe_3[9]ane$N_3OCl_2^+$ cation [300]. This is the only example of distortional isomerism currently known for tungsten; some molybdenum examples have already been discussed. Blue and green forms of the WMe_3[9]aneN_3-OCl_2^+ cation have been structurally characterized, and the W=O bond lengths differ considerably (172 pm in the blue isomer and 189 pm in the green) [300]. The bond to the nitrogen *trans* to the W=O bond is longer in the blue form of the complex but the other bond distances around the tungsten are identical. Solutions of both isomers in acetonitrile are stable for days but the addition of water to these solutions results in rapid conversion of the green to the blue form.

The $W_2L_2O_5^{2+}$ species are the first examples of this moiety established for tungsten, although molybdenum complexes of this type are well known. Comparison of the electrochemistry of the molybdenum and tungsten complexes indicates that the lower oxidation states, M(III) and M(IV), are much more accessible for molybdenum than for tungsten. These electrochemical investigations have disclosed the presence of species in solution, e.g. $LWOX_2$ and $LW^{II}(NO)Br(OEt)$, which have not as yet been isolated as solid complexes [299]. A trinuclear cluster $L_3W_3O_4^{4+}$ and *trans*-$W_2L_2(\mu\text{-}OH)_2Br_2^{2+}$ (L = [9]aneN_3) have been isolated and structurally characterized [298].

(c) Other elements

Re(I) and Re(VII) complexes of [9]aneN_3 have been prepared [301]. $Re(CO)_5Br$ reacts with [9]aneN_3 to give $LRe(CO)_3^+$ which in turn reacts with $NOBF_4$ to yield $ReL(CO)_2NO^+$. Oxidative decarbonylation reactions of these complexes yields $ReLO_3^+$ and the structure of this complex ion has been determined [301]. Rh(III) complexes of [9]aneN_3 [200,302] and Me_3[9]aneN_3 [179] have been prepared and the kinetics of the decarboxylation of $Rh_2([9]aneN_3)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2^{2+}$ have been studied [200]. A structure of the *trans*-$Rh_2L_2(\mu\text{-}OH)_2(H_2O)_2^{4+}$ cation has been determined and the bonding is unusual for second- and third-row transition metal complexes of this type in that it does not contain a metal–metal bond. With Me_3[9]aneN_3, only the $Rh_2L_2(\mu\text{-}OH)_3^{3+}$ cation has been reported and this ion does not react with acid to give the di-μ-hydroxo species. Kinetic studies of the decarboxylation reaction of $Rh_2([9]aneN_3)_2(\mu\text{-}CO_3)(\mu\text{-}OH)_2^{2+}$ have been reported [200].

Ru(III) complexes of [9]aneN_3 are of interest because they are the first examples of Ru(III) complexes containing μ-hydroxy bridges. Both $L_2Ru_2(\mu\text{-}OH)_2Cl_2^{2+}$ and $L_2Ru_2(\mu\text{-}OH)_2(\mu\text{-}OAc)^{3+}$ have been isolated as solids and the structure of the latter has been determined and shown to contain a Ru–Ru bond. Other Ru(III) complexes characterized include $LRuX_3$ (X = Cl or Br), RuLIox (ox = oxalate), RuL_2^{3+} and the mixed-valence species $Ru_2L_2(\mu\text{-}Cl)_3^{2+}$. RuL_2^{3+} is a better oxidant than $Ru(NH_3)_6^{3+}$ by 0.3 V [303].

Coordination of cyclic triamines to metal ions which prefer square-planar coordination geometries is of interest because the metal might bind the third nitrogen of the macrocycle out of the square plane. There has also been interest in seeing whether a sufficiently long alkyl chain between the nitrogen atoms will enable the nitrogen atoms to be bound in a planar arrangement. Isolated complexes of [9]aneN_3 with Pd(II) [187] and Pt(II) [304] show that only two nitrogen atoms are coordinated to the metal, and with Pt(II) a protonated complex can be isolated from acid solutions. NMR evidence suggests that the uncoordinated nitrogen in the Pt(II) complex is involved in a weak interaction with the metal in solution but in the solid this is not the case [304]. With Pd(II) and ligands of larger ring size, 1,4,7-[13]aneN_3, 1,4,7-[14]aneN_3, 1,4,7-[15]aneN_3 and 1,4,7-[17]aneN_3, the complexes isolated have the formula $PdLCl^+$. With the two largest macrocycles the electronic spectra of the complexes are very similar to that of Pd(dien)Cl^+ and hence a planar PdN_3Cl chromophore is likely. With smaller ring sizes the spectra are different but the structure is not known [187]. PtL_2^{2+} (L = [9]aneN_3) is readily oxidized with air to PtL_2^{4+} in which all three nitrogen atoms of the macrocycles are coordinated to the metal. This complex can be deprotonated in basic solution to give the $PtL(H_{-1}L)^{3+}$ ion, thé iodide salt of which has been isolated [304].

Ga(III) complexes of both [9]aneN_3 and Me_3[9]aneN_3 have been studied and mononuclear $GaLCl_3$ complexes isolated from non-aqueous solvents for both ligands [305]. From alkaline aqueous solution, binuclear $Ga_2L_2(\mu\text{-}OH)_2(H_2O)_2^{2+}$ and $Ga_2L_2(\mu\text{-}OH)_2(\mu\text{-}OAc)^{3+}$ complexes have been isolated with [9]aneN_3. With Me_3[9]aneN_3 a complex formulated as $[Ga_2L_2(\mu\text{-}H_2O)(\mu\text{-}OAc)_2](ClO_4)_4 \cdot H_2O$ containing a bridging water molecule was isolated. The structure of the cation $L_2Ga_2(\mu\text{-}OAc)(\mu\text{-}OH)_2^{3+}$ has been determined [305].

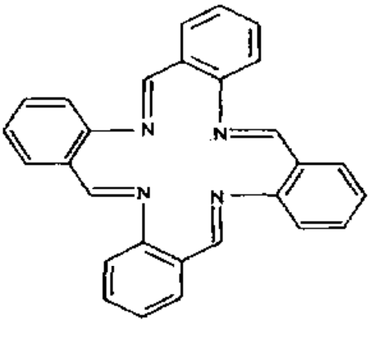
Complexes similar to $GaLCl_3$ have been prepared with In(III), [9]aneN_3 and Me_3[9]aneN_3, and in aqueous alkaline solution the [9]aneN_3 complex hydrolyses to give the first well-characterized μ-OH complex of indium, $[In_4(\mu\text{-}OH)_6]^{6+}$. The $In_4(OH)_6$ core has an adamantane-like skeleton. Hydrolysis of In([9]aneN_3)Br_3 in sodium acetate solution yields $L_2In_2(OAc)_4(\mu\text{-}O)$ the structure of which has been determined [306].

Tl(I) complexes of Me_3[9]aneN_3 and Tl(III) complexes of both [9]aneN_3 and Me_3[9]aneN_3 have been prepared and characterized [307]. The Tl(I) complex is unusual in that the thallium is three-coordinate, bound only to the three nitrogen atoms of the macrocycle. $TlLX_3$ (X = Cl, Br and I) (L = [9]aneN_3 or Me_3[9]aneN_3) and $TlL_2(ClO_4)_3$ (L = [9]aneN_3) have been prepared from Tl(III). Kinetic studies of the reduction of Tl([9]aneN)$_3^{3+}$ with Co([9]aneN_3)$_2^{2+}$ have shown that the reaction is first order in both complexes, implying the formation of Tl([9]aneN_3)$_2^{2+}$ as a reaction intermediate. Electrochemical studies, however, failed to find any evidence for the putative Tl([9]aneN_3)$_2^{2+}$ species [307].

Two complexes of Pb(II), Pb[9]ane$N_3(NO_3)_2$ and Pb[9]ane$N_3(ClO_4)_2$, have been characterized structurally [308]. In both complexes, [9]aneN_3 is strongly bonded to the lead, with the coordination sphere being completed by weakly bonded nitrate or perchlorate anions. In both complexes the coordination geometry is very irregular due in part to a stereochemically active lone pair of electrons.

(ii) Other triaza macrocycles

The first triaza macrocycle to be prepared was the ditosyl derivative of [9]aneN_3 [1] but the first such macrocycle to have its complexes investigated was tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine, **36**, which is prepared via a template reaction with *o*-aminobenzaldehyde [309]. *o*-Aminobenzaldehyde undergoes a variety of self-condensation reactions depending on the experimental conditions to form bis anhydrotrimers [310], tris anhydrotetramers [309,311] and bis acid salts of a tetrameric condensate [312]. In the presence of metal ions or BF_3 the self-condensation can lead to either complexes of **36** (with VO^{2+} as template) [313], the tetraaza macrocycle **73** (with Cu(II) [309,314,315], Zn(II) [314] or Mo_2Cl_8 [316] as templates), the tetrafluoroborate salt of **73** [311] or a mixture of complexes of **36** and **73** (Co(II) [310,314] or Ni(II) [309,313,317] as templates). Reaction of Ni(II) with the diacid salt of *o*-aminobenzaldehyde [312] or the bis anhydrotrimer [315,318] leads exclusively to the Ni(II) complexes of **36** and **73** respectively. Ni(II) complexes of **74** have been prepared by reaction of Ni(II) salts with the bis anhydrotrimer of 5-chloro-*o*-aminobenzaldehyde but not via the direct template condensation reaction [318].



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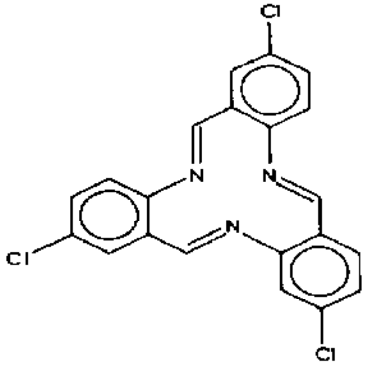
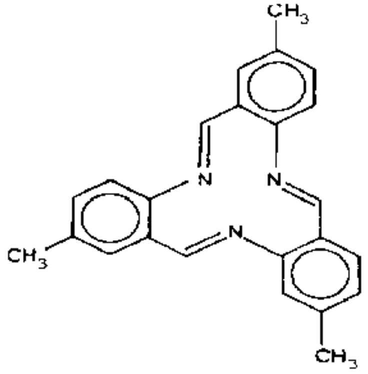


(74)

The selectivity of vanadium for **36** has been accounted for by the small size of the V(V) ion and by the fact that VO_2^+ has a *cis* configuration so that square-planar complexes of **73** are unlikely to form [313]. V(IV) was the templating ion in this preparation but the product isolated was the V(V) complex.

Mertes and coworkers [319,320] have shown that the diacid salt of 5-methyl-2-[(triphenylmethyl)amino]benzaldehyde reacts with Cu(II) to give a mixture of the complexes of **75** and **76**. Other metal ions give only complexes of **76** under the same conditions.

Bis complexes of **36** with Ni(II) [318], Co(II) [227], Cu(II) [310] and of **75**



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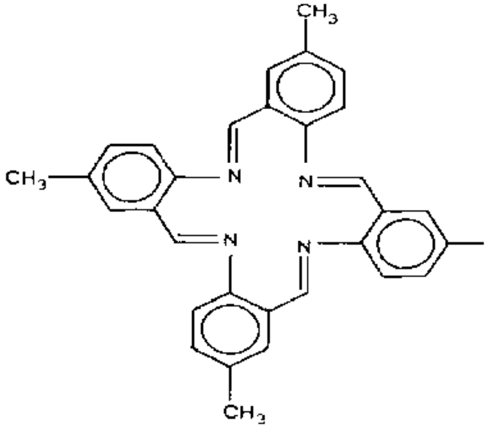
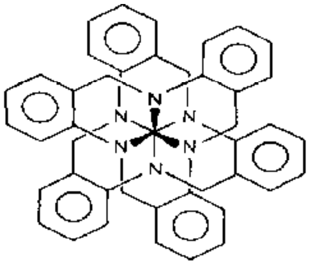


(76)

with Cu(II) have been prepared [319]. These complexes may exist in two isomeric forms, *meso*, **77**, and racemic, **78**, and both forms have been



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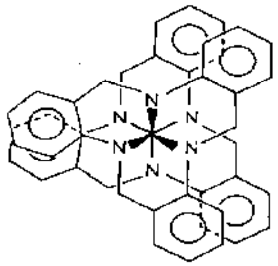
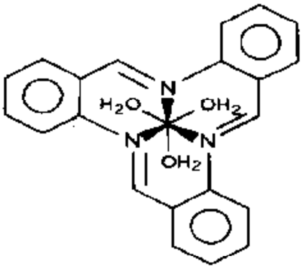


(78)

isolated as Co(III) complexes. A crystal structure of one of the racemic isomers (+) − CoL$_2^{3+}$ (L = **36**) has been determined [321]. Interactions between the benzene rings of the two ligands are maximized in the racemic form of the molecule and it was suggested that the interactions between the benzene rings are attractive rather than repulsive [321]. NiL$_2^{2+}$ (L = **36**) could not be resolved, nor could isomers be separated so that the complex was assigned the *meso* configuration [318]. CuL$_2^{2+}$ (L = **75**) has been shown to have the *meso* structure [319]. This ion is interesting because the complex has D_3 symmetry, which requires an E_1 ground state for the Cu(II) not allowed by the Jahn–Teller effect. The thermal ellipsoids of the nitrogen atoms in the structure determined at 110 K suggest that the molecule is undergoing a dynamic Jahn–Teller distortion [319].

Techniques for the separation of the Co(III) isomers have been improved [227] and the Co(II) isomers have been prepared by reduction of the Co(III) isomers. Redox potentials for the Co(III)/Co(II) couple have been determined for both isomers [227]. Both Co(II) complexes are low spin but the complex ESR spectra suggest that the energy gap between the high spin and low spin states is not large. These isomeric forms of the complexes have been shown to have quite different reactivities with other redox reagents [227,228,322].

Two isomeric forms (D and L) of the $NiL(H_2O)_3^{2+}$ ($L = \mathbf{36}$) ion may also exist, **79** and **80**, and the complex has been resolved and the structure determined [323–325]. This resolved complex can be used to resolve amino acids [324]. Solvent-exchange rate constants for the $NiL(solvent)_3^{2+}$ ($L = \mathbf{36}$) ions have been determined by NMR techniques [326,327] and the kinetics of the reaction in aqueous solution of $NiL(H_2O)_3^{2+}$ ($L = \mathbf{36}$) with a variety of bidentate and tridentate ligands have shown that the rate-determining step in the substitution reaction is chelate ring closure [328]. Electron spin delocalization in NiL^{2+} and NiL_2^{2+} ($L = \mathbf{36}$) complexes has been studied by proton NMR [329].



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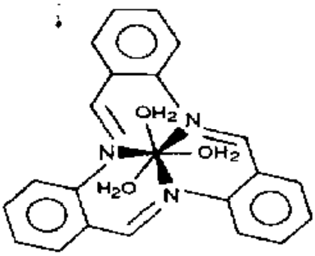

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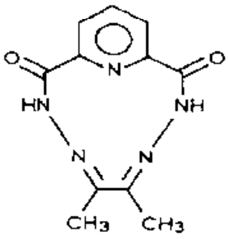
Interpretation of the CD of the CoL_2^{3+} ($L = \mathbf{36}$) ion has been the subject of some debate. Spectra were initially interpreted in terms of the optical activity arising from a twisted crystal field [321], but a mixed-ligand $CoL([9]aneN_3)^{3+}$ complex has been prepared and it is claimed that the CD spectra of this species show that the optical activity is derived from the chiral arrangement of the benzene ring moieties [330].



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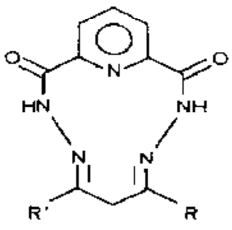

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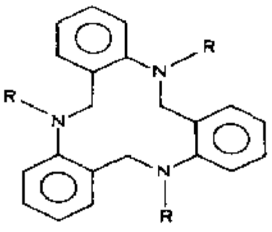


(83)

Complexes of macrocycles **81** and **82** have been prepared from dipicolinyl dihydrazine and either 2,3-butanedione or β-diketones in the presence of metal ions as templates. For **81**, Co(II), Ni(II) and Cu(II) are effective templating ions [331] whereas for **82**, VO^{2+} [332], ZrO^{2+} [333], Zn(II), Cd(II), Hg(II) [334], Co(II), Ni(II) and Cu(II) [335] all act as templates. Upon coordination to the metal the amide nitrogen is deprotonated and therefore the pyridine and two amide nitrogen atoms must be planar. This should prevent the ligand occupying three facial positions of an octahedron. On the basis of chemical evidence, the complexes isolated are thought to have a trigonal bipyramidal structure. A crystal structure determination would be of considerable interest.

Cyclic triamines **83** ($R = CH_3$ or CH_2Ph) have been prepared and structurally characterized but complexes have not been reported [336,337].

(iii) Mixed-donor tridentate macrocycles containing nitrogen donor atoms

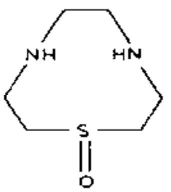
Although the complexes of [9]aneN_2O, **5**, have been studied only recently, the ligand was first synthesized in 1976 [77,80]. Formation constants of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) complexes have been determined [91,338] and the ligand has been shown to display a pronounced macrocyclic effect with small metal ions but not with Cd(II) and Pb(II). In common with other tridentate macrocycles, [9]aneN_2O has a larger than expected ligand-field strength [61,91]. This will be discussed in detail in Section E (i). CD spectra of the Ni([9]ane$N_2O)_2^{2+}$ ion have been interpreted as indicating that the chelate rings have a more flexible conformation than that present in Ni([9]ane$N_3)_2^{2+}$ [61]. Co([9]ane$N_2O)_2^{3+}$ could not be isolated, probably because of facile reduction to Co(II) [61], but mixed complexes, e.g. Co[9]aneN_3([9]ane$N_2O)^{3+}$, have been isolated. Complexes of 2-methyl[9]ane-N_2O have been prepared in low yield and the CD spectra of the Ni(II) and Cu(II) complexes studied [61].

Ni([9]ane$N_2O)_2^{2+}$ has been the subject of an X-ray structural investigation and the coordination of the nickel has been shown to be octahedral with a *trans*-N_4O_2 donor set [339].

Co(III), Cu(II) and Ni(II) complexes of **84** have been described by Nonoyama and Nonoyama [340]. Spectral evidence from all the complexes suggests that the sulphoxide oxygen is coordinated to the metal which in each case has a *trans*-N_4O_2 donor set. This ligand has a weaker ligand field than [9]aneN_3 or [9]aneN_2S.

Macrocycles [9]aneNO_2 [77], **85** [341], **86** [342,343], **87** [344], **88** [345], **89** [342] and **90** [346] have all been prepared in reasonable yields but complexes of these molecules have not yet been reported.

[9]aneN_2S has been the subject of a number of different investigations



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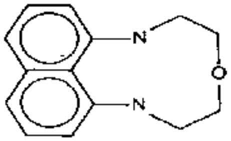

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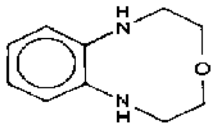

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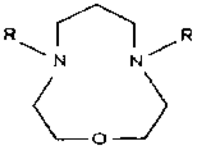
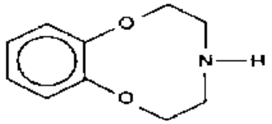


(87)

R = Me, Et, Pr, Bu



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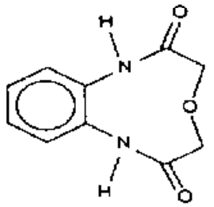

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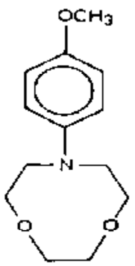


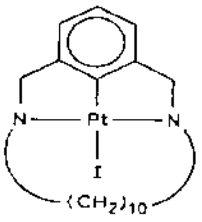
(90)

and Cu(II) [61,62], Ni(II) [61,347] and Co(III) complexes [61,348,349] have been described together with some mixed-ligand species, e.g. Co([9]aneN$_3$)([9]aneN$_2$S)$^{3+}$. Formation constants [374] and structures of the bis complexes with Co(III) [349], Cu(II) [62] and Ni(II) [347] have been determined. All three isolated complexes have the *trans-S* configuration. The Co(III) complex occurs in solution as a mixture of the *cis-* and *trans-S* isomers (in a 4 : 1 ratio) and isomerization is facile. Attempts to separate the two forms were initially unsuccessful but have recently succeeded [349]. Visible spectra of the Ni(II) complex of both [9]aneN$_2$S and its linear analogue have been analysed in some detail [256,347] and have been explained in terms of mixing of the ^1E_g and $^3T_{2g}$ excited states.

N$_2$P macrocycles **31**, the preparation of which was described in Section B (ii), form mononuclear and possibly dinuclear Rh(I) complexes [154]. It is thought that the dinuclear complexes contain a bidentate macrocycle but the mononuclear LRh(CO)Cl (R = CH$_3$) contains a tridentate macrocycle. Both Rh–N bonds are very long (longer than the Rh–P bonds) and it is probable that this is a structural requirement of the ligand although it may be a manifestation of the *trans* effect. These complexes show promise as hydroformylation catalysts [154].

Recently a novel carbodiaza macrocycle and its Pt(II) complex, **91**, has been prepared and the complex structurally characterized [350].

Two related ligands, **92** and **93**, are the only dithiaaza macrocycles that



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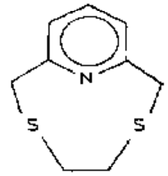

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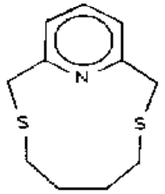


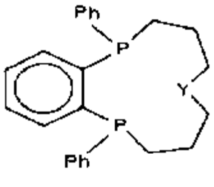
(93)

have been studied. Ligand **92** was first prepared by Weber and Vögtle who described a zinc complex $Zn_3L_4I_6$ [351], and Rh(I) and Pd(II) complexes of both ligands have been described [352]. $RhLCO^+$ (L = **93**) and $PdLCl^+$ (L = **93**) are apparently square planar with **93** acting as a tridentate ligand. Complex $\{RhL(CO)_2\}_2^{2+}$ (L = **92**) has both bridging and terminal CO groups and the macrocycle acts as a bidentate with NS coordination. This molecule displays complex fluxional behaviour which is believed to occur via on/off exchange of the sulphur atoms. $PdLCl_2$ (L = **92**) is probably oligomeric and the macrocycle is probably bidentate with SS coordination [352].

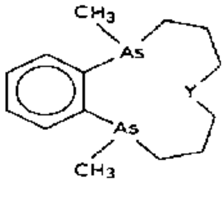
(iv) Complexes of phosphorus and arsenic donor macrocycles

Diel et al. [353] have reported the crystal structure of the Mo[12]aneP_3(CO)$_3$ complex prepared by a template reaction but this is the only report of complexes of this ligand. Complexes of the triarsena macrocycle **29** prepared by Ennen and Kauffmann [150,151] have not yet been described.

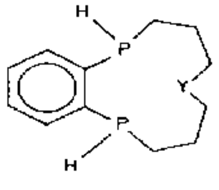
Complexes of the tertiary phosphino- and tertiary arsino-containing macrocycles prepared by Kyba and coworkers and described in Section B (ii) have been prepared with first-row transition metal ions and with chromium, molybdenum and tungsten carbonyls.



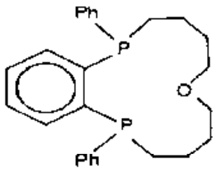
94 Y = N–Ph
95 Y = N–H
96 Y = N–CH_3
97 Y = S
98 Y = P–Ph
99 Y = As–Ph
100 Y = O
101 Y = P–H
102 Y = N–C_6H_4Br



103 Y = S
104 Y = As–Ph
105 Y = P–Ph
106 Y = O
107 Y = N–CH_3



108 Y = S
109 Y = N–CH_3



(110)

Ligands **94–100** all form complexes with $Mo(CO)_6$ (and some have been reported with $Cr(CO)_6$ and $W(CO)_6$] but **94**, **95**, **99** and **100** act as bidentate ligands [140,149]. The bidentate nature of these ligands is a result of either the poor donor properties of the third donor atom or the fact that the ligand prepared is the *meso-trans* conformer which cannot act as a tridentate ligand [141]. Ligands **96–98** act as tridentates although bidentate complexes were observed as intermediates in the reaction with **96** and **98** [149]. The crystal structure of the complex $MoL(CO)_3$ (L = **96**) has revealed an extremely long Mo–N bond (244 pm) [140]. Square-pyramidal $NiLCl_2$ (L = **95**) also has an extremely long axial Ni–N bond (242.8 pm) which is 30 pm longer than the Ni–P bonds in the complex. Reasons for these extraordinary bond lengths are not clear. The three W–P bond lengths in $WL(CO)_3$ (L = **98**) are the same within ±5 pm [141] and therefore they are probably not imposed by the ligand. Ligand **101** also forms complexes of the type $MoL(CO)_3$ [144] but full details of the coordination behaviour of this ligand have not yet appeared. An electrochemical investigation of the $ML(CO)_3$ complexes (M = Cr, Mo, W and L = **96**, **97** and **98**) has been reported [147]. The ease of oxidation of the complexes is greatest for **96** and least for **98**.

Ni(II) complexes of **108** and **109** have been prepared and it has been shown that the *cis* isomer of the ligand which can complex a metal ion as a tridentate ligand without steric strain can be enriched by a series of complexation–decomplexation reactions [146].

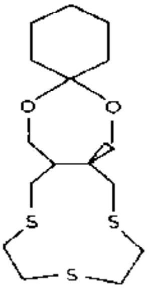
Co(II) complexes of **94**, **96**, **100**, **102** and **110** have been investigated and a range of different complexes isolated with bidentate and tridentate macrocycles and a variety of coordination geometries [145]. Ligands **94**, **102** and **110** act as bidentate ligands whereas **96** acts as a tridentate. Ligand **100** is able to form complexes with Co(II) in which it acts as either a bidentate or a tridentate ligand. A Cu(I) complex of **97** has also been isolated and the crystal structure has shown that this ligand acts as a tridentate ligand with this metal ion [141,148].

The *meso-cis* forms of the arsenic donor macrocycles **104** and **105** also form complexes of the type $MoL(CO)_3$ (as do **103** and **107**), and the electrochemistry of the $MoL(CO)_3$ (L = **103**) complex has been studied [147]. The *meso-trans* forms of the ligands **104**, **105** and **106** give complexes of the type $MoL(CO)_4$ with a bidentate macrocycle [138,140].

(v) Complexes of sulphur-containing macrocycles

(a) Trithia macrocycles

Only four examples of ligands forming trithia macrocyclic complexes are known; these are formed by [9]aneS_3, **2**, [12]aneS_3, **33**, **35** and **111**. Ligand **34**

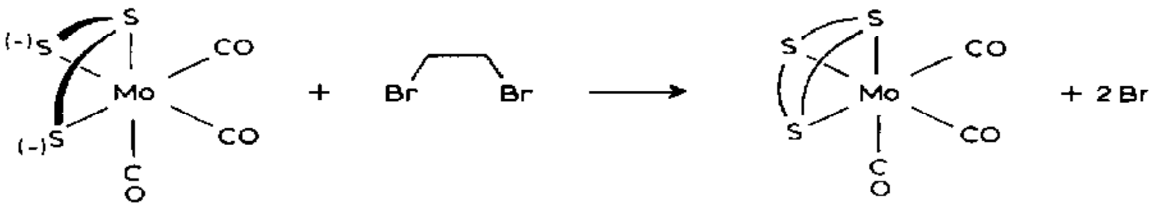


(111)

has been prepared and its crystal structure determined but no complexes have been described [139]. Vriesema et al. have reported the use of the Ni(II) complex of **111** as a catalyst in the cross-coupling reaction of the Grignard reagent of 1-phenyl-1-chloroethane and vinyl bromide [354]. The complex itself has not been described.

Rosen and Busch [159] prepared and characterized the Ni([12]aneS_3)$_2^{2+}$ complex and showed that the complex is octahedral with a ligand-field D_q value of 1110 cm^{-1}, a value consistent with that for other thioether complexes. The Cu^{2+}/Cu^+ redox potential (0.789 V) [355] and the Raman spectrum of Cu[12]aneS_3^{2+} [356] have been measured but the complex has not been described in detail.

Complexes of [9]aneS_3 have been much more thoroughly characterized. Structures of the free ligand have been determined in both the solid [357] and the gas phase [358]. In both phases the S atoms are endodentate, so that, unlike most other thioether ligands, [9]aneS_3 can complex metal ions without conformational change. Structures of the complexes M([9]aneS_3)$_2^{n+}$ (M = Co(II), Ni(II), Cu(II) [162], Fe(II) [359], Pt(II) [360], Pd(II) [361] and Co(III) [223], Ru(II) [362,363]) and of Pd[9]aneS_3Br$_2$ [361] and Mo(CO)$_3$[9]aneS_3 [364] have all been determined. An In(III) complex, In[9]aneS_3Cl$_3$, has also been prepared [304]. Mo[9]aneS_3(CO)$_3$ is readily prepared in high yield by the template reaction



and the free ligand is isolated by reaction of the complex with the tetramethylammonium salt of 1,4,7-trithiaheptane [165,166]. [9]aneS_3 is an unexpectedly good ligand for first-row transition metal ions. Bis complexes have been formed with many of the first-row transition metal ions and the properties of these complexes are unusual. Fe[9]aneS_3Cl_3 is high spin with a temperature-independent magnetic moment of 5.93 μ_B [359]. Fe([9]ane$S_3)_2^{2+}$ and Co([9]ane$S_3)_2^{2+}$ are both low spin; the iron complex is the only known FeS_6^{2+} complex with a low spin electron configuration [359,365]. Analysis of the electronic spectra of the bis complexes of Fe(II) indicates that [9]aneS_3 exerts a strong ligand field.

The ESR spectrum of the Co(II) complex has been studied [366]. Values of the formation constants of the Co(II) complexes are four orders of magnitude higher than other reported constants for thioether complexes of Co(II). Unusually, the constant for the formation of the bis complex from the monocomplex is higher than the constant for the formation of the monocomplex [365]. This anomaly is probably associated with the fact that the bis complex is low spin. Oxidation of the Co(II) complex to the Co(III) species requires a strong oxidant such as peroxydisulphate. Cyclic voltammetry in nitromethane reveals the oxidation potential of the Co(II) complex to be +0.68 V (vs. NHE) and the complex has a reduction potential of −0.214 V [366]. A Co(I) complex, however, has not been isolated. Similar observations have been reported for acetonitrile [359] and aqueous solution [223]. Cyclic voltammetry of the Ni(II) and Fe(II) complexes reveals that the metal centres in these complexes are not oxidized [359]. Rate constants for the self-exchange reaction of the Co([9]ane$S_3)_2^{(2+/3+)}$ couple have been shown to be five orders of magnitude greater than the Co([9]ane$N_3)_2^{(2+/3+)}$ couple self-exchange rate constants [223]. This difference is accounted for by the reduced difference in the Co–S distances in the former complexes compared with the Co–N distances in the latter complexes.

Analysis of the visible spectrum of the Ni(II) complex revealed a D_q value (1276 cm^{-1}) which is much higher than that observed for the corresponding [12]aneS_3 complex and slightly higher than that for the [9]aneN_3 complex [359]. The origin of the strong ligand field for the [9]aneS_3 complexes will be discussed in Section E (i).

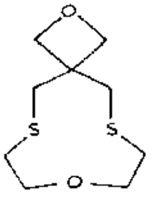
Cu([9]ane$S_3)_2^{2+}$ has an intense charge transfer transition at 446 nm ($\epsilon = 4696$), a property common to other thioether macrocycles [162,367]. The redox potential of the Cu([9]ane$S_3)_2^{2+}$ ion has been measured and shown to differ by 120 mV from that of the [18]aneS_6 complex. Despite large structural differences between the Cu([9]ane$S_3)_2^{2+}$ and Cu[18]aneS_6^{2+} ions, the ESR spectra and the spin Hamiltonian parameters of the two complexes are similar [162,163].

Three complexes of Pd(II) have had their structures determined: green Pd([9]ane$S_3)_2(PF_6)_2$, blue Pd([9]ane$S_3)_2(PF_6)_2 \cdot H_2O$ and brown Pd([9]ane-

$S_3)Br_2$. In each case the ligand is tridentate but there are four short equatorial bonds and two or one weak axial interactions with the third sulphur of the ligand. The difference in colour of the blue and green complexes is due to a change in the charge transfer transitions and is probably strongly dependent on the weak axial interactions [361]. Pt([9]aneS_3)$_2^{2+}$ has recently been reported by Blake et al. [360]. The platinum has an unusual square-pyramidal geometry in which one of the [9]aneS_3 ligands acts as a bidentate and the other is tridentate. Controlled potential electrolysis of this complex in acetonitrile gives the monomeric Pt(III) complex which has been characterised by ESR [360]. Ru([9]aneS_3)$_2^{2+}$ is extremely resistant to oxidation or reduction. This resistance has been attributed to the matching of the stereochemical and electronic demands of the ligand and the Ru(II) ion [362,363]. Complexes of the crown conformer of **110** with Cu(I) [368], Pt(II) [369] and Rh(III) [370] have been structurally characterized and shown to have tetrahedral, square-pyramidal and octahedral coordination respectively. PtL^{2+} (L = **110**) is particularly interesting because the metal interacts with the saddle conformer of the ligand in toluene and with the crown conformer in $CHCl_3$. Crystals isolated from dimethylacetamide solution revealed a distorted square-pyramidal coordination geometry around the Pt(II) with the Pt(II)–S(axial) bond distance being quite long.

(b) Other macrocycles containing sulphur

The only complexes of this type that have been reported are the Ag(I), Tl(I), Hg(II) and Pb(II) complexes of [9]aneS_2O and [9]aneSO_2 [371]. These large metal ions are believed to be too large to fit inside the ligand cavity, but the structures of the complexes are unknown. Enthalpies of formation and formation constants have been determined in 70% methanol [371]. Both 1 : 1 and 1 : 2 metal : ligand complexes are formed. The Hg(II) complex with [9]aneSO_2 is unusual in that only the 1 : 2 complex is observed. A ten-membered macrocycle, **112**, has been prepared, but complexes of this potential ligand have not been isolated [372].



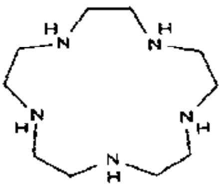
(112)

D. PENTADENTATE MACROCYCLIC COMPLEXES

(i) Nitrogen-containing macrocycles

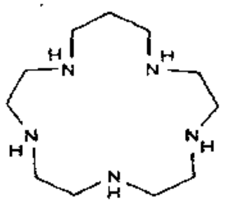
(a) Pentaaza macrocyclic complexes of [15]aneN_5 to [20]aneN_5

The pentaaza macrocycle [15]aneN_5 was originally prepared by Richman and Atkins [45–47], and the same general method has been used to prepare all the ligands described in this section. Ligands with all the possible



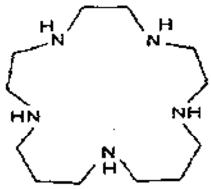
(113)

[15] ane N_5



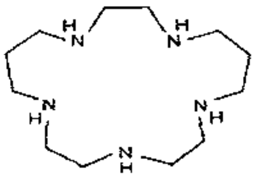
(114)

[16] ane N_5



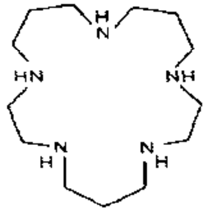
(115)

[17A] ane N_5



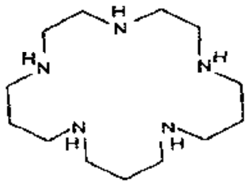
(116)

[17B] ane N_5



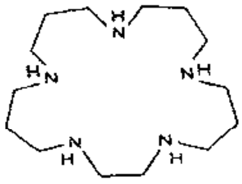
(118)

[18B] ane N_5



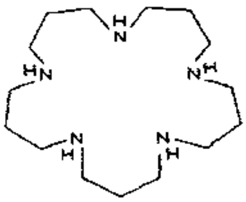
(117)

[18A] ane N_5



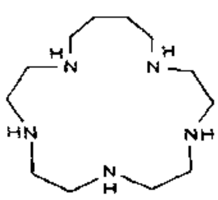
(119)

[19] ane N_5



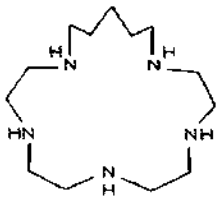
(120)

[20] ane N_5



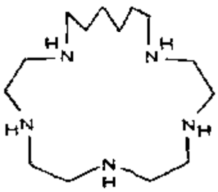
(121)

[17C] ane N_5



(122)

[18C] ane N_5



(123)

[19B] ane N_5

combinations involving two or three carbon atoms between adjacent nitrogen atoms have recently been described [59]. Some of these macrocycles and others with an extended methylene chain between two adjacent nitrogen atoms had been described earlier by Machida et al. [58] and by Kodama and Kimura [373]. Abbreviated names for these ligands are shown in structures **113–123**. A selectively substituted analogue of [15]aneN$_5$, Me$_4$[15]aneN$_5$, **24**, has been prepared as described in Section B (i) [132], and although Co(II), Ni(II), Cu(II) and Rh(III) complexes of this ligand have been prepared, they have not been fully characterized.

The majority of investigations into the complexes of the ligands **113–120** have been concerned with the metal ions Co(III), Ni(II), Ni(III), Cu(II) and Cu(III). Kodama and Kimura have measured formation constants for complexes with Cu(II), Zn(II), Hg(II), Pb(II) and Cd(II) [373,374]; these results are discussed in Section E (ii). Complexes of [16]aneN$_5$ with Mg(II), Ca(II), Na(I) and K(I) have been shown not to form [375]. Most of the complexes formed have a pseudo-octahedral structure with the pentaaza macrocycle occupying five of the six coordination sites. Three different dispositions of the chelate rings are possible in such complexes for all the ligands (except [15]aneN$_5$ and [20]aneN$_5$) as shown in Fig. 3 for [17A]aneN$_5$. For each of these complexes, three different configurations of the "planar" N–H bonds are possible (*syn-meso, anti-meso* and racemic) [376–378]. There are therefore nine isomers for most of the complexes, and when the arrangement of chelate rings in the equatorial plane is 5,5,6 or 5,6,6, then a further pair is possible [376]. For the ligands [15]aneN$_5$ and [20]aneN$_5$, only one di-

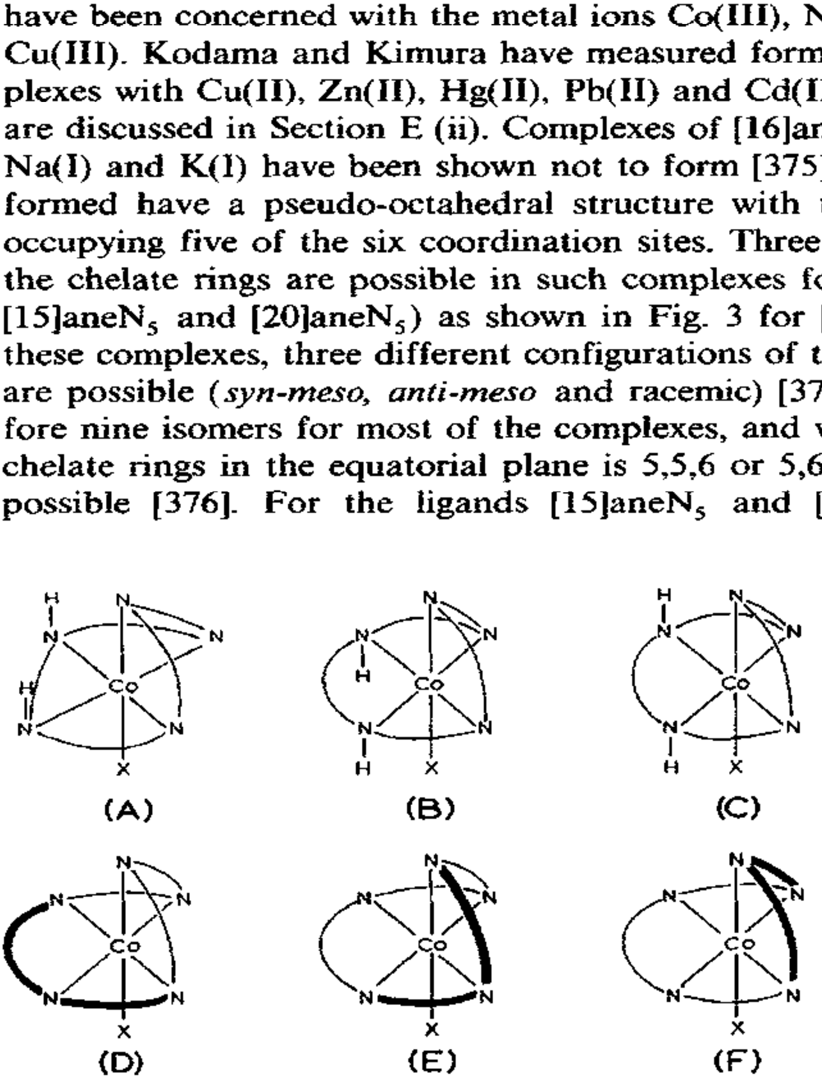


Fig. 3. Possible isomers of the Co[17A]aneN$_5$X^{n+} complex ion. The three configurations of the planar NH bonds are shown: **A**, *meso-syn*; **B**, *meso-anti*; **C**, racemic. Three dispositions of chelate rings are shown in **D**, **E** and **F**. Heavy lines represent six-membered chelate rings.

astereoisomeric pair and two mesomeric isomers are possible. Only for the Co(III) complexes has information about the isomers formed been obtained and we therefore consider complexes of these ligands with cobalt first.

Cobalt. $CoLCl^{2+}$ complexes (L = $[15]aneN_5$, $[16]aneN_5$ and $[17B]aneN_5$) have been prepared by reaction of the ligand hydrochloride with $Na_3[Co(CO_3)_3] \cdot 3H_2O$, and the aquo, formato and DMF complexes have been prepared by replacement of the coordinated chloride [377,379–381]. Chloro and bromo complexes of these ligands together with those of $[17A]aneN_5$ have been prepared by other methods [376]; reaction of the ligand with $Co(NH_3)_5X^{2+}$ (X = Cl or Br) or reaction of Co(II) with the pentaamine followed by oxidation with H_2O_2. Various other monodentate ligands can be substituted into the sixth coordination site.

For the 18-membered macrocycles $[18A]aneN_5$ and $[18B]aneN_5$, none of the above methods were successful [376]. Bromo complexes of these ligands and of the $[15]aneN_5$, $[16]aneN_5$, $[17A]aneN_5$ and $[17B]aneN_5$ ligands have been readily prepared in excellent yield by bromine oxidation of the Co(II) complexes. Chlorine oxidation has been used to prepare $Co[15]aneN_5Cl^{2+}$ in good yield [376].

Information about the isomers present in these complexes has been obtained from ^{13}C NMR spectrometry [376,377,380] and for four complexes by X-ray crystallography [378,382,383]. $Co[15]aneN_5Cl^{2+}$ was initially reported to be a mixture of all three possible isomers [380] but it was later shown that only two isomers (one racemic and one *meso*) are formed. Furthermore, the bromo complex is obtained only as the racemic isomer via a number of different preparative methods [376].

The crystal structure of $\{Co[16]aneN_5Cl\}(ClO_4)_2$ has been reported [378] and the complex is the *meso-syn* isomer of the most symmetric geometric isomer with the 5,6,5 arrangement of chelate rings in the equatorial plane. Coordination around the cobalt is close to octahedral and bond lengths and angles within the complex are unremarkable. All preparative methods used have been shown (using ^{13}C NMR spectroscopy) to yield a single product of the same isomeric form, and there is no evidence for the presence of any of the other ten possible isomers [376,377].

The preparation of Co(III) complexes of $[17B]aneN_5$ from $Na_3[Co(CO_3)_3] \cdot 3H_2O$, and metathesis reactions of the chloro complex have been described [376,379]. One or two isomeric forms are produced [376] (on the basis of ^{13}C NMR evidence the second form has a plane of symmetry). The isomeric chloro complexes can be readily separated on the basis of their solubility in water. A crystal structure of the bromo complex of the unsymmetric isomer has been determined (Fig. 4) [383]; both six-membered chelate rings are in the equatorial plane and again bond lengths and angles are unremarkable.

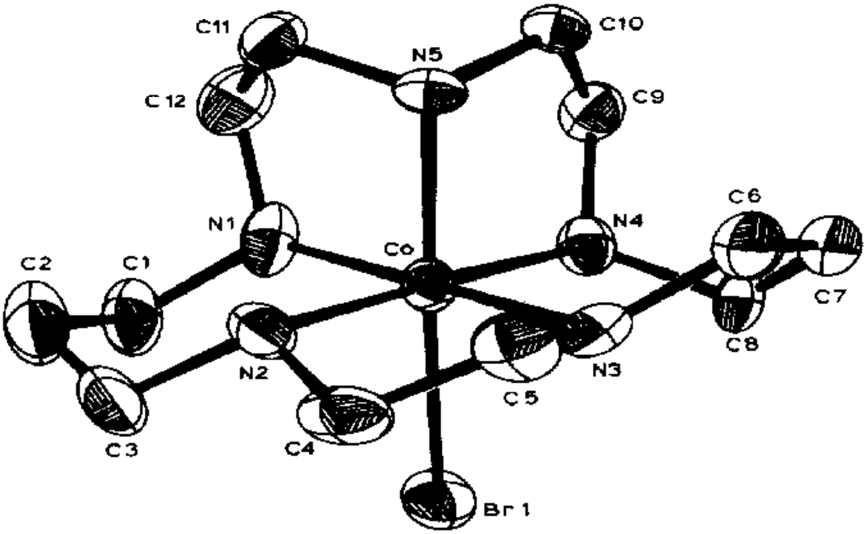


Fig. 4. Structure of the $Co[17B]aneN_5Br^{2+}$ cation.

The symmetric isomer must have the same arrangement of five- and six-membered chelate rings around the Co(III) so that the two isomers differ only in the configuration of the N–H bonds.

Only one of the possible isomeric forms of the chloro and bromo complexes of $[17A]aneN_5$ with Co(III) is observed [376]. The structure of $Co[17A]aneN_5Cl^{2+}$ has been determined and both six-membered chelate rings are in the equatorial plane; the complex has the racemic configuration. There are some severe non-bonded interactions between hydrogen atoms of one of the six-membered chelate rings (with a boat configuration) but the Co(III) ion has a pseudo-octahedral coordination geometry with bond angles close to 90° [376].

Co(III) complexes of $[18A]aneN_5$ and $[18B]aneN_5$ are significantly less stable than those of the smaller macrocyclic rings. Significant decomposition of the bromo complexes is observed in aqueous solution. $Co[18A]aneN_5Br^{2+}$ is green in colour whereas most other bromopentaamine complexes are purple. $Co[18A]aneN_5Br_3$ has been structurally characterized; all six-membered chelate rings are in the equatorial plane with the N–H bonds displaying the *meso-anti* configuration [382]. This structure reveals that the ligand experiences considerable steric hindrance in trying to coordinate to Co(III), two Co–N bonds are very long, and there are numerous non-bonded interactions between the hydrogen atoms of the ligand. $Co[18B]aneN_5Br_3$ also has an unusual electronic spectrum and the ^{13}C NMR spectrum indicates that only one isomeric form of the complex is present. Indirect evidence suggests that this complex has two six-membered chelate rings in the equatorial N_4 plane [376].

Rates of acid hydrolysis of these complexes are very dependent on ring size. Co[15]aneN_5Cl^{2+} is slow to react ($k = 1.66 \times 10^{-4}$ s^{-1} at 50 °C) [380] but the rate for Co[18A]aneN_5Br^{2+} is rapid ($k > 0.05$ s^{-1} at 25 °C) [67]. For Co[18B]aneN_5Br^{2+} the rate is several orders of magnitude slower ($k \approx 5 \times 10^{-5}$ s^{-1} at 25 °C). Hg^{2+}-catalysed hydrolysis rates have been measured for Co[17B]aneN_5Cl^{2+} [379] but the uncatalysed reaction rates have not been reported. Acid hydrolysis reactions of these complexes are accompanied by extensive competition for the vacant coordination sites by anionic species in solution but this interesting aspect of these reactions has not been studied.

Co(III) complexes of [19]aneN_5 and [20]aneN_5 have not been isolated. Co(II) solutions with [19]aneN_5 are air sensitive, but solutions with [20]aneN_5 are air stable. Solid Co(II) complexes with both ligands have been isolated, and solid state and non-aqueous solution spectra, IR spectra, magnetic susceptibility and conductivity data are consistent with high spin five-coordinate Co(II) complexes [376]. Data for Ni(II) and Cu(II) complexes of these ligands also suggest five-coordination so that the potential for steric strain in the pseudo-octahedral complexes is apparently relieved by reducing the metal coordination number.

Oxygen uptake by the Co(II) complexes of [15]aneN_5, [16]aneN_5, [17C]aneN_5, [18C]aneN_5 and [19B]aneN_5 to form μ-peroxo complexes has been investigated [58,384]. The reaction with [15]aneN_5 is irreversible as are the reactions with [16]aneN_5, [17C]aneN_5 and [18C]aneN_5 complexes. With [19B]aneN_5, oxygen uptake is reversible in the presence of CO_2. Equilibrium constants for the reaction have been determined and the rate of oxygen uptake measured. Oxygen binding is not as strong as for the Co(tetren)$^{2+}$ complex but the rates of oxygen uptake by the two complexes are very similar.

Base-catalysed hydrolysis reactions of the chloro, formato and DMF complexes with [15]aneN_5, [16]aneN_5 and [17B]aneN_5 have all been studied [377,379–381]. Other than the expected and observed acceleration of the rates compared with those for the Co(tetren)X^{n+} complexes, no pattern is discernible. The acid-catalysed decarboxylation of $CoLCO_3^+$ complexes (L = [15]aneN_5, [17B]aneN_5) has also been investigated. The reactions occur at rates similar to that of the linear pentaamine analogue at 25 °C as the ΔH and ΔS values exert compensating effects [379,380]. Co[15]aneN_5OH^{2+} is able to hydrolyse 4-nitrophenyl acetate and Hay and Bembi have reported a kinetic study of the reaction [385]. The macrocyclic complex is six times more reactive than the $Co(NH_3)_5OH^{2+}$ complex.

Nickel. Ni(II) complexes of [15]aneN_5, [16]aneN_5 and [17B]aneN_5 were first described by Paoletti and coworkers [386] and subsequent investigations by Fabbrizzi and coworkers [387–389], Hay et al. [377,379,380] and Osvath et al. [59] have confirmed and extended the original reports. Electronic spectra of the complexes show that they have a distorted pseudo-octahedral geometry in solution, with a water molecule occupying the sixth coordination site. With [15]aneN_5 the distortion from a regular octahedron is thought to be severe. Paoletti proposed, on the basis of enthalpy measurements and an analysis of the electronic spectra, that the [16]aneN_5 and [17B]aneN_5 complexes have one six-membered chelate ring in the equatorial N_4 plane [386]. This is the same arrangement as that observed in the crystal structure of the Co[16]aneN_5Cl^{2+} complex but different from that of the Co[17B]aneN_5Br^{2+} complex described above. Solution spectra of the Ni[17A]ane$N_5H_2O^{2+}$, Ni[18A]aneN_5^{2+} and Ni[18B]aneN_5^{2+} complexes are also consistent with a pseudo-octahedral structure. However, the two [18]aneN_5 complexes show slightly anomalous spectra which it is presumed arise from increased steric strain due to the requirement to accommodate the additional six-membered chelate rings [59]. IR, solid state reflectance spectra and conductivities in non-coordinating solvents of the $NiL(ClO_4)_2$ salts of these ligands are, however, consistent with a five-coordinate geometry in the solid state. $NiL(NO_3)_2$ salts apparently contain a coordinated nitrato group and the complexes are six-coordinate [59].

Ni(II) complexes of [19]aneN_5 and [20]aneN_5 have aqueous solution spectra consistent with a five-coordinate square-pyramidal geometry. With these two ligands, five-coordination is also observed in the solid nitrate salts, and in non-coordinating solvents the nitrate salt is a 2 : 1 electrolyte [59].

A notable feature of macrocyclic tetraamines is their ability to stabilize unusual oxidation states. Ni(II) complexes of [15]aneN_5, [16]aneN_5, and [17B]aneN_5 are more readily oxidized than any tetraaza macrocyclic complex with the exception of Ni[14]aneN_4^{2+} [379,387–389]. Oxidation of Ni[16]aneN_5^{2+} by OH radicals is followed by a very slight change in the absorption spectrum of the product and it has been suggested that the reaction involves some sort of isomerization of the five-coordinate Ni(III) product [387]. Unlike the tetraaza macrocyclic complexes, there is little dependence of $E_{1/2}$ values upon the macrocyclic ring size and it has been suggested that this is a reflection of the absence of in-plane ring-size effects in the pentaamine complexes. For the Ni[16]aneN_5^{2+} complex, changing from acetonitrile to DMSO solvent results in a 350 mV stabilization of the Ni(III) state. This is not simply a result of the greater coordinating tendency of DMSO, as changes of similar magnitude in the redox potentials have been observed for coordinatively saturated bistriaza macrocyclic complexes. Stabilization of the Ni(III) state is observed on increasing the perchlorate ion concentration. This is thought to be the result of an increasing negative environment not involving the inner coordination sphere [68].

The ESR spectra of frozen acetonitrile solutions of Ni(III) complexes of [15]aneN_5, [16]aneN_5 and [17B]aneN_5 have been recorded [388] and all three complexes have $g_\perp > g_\parallel$ ($g_\perp = 2.17$; $g_\parallel = 2.03$). A five-line $g_\parallel$ feature is observed in each case. This is attributed to the interaction of the unpaired electron with the two inequivalent nitrogen atoms (the axial macrocyclic nitrogen and an acetonitrile nitrogen). This is supported by the ESR spectrum of the Ni(III) complex of [16]aneN_5 in methanol at 77 K showing three $g_\parallel$ lines of equal intensity, which is the pattern expected for a folded macrocycle with four equatorial and only one axial donor nitrogen. Similar observations are reported for the Ni[15]aneN_5^{3+} complex at 77 K in frozen aqueous borate buffer [390].

Acid dissociation reactions of Ni(II) complexes of [15]aneN_5, [16]aneN_5 and [17B]aneN_5 are considerably more facile than those of tetraaza macrocycles [377,379,380]. Dissociation of Ni[15]aneN_5^{2+} shows a second-order dependence on hydrogen ion concentration ($k = 0.63$ dm^6 mol^{-2} s^{-1}) [380], whereas the reactions of [16]aneN_5 and [17B]aneN_5 complexes in the same concentration range show a first-order dependence on hydrogen ion concentration (for Ni[16]aneN_5, $k = 9.4 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} [377]; for Ni[17B]aneN_5, $k = 0.23$ dm^3 mol^{-1} s^{-1} [379]). It has been suggested that this difference arises because the apical nitrogen in complexes of [16]aneN_5 and [17B]aneN_5 is protonated throughout the acidity range investigated [379]. Fabbrizzi and coworkers, however, failed to observe protonation of these complexes [386] and further suggest that steric strain is relieved when a six-membered chelate ring replaces a five-membered chelate ring in the distorted Ni[15]ane$N_5H_2O^{2+}$ complex. This would suggest that the Ni[15]aneN_5^{2+} complex should be more readily protonated than, for example, Ni[16]aneN_5^{2+} which is not in accord with the above suggestion.

Copper. Analysis of the conductivity of non-aqueous solutions, IR and solid state and solution electronic spectra of the copper complexes of [15]aneN_5, [16]aneN_5, [17A]aneN_5, [17B]aneN_5, [18A]aneN_5, [18B]aneN_5, [19]aneN_5 and [20]aneN_5 suggests six-coordinate salts are formed with nitrate anion. A coordinated nitrato group occupies the sixth coordination site. Perchlorate salts of complexes with these ligands are all 2 : 1 electrolytes, so that the perchlorate anion is apparently not coordinated. It has been suggested that the less sterically demanding Cu(II) ion can accommodate pseudo-octahedral coordination geometries as the number of six-membered chelate rings is increased, whereas Ni(II) becomes five-coordinate [59].

The structure of the Cu[15]aneN_5^{2+} and Cu[16]aneN_5^{2+} complexes has been probed by ESR and the presence of one axial nitrogen donor and the off-plane distortion of the square-planar basal plane are suggested by the $A_\parallel$ parameter [390].

Oxidation of the Cu(II) complexes of [15]aneN_5, [16]aneN_5 and [17B]aneN_5 is substantially less favoured than that of the corresponding Ni(II) complexes and controlled potential electrolysis in acetonitrile solution leads to demetallation and fragmentation of the complexes in a multielectron process. With rapid potential scan cyclic voltammetry (> 5 V s^{-1}), it is possible to observe the first step in this process, i.e. the oxidation of the metal centre [391]. The order of the $E_{1/2}$ values is the same as for the Ni(II)/Ni(III) couples and similar changes are observed for increasing macrocyclic ring sizes. With copper it is clear that the addition of the fifth axial donor nitrogen does not favour the Cu(III) oxidation state. Reduction of the Cu(II) complexes of these ligands has been studied by cyclic voltammetry [5,390]. Cu(I) complexes are slightly more accessible than in the corresponding tetraaza macrocyclic systems and the stabilization is attributed to the apical nitrogen.

Reaction of the Cu(II) complexes of the ligands [15]aneN_5, [16]aneN_5, [17A]aneN_5, [17B]aneN_5, [18A]aneN_5, [18B]aneN_5, [19]aneN_5, and [20]aneN_5 with acid has been studied in perchlorate (for [15]aneN_5, [16]aneN_5 and [17B]aneN_5 only) and nitrate media [67,377,379,380]. Cu[15]aneN_5^{2+}, Cu[16]aneN_5^{2+} and Cu[17B]aneN_5^{2+} show a second-order dependence on hydrogen ion concentration at low hydrogen ion concentration but at higher concentrations (up to 1 M) limiting kinetics are observed with Cu[16]aneN_5^{2+} and Cu[17B]aneN_5^{2+}. Cu[17A]aneN_5^{2+} shows a first-order dependence on hydrogen ion concentration over the range 0.02–1 M but all the other complexes have a more complex acid dependence over the acidity range studied [67].

Rates of complex formation of the Cu(II) complexes of [15]aneN_5, [16]aneN_5 and [17B]aneN_5 have been measured in acetate buffer solutions. Under the experimental conditions chosen the reactive forms of the ligands are H_2L^{2+} and H_3L^{3+} and these react with $CuOAc^+$ [373]. Rate constants increase by a factor of 100 as the macrocyclic ring size increases. Tabushi and Fujiyoshi [124] have measured the rate of formation of the Cu[15]aneN_5^{2+} complex in 0.5 M NaOH solution ($k = 4.6 \times 10^5$ M^{-1} s^{-1}) but a more detailed study of this reaction over a range of hydroxide concentrations is necessary before any meaningful comments can be made. Ligand-exchange reactions of copper complexes of aminocarboxylates with [15]aneN_5 have been reported [392]. The rate constants are smaller than those for similar reactions with linear polyamines but a similar mechanism has been used to explain the results.

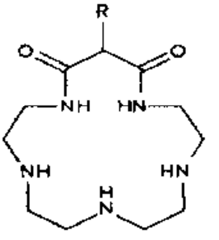
Interactions with anions and biological implications. These macrocycles have been shown to have a number of interesting properties, which mean that they can serve as useful models of biological systems and may have some theraputic value. Kimura et al. have made extensive investigations of the interactions of a wide range of polyamines including [15]aneN_5, [16]aneN_5, and [17B]aneN_5 with anions [393–395]. The macrocyclic polyamines are selective receptors for most tricarboxylic acid–cycle intermediates and their analogues [395]. It is the triprotonated form of the macrocycle which interacts with the anions and ring size effects have been demonstrated for the formation constants. The physiological implications of the interaction with bicarbonate ion have been discussed in some detail [393].

[16]aneN_5 has been shown to solubilize calcium phosphate and urinary calculii and may find some use in the removal of such calculii [396]. [15]aneN_5 has been shown to be a particularly effective agent for enhancing the urinary excretion of copper in rats and its use as an improved drug in the treatment of Wilson's disease has been suggested [397].

(b) Other pentaaza macrocycles

Ligands prepared by non-template methods. Kimura and coworkers have studied Ni(II) and Cu(II) complexes of the oxapentamine ligands **14**–**17** and **124**–**129** together with related macrocyclic tetraamines [121,125,398–402]. Amide nitrogen atoms are deprotonated upon coordination to these metal ions; an Ni(II) complex of **14** has a square-pyramidal structure [398,400] with the two imide anions in the basal plane. Ni(II) and Cu(II) complexes of **14**–**17** and **123**–**128** are expected to have similar structures. Coordination of the pyridine nitrogen of **128** to Ni(II) is observed, and complexes of this ligand are discussed in Section E (iv).

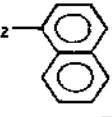
$NiH_{-2}L$ (L = **129**) exists as a mixture of high spin and low spin Ni(II)

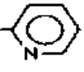


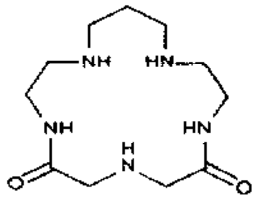
(124) R = CH_3

(125) R = CH_2CH_3

(126) R = CH_2—


(127) R = CH_2—


(128) R = CH_2CH_2—




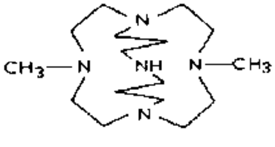
(129)

[121]. As bonding to the amide nitrogen atoms is planar, it is likely that the fifth nitrogen is unable to coordinate to the nickel and the ligand is tetradentate. Ligand **17** is of interest because the imide anions must be in the basal plane, which requires the pyridine nitrogen to occupy an axial position, and molecular models indicate that this must involve considerable strain. Ni(II) complexes of **17** and **16** have very different visible spectra, thought to result from strain in the $NiH_{-2}L$ (L = **17**) complex [121].

Ni(II) complexes of **14** and **124–128** have been thoroughly characterized, the stability constants, redox potentials, magnetic susceptibilities, ESR spectra and kinetics of the reaction of $NiH_{-2}L$ (L = **14**) with oxygen all having been studied [121]. Redox potentials of the Ni(III)/Ni(II) couples are similar and are the lowest known for nickel complexes. These potentials are lower than potentials of the Cu(III)/Cu(II) couple indicating that the coordination environment of these ligands is more favourable for Ni(III) than Cu(III). The R substituents have little effect on the redox potentials but the nature of R does affect the reactivity of the complex. Freshly prepared Ni(III) complexes are stable in aqueous solution for 4–5 h at pH 7 but decompose rapidly at pH 10. If the Ni(III) complexes are first isolated, then the complexes are stable in solution for 24 h at room temperature [398]. The structure of the $NiH_{-2}LH_2O^+$ (L = **126**) complex has been determined, and Ni(III) shown to have tetragonally distorted octahedral coordination [398]. Superoxide dismutase activity of the Cu(II) and Ni(II) complexes of **14**, **15**, **124–127** and **129** has been investigated and the Ni(II) complexes shown to be extremely effective in this role [125,402].

Even more remarkable is the fact that the Ni(II) complexes of **14** and **124–127** can react with air to give a 1:1 $NiH_{-2}LO_2$ adduct [121,399] and with **125** the formation of this adduct is reversible. The bound oxygen is activated and is able to oxygenate aromatic substrates to produce phenols, and it has been shown that the oxygen is directly incorporated into the aromatic ring [399,401]. Oxygen uptake at 35 °C is quite slow ($k = 0.017$ M^{-1} s^{-1}) and is independent of pH. Magnetic susceptibility measurements of the O_2 adduct indicate $S = 1$, for the Ni(III) complex $S = 1/2$ and for the Cu(III) complex $S \approx 0$. The last value raises the possibility that Cu(III) complexes with these ligands might be four-coordinate but the Cu(III) complexes have not been thoroughly characterized [121].

A pentaaza macrobicyclic ligand, **130**, has been described by Ciampolini

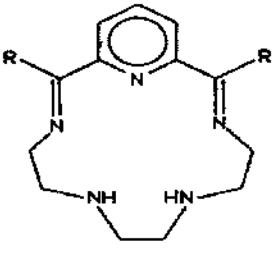


(130)

et al. [403,404]. Crystal structures of the free ligand [404] and the Cu(II) complex [403] have been determined; the copper is in a distorted square-pyramidal geometry with the secondary nitrogen in the axial position. Complexes with Cu(II), Zn(II), Ni(II), Co(II), Li(I) and Mg(II) have been described but complexes with Na(I), K(I), Be(II) and Al(III) were not observed [403]. Electronic spectra of the Co(II) and Ni(II) complexes are consistent with a square-pyramidal geometry.

Ligands prepared by template reactions. Considerable effort has been devoted to the study of pentaaza macrocycles formed by Schiff's base condensation reactions in the presence of a metal ion which acts as a template. Successful preparation of macrocyclic complexes via these methods is dependent on a number of factors which have been discussed in detail [37,38]. Preparation of pentaaza macrocyclic ligands has usually involved relatively rigid molecules as precursors and metal ions which have no preference for a particular coordination geometry. This has been suggested as a rule [405] but there are enough exceptions to the rule to suggest that its validity is doubtful. In the absence of protons or metal ions the organic precursors generally yield polymeric materials of variable composition. 2,6-Diacetylpyridine and pyridine-2,6-dicarbaldehyde are the most widely studied precursor molecules and they react with a wide variety of tetraamines or dihydrazines to give macrocycles. If terminal diamines with other potential donor groups are used in these template reactions, mixed-donor macrocycles of the type N_3X_2 are formed. These complexes are discussed in Section D (i) (d).

Complexes of the ligand [15]pydieneN$_5$, **131**, were first prepared by Curry and Busch in 1964 [3] and complexes of this ligand have continued to be the subject of investigations ever since. Much of the work performed by Nelson and Drew and their groups has been reviewed [11,38,406] and so will not be discussed in great detail here. Condensation of 2,6-diacetylpyridine and triethylenetetraamine gives complexes of **131** in the presence of the following metal ions: Mg(II) [407], Mn(II) [408–411], Zn(II) [411], Fe(II) [405,412–414], Fe(III) [3,415–418], Co(II) [419], Sn(IV) [420], Cd(II) [421–423] and Pb(II)

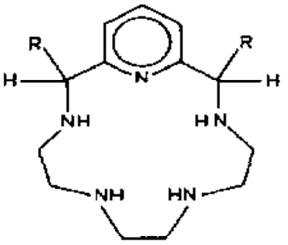


(131) R = CH$_3$

[424]. Complexes of these metals in different oxidation states have been prepared by electrochemical or chemical means [405,411]. Structural determinations have been reported for complexes of Fe(III) [415,417], Fe(II) [414,417,425], Mg(II) [407], Zn(II) [426] and Cd(II) [422]. The rigidity of the ligand imposes a pentagonal bipyramidal coordination geometry on all of the metal ions.

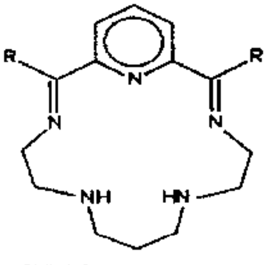
Recently, interest in complexes of this ligand has focused on iron and Mn(III) complexes and follows earlier work on Mössbauer [427] and ESR spectra [428] of the iron complexes. Recent work on the iron complexes includes a study of charge-transfer photochemistry (which is largely dependent on the nature of the axial ligands) [429], low temperature magnetic susceptibility [418], possible use of the complexes in electrochemical devices [430–432] and unusual magnetic behaviour of $FeL(CN)_2$ complexes [413]. It is suggested that this magnetic behaviour can be explained by a structure in which the macrocycle acts as a quadridentate ligand with one of the secondary amino groups not coordinated. Low temperature magnetic susceptibility measurements and ground state zero-field splitting parameters of the $MnLCl_2^+$ and $MnLBr_2^+$ complex ions have been reported [433].

Hydrogenation of complexes of **131** gives complexes of ligand **132** [434–436] which is much less rigid than **131** and as a consequence is able to form complexes with a variety of coordination geometries. Ni(II) complexes have been prepared and have a pseudo-octahedral structure [435]. $CuL(PF_6)_2$ (L = **132**) has a trigonal bipyramidal coordination geometry with all five nitrogen atoms coordinated to Cu(II) [436,437]. $CoLCl(ClO_4)_2$ (L = **132**) has octahedral Co(III) with an approximate square pyramid formed by the five nitrogen atoms of the ligand [436,437] and $FeL(NCS)_2^+$ (L = **132**) has a pentagonal bipyramidal geometry [434]. Structures of Cu(II) and Co(III) complexes are apparently determined by preferences of the metal ion whereas that of the Fe(III) complex is determined by ligand preference [436]. Photochemical reactions of $FeLX_2^+$ (L = **132**) have also been studied [429].



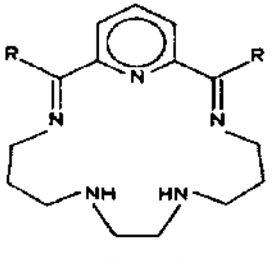
(132) R = CH_3

Reaction of 2,6-diacetylpyridine with the tetraamines 1,9-diamine-3,7-diazanonane (2,3,2-tet) and 1,10-diamine-4,7-diazadecane (3,2,3-tet) in the presence of metal ions gives complexes of the macrocyclic ligands [16]pydieneN$_5$, **133**, and [17]pydieneN$_5$, **134**. Complexes of **133** are formed using the following metal templates: Mg(II) [407], Fe(III) [416,417], Fe(II) [405,412–414], La(III) [419], Co(II) [419], Ag(I) [438], Zn(II) [411], Hg(II) [439], Cd(II) [421,439], Sn(IV) [420] and Mn(II) [407,409,411,440]. Structural studies have been reported for complexes of the following metal ions: Ag(I) [438], Mn(II) [440], Fe(II) [414], Fe(III) [417] and Cd(II) [439]. In contrast to the situation with **131**, the increase in the macrocyclic ring size results in structural diversity. Mn(II), Fe(II), Fe(III) and Cd(II) complexes are still seven-coordinate but the plane containing the five nitrogen atoms and the metal ion is more distorted. Ag(I) is bound to the five nitrogen atoms of the ligand in a plane and there is a sixth nitrogen from an adjacent ion at a distance just longer than the equatorial Ag–N distances. The coordination geometry is thus pentagonal pyramidal [438].



(133) R = CH_3

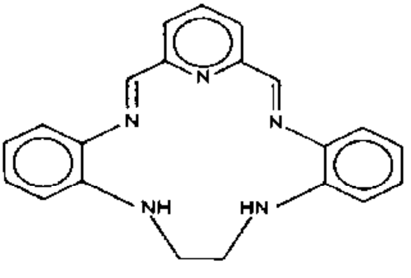
Complexes of **134** are formed using the following metal templates: Mg(II), Ca(II), Sr(II), Ba(II) [441], Pb(II) [424,442], Cd(II) [421,439], Hg(II) [421,439], Mn(II) [409,411], Zn(II) [411] and Ag(I) [439,443]. Structures of complexes with the following metals have been determined: Mn(II) [409], Cd(II) [421,439], Hg(II) [421,439], Ag(I) [439] and Pb(II) [424,442]. Only MnL(NCS)$_2$ (L = **134**) is seven-coordinate although its structure is not a regular pentagonal bipyramid. The pyridine nitrogen lies below the plane of the other four nitrogen atoms and the metal ion is above the plane. Chemical evidence suggests that other manganese complexes may be six-coordinate [409]. Cd(II) and Hg(II) complexes of **134** are both six-coordinate



(134)

with a planar array of four nitrogen atoms from the macrocycle; the fifth nitrogen is below the plane and there is a sixth ligand above the nitrogen plane [421,439]. $PbL(SCN)_2$ (L = **134**) has a similar structure but is even more distorted owing to a stereochemically active lone pair of electrons [442]. AgL^+ is five-coordinate with all five nitrogen atoms of the macrocycle bound to the metal [439]. Thus **134** can adopt three different conformations suitable for five-, six- and seven-coordination geometries. Cu(II) and Ni(II) complexes of **134** can be prepared via transmetallation reactions with the Ag(I) complex [443]. These complexes are the only examples of these metals complexing the pydieneN_5 ligands, and the visible spectra of the nickel complexes suggest that nickel is six-coordinate. PbL^{2+} (L = **134**) has been reduced using borohydride but no details of complexes of the reduced ligand have been published [424].

Mn(II) and Zn(II) complexes of the ligand **135** formed by condensation of pyridine-2,6-dicarbaldehyde with the appropriate tetraamine have been prepared. The Mn(II) complex has been structurally characterized and shown to have a pentagonal bipyramidal structure with perchlorate ions in the axial positions [444].



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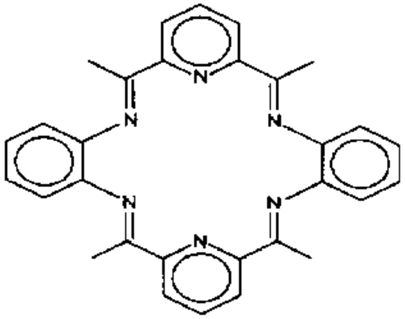

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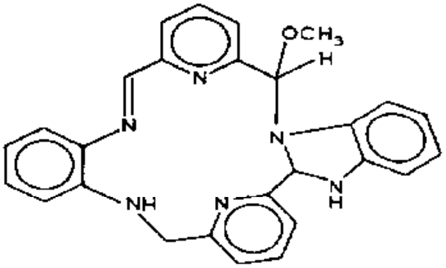

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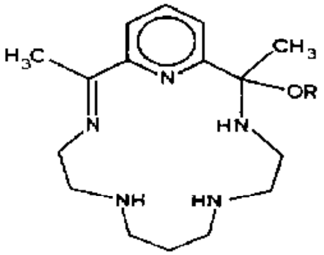

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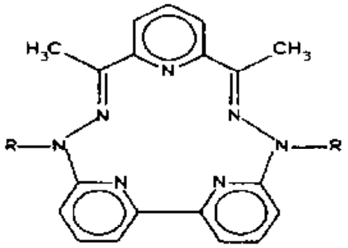
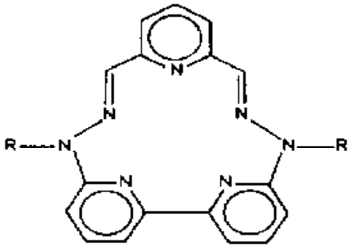
Barium complexes of the 18-membered macrocycle **136** react with Pb(II) salts in a transmetallation reaction to give the Pb^{2+} complex of **136**, but treatment of BaL^{2+} (L = **136**) with manganese, iron, cobalt or zinc salts in methanol results in ring contraction to the 15-membered macrocycle **137** [445,446]. The structure of $CoL(H_2O)_2^{2+}$ (L = **137**) has been determined and the Co(II) is in a pentagonal bipyramidal environment. Complexes with the other metal ions are believed to have similar structures [445]. A mismatch in size between the small transition metal ions and the hole size of the ligand **136** is believed to be the driving force for the rearrangement. A similar reaction has been observed with the ligand **133**. In this case the attempted preparation of an Ni(II) complex by treatment of the AgL^+ (L = **133**) complex with Ni(II) salts in dry alcohol solutions results in the formation of the Ni(II) complex of macrocycle **138** (R = CH_3 or C_2H_5). If the alcohol is wet, a non-macrocyclic ring-opened product is obtained [443].

Pentaaza macrocyclic complexes formed by condensation of 2,6-diacetylpyridine or 2,6-diformylpyridine with bishydrazines have been investigated by Lewis and coworkers. They have used a number of bishydrazines derived from 1,10-phenanthroline and 2,2′-bipyridyl to form complexes of the ligands **139**–**152**. Reaction, in aqueous or methanol solutions usually containing a few drops of mineral acid, in the presence of Ni(II) [447,448], Mn(II) [449–452], Zn(II) [453–456], Cd(II) and Hg(II) [453,455], Co(II) [457–459], Fe(II) [460,461] and Cr(III) [462] results in the formation of complexes of these ligands. Uncertainty has surrounded the role played by the metal ion in these condensation reactions because acid is usually necessary, and in the presence of Cr(III) the free macrocyclic ligands **139** [463], **141**–**143** and **147**–**149** [462] have been isolated. This suggests that ligand formation may be mediated by protons rather than the metal ion. In the absence of the metal ion template, macrocyclic products are not isolated unless the pH of the solution is below about four. Above this pH the carbanolamine form of the macrocycle is favoured, and facile hydrolysis is likely [463]. Proton involvement is supported by the fact that if the Cr(III) complex of the dihydrazine is prepared and allowed to react with 2,6′-diacetylpyridine, the Cr(III) macrocyclic complex and not the free ligand is obtained. This latter observation suggests that Cr(III) can act as a templating ion but that protons have a kinetic advantage. Reaction may proceed via the carbanolamine, as the $ZnL(NO_3)^+$ (L = **150**) complex has been isolated and structurally characterized during the preparation of ZnL^{2+} (L = **142**) [456]. Carbanolamine **151** has been isolated as a Co(III) complex but details have not been published [463]. Single-crystal paramagnetism of NiL and CoL (L = **145**) complexes has been studied and the ligand field around the metal ion described in terms of a significant σ and π donor role for the ligand [448]. Proton NMR spectra of the zinc and cadmium complexes of **145** and **148** have been interpreted as indicating extensive π-electron delocalization in the complexes [455]. With the bipy derivative, **140**, the interpretation of the spectra is not as straightforward [453].

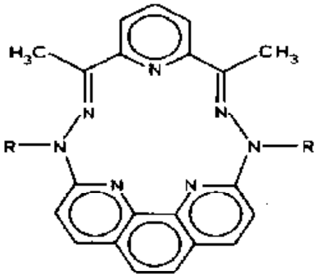
Electrochemical reduction of Ni(II) and Co(II) complexes of **145** gives the Ni(I) and Co(I) complexes [447,459] and the crystal structure of



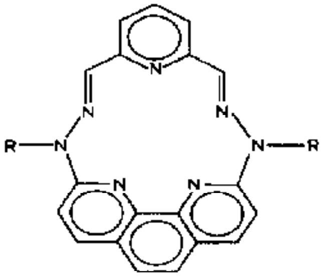
(139) R = H
(140) R = CH_3



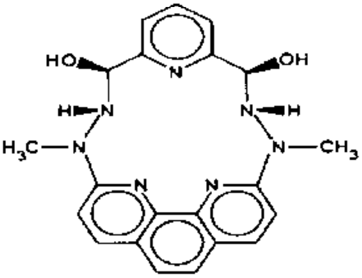
(141) R = H
(142) R = CH_3
(143) R = C_2H_4OH
(144) R = C_2H_4



(145) R = CH
(146) R = C_2H_4OH



(147) R = H
(148) R = CH_3
(149) R = C_2H_4OH



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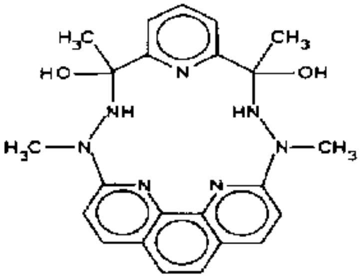

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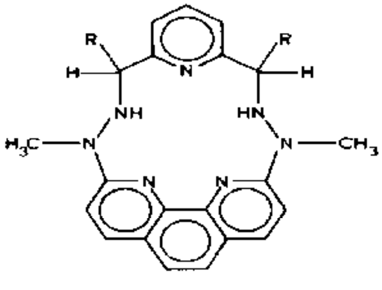


(152) R = CH_3
(153) R = H

$CoL(P(OCH_3)_3)BF_4$ has been determined [459]. Reduction of the Mn(II) complex results in a one-electron-reduced ligand species [450]. Chemical reduction of the hydrazone bonds of zinc and manganese complexes of **145** and **148** [449,455] results in the formation of complexes of the ligands **152** and **153**. Complexes of these ligands can exist in a number of isomeric forms owing to the asymmetric centres present. Evidence from NMR spectra of the zinc complex of **152** suggests that only one isomer is present and the macrocycle is folded. Both N–H bonds formed are on the same side of the macrocycle. Ligand **152** exists in three isomeric forms in which the protons are on the same side of the macrocycle, but the methyl groups on the carbon may be on the less-hindered side of the macrocycle, the more-hindered side or one on each side [455].

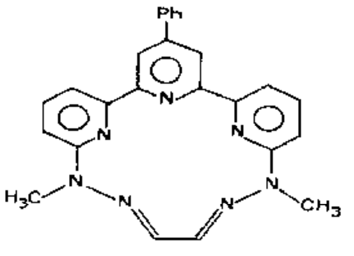
It is interesting that these 15-membered macrocyclic ligands are able to form complexes with Ni(II), whereas Ni(II) complexes of **131** and **132** are unknown. Ni(II) prefers octahedral over pentagonal bipyramidal coordination and this may account for the inability of **131** and **132** to form Ni(II) complexes [443]. $NiL(H_2O)_2^{2+}$ (L = **145**) has been shown to be a pentagonal bipyramidal complex [447] and it has been suggested that this ligand has a cavity which is larger than ideal for Ni(II) [464]. Ligand **131** has a larger cavity than **145** (225 pm for **131** [434] and 218 pm for **145**) so that interactions with the nickel ion would be even weaker. It is suggested that ligand **134** complexes Ni(II) because it is able to fold and adopt a square-pyramidal conformation with a smaller hole size [434]. $NiL(H_2O)_2(BF_4)_2$ is seven-coordinate and is isostructural with $CoL(H_2O)_2(BF_4)_2$ [458] and $FeL(H_2O)_2(BF_4)_2$ (L = **145**) [460,461]. The metal ions and the seven nitrogen atoms are coplanar and the ligand is almost planar [447]. Pentagonal bipyramidal structures have been established for the $CrL(H_2O)_2^{3+}$ (L = **143**) [462], $CoL(CH_3OH)_2^{2+}$ (L = **145**) [459], $CoL(H_2O)_2^{2+}$ (L = **148**) [457] and $ZnL(H_2O)_2^{2+}$ (L = **139**) [454] complex ions. Comparison of the structures of $CoL(H_2O)_2^{2+}$ (L = **145**) and $CoL(H_2O)_2^{2+}$ (L = **148**) reveals that there are steric interactions between the methyl groups of **145** which cause a slight distortion of the macrocycle in the complex [457]. The free ligand **145** is planar in the solid and has a very similar cavity size to that observed in the metal complexes [465].

$MnLCl(BF_4)_2$ (L = **145**) has a slightly distorted pentagonal pyramidal structure with the Mn 53 pm above the N_5 basal plane and a chloride ion at the apex [449,452]. A similar structure has been determined for the Co(I) complex $CoL(P(OMe)_3)^+$ (L = **145**) [459] and $MnLCl^+$ (L = **146**) [451], and chemical evidence suggests that the Zn(II), Cd(II) and Hg(II) complexes of **145** and **148** [455] and $CdLCl^+$ (L = **140**) [453] have similar structures. Six-coordination of the metal ion has also been reported for the complexes $CuL(H_2O)(BF_4)_2$, $MnL(H_2O)(BF_4)_2$, $ZnLCl(BF_4)$ (L = **145**) [466] and

$LiL(CH_3OH)^+$ (L = **144**) [467]. This complex was prepared by conversion of **143** to **144** and then reaction with lithium salts.

Reaction of the dimethylhydrazine of 4′-phenyl-2,2′:6′,2″-terpyridine with $SnMeL_2Cl_2$ in aprotic solvents produces a complex of the dihydrazone with $Me_2Sn(IV)$ [468,469]. Reaction of this complex with glyoxal and a trace of mineral acid results in the isolation of a salt of the uncomplexed macrocycle **154**. Condensation in the presence of $Cr(H_2O)_6^{3+}$ gives the same product. Reaction of the precursors in the presence of Ni(II) and Mn(II) forms complexes of **154** with these metals. In the presence of other metal ions, reaction usually produces only complexes of the bismethylhydrazine but with Co(II) a complex thought to be a pseudo-octahedral complex of the ligand **155** is formed [468,470]. Attempted condensation reactions using either butane-2,3-dione or benzil instead of glyoxal did not lead to macrocyclic products. Constable et al. have reported the preparation of the unsubstituted ligand **156** derived from 2,2′:6′,2″-terpyridine [471].

The structure of **154** has been determined [469] and treatment with Mn(II), Ni(II) and Co(II) produces the known Mn(II) and Ni(II) complexes and the previously unknown Co(II) complexes. An X-ray analysis of an Ni(II) complex of **154** confirms the presence of a seven-coordinate pentagonal bipyramidal centre with two axial ethanol molecules [472]. Controlled potential electrolysis of a solution of NiL^{2+} (L = **154**) in the presence of $P(OCH_3)_3$ or CO in acetonitrile gives the Ni(I) complex [472]. If more negative potentials are used for the reduction, an Ni(I) ligand radical species with two paramagnetic centres is formed. Metal complexes of **156** are very similar to the complexes of **154**, and their properties are also similar. However, the electrochemistry of the Ni(II) complexes differs in interesting ways [471]. Reduction of the Ni(II) complex of **156** is quasi-reversible so that the phenyl substituent of **154** apparently stabilizes the Ni(I) oxidation state. The phenyl substituent may stabilize the radical species and may also act as an electron sink for the excess electrons on the nickel. $CuL(CH_3CN)_2^{2+}$ (L = **156**) undergoes quasi-reversible oxidation and a reversible reduction. A



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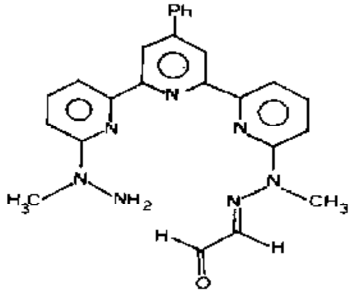

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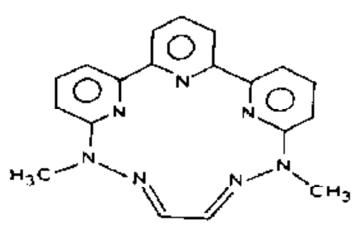
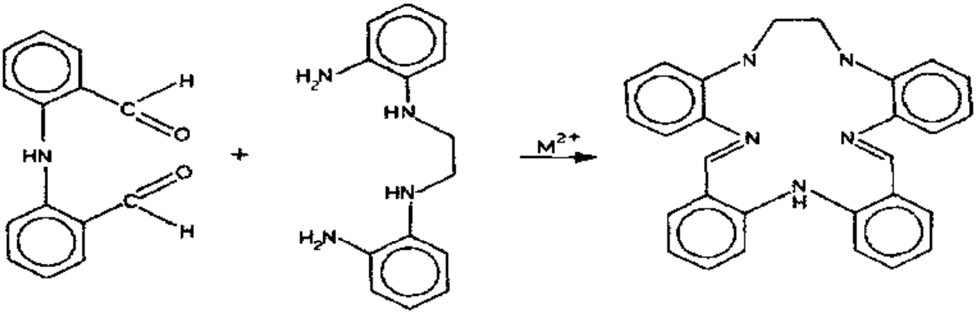


(156)

Cu(III) complex is indicated, but the nature of the product has not yet been reported.

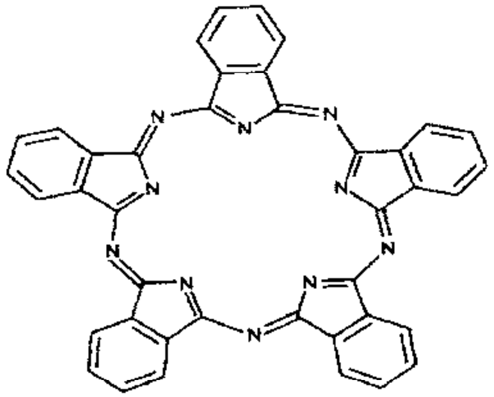
A 20-membered macrocycle **157** has been prepared via the template reaction



(157)

and the rather unstable Cu(II) complex has been shown to have a very irregular coordination geometry [473,474].

Ligand **158** can be prepared from dicyanobenzene in the presence of UO_2^{2+} to give a pentagonal bipyramidal complex of UO_2^{2+} [475]. Pentapyrrolic macrocycles (sapphyrins) have been prepared and indications obtained that the decamethylsapphyrin **159** forms complexes with Ni(II), Fe(II),



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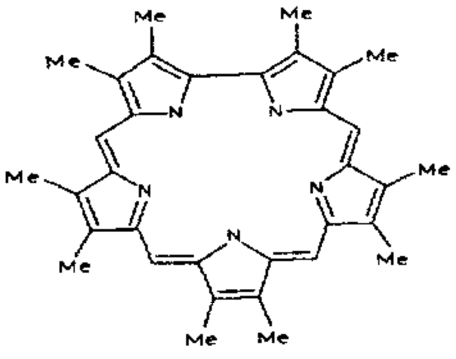
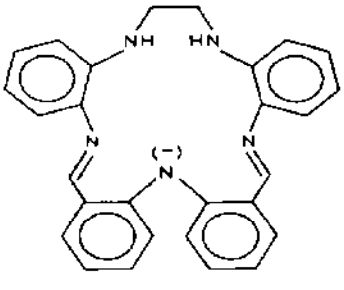


(159)

Cd(II), Mn(II), Co(II), and Zn(II) but not with UO_2^{2+} or Pb(II). The Co(II) and Zn(II) complexes may, however, have only four nitrogen atoms coordinated to the metal [476].

Black and Rothnie [477,478] have prepared **160** using 2,2′-iminobisbenzaldehyde, the tetraamine 1,2-di(*o*-aminophenylamino)ethane and either Cu(II) and Zn(II) ions as templates. The 2,2′-iminobisbenzaldehyde moiety adds greater flexibility to the macrocycle than the pyridine-2,6-dicarbonyl moiety and increases the size of the macrocylic ring to 17 members which is also expected to increase flexibility. A pentagonal pyramidal structure with coordinated anions at the apices was suggested; however, structures of complexes of this ligand have not been determined. Ansell et al. [479] have also used 2,2′-iminobisbenzaldehyde and the bisdimethylhydrazine of 1,10-phenanthroline to prepare Co(II) complexes of the ligand **161**. Both **160** and **161** deprotonate on coordination to a metal ion and the Co(II) complex CoL(py)$_2^+$ (L = **161**) has been shown to have a distorted pentagonal bipyramidal structure [479].



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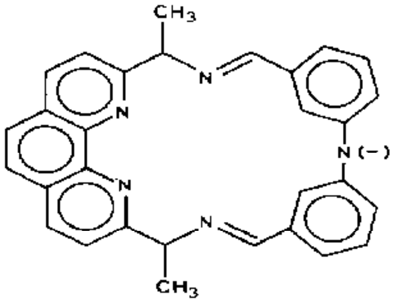
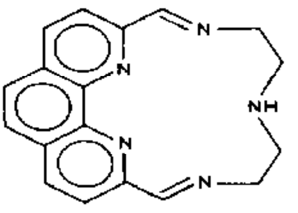


(161)

Bishop et al. [452] have reported preparation of complexes of the ligands **162** and **163** via a template reaction with Mn(II), but no subsequent reports on these complexes have appeared. An Mg(II) complex of **164** has been reported to be formed as a result of the reaction between 4,4,9,9-tetramethyl-5,8-diazadodeca-2,11-dione and dien in acetonitrile in the presence of Mg(ClO$_4$)$_2$. The free ligand is formed when the reaction is carried out in the presence of Ca(II), Sr(II) and Ba(II) [480].



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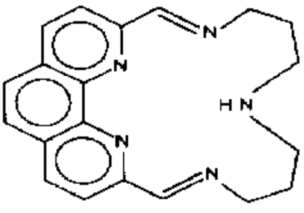

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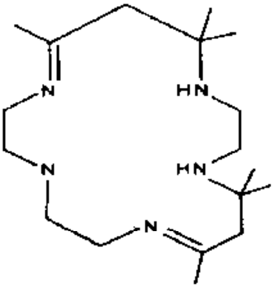
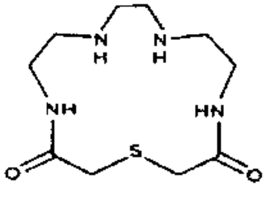


(164)

(c) N_4X macrocycles

Only a limited number of macrocycles of this type have been synthesized. Rasshofer et al. [80], Pelissard and Louis [481] and Tabushi et al. [482] have all prepared 15-membered N_4X macrocycles ($X = O$ or S) but only Cu(II) complexes of [15]aneN_4O and **165** have been prepared [390]. On the basis of visible, ESR and CD spectra these ligands are thought to be pentadentate with oxygen or sulphur atoms in an apical coordination site. Complexes of these ligands can exist in a number of isomeric forms but none have been reported to date. An Ni(II) complex of **166** has been prepared, and chemical evidence suggests a pseudo-octahedral structure with a methanol molecule completing the octahedron [483].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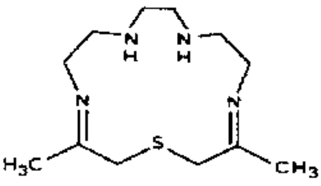
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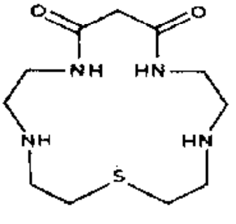
Kimura and coworkers have prepared [16]aneN_4O and [16]aneN_4S [121,123,384] ligands and have reported the protonation and complex formation of these ligands with Fe(II), Ni(II), Co(II), Cu(II) and Hg(II). These ligands are considerably less basic than [16]aneN_5 and the stability trend for the metal complexes is $N > S > O$ [123]. The Hg(II) complex of [16]aneN_4S is particularly stable, and unusually, the Ni(II) complex of this ligand is less stable than its linear counterpart. Both Co(II) complexes react with dioxygen to form a $[CoL]_2O_2$ adduct, and oxygenation constants K ($= [\{CoL\}_2O_2]/[CoL]^2[O_2]$) also follow the order $N > S > O$. The rate of formation of the [16]aneN_4S complex is two orders of magnitude slower than the rate for the [16]aneN_5 complex (H_2L^{2+} is the reactive species in each case) but the reason for the difference in rates is not clear [123,384].

Kimura et al. have also reported the Ni(II) complex of **167** [121]. This complex is diamagnetic which suggests that the sulphur is not coordinated to the Ni(II). An unusual N_4S macrobicycle **168** has been prepared by Bianchi et al. [484]. Protonation constants of the ligand, formation constants of the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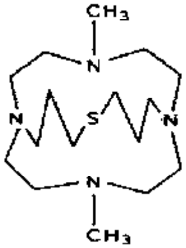
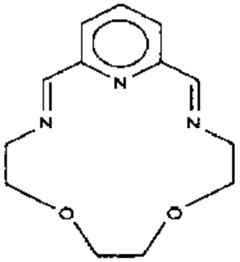

(168)

Cu(II) complex and associated thermodynamic parameters have been determined and although the stability of the complex is not high, the large favourable entropy change for the reaction supports the hypothesis that Cu(II) is incorporated into the ligand cavity.

(d) N_3X_2 macrocycles

It is remarkable that although the molecules [15]aneN_3O_2 and Ts_3[17]aneN_3O_2 have been prepared by a number of different groups [77,80,90,482], complexes of these ligands have not been described. Complexes of ligands **169** and **170** are formed by template condensation reactions of pyridine-2,6-dicarbaldehyde and 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine. With **169**, only Mg(II) has been reported as a templating ion; Ca(II) does not give the desired products [485]. With **170**, Fe(II) [413,486], Fe(III) [486], Mn(II) [486], Zn(II) [486], Cd(II) [486,487] or Mg(II) [485] all act as templates. Complexes of other metals can be produced by transmetallation reactions. Cation size is important in these templating reactions as ions with an ionic radius greater than 95 pm do not facilitate macrocycle synthesis. Large cations, e.g. Hg(II), Pb(II) and Ag(I), give rise to a 30-membered N_6O_4 macrocycle (a 2 + 2 addition product) [11,424,487–489] and Ba(II) and Sr(II) ions give rise to open chain 1 + 2 addition products [487].



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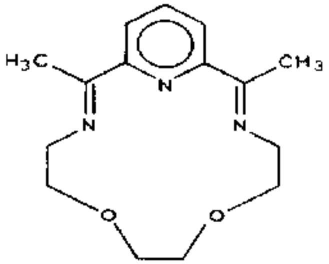
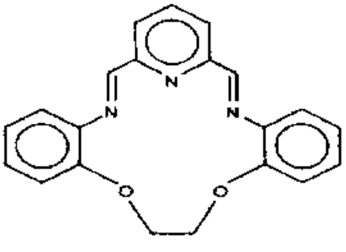


(170)

$MgL(NCS)_2$ (L = **170**) is isostructural with the corresponding Fe(II), Co(II) and Zn(II) complexes and it was concluded on the basis of chemical evidence that these complexes have a pentagonal bipyramidal structure [485]. $MnL(NCS)_2$ (L = **170**) (isostructural with the Cd(II) complex) has a pentagonal bipyramidal structure with the Mn atom and the five donors almost coplanar [486]. Mössbauer spectra and the temperature dependence of the magnetic properties of $FeL(CN)_2$ (L = **170**) suggest that this complex is octahedral with a quadridentate macrocycle (N_3O donor set) and two cyanide groups bound to the iron at temperatures below 150 K but either a six- or seven-coordinate structure is possible at ambient temperatures [413].

Complexes of **171** are prepared by a template reaction between pyridine-

2,6-dicarbaldehyde and the primary diamine, with Mn(II) and Zn(II) ions serving as templates [444,490]. Carbanolamines **172** and **173** (R = Me, Et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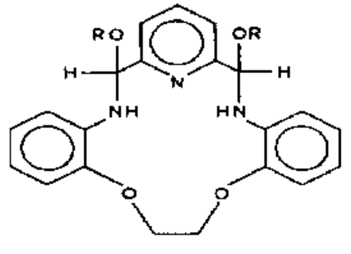
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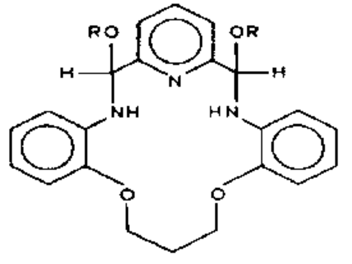
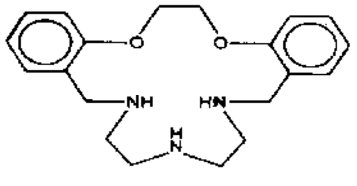

(173)

and *n*-Bu) can be obtained in the absence of the templating ion.

Complexes of the 17-, 18- and 19-membered macrocycles **174–181** have been prepared and structures of complexes with Cu(II) [491], Cd(II) and Zn(II) [492] and Ni(II) [493,494] have been determined. Lindoy has reviewed the work on these ligands and only a brief outline will be given here [495]. $NiL(H_2O)(ClO_4)_2$ (L = **174**) is a pseudo-octahedral complex with all five donors of the macrocycle bound to nickel; the three nitrogen donors of the ligand adopt a *mer* configuration and a water molecule occupies the sixth coordination site [494]. Only one other complex in which all five donors of the macrocycle are bound to the metal ion is known, $[CdL(NO_3)_2]$ (L = **174**), which has a very distorted pentagonal bipyramidal coordination geometry with the nitrate ions axial [492]. The ether oxygen atoms are only weakly bound to the cadmium. $NiL(NCS)_2$ (L = **174**) is dimeric and the ether oxygen atoms of the macrocycle are not coordinated. The pseudo-octahedral coordination is completed by an isothiocyanato ion and two bridging isothiocyanates. $NiL(NCS)_2H_2O$ (L = **175**) also has the ether oxygen atoms uncoordinated; the other three ligands are two thiocyanate groups and a water molecule. $NiL(NCS)_2$ (L = **176**) has a very irregular five-coordinate geometry with the three nitrogen atoms of the macrocycle in a *mer* configuration and two isothiocyanate groups bound to the metal. Two ether oxygen atoms lie approximately in the NiN_3 plane but are too far from the nickel to be bound to it [493]. $ZnL(NO_3)_2$ (L = **174**) has a pseudo-octahedral structure with three nitrogen atoms of the macrocycle bound to the metal in a facial conformation and a monodentate and a bidentate nitrate taking up the other three coordination positions [492]. Cu(II) binds the macrocycle via the three nitrogen atoms, and a water molecule completes the Cu(II) coordination sphere [491]. The uncomplexed macrocycle has been structurally characterized [496].



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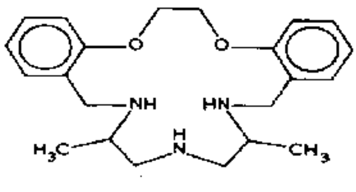

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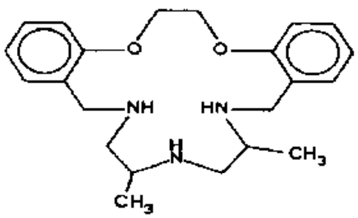

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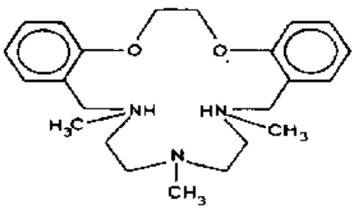

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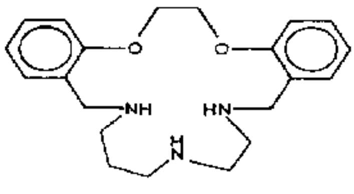

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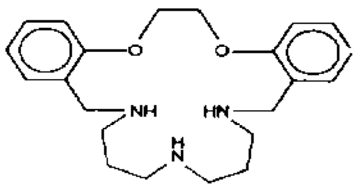

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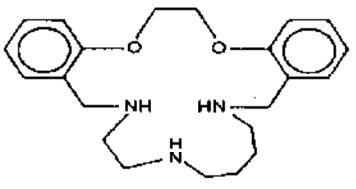

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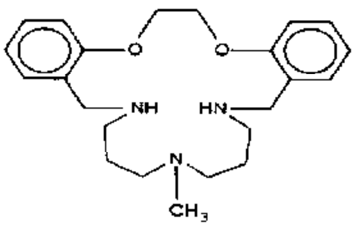

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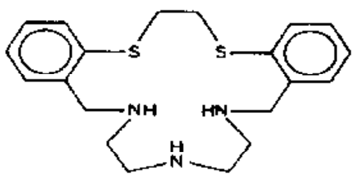


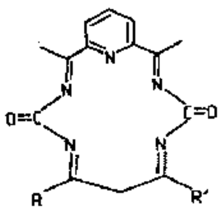
(182)

Formation constants for complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the ligands **174** and **176–181** have been determined [491,492,495,496]. With some metal ions the formation constants display sudden changes in passing from one ligand to another in the series **174–181**. These changes are believed to be due to changes in the coordination geometry of the complexes. For example, values for the formation constants of the 1 : 1 complex of Ni(II) with **174** and **176** are $10^{9.96}$ and $10^{6.89}$ respectively. $NiL(H_2O)^{2+}$ (L = **174**) has a *fac* arrangement of the three nitrogen atoms. On the basis of molecular mechanics calculations and the crystal structure of the thiocyanate complex, it is believed that **176** is not able to coordinate to nickel in the same fashion as **174**. This is due to steric crowding in the N_3 portion of the macrocycle and a *mer* configuration of the three nitrogen donor atoms seems probable [494]. A similar dislocation in stabilities of the Co(II), Ni(II) [496] and Cd(II) [492] complexes occurs as the ring size is increased from 18 to 19 members and a change in coordination, possibly involving the ether oxygen atoms, has been suggested as the cause of the dislocation. It has been shown independently that the complexes $NiLI_2$ (L = **174**) and $NiLI_2$ (L = **178**) are 1 : 1 electrolytes in nitromethane, and $NiL(NCS)_2$ (L = **178**), $NiL(NCS)_2$ and $NiLCl_2$ (L = **179**) are non-electrolytes. Therefore it is probable that **178** and **179** behave as tetradentates in the thiocyanato complexes [497]. These dislocations are not observed in the stabilities of the Cu(II) complexes. A sulphur analogue of ligand **174**, **182**, has been prepared and the stability constant of the Cu(II) complex shown to be very similar to the value for **174** [496].

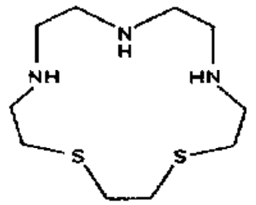
Interactions of Co(II), Ni(II) and Cu(II) with ligand **174** bound to a polystyrene matrix has also been investigated by Paredes et al. [498]. Metal binding properties are altered significantly upon incorporation into the matrix.

Ligands **183**, which are formed by a template reaction between the 2,6-diacetylpyridine-bis(semicarbazide)zirconium(IV) complex and β-diketones are believed, on the basis of IR evidence, to coordinate to the metal through the pyridine nitrogen, two azomethine nitrogen atoms and two amido oxygen atoms [499]. The semicarbazide precursor complex has also been reacted with 2,6-diacetylpyridine forming what is believed to be a macrocyclic complex, but the exact nature of the product is not clear [499].

[15]aneN_3S_2, **184**, has been prepared [482] and the ligand exchange reaction between CuL^{2+} (L = **184**) and [16]aneN_4 has been used to calculate the formation constant of the CuL^{2+} complex [124]. This value is in reasonable agreement with a directly determined value. Both **185** and **186** have been prepared but metal complexes have not been reported [484].



$R = CH_3, C_6H_5, C_4H_3S$
$R = CH_3, CF_3, C_6H_5$
(183)



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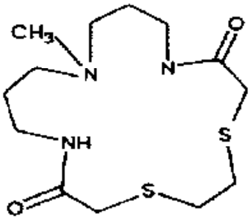

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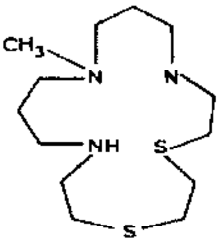

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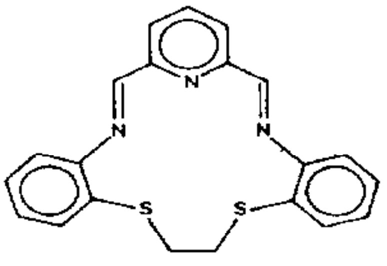
A 15-membered N_3S_2 analogue of **171**, **187**, has been prepared and while the zinc and manganese complexes of **187** have not been studied in detail [444], the Cu(II) complex has been fully characterized and shown to have



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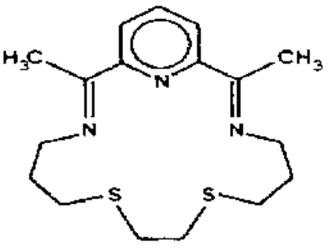


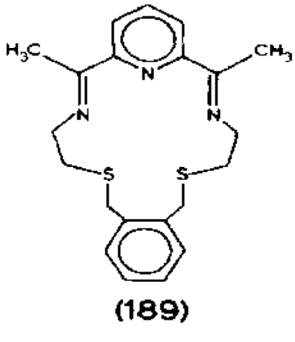
(188)

spectroscopic and electrochemical properties very similar to those of CuL^{2+} (L = **188**) [500].

The N_3S_2 macrocycle studied in greatest detail is the 17-membered macrocycle, **188**, which was chosen for study because studies with **135** suggested that **188** would be more flexible in its coordination demands than a smaller macrocycle [501]. This expected flexibility was borne out in practice in that Ag(I) [501], Fe(II) [502] and Pb(II) [424] can act as templating ions (complexes of other metals are prepared by transmetallation reactions) and the structures of the complexes reported show a wide range of possible coordinating behaviour.

Two distorted octahedral Fe(III) complexes have been prepared; the $FeL(NCS)^+$ (L = **188**) ion has a pentadentate macrocycle with one of the S donor atoms of the macrocycle *trans* to the N of the isothiocyanate ion. $FeLCl(CH_3OH)^+$ (L = **188**) is also six-coordinate but the metal ion is bound to four donor atoms of the macrocycle (one S atom is not bound), to a chloride ion and a methanol molecule [502]. $[AgL](BPh_4)$ and $[CuL](ClO_4)$ (L = **188**) also have all five donor atoms of the macrocycle bound to the metal atoms in structures best described as distorted trigonal pyramids [501]. Structures of two Cu(II) complexes have also been determined [503]. Both compounds have distorted square-pyramidal structures in which the trimethine unit of the macrocycle occupies three positions of the square plane. $CuL(ClO_4)_2$ (L = **188**) has one S atom of the macrocycle in the plane (Cu–S 238 pm) and the other S atom is axial (Cu–S 247 pm). $CuL(NCS)^+$ (L = **188**) has the three macrocyclic nitrogen atoms and an isothiocyanate comprising the plane, and the axial position is occupied by a ligand S atom (Cu–S 275 pm) [503]. Reduction of the Cu(II) complex with borohydride gives the Cu(I) complex but reduction of the Ag(I) complex gives the reduced free macrocycle.

Zn(II) and Cd(II) complexes of **189** and Zn(II) complexes of **190** have been prepared [504,505]. Attempts to perform the cyclization with fewer



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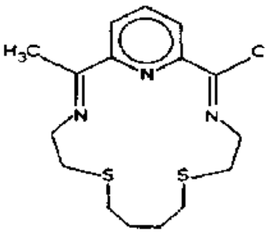

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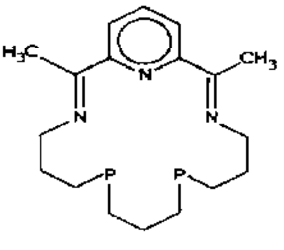

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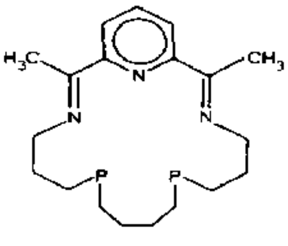
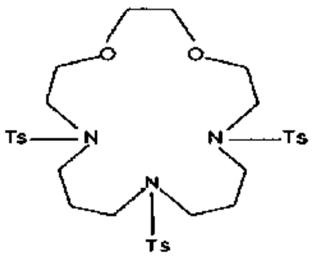


(192)

than four carbon atoms between the sulphur atoms were unsuccessful. This result is puzzling because preparation of the 15-membered macrocycle **187** was described above. The structure of $ZnLI_2$ (L = **190**) revealed that the sulphur atoms are not coordinated to the zinc which is five-coordinate with an N_3I_2 donor set [505].

Preparation of N_3P_2 macrocycles, [X]pydieneN_3P_2 (X = **15**–**18**), was attempted using Mn(II), Fe(II), Zn(II), Cd(II), Hg(II) and Ag(I) as templates. However, only with the silver and cadmium ions and the 17- and 18-membered macrocyclic ligands **191** and **192** could products be isolated. Unfortunately, single crystals suitable for X-ray investigation were not obtained [142].



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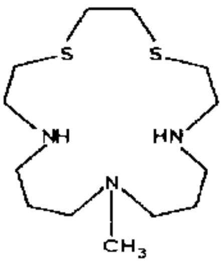

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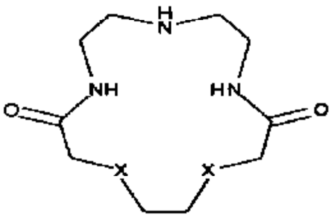
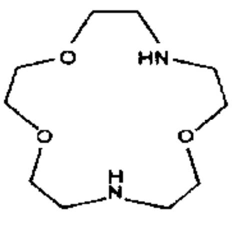


(195) X = S or O

Many other ligands of the N_3X_2 type, e.g. **193**–**195** [80,481,482,506], have been prepared but no metal complexes have been reported.

(e) N_2X_3 macrocycles

Two different arrangements of X groups are possible for 15-membered macrocycles of this type as shown for ligands **196** and **197**. Formation constants in both water and non-aqueous solvents have been determined for a large number of complexes of the ligand **196**, and complexes of both **196** and **197** have been investigated in aqueous solution. In methanol, **196** has been shown to form complexes with a wide variety of metal ions but the interaction with group I metal ions and UO_2^{2+} [507,508] is too weak to observe. However, formation constants of Na^+ and K^+ complexes with **196** in acetonitrile and in water have been determined [509,510] and Li^+ forms a complex in chloroform [511]. The earliest published formation constants for



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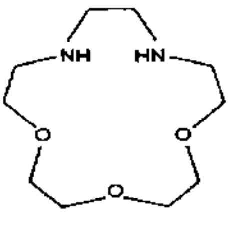

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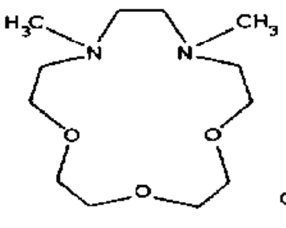

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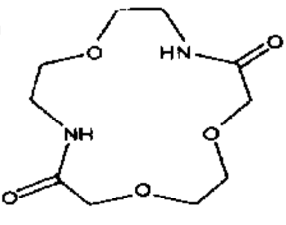

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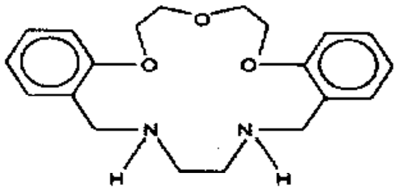
196 and all the published work for **197** and **198** have been tabulated [17]; subsequent results and results omitted from the previous tabulation for **196** are found in refs. 509–518.

N-substituted derivatives of **196** have recently been reported and binding constants for the sodium and potassium complexes of the dibenzyl derivative determined [519]. Ligand **196** is unusual in that the stability of the Co(II) complex is greater than that of the Ni(II) complex [516,520] and the enthalpy of formation of these two complexes [513,516,520] and of the Sr(II) and Ba(II) complexes [516,518] has been shown to be positive. These enthalpy values have been explained by the necessity for the ligand to undergo conformational change before binding the metal ions and by weak interactions between the ether oxygen atoms and the Ni(II) and Co(II) ions on the one hand [513,520] and the nitrogen donors and the Ba(II) or Sr(II) ions on the other [516]. Formation constants of the alkaline earth metal complexes are similar to those of 15-crown-5 but enthalpy values for the reaction are smaller [518]. A macrocyclic effect is not observed for **196** or **197** with the transition metals Co(II), Ni(II), Cu(II) and Zn(II) [511] or with Pb(II), Ba(II) or Ag(I) [515,518].

Ligand **199** does not form complexes in either methanol or acetonitrile solutions with Ag(I), Pb(II), group I or group II metal ions. Dilactam-type ligands form complexes whose formation constants are reduced by a factor of 10^5–10^{10} compared with the unsubstituted ligands so that stable complexes of **199** are expected for only a few metal ions which form complexes with **196** with log $K > 5$, e.g. Cu(II) [510].

Formation constants of Ni(II) complexes of **200** and **201** have been determined [496]. Complexes of **201** with Co(II), Ni(II), Cu(II) and Zn(II) have been investigated in more detail. Formation constants follow the Irving–Williams series and solid complexes isolated for these metals have stoichiometries which indicate that not all ligand donor atoms are bound to the metal [521]. Complexes of **202** with Cu(II), Ni(II), Co(II) and Pd(II) have been prepared [522]. The copper, nickel and cobalt complexes have a metal : ligand stoichiometry of 1 : 2 and the metal is believed to be coordinated to the ligand via the dioxime nitrogen atoms. Pd(II) and UO_2^{2+} ions form complexes with a metal-to-ligand stoichiometry of 3 : 2 and are believed to have the metal bound to both the macrocyclic cavity and the dioxime. Complexes of alkali and alkaline earth metal ions with the ligands **203**–**205** have been investigated [106,107] and the ligands have been incorporated into poly(vinyl chloride) membrane electrodes in order to study the selectivity of the ligands for Ca(II) [107].

Structural characterization of the Hg(II) complex of the 19-membered macrocycle **206** has shown that the mercury is not incorporated into the macrocyclic ring but is bound to nitrogen atoms of two bridging macro-



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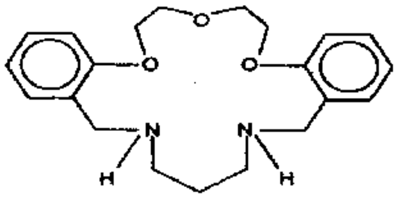

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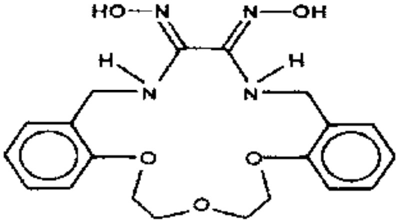

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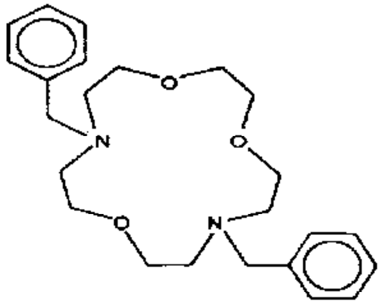

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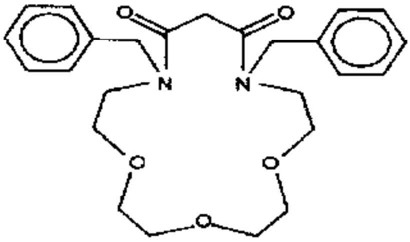

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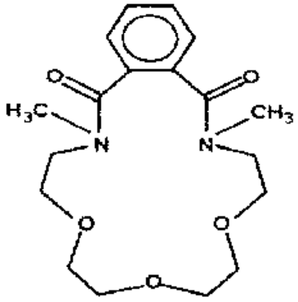

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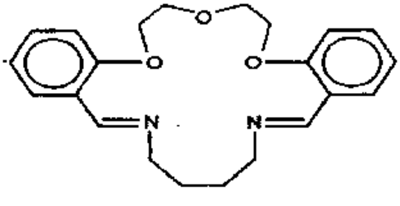
cycles and to two iodide ions in a distorted tetrahedral arrangement [523]. Ag(I) may be bound inside the macrocyclic cavity because **206** can extract Ag(I) (but not a wide range of other metal ions) from water into non-aqueous solvents [524].

Sodium complexes of **207** have been structurally characterized [525]; the Na^+ ion lies above the 15-membered macrocyclic ring, whereas the Li^+ ion in the lithium complex lies in the macrocyclic cavity [526]. ^{13}C NMR spectra



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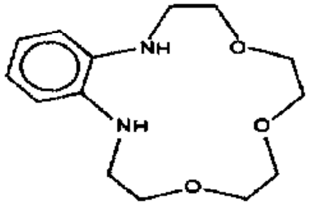

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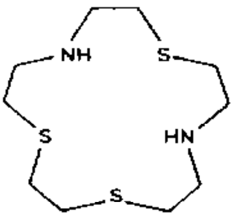
indicate that these structures are retained in solution [525]. Formation constants of the Na^+ complex, which vary considerably with the nature of the solvent, have been determined [526] and formation rate constants in a variety of solvents have also been measured [527]. Variations in the formation constants are much larger that the variations in rate constants so that the former must be controlled by the dissociation rate constant. These observations have been used to postulate reaction mechanisms for the complexation process [527].

Interactions between N_2O_3 macrocycles and quaternary ammonium cations have been investigated [528–532]. In most cases 1:1 complexes are observed. Complexes of **208** with sodium iodide have been shown to exist but they are less stable than complexes with crown ethers [533] and it was suggested that hydrogen bonding stabilizes the nitrogen macrocycles. Other N_2O_3 macrocycles have been prepared [79,534–538] but their complexing properties have not been investigated.

Cu(II) [539,540] and Ni(II) [541] complexes of the N_2S_3 ligands **209** and **210** have been reported and the electrochemistry of these complexes in water and propylene carbonate has been investigated [539,541]. Another N_2S_3 ligand **211** was the second example of a pentadentate macrocyclic ligand to be prepared [542] and it is thought that the Fe(II) complex is octahedral with a CH_3CN molecule completing the coordination sphere.



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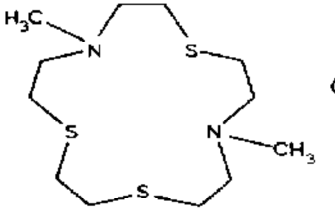

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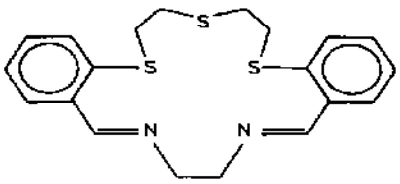

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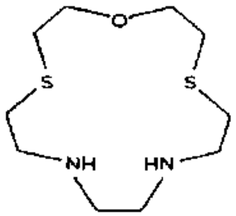

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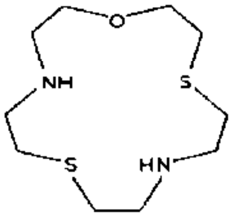

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Ligands **212** and **213**, which were first prepared by Pelissard and Louis [481], can coordinate to a metal ion to give a square-pyramidal or octahedral complex in a number of different ways (Fig. 5). Structures **II** and **III** and **IV** and **V** respectively differ in the configuration of the coordinated NH groups.

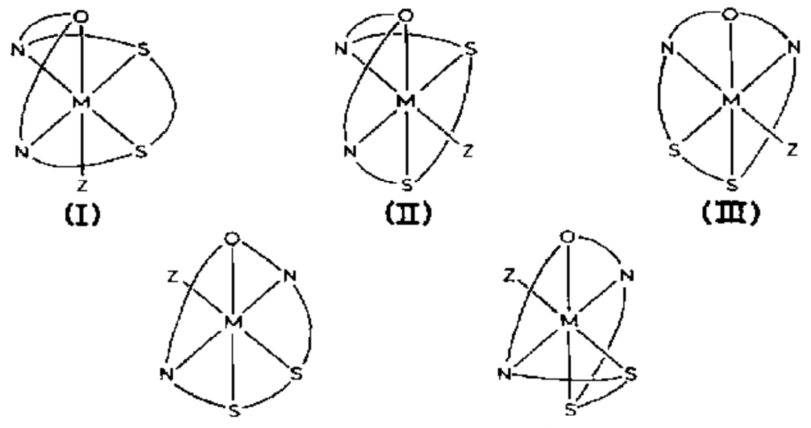


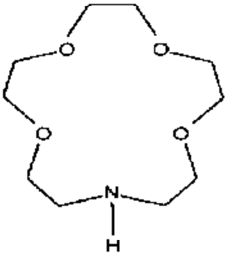
Fig. 5. Different modes of coordination of an N_2S_2O macrocycle to a metal ion.

Structures of the following complexes have been determined: AgLNCS [543,544], $NiL(NO_3)_2$ [545], $CuL(ClO_4)_2$ [546] (L = **212**) and AgL′NCS [547], $[NiL'(H_2O)](ClO_4)_2$ [548] and $PdL'(NO_3)_2$ (L′ = **213**) [549]. Both the CuL^{2+} and NiL^{2+} cations have been shown to have structure I with a vacant sixth coordination site in the Cu(II) complex and a nitrate oxygen in the sixth site in the Ni(II) complex. $NiL'(H_2O)^{2+}$ has structure V. $PdL'(NO_3)_2$ also has structure I although the Pd–O bond is long (277.9 pm). With both the silver complexes the Ag(I) ion is bonded to both nitrogen atoms and both sulphur atoms of the macrocycle and a sulphur of the thiocyanate ion. The complexes differ in that with L′ the Ag–O distance is 290 pm, suggesting a weak bond, whereas with L the distance is 372 pm.

Formation constants for both L and L′ [544,550,551] with Co(II), Cu(II), Zn(II), Pb(II), Cd(II) and Ag(II) have been determined and enthalpy changes for the reactions of L with Cu(II) and Pb(II) have been measured [546]. Formation constants for the two ligands are not appreciably different except for the complexes of Cu(II), Pb(II) and Ag(I) which are about ten times more stable for L than for L′ [550,551]. There is a strong macrocyclic effect observed for L with Cu(II), Ni(II) and Co(II). A moderate macrocyclic effect is observed with Cd(II) and Ag(I) but no macrocyclic effect is observed with Pb(II) and Zn(II). An attempt has been made to correlate the observed formation constants with the solid state structures of these complexes [550].

(f) NX_4 macrocycles

Although ligands of the NO_4 type are readily prepared [40,41,170,537, 552–560], few studies of metal complexes apart from group I and group II metal ions with these ligands have appeared. [15]aneNO_4, **214**, has been little



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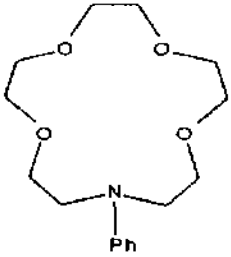

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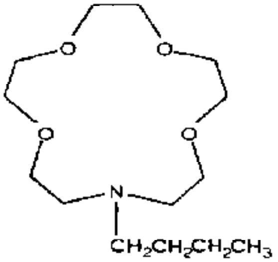

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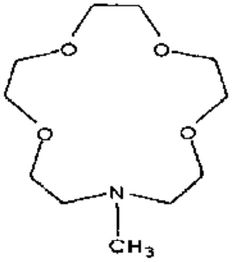
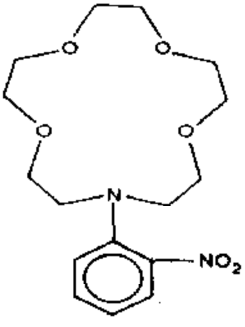


(217)

studied as a ligand for metal ions but the formation constant for the ammonium complex has been measured [529,532,561]. An Na^+ complex of **215** has been structurally characterized [562,563] and all five donor atoms are bound to the sodium. Formation constants of **215** with Ba^{2+}, Ag^+, Na^+, K^+, Rb^+, Cs^+ and Sr^{2+} [552,564] and **216** with Na^+, K^+ and Ca^{2+} [565] in methanol have been determined. Complete details of the method for the determination of these constants have recently appeared [566]. Cu(II) and Fe(III) complexes with **215** have been reported [567]. ^{13}C NMR relaxation times of the sodium complex of **216** and **217** have been compared with those of the free ligands. With **217** neither the ring nor methyl carbon mobility is much affected by complexation but this is not the case for **216**. ^{23}Na NMR has shown that sodium exchange in the **216** complex is slow on the NMR time scale [568].

Reduction of the nitro group in **218** is 0.26 V more positive when an Na^+ ion is bound to the macrocycle. This indicates that the Na^+ binds 2.5×10^4 times more strongly to the reduced compound than to the non-reduced



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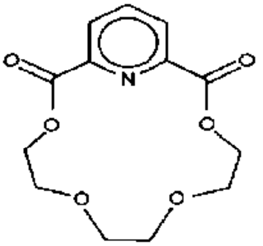

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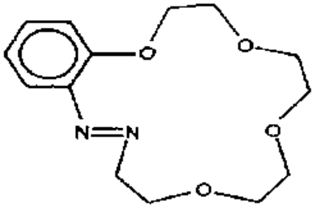
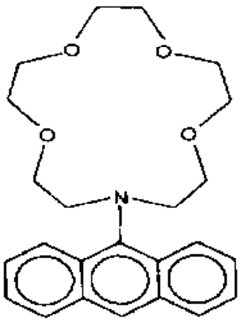


(220)

species [569]. Interactions of the Na^+ ion with the reduced ligand have been studied using ESR [570]. Formation constants of **219** with Na^+, K^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+} and Ag^+ have been measured by Buschmann [571,572]. These complexes have lower stability than those of 15-crown-5 but higher than those of **215**. Formation constants in acetonitrile with group I metal ions have been measured for **220**, a 16-membered macrocycle. Li^+ forms the most stable complex, which is attributed to the fact that interaction between the metal ion and the macrocycle is ion-dipolar in character rather than a macrocycle encapsulating reaction [573]. This ligand has been used to separate metal ions by ion–dipole association chromatography [113]. The fluorescence quantum yield of the anthracene portion of **221** is enhanced by binding Na^+ or K^+ but not Li^+ to the macrocycle [574].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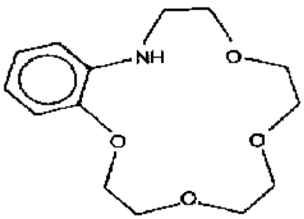
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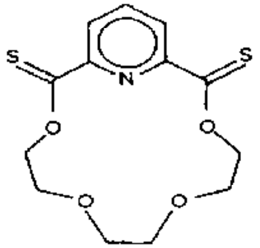
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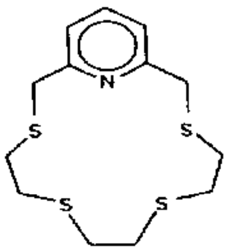
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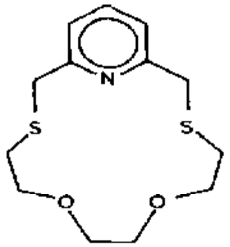
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Sodium and potassium complexes of **222** have been studied by observing the effect of complexation on the NMR spectrum of the ligand. Signals shift upfield in the presence of Na^+ and downfield with K^+ which suggests the formation of a 1 : 1 complex with sodium and a 1 : 2 complex with potassium [575]. **223** has been shown to form complexes with $NaClO_4$ and NaSCN [576].

NS_4 macrocyclic ligands have hardly been studied. Weber and Vögtle [351] have reported Ni(II), Cd(II) and Co(II) complexes of **224**. Vögtle and Weber have also shown that the NS_2O_2 macrocycle **225** complexes Na^+ because $NaMnO_4$ is soluble in organic solvents in the presence of **225** [577].

(ii) Sulphur-containing pentadentate macrocycles

(a) Pentathia macrocycles

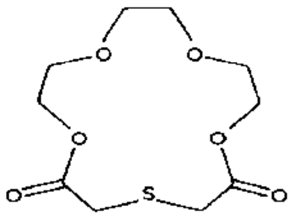
Cu[15]aneS_5^{2+} is the only complex considered in this section. No complexes of [15]aneS_5 with other metals or complexes of other ligands have yet been reported, although Co(II) complexes of [18]aneS_6 and Ni(II) complexes of both [18]aneS_6 and [24]aneS_6 have been prepared [163,366,578–580]. Formation constants for Cu[15]aneS_5^{2+} and complexes with other thia macrocycles have been determined [581,582]. Visible and Raman spectral data for the Cu[15]aneS_5^{2+} complex together with data for other thia ether complexes were used to identify the nature of the intense absorption band and the Cu–S stretching frequency in spectra of blue copper proteins [356,367,583]. Positive potentials for the Cu^{2+}/Cu^{+} couple of Cu[15]aneS_5 and other thia ether complexes have been related to the positive potentials observed for these proteins [355].

Rates of formation of the Cu[15]aneS_5^{2+} ion have been measured in methanol–water solvent mixtures and the variation of the rate with solvent composition analysed to give the rate for $Cu(aq)^{2+}$ reacting with [15]aneS_5. Initial Cu–S bond formation is not rate determining and therefore chelate ring closure (second bond formation) is probably the rate-determining step. From the formation rate constant and the measured stability constant, it is possible to calculate the dissociation rate constant. This value, 49 s^{-1}, is high for a macrocyclic complex [584,585].

Structures of both the Cu(II) and Cu(I) complexes have been determined [176]. The Cu(II) complex has a square-pyramidal coordination geometry with the copper ion situated above the basal plane and on the same side of the plane as the apical sulphur. The Cu(I) complex has a distorted tetrahedral geometry which approximates the Cu(II) geometry except that one of the ligand sulphur atoms is not coordinated. Studies on electron transfer reactions of these two complexes [585] have shown that the Cu[15]ane$S_5^{(2+/+)}$ couple is more labile in its electron transfer reactions than any other copper–polythiaether complex studied to date and this has been related to the minor structural changes that occur upon oxidation [176].

(b) Other macrocycles containing sulphur

Reports of complexes of other pentadentate sulphur-containing macrocycles are fragmentary. Lamb et al. [586] have studied the formation of complexes of **226** with alkali metals and observed no enthalpy change for the reaction (if any reaction occurred). Pedersen [587] prepared **227** and has shown that the interaction of this ligand with alkali metal ions is much weaker than the interaction of the same ions with crown ethers but that Ag(I) interacts with **227** and crown ethers to about the same extent. Ligand **228** has been shown to solubilize $NaMnO_4$ in $CHCl_3$ and C_6H_6 but no other reports of the complexing ability of this ligand have appeared [577]. A number of other S_2O_3 and SO_4 macrocycles have been prepared but no complexes have been reported [155,170,171,506,588].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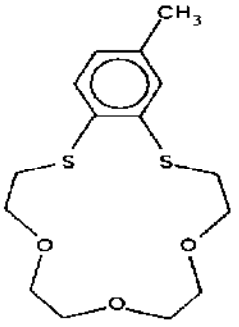
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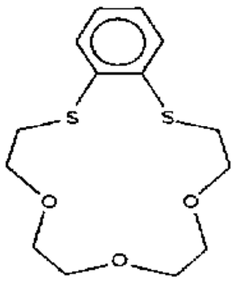
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E. PROPERTIES

(i) Ligand-field effects

Macrocyclic ligands may impose a stronger than expected ligand field on a variety of metal ions. This effect was first noted for the macrocycles considered in this review with [9]aneN$_3$ [253,255] and has been observed with a number of other tridentate macrocycles, [9]aneN$_2$O [61,91,338], [9]aneN$_2$S [61,62] and [9]aneS$_3$ [359,365]. However, this effect is not general. Some macrocyclic ligands impose weaker than expected ligand fields on a particular metal ion, e.g. [18A]aneN$_5$ with Co(III) [376], and other macrocyclic complexes, e.g. Ni([12]aneS$_3$)$_2^{2+}$ [159], have D_q values which are comparable with their linear counterparts. With the reduced ligand-field parameters a mismatch between the size of the metal ion and the hole size of the macrocycle is the generally accepted explanation for the effect and there is good evidence that this explanation is correct [382].

In Section C (v) the strong ligand-field effect of the [9]aneS$_3$ ligand was mentioned. Both the Fe(II) and Ni(II) complexes display much larger than expected D_q values [359,365] and the Co(II) and Fe(II) complexes are low spin so that it is unlikely that the spectra have been misinterpreted. Thöm et al. [226] have persuasively argued that the origin of the ligand-field effect for aza macrocycles is the greater donor ability of a secondary nitrogen in a situation of low strain, but this is irrelevant for the thia macrocycles and another explanation must be sought. Cooper and coworkers [163,366,579,580] have suggested that the strong ligand field in thia macrocycles is produced by steric compression of the M–S bonds. Structures of the Ni(2,5,8-trithianonane)(H$_2$O)(picrate) [589], Ni[18]aneS$_6^{2+}$ [579] and Ni[24]aneS$_6^{2+}$ cations [578] have shown that the Ni–S bond lengths in the Ni(2,5,8-trithianonane) complex (range, 239.2–241.8 pm) and the Ni[24]aneS$_6^{2+}$ complex (range, 241.5–244.5 pm) are longer than the Ni–S bonds in the Ni[18]aneS$_6^{2+}$ complex. The average bond length in the Ni([9]aneS$_3$)$_2^{2+}$

complex is 238.6 pm (range, 237.7–240.0 pm) [580]. In addition, structures of the Co[18]aneS$_6^{2+}$, Co(2,5,8-trithianonane)$_2^{2+}$ and Co([9]aneS$_3$)$_2^{2+}$ complexes have been determined [366,579]. All three complexes have low spin Co(II) with six thiaether donors and all display a marked Jahn–Teller distortion expected for low spin Co(II) complexes. It is interesting that the tetragonal distortion of the Co([9]aneS$_3$)$_2^{2+}$ complex (equatorial bonds longer than axial bonds) is different from the distortion on the other two complexes (equatorial bonds shorter than axial). Comparison of the macrocyclic complexes with the complex with the linear thiol reveals that the latter has longer axial bonds (by more than 10 pm) than the macrocyclic complex, a difference attributed to steric compression by the macrocyclic ligand [366].

That steric compression of metal–ligand bonds in macrocyclic complexes can produce large ligand fields was first suggested by Busch [7] for a series of tetraaza macrocycles. There are difficulties with this steric compression argument for the tetraaza macrocycles which have been enumerated by Thöm et al. [226]. Perhaps the most telling of these arguments is that with low spin Ni(II) complexes the largest ligand field is produced by a ligand with a hole size too large to produce steric compression. Furthermore, compression of the M–L bonds would produce a large unfavourable strain energy in the bonds. This is expected to lower the enthalpy of formation, which is not in accord with the enhanced stability of these macrocyclic complexes. With thiaether ligands, only two stability constant determinations are available, Co(II) with [9]aneS$_3$ and Cu(II) with [15]aneS$_5$, but the results indicate that the stability is enhanced by three to four orders of magnitude [365,581,582].

It seems that the most probable explanation for the high ligand fields observed with [9]aneS$_3$ is that this ligand is able to coordinate first-row transition metals without significant steric strain. The structure of the free ligand has been determined [357], and the orientation of the sulphur atoms is into the ring (endodentate) as opposed to exodentate. Exodentate orientations are observed with most other thiaethers but significantly not with [18]aneS$_6$ [590]. Structures of the metal complexes of [9]aneS$_3$ with the first-row transition metal ions have revealed that the S–M–S bond angles are close to 90°. Complexes of [9]aneN$_3$ typically have N–M–N bond angles with the first-row transition metal complexes of $82° \pm 2°$ (slightly larger for the smaller Co(III) ion) and this indicates some metal–ligand bond strain. With Mo[9]aneS$_3$(CO)$_3$, which has much longer M–S bonds, the S–Mo–S bond angles are reduced to 82–83° [364]. If this bond angle were to be increased towards the octahedral value the M–N or M–S bond length would decrease, i.e. steric compression would occur. In complexes of the tridentate macrocycles the compromise which is reached suggests that steric compression is much less favourable energetically than angle bending. There is no evidence for steric compression in any complex of [9]aneN_3 and for the +3 metal ions; bonds which are longer than ideal for the metal ion are normal [226]. With [9]aneS_3, because the macrocyclic hole is larger and/or because the force constants for S–M–S angle bending are lower, the S–M–S bond angles are close to their ideal values of 90°. [18]aneS_6 also coordinates to Ni(II) and Co(II) with bond angles which are very close to 90° (90° ± 1.5° for Ni(II) [580], 90° ± 2.2° for Co(II) [366]) but with the Cu(II) complex the deviations from 90° are larger (±4.2°) because of the irregular coordination geometry of the copper complex [163].

Similar effects are observed in the structures of complexes of the [9]aneN_2S ligand [347,349]. N–M–N bond angles are very similar to the N–M–N bond angles in the [9]aneN_3 complexes with these metals but the S–M–N bond angles are closer to 90°. This is not the case with the Cu(II) complex but the very long axial Cu–S bond in that complex makes comparisons meaningless [62].

Large ligand-field effects are therefore observed for the thia macrocycles which have S–M–S or N–M–S bond angles close to 90° and the evidence suggests that bond-angle deformation will occur before steric compression. Therefore [9]aneS_3 and [18]aneS_6 apparently coordinate to first-row transition metal ions with little steric strain. It is probable therefore that short M–S bond lengths which are observed in these complexes represent the unstrained covalent metal–sulphur bond lengths and the longer bonds observed in other S-donor ligands are the result of steric strain within these complexes. Thus it seems likely that the ligand field imposed by [9]aneS_3 and [18]aneS_6 reflects the true donor ability of thiaether sulphur and earlier conclusions about the position of thiaether in the spectrochemical series are in error.

(ii) Formation constants and the macrocyclic effect

The macrocyclic effect, an enhanced stability of complexes of macrocyclic ligands compared with complexes of linear analogues, was discovered in studies of tetraaza macrocycles [27]. The first studies of formation constants of triaza macrocycles [591,592] noted that formation constants of the Ni(II) and Cu(II) complexes of [9]aneN_3 were much higher than values for linear triamines such as dien, dpt and *cis,cis*-tach. Later studies of the formation of complexes of ligands [9]aneN_3 to [12]aneN_3 have been performed by various groups of workers and unfortunately results obtained are not always in agreement [271,272,280,374,591–596] (Table 1). These difficulties seem to be partly due to different methods used for the determination of the constants, slow equilibration in some systems and the possibility that not all complexes present in the solution have been taken into account in the calculations, but

TABLE 1

Formation constants for triaza macrocyclic complexes

Ligand	Metal	Constant	Log K	Medium[a] (M)	Reference
[9]aneN_3	Co(II)	K_1	11.2	0.1 KNO_3	591
		K_2	7.8	0.1 KNO_3	
	Ni(II)	K_1	16.24	0.1 KNO_3	280
		K_1	13.6	0.1 KNO_3	591
		K_1	16.2	0.1 KNO_3	253
		K_2	11.8	0.1 KNO_3	591
	Cu(II)	K_1	15.52	0.1 KNO_3	280
		K_1	15.5	0.1 KNO_3	253
		K_1	15.7	0.1 KCl	592
		K_1	15.1	0.1 KNO_3	591
		K_1	15.6	0.1 KNO_3	594
		K_1	16.2	0.2 $NaClO_4$	272
		K_1		$\Delta H = -54.3\ \text{kJ mol}^{-1}$	
				$\Delta S = 130\ \text{J K}^{-1}\ \text{mol}^{-1}$	
		K_1		$\Delta H = -59\ \text{kJ mol}^{-1}$	595
				$\Delta S = 98\ \text{J K}^{-1}\ \text{mol}^{-1}$	
		K_1	15.84	0.5 KNO_3	271
		K_2	10.69	0.5 KNO_3	
		K_2	11.8	0.1 KCl	592
		K_2	12.1	0.1 KNO_3	591
	Cu(I)	K_1	8.28	Aqueous CH_3CN	593
	Zn(II)	K_1	11.3	0.2 $NaClO_4$	374
				$\Delta H = -30.5\ \text{kJ mol}^{-1}$	
				$\Delta S = 113\ \text{J K}^{-1}\ \text{mol}^{-1}$	
				$\Delta H = -29\ \text{kJ mol}^{-1}$	
				$\Delta S = 121\ \text{J K}^{-1}\ \text{mol}^{-1}$	
				$\Delta H = -50\ \text{kJ mol}^{-1}$	595
				$\Delta S = 55\ \text{J K}^{-1}\ \text{mol}^{-1}$	
		K_1	11.4	0.2 $NaClO_4$	374
		K_1	11.62	0.1 KNO_3	280
		K_1	11.6	0.1 KNO_3	253
		K_1	11.7	0.1 KNO_3	591
		K_2	10.0	0.1 KNO_3	
	Cd(II)	K_1	9.2	0.2 $NaClO_4$	374
				$\Delta H = -32\ \text{kJ mol}^{-1}$	
				$\Delta S = 71\ \text{J K}^{-1}\ \text{mol}^{-1}$	
		K_1	9.5	0.1 KNO_3	591
		K_2	8.4	0.1 KNO_3	
	Pb(II)	K_1	10.8	0.2 $NaClO_4$	374
				$\Delta H = -34\ \text{kJ mol}^{-1}$	
				$\Delta S = 113\ \text{J K}^{-1}\ \text{mol}^{-1}$	
[10]aneN_3	Ni(II)	K_1	14.58	0.1 KNO_3	280
	Cu(II)	K_1	16.14	0.5 KNO_3	271
		K_1	14.4	0.2 $NaClO_4$	374
				$\Delta H = -62\ \text{kJ mol}^{-1}$	
				$\Delta S = 67\ \text{J K}^{-1}\ \text{mol}^{-1}$	
		K_1	15.5	0.1 KNO_3	594
		K_1	15.48	0.1 KNO_3	280

TABLE 1 (continued)

Ligand	Metal	Constant	Log K	Medium [a] (M)	Reference
[10]aneN_3		K_1	16.22	0.5 KNO_3	593
		K_2	10.26	0.5 KNO_3	271
	Zn(II)	K_1	11.28	0.1 KNO_3	280
		K_1	11.2	0.1 KNO_3	594
		K_1	10.3	0.2 $NaClO_4$ $\Delta H = -28$ kJ mol^{-1} $\Delta S = 105$ J K^{-1} mol^{-1}	374
	Cd(II)	K_1	7.8	0.2 $NaClO_4$ $\Delta H = -30.5$ kJ mol^{-1} $\Delta S = 46$ J K^{-1} mol^{-1}	374
	Pb(II)	K_1	8.8	0.2 $NaClO_4$ $\Delta H = -30.5$ kJ mol^{-1} $\Delta S = 67$ J K^{-1} mol^{-1}	374
[11]aneN_3	Ni(II)	K_1	12.88	0.1 KNO_3	280
	Cu(II)	K_1	14.44	0.1 KNO_3	280
		K_1	14.4	0.1 KNO_3	594
	Zn(II)	K_1	10.41	0.1 KNO_3	280
			10.4	0.1 KNO_3	594
[12]aneN_3	Ni(II)	K_1	10.93	0.1 KNO_3	280
	Cu(II)	K_1	12.63	0.1 KNO_3	280
		K_1	12.6	0.1 KNO_3	594
		K_1	13.16	0.5 KNO_3	270
		K_2	7.68	0.5 KNO_3	271
	Zn(II)	K_1	8.75	0.1 KNO_3	280
		K_1	8.8	0.1KNO_3	594
Me_3[12]aneN_3	Cu(II)	K_1	11.58	0.1 $NaNO_3$	185
	Zn(II)	K_1	7.68	0.1 $NaNO_3$	185
[9]aneN_2O	Ni(II)	K_1	8.59	0.1 $NaNO_3$	338
			8.49	0.1 $NaNO_3$	91
		K_2	7.27	0.1 $NaNO_3$	338
		K_2	7.2	0.1 $NaNO_3$	91
	Cu(II)	K_1	10.85	0.1 $NaNO_3$	338
		K_1	10.86		91
		K_2	8.64	0.1 $NaNO_3$	338
			8.68	0.1 $NaNO_3$	91
	Zn(II)	K_1	6.32	0.1 $NaNO_3$	338
			6.36		91
		K_2	5.07	0.1 $NaNO_3$	91, 338
	Pb(II)	K_1	5.17	0.1 $NaNO_3$	91
[9]aneN_2S	Ni(II)	K_1	10.45	0.1 $NaNO_3$	347
		K_2	9.60	0.1 $NaNO_3$	
	Cu(II)	K_1	12.42	0.1 $NaNO_3$	
		K_2	9.87	0.1 $NaNO_3$	
[9]aneS_3	Co(II)	K_1	6.96	CH_3CN	365
		K_2	7.00	CH_3CN	

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[a] All measurements at 25 °C unless otherwise stated.

may be mainly due to different values of the protonation constants of the triamines determined by different groups. There seem to be two reasons for the inability to obtain apparent agreement on the protonation constants:

(1) pK_a values are often very high (greater than 11) so that normal pH titration techniques do not give accurate results.

(2) Formation of complexes with Na^+ and K^+ ions so that ionic strength variations can lead to apparently very different pK_a values.

Despite the above difficulties, certain trends in the formation constants of [X]aneN_3 complexes are clear; a macrocyclic effect is observed, the Irving–Williams order of stability is obeyed for the [X]aneN_3 and [X]aneN_5 ligands, except for [9]aneN_3 with Cu(II) where the special steric demands of the ligand lead to a lower stability, and formation constants decrease with increasing macrocyclic ring size for triaza macrocycles [280,374,384].

Formation constants of pentaaza macrocyclic complexes have been much less thoroughly investigated. Polarographic and potentiometric investigations by Kodama, Kimura and coworkers [122,123,373,374] and calorimetric studies by Fabbrizzi et al. [386] are the only reports to date. These results are given in Table 2. Formation constants of the macrocycles [15]aneN_5, [16]aneN_5 and [17B]aneN_5 follow the sequence [15]aneN_5 > [16]aneN_5 > [17B]aneN_5 for all metal ions, with the possible exception of Ni(II). Increasing the macrocyclic ring size from 15 to 19 members in the sequence [15]aneN_5, **113**, [16]aneN_5, **114**, [17C]aneN_5, **121**, [18C]aneN_5, **122**, and [19B]aneN_5, **123**, results in a decrease in the formation constants of Co(II) complexes [58]. [19B]aneN_5 apparently acts as a quadridentate ligand because the only complex identified is the $CoHL^{3+}$ species.

Enthalpies of complex formation of the Ni(II) complexes have been measured directly and follow the sequence [16]aneN_5 > [17B]aneN_5 > [15]aneN_5 [386]. Indirectly determined values for the enthalpy of formation of the Cu(II) complexes with these ligands follow the sequence [15]aneN_5 ≈ [16]aneN_5 > [17B]aneN_5, and with Zn(II), Pb(II) and Cd(II) the enthalpy values are the same for all three ligands [374]. Fabbrizzi et al. [386] suggest that as the enthalpy of formation of the Ni[15]aneN_5^{2+} complex is 11.7 kJ mol^{-1} lower than the value for the Ni(tetren)$^{2+}$ complex, the formation constant is likely to be lower (a reverse macrocyclic effect). However, the value for log K in Table 2 is higher than the value for Ni(tetren)$^{2+}$. While details of the determination of this value have not been published, it seems likely that a major contribution to the stability of the Ni[15]aneN_5^{2+} complex is the entropy term. The low ΔH value is likely to be due to steric strain in the complex, a suggestion supported by a somewhat unusual electronic spectrum of this species. Ni[16]aneN_5^{2+} has a much more negative ΔH, probably owing to relief of steric strain. However, the reported formation constant, log $K = 18.1$, (again no details have been published) is the same as

TABLE 2

Formation constants of pentaaza macrocyclic complexes

Ligand	Metal	Constant	Log K	Medium [a]	Reference
[15]aneN_5	Co(II)	K_1	16.76	0.2 $NaClO_4$ 35 °C	384
	Ni(II)	K_1	18.1	0.2 $NaClO_4$	606
				$\Delta H = -67.3$ kJ mol^{-1}	386
	Cu(II)	K_1	28.3	0.2 $NaClO_4$ $\Delta H = -137.7$ kJ mol^{-1} $\Delta S = 92$ J K^{-1} mol^{-1}	373
		K_1	25.9	0.1 NaOH	124
	Zn(II)	K_1	19.1	0.2 $NaClO_4$ $\Delta H = -57$ kJ mol^{-1} $\Delta S = 171$ J K^{-1} mol^{-1}	374
	Cd(II)	K_1	19.2	0.2 $NaClO_4$ $\Delta H = -54$ kJ mol^{-1} $\Delta S = 184$ J K^{-1} mol^{-1}	374
	Pb(II)	K_1	17.3	0.2 $NaClO_4$ $\Delta H = -42$ kJ mol^{-1} $\Delta S = 191$ J K^{-1} mol^{-1}	374
	Hg(II)	K_1	28.5	0.2 $NaClO_4$ $\Delta H = -137$ kJ mol^{-1} $\Delta S = 84$ J K^{-1} mol^{-1}	374
[16]aneN_5	Fe(II)	K_1	14.57	0.2 $NaClO_4$ 35 °C	122
	Co(II)	K_1	15.95	0.2 $NaClO_4$ 35 °C	384
	Ni(II)	K_1	18.1		123
				$\Delta H = -96$ kJ mol^{-1}	386
	Cu(II)	K_1	27.1	0.2 $NaClO_4$ $\Delta H = -137$ kJ mol^{-1} $\Delta S = 59$ J K^{-1} mol^{-1}	373
	Zn(II)	K_1	17.9	0.2 $NaClO_4$ $\Delta H = -56$ kJ mol^{-1} $\Delta S = 155$ J K^{-1} mol^{-1}	374
	Cd(II)	K_1	18.1	0.2 $NaClO_4$ $\Delta H = -54$ kJ mol^{-1} $\Delta S = 163$ J K^{-1} mol^{-1}	374
	Hg(II)	K_1	27.38	0.2 $NaClO_4$	123
				$\Delta H = -144$ kJ mol^{-1} $\Delta S = 42$ J K^{-1} mol^{-1}	374
	Pb(II)	K_1	14.3	0.2 $NaClO_4$ $\Delta H = -44$ kJ mol^{-1} $\Delta S = 125$ J K^{-1} mol^{-1}	374
[17B]aneN_5	Ni(II)	K_1		$\Delta H = -81$ kJ mol^{-1}	386
	Cu(II)	K_1	23.8	0.2 $NaClO_4$ $\Delta H = -114$ kJ mol^{-1} $\Delta S = 372$ J K^{-1} mol^{-1}	373
	Zn(II)	K_1	15.8	0.2 $NaClO_4$ $\Delta H = -53$ kJ mol^{-1} $\Delta S = 125$ J K^{-1} mol^{-1}	374

TABLE 2 (continued)

Ligand	Metal	Constant	Log K	Medium [a]	Reference
[17B]aneN_5	Cd(II)	K_1	15.5	0.2 $NaClO_4$ $\Delta H = -53$ kJ mol^{-1} $\Delta S = 121$ J K^{-1} mol^{-1}	374
	Hg(II)	K_1	26.5	0.2 $NaClO_4$ $\Delta H = -140$ kJ mol^{-1} $\Delta S = 38$ J K^{-1} mol^{-1}	374
	Pb(II)	K_1	11.6	0.2 $NaClO_4$ $\Delta H = -41$ kJ mol^{-1} $\Delta S = 125$ J K^{-1} mol^{-1}	374
[17C]aneN_5	Co(II)	K_1	15.38	0.2 $NaClO_4$	58
[18B]aneN_5	Co(II)	K_1	11.54	0.2 $NaClO_4$	58
[19B]aneN_5	Co(II)	$K_{(MHL)}$	7.36	0.2 $NaClO_4$	58

[a] All measurements at 25 °C unless otherwise stated.

for the Ni[15]aneN_5^{2+} complex. Reasons for this behaviour are not clear. Equilibrium in these nickel systems is attained only slowly so that some caution should be exercised in interpreting these results, particularly as experimental details have not been forthcoming. Studies with pentaaza macrocycles [17A]aneN_5 to [20]aneN_5 have not been performed but would be of considerable interest.

Formation constants of the Fe(II) and Co(II) complexes of **17** have been measured, and the cobalt complex has approximately the same formation constant as the complex with its linear analogue, i.e. a macrocyclic effect is not observed [122]. A constrained ligand configuration has been suggested as the explanation of this effect.

Studies with the tridentate macrocycles [9]aneN_2O [91], [9]aneN_2S [347] and [9]aneS_3 [365] and with the pentadentate macrocycles [16]aneN_4O [123,384], [16]aneN_4S [123] and [15]aneS_5 [581,582] have established that macrocyclic effects exist for these ligands and that the order of stability is $N_x > N_{(x-1)}S > N_{(x-1)}O \gg S_x$.

Considerable debate has taken place as to whether the macrocyclic effect is due to more favourable enthalpy or entropy changes in the complex-formation reaction. With triaza and pentaazamacrocycles, the macrocyclic effect can be large (3–7 orders of magnitude) and has been attributed largely to an entropy effect [374]. However, for Cu(II) complexes of [15]aneN_5, [16]aneN_5 and [17B]aneN_5, it has been claimed that the enthalpy change is the principal contributor to the effect [373]. The polarographic technique which was used to obtain both these results has, with triaza and tetraaza macrocycles, been shown to give results which are in poor agreement with thermodynamic parameters determined by apparently more reliable techniques [374,595]. These conclusions must therefore be treated with considerable caution. With tetradentate and crown ether systems both an enthalpy and an entropy contribution to the macrocyclic effect have been demonstrated [596,597]. It is generally agreed that the entropy contribution is due to a smaller configurational entropy of the macrocycle compared with that of the open-chain ligand. A favourable macrocyclic enthalpy was originally suggested as being due to steric hindrance to solvation of the free macrocyclic ligand [598], and measurements of enthalpies of solvation of tetraaza macrocycles and their linear counterparts have tended to support this suggestion [599,600]. However, reservations about this conclusion have been expressed [226].

Much less attention has been given to kinetic aspects of the macrocyclic effect; either the formation or dissociation rate constants or both could be affected. Studies with unprotonated aza macrocycles have not been possible because protonated forms of the macrocycle are the principal reactive species under the experimental conditions where formation reactions have been studied. Studies of the dissociation of the macrocycle from the metal have only been performed in strongly acidic solution so that acid assistance in the dissociation process is expected and found. Extrapolation of the acid-dependent rates to zero $[H^+]$ usually gives a rate constant which is experimentally indistinguishable from zero but occasionally a non-zero rate constant is obtained, e.g. for $Cu(Me_3[12]aneN_3)^{2+}$ [87], and these rates suggest that it is the dissociation rate constant which is the principal contributor to the kinetic macrocyclic effect. What evidence there is suggests that formation rates are lower for macrocycles than for linear molecules, a result not unexpected.

Studies with thia macrocycles which are not affected by protons have shown that a kinetic macrocyclic effect is associated with the final stages of the complexation process, and this effect thus parallels the dissociation rate constants [584]. Fast dissociation rate constants were associated with ligands which qualitatively were more soluble in the solvent, suggesting that the dissociation process is aided by solvation of the partly dissociated macrocycle. Such effects should be more important for polyamines and provide a kinetic explanation for the solvation contribution to the macrocyclic effect.

(iii) Macrocyclic hole sizes

The importance of a match in size between the metal ion and the macrocyclic hole has been demonstrated for a large number of template reactions which result in macrocycle formation. Some metal ions are apparently too small or too large to act as templating ions [38]. Some large metal ions act as templates for macrocycles which are different from those that are formed with smaller metal ions [424,487–489]. In other cases it has been suggested that the metal ion is able to act as a templating ion in the formation of the macrocycle but is too small to bind to the macrocycle so that the free ligand is isolated [462,469,471].

Determination of macrocyclic hole sizes and the manner in which the mismatch or match in the size of the metal ion and the macrocyclic hole influences the properties of metal complexes have been the subject of much recent interest. Hancock has reviewed metal ion selectivity and macrocyclic hole sizes in tetradentate macrocycles [601]. Hole sizes have been calculated in two different ways, using the results of crystal structure determinations and using molecular mechanics calculations. Determinations based on crystal structures have been reviewed [464] and give consistent results, but there are dangers in the uncritical use of this method. It has been shown that hole size calculations based on the structure of an uncomplexed macrocycle give different results from calculations based on metal complexes, and different conformations of the macrocycle in metal complexes may have different hole sizes [434].

Molecular mechanics calculations have been the subject of lively debate because reliable force constants for the bond stretching and bond bending modes involving the metal are hard to obtain [602–605]. Some calculations have been performed using a value of zero for the force constants, which allows the ligand to adopt the conformation of the uncomplexed ligand. Other workers have used what is hoped are physically realistic values for these force constants but have used the same values for all metal complexes [602]. Others have chosen to use values which appear unreasonably high [603,604]. These values have the result of forcing the macrocycle to adopt a conformation that will fit the metal–ligand bond lengths. If these bond lengths are known, then this approach may have some merit. However, bond lengths cannot be transferred uncritically from one complex to another; the structure of $Co([18A]aneN_5)Br^{2+}$ has shown that the metal–ligand bond lengths can vary by at least 10 pm owing to macrocyclic hole size constraints [382]. However, similar results are obtained as a result of these different assumptions, and it has been claimed that the same hole size should be calculated regardless of the values of the force constants used [602]. However this claim has been disputed [603].

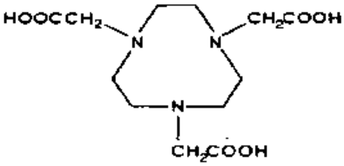
Molecular mechanics calculations have been used with tetraaza macrocycles to calculate what happens when the metal ion becomes too large for the macrocycle. Three scenarios have been considered. If the metal ion is not obliged to be octahedral, then a different ligand conformation can be adopted with the metal ion lying out of the plane of the four donor atoms. This results in a reduced coordination number. Secondly, the macrocycle may fold, adopting a different conformation with presumably an effectively larger hole size. Finally, the macrocycle may compress the metal so that the metal-to-ligand bonds are shortened. Experience with tetraaza macrocycles suggests that the last possibility is never adopted [605]. Studies with the [X]aneN_3, [X]aneN_4 and [X]aneN_5 macrocycles have all shown that increasing the size of the macrocyclic hole by increasing the number of six-membered chelate rings in the macrocycle eventually leads to a decrease in the coordination number of the metal ion. Structural studies have shown that the increasing bulk of the macrocyclic ligand forces a conformation in which one of the coordination sites is blocked. This has been observed even with metal ions which have a strong preference for octahedral coordination such as Ni(II).

For triaza macrocycles the concept of hole size is probably less appropriate as the metal ion does not sit in the plane of the donor atoms. Wieghardt and coworkers have performed numerous structural determinations of complexes of [9]aneN_3 and have shown that this ligand is extremely flexible in its coordination requirements. In a number of structures of [9]aneN_3 complexes [210,276,298] the three M–N distances are not equivalent, demonstrating the coordination flexibility of this ligand.

(iv) Pendent arms on tridentate and pentadentate macrocycles

Preparation of tetraaza macrocycles with pendent arms and their metal complexes have been reviewed [30,31]. Triaza macrocycles have been used to prepare a variety of hexadentate, pentadentate and tetradentate ligands with three pendent arms, two pendent arms and one pendent arm respectively. These ligands contain the following pendent arms: acetato, **229–231**, [607–618]; aminoethyl, **232–234**, [348,619,620]; 2-hydroxyethyl, **235**, [621]; 2-hydroxypropyl, **236**, [622]; 2,3-dihydroxybenzoyl, **237**, [623]; ethanesulphinate, **238**, [624]; ethylacetate, **239**, [624]; diphenylphosphinylmethyl, **240**, [625,626]; dihydroxyphosphorylmethyl, **241**, [627–629]; pyridylmethyl, **242** and **243** [630,631] and phenol, **19** [126]. The hexadentate ligand 1,2-di(1,4,7-triazacyclononyl)ethane, **22**, can be regarded as a triaza macrocycle with one pendent arm and so will be considered in this section. 1,2-di(1,4,7-triazacyclononyl)propane, **23**, has also been prepared [129].

Takamoto and coworkers have reported the preparation of Fe(III), Cr(III) and Co(III) complexes with **229** and **230** and determined formation constants of complexes of **229** using a polarographic technique. Attempts to prepare complexes of triacetato derivatives of [11]aneN_3 and [12]aneN_3 were unsuccessful [607,608]. Cacheris et al. have reported formation constants of this ligand with lanthanide ions [632]. Wieghardt et al. have also prepared complexes of **229** with Fe(III), Cr(III) and Co(III) and have prepared



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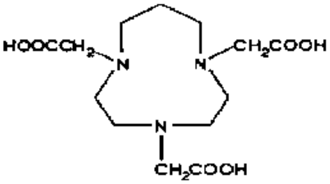

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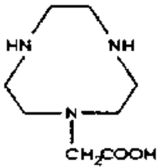

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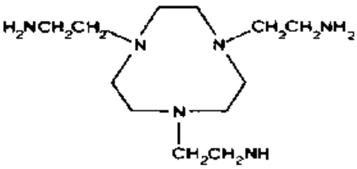

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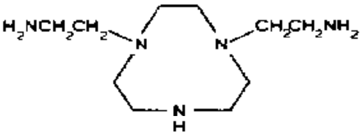

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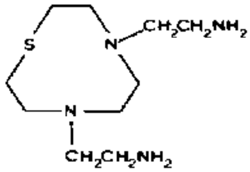

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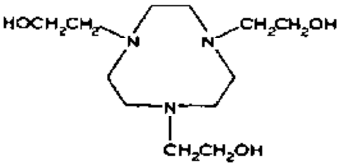

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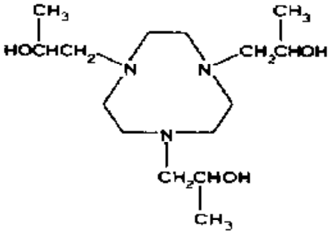

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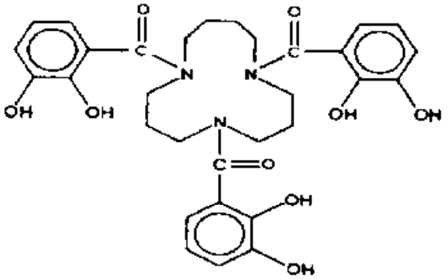

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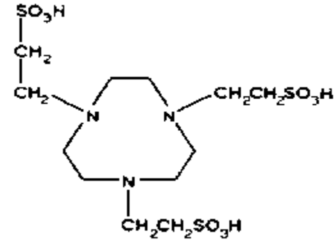

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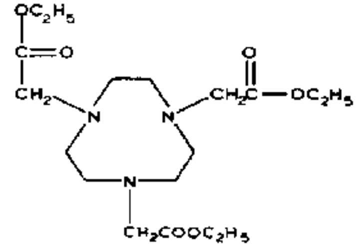

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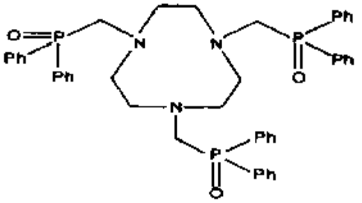

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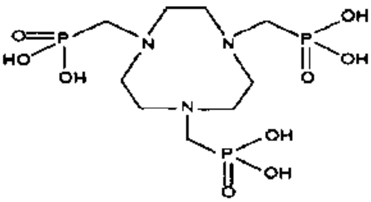

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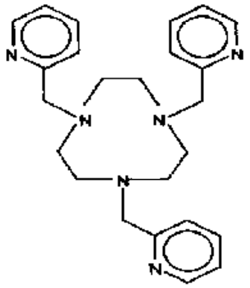

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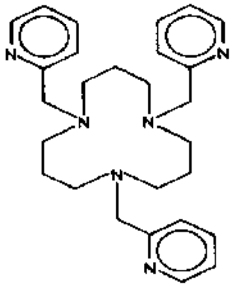


(243)

complexes with Mn(III), Mn(II), Al(III), V(IV), Co(II), Ni(II) and Cu(II). Crystal structures of Cr(III), Fe(III) and Cu(II) complexes have been determined [612]. Van der Merwe et al. have independently prepared and characterized structurally Ni(III) [609], Fe(III), Ni(II) and a different Cu(II) complex [613]. They have also determined formation constants of the Mg^{2+} and Ca^{2+} complexes of **229**, and surprisingly the Mg^{2+} complex is more stable [613].

Ligand **229** behaves as a pentadentate ligand in the V(IV) complex; the sixth coordination site is occupied by a terminal oxo group and the complex isolated has the uncoordinated carboxylate group protonated [612]. A Cu(II) complex, isolated by Wieghardt and coworkers from neutral solution, contains hexadentate **229**, whereas the complex isolated at low pH by Van der Merwe et al. [613] contains two uncoordinated protonated acetate groups, tetradentate **229** and coordinated chloride ion. The coordination sphere of the copper in the complex with the hexadentate form of the ligand is less distorted than the coordination sphere in the five-coordinate complex, a phenomenon attributed to the steric constraints imposed by the ligand.

Complexes of **229**, whose structures have been determined, show a range of distortion in their coordination geometry from octahedral towards trigonal prismatic geometry. This distortion is largest for Fe(III) and smallest for Ni(II) and suggests that **229** experiences considerable strain in coordinating to metal ions which prefer octahedral coordination geometries. Two possible arrangements exist for the acetato groups in the pseudo-octahedral complexes depending on whether the acetate groups are oriented in a clockwise (**VI**) or an anticlockwise fashion (**VII**) (Fig. 6). Ni(III) [609], Ni(II) [613] and Cr(III) [612] complexes are type **VI** and the Fe(III) complex is type **VII**; the Cu(II) complex is a distorted form of type **VII** [613]. This change from type **VI** to **VII** comes in response to increasing M–N bond lengths [613]. NiL^- ($L = $ **229**) is unusual in a number of ways. The ligand-field strength is higher than that for $Ni([9]aneN_3)(H_2O)_3^{2+}$ which is attributed to two factors: (a) the presence of tertiary rather than secondary nitrogen atoms and (b) the absence of steric strain because the carboxylate oxygens carry no hydrogen atoms [613]. The solid complex isolated was a salt of the hydronium cation H_3O^+, which indicates considerable kinetic stability of the complex in the presence of acid. All hexadentate complexes formed are kinetically very stable; no change in the visible spectrum of the complexes occurs for at least 24 h at pH 1 [612].

(VI) (VII)

Fig. 6. Two different modes of coordination in octahedral complexes of **229**.

Redox potentials for chromium, manganese, iron, cobalt and nickel complexes have been measured. Reduction potentials are more positive than those for the $M([9]aneN_3)_2^{n+}$ complexes, with the exception of the chromium complexes which have approximately the same potential [196,612].

Geraldes et al. [611] have investigated the protonation equilibria of **229** using NMR. The protonation shifts observed are very different from the shifts observed with similar compounds formed with tetraaza macrocycles, a difference attributed to conformational effects. Lanthanide and Mn^{2+} complexes of **229** have been studied using NMR [610,611,614,616–618] in order to investigate the possibility of using the complexes as lanthanide shift reagents and as agents for the enhancement of contrast in NMR images. Small trivalent lanthanides (Dy–Yb) appear to form complexes containing only hexadentate **229** but the early members of the series form a mixture of complexes with pentadentate and hexadentate **229**. Luminescence lifetimes of the Eu(III) complex have been measured [610]. This work and NMR investigations [614] suggest that the water coordination number of the complex is three. Hydroxy complexes of lanthanum and lutetium have also been observed in solution above pH 9 [611].

Studer and Kaden [615] have prepared the quadridentate ligand **231** by reacting chloroacetic acid with an excess of $[9]aneN_3$ and have described the preparation of the Cu(II) complex but no other details have appeared.

Hexadentate Co(III) complexes of **232** have been prepared by Hammershoi and Sargeson [620]. A major byproduct of the ligand preparation is **233** and the two ligands are conveniently separated as their Co(III) complexes [348,620]. CoL^{3+} (L = **232**) has been resolved and the ^{13}C NMR spectrum indicates that the complex has C_3 symmetry. An X-ray structural characterization confirmed this symmetry and energy minimization calculations have shown that the observed structure has considerably less strain than other structures considered [619]. CoL^{3+} (L = **232**) has been used as the starting material for the preparation of a number of different macrotricyclic hexamine cage complexes of cobalt [620]. The electrochemical behaviour of the CoL^{3+} complex and these macrotricyclic complexes has been studied and it has been suggested that the strain involved in binding the small Co(III) ion in the macrocyclic cavity influences the redox potentials [633].

Co(III) complexes of **233** and **234** have been prepared and base hydrolysis of the chloro complex studied. Two possible isomeric forms are possible for complexes of these ligands and ^{13}C NMR spectra indicate that the unsymmetrical form is the only isomer present. Base hydrolysis of both complexes proceeds in two steps. The first step corresponds to the loss of chloride ion in both complexes. The second step in the reaction of the **233** complex is thought to correspond to the loss of one of the pendent arms from the coordination sphere. The second step in the base hydrolysis of **234** is believed to result in the loss of the S atom from the cobalt coordination sphere [348].

Sayer et al. have prepared **235** and have determined complex formation constants for Cu(II) and Zn(II) complexes of this ligand [621]. These constants are the same or larger than the constants of [9]aneN_3 despite the large steric strain expected for this ligand. Co(III) complexes of chiral **236** have also been prepared [622]. Absorption and CD spectra of these complexes, which were analysed in some detail, are pH dependent. At low pH, one of the OH groups is protonated (pK_a 8.2) and the sixth coordination site is then occupied by water.

Ligand **237** was designed as a ligand which can readily form an octahedral cavity composed of catechol oxygen atoms suitable for complexation to Fe(III) [623]. A red Fe(III) complex is not fully formed until pH 10 and hydroxy complexes form above this pH [634]. Potentiometric and spectrophotometric (visible and IR) measurements of the Fe(III) complexes have shown that complexes formed by **237** and its 5-sulphonated derivative [635,636] include FeH_3L, FeH_2L and FeHL in addition to FeL. Binding to the iron in the protonated complexes is believed to be via one deprotonated hydroxy group and the carbonyl oxygen of the amide function [634]. The overall formation constant of the FeL (L = **237**) complex is lower than expected, probably because all six phenolic oxygen atoms do not coordinate the iron simultaneously [635,636].

Wieghardt et al. have prepared Cu(II) and Ni(II) complexes of **238** and Co(II), Ni(II), Cu(II) and Zn(II) complexes of **239**. All complexes of **239** apparently contain pentadentate **239** with a water molecule occupying the sixth coordination site. Structures of complexes isolated with **238** also reveal that the ligand is acting as a pentadentate ligand; the Cu(II) complex is five-coordinate and a water molecule completes the pseudo-octahedral coordination sphere of the nickel complex. Rates of the reactions of Co(II) complexes of both ligands with $Fe(CN)_6^{3-}$ have been studied; CoL^- (L = **239**) reacts via an outer-sphere pathway whereas with CoL^- (L = **238**) a stable binuclear complex $CoLFe(CN)_6$ is formed so that an inner-sphere pathway is indicated [624].

Complexes of **240** and **241** have been investigated by Russian workers. Ligand **240** is apparently too bulky to coordinate to a single metal ion as a hexadentate ligand so that mononuclear complexes have **240** acting as a quadridentate ligand, although binuclear four-coordinate Co(II) complexes in which **240** acts as a bridging ligand tridentate to each Co(II) ion can apparently be formed [625]. Ligand **241** is formed by reaction of [9]aneN_3, formalin and phosphorus acid, and protonation equilibria and complex formation constants with a wide variety of metal ions have been investigated [627,628]. This ligand forms particularly stable complexes with Zn(II), and the Mg(II) complex is more stable than the Ca(II) complex by five orders of magnitude [628]. This is believed to be due to the magnesium complex having a hexadentate ligand, whereas not all the potential donors are bound to Ca(II) [629]. A crystal structure of the Fe(III) complex has been reported; the ligand is hexadentate and the Fe(III) coordination is distorted towards a trigonal prism [637]. Complexation selectivity of these and similar ligands has been investigated using molecular mechanics computations [638].

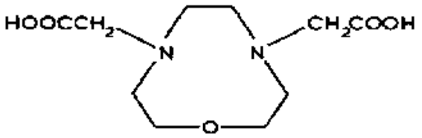
Complexes of **242** and **243** have been prepared by Christiansen et al. [631] and complexes of **242** have been independently synthesized by Wieghardt et al. [630]. Complexes have been prepared with a wide variety of transition metal ions, and in most cases chemical evidence supported by some structural evidence suggests that the ligand is hexadentate. An exception to this behaviour is the Pd(II) complex which has been shown to have a square-based pyramidal geometry which is unique for Pd(II) [630]. Electronic spectra of the iron, cobalt and nickel complexes have been analysed; the ligand-field strength of the **242** ligand is high, almost as large as that of bis [9]aneN_3 complexes. Ligand **243** has a much lower ligand-field strength [631]. Fe(II) complexes of **242** are low spin whereas complexes of **243** are high spin. Ligand **242** is expected to favour a trigonal prismatic structure and the observed structure of the Mn(II) complex supports this expectation. Structures of Fe(II) and Ni(II) complexes are closer to octahedral than trigonal prismatic because low spin Fe(II) and Ni(II) have a large ligand-field preference for octahedral geometry. Mössbauer spectra of Fe(II) complexes of **242** and **243** have been measured and the spectrum of FeL (L = **243**) indicates that inequivalent cations are present in the solid. Racemization of FeL (L = **242**) has been studied; at 5 °C the rate constant is 0.0027 s^{-1} which is fast for low spin Fe(II) complexes. A Bailar twist mechanism is favoured for this reaction [631].

Preparation of **19** was described in Section B (i). Studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes of this ligand have revealed that complexation results in the loss of the proton from the phenol pendent arm and formation constants are much larger than those of complexes of [12]aneN_3 [126].

Complexes of **22** have been studied in detail by Wieghardt et al. [129]; earlier work on this ligand by Tanaka et al. [639] was concerned with aqueous equilibria of complexes with Mn(II), Cd(II), Co(II), Zn(II) and Ni(II). Formation constants are high but, with the exception of the Cd(II) complex, are slightly less than the β_2 values of the [9]aneN_3 complexes. Wieghardt et al. have shown that **22** forms complexes with metal ions which have many similarities to complexes formed by [9]aneN_3. Mononuclear complexes in which **22** acts as a hexadentate ligand to one metal ion have been isolated for Cr(III), Mn(II), Fe(III), Co(III), Ni(II), Ni(III), Cu(II) and Zn(II). Electronic spectra of these complexes are consistent with octahedral coordination although molar absorption coefficients are high which is attributed to distortion of the octahedron. Ligand **22** has a ligand-field strength comparable to bis [9]aneN_3 complexes. Electrochemical investigations of these complexes indicate that they undergo reversible one-electron processes except for the Mn(II)/Mn(III) couple where the electrochemical behaviour indicates that a chemical change occurs in the oxidized species. Reduction potentials of complexes of **22** are 0.3 V more positive than the corresponding $M([9]aneN_3)_2^{n+}$ complexes. Two factors have been suggested as being responsible for this difference; an electronic effect due to tertiary vs. secondary nitrogen atoms and the relief of steric strain in the reduced form of the complexes. This steric strain argument is supported by the fact that the reduction potential of the Co(III) complex of **23**, which should be less strained, is more negative than that of the corresponding complex of **22** [129].

Binuclear complexes of the type Cl_2MLMCl_2 (M = Mn or Cu, L = **22**) with five-coordinate metal centres and of the type Cl_3MLMCl_3 (M = Cr(III), Fe(III) and Co(III)) with six-coordinate metal centres have been prepared. Hydrolysis of the Fe(III) complex in sodium acetate solution leads to a complex originally formulated as $Fe_2L(\mu\text{-}O)(\mu\text{-}OAc)Br \cdot 2H_2O$ (L = **22**). However, a tetranuclear formulation containing two binuclear $\{Fe_2(\mu\text{-}O)(\mu\text{-}OAc)_2\}$ units has recently been suggested as more likely [26]. An oxo-bridged oligomeric Mn(IV) complex which is believed to have the same structure as $Mn_4([9]aneN_3)_4O_6^{4+}$ ion (Section C (i) (a)) has also been isolated. Oligomeric complexes of the type $(CO)_3MLM(CO)_3$ (M = Cr, Mo and W; L = **22**) are formed by reacting $M(CO)_6$ with **22** and oxidative decarbonylation reactions of the types discussed in detail in Section C (i) (b) have been observed also for these complexes [129].

Formation constants and associated thermodynamic parameters of complexes of the alkaline earth metals with the diacetic acid derivatives of



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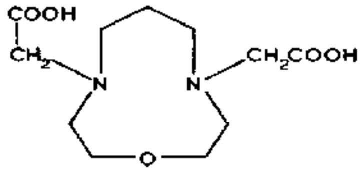

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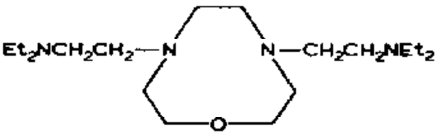

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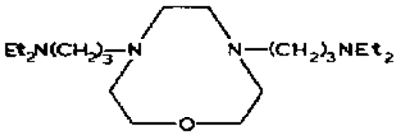

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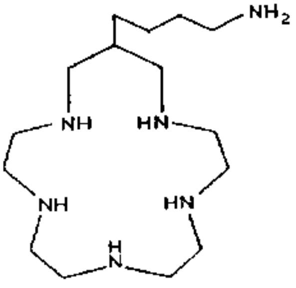
[9]aneN_2O, **244**, and [10]aneN_2O, **245**, have been measured [640]. The most stable complexes are formed by **244**; **245** apparently does not complex Sr(II) or Ba(II). Molecules **246** and **247** have been prepared [344] and their effect on the central nervous system of mice investigated [641] but metal complexes have not been reported.

Only three pentaaza macrocycles with pendent arms have been described. Ni(II) complexes of **128** have been prepared and characterized [121]. Coordination of the pyridine arm is indicated by the complex formation constant and the fact that the complex does not react with molecular oxygen. Oxidation to the Ni(III) complex is not, however, affected by pyridine coordination. Metal complex formation constants for **248** have been determined for a limited number of metal ions [375]; the ligand selectively binds Mg(II) but it does not bind Ca(II). Pentakis(2-hydroxyethyl)-[15]aneN_5, **249**, has been prepared but metal complexes have not been reported [116].



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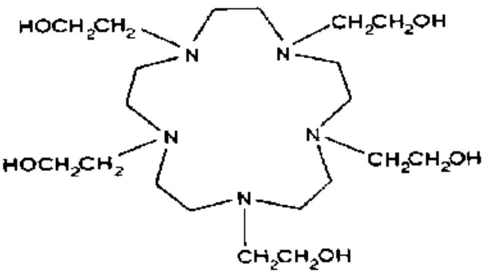

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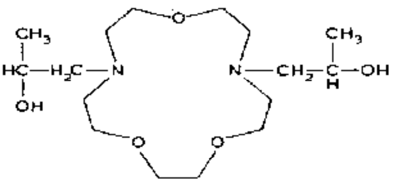
Hancock and coworkers have described a [15]aneN_2O_3 macrocycle, **250**, which has two pendent 2-hydroxypropane groups [91,642,643]. Formation constants of Ca(II), Sr(II), Ba(II), Pb(II), Cu(II), Zn(II) and Cd(II) complexes of this ligand have been determined [642]. Complexes of the *N*,*N*′-diacetic acid derivative of this macrocycle, **251**, have been studied by Chang and coworkers [644–648] and others [649]. Chang has shown that the ligand shows selectivity towards some of the lanthanide ions, in particular Eu(III),



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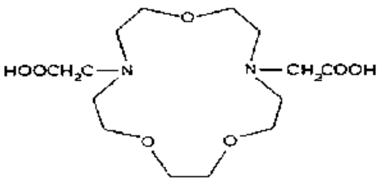

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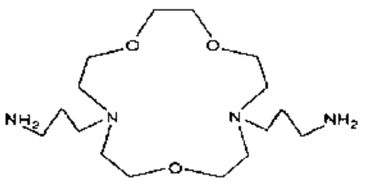

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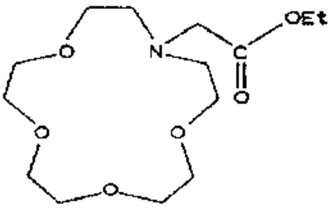
and that ternary complexes of **251**, theonyltrifluoracetone and lanthanide ions may be extracted from aqueous into non-aqueous solution. Kinetics of the dissociation of the lanthanide complexes have been studied [647], both an acid-dependent and acid-independent pathway were observed. Molecule **252** has been prepared and used to cap a porphyrin molecule but no reports of the behaviour of this ligand have been reported [650].

Nitrogen-pivot lariat ethers of the type **253–258** have been extensively



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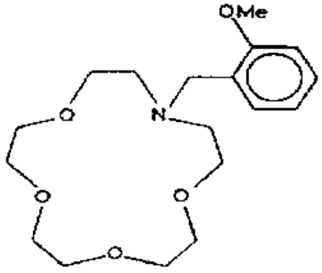

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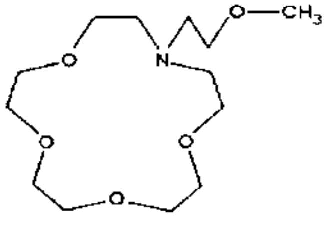

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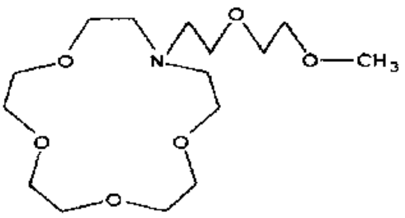

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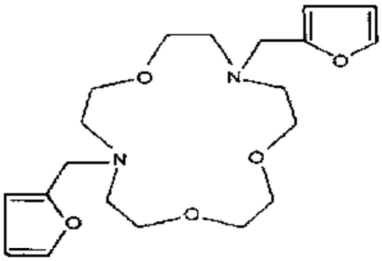

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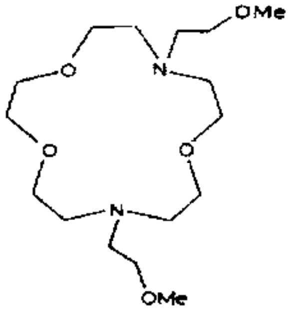

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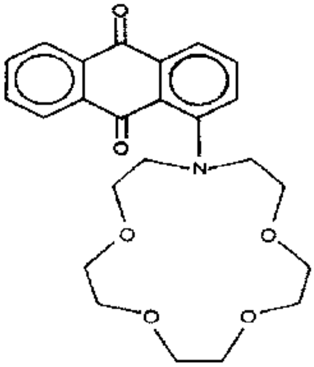
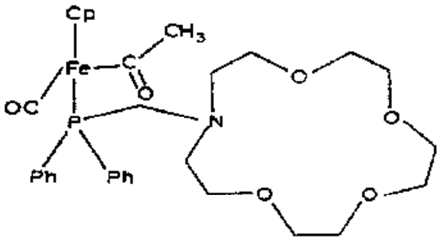
studied by Gokel and coworkers [519,552,563,568,569,651–655] and other workers [40,78,656–658]. The presence of donor groups on the flexible arm has been shown to enhance (via an enthalpy effect) binding to metal ions and NH_4^+ [519,563,651,653,655]. Factors influencing the magnitude of the binding are thought to be the type of donor atoms on the flexible arm, steric accessibility of the donor group to the macro-ring-bound cation, and the number and stability of the three-dimensional geometries the complex can adopt [519,655]. Crystal structures of the complexes NaLBr (L = **253**) [653,654], KLI (L = **256**), KLI (L = **256**) and NaLBr (L = **257**) [654] have shown that the donor atoms of the macrocycle and the flexible arm are bound to the metal ion which lies significantly out of the best plane through the five donor atoms of the macrocycle. ^{13}C NMR relaxation studies have shown that the Ca^{2+} complexes of the ligand **254** is rigid, all the carbons having the same relaxation times [568]. The sodium complex of this ligand is much more flexible.

Vögtle has attached dye molecules to the nitrogen of **215** to give, for example, **259** and has investigated the effects of complexation on the absorption spectra of the dye [659]. Both bathochromic and hipsochromic shifts are observed, depending on the nature of the dye, and the extent of change observed is metal-ion dependent. A ligand of this type has been used as a photometric reagent for the determination of sodium [660].

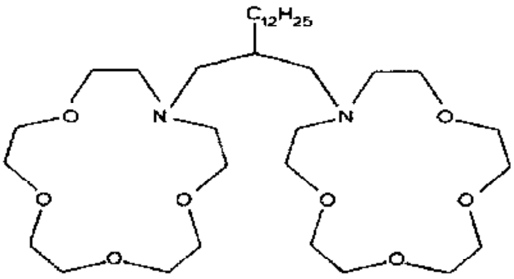


(259)

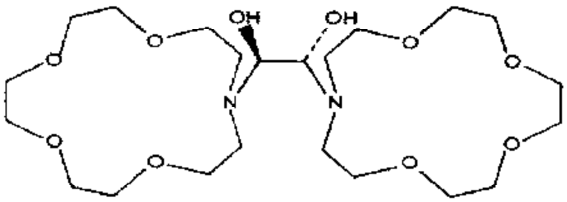


(260)

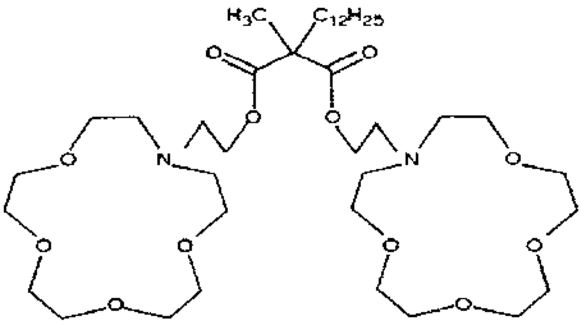
Unusual side-arms have been developed by McLain [661,662] who has prepared phosphinoaza crown ethers and has used this ligand to prepare organometallic derivatives, e.g. **260** [662]. Reaction of these derivatives with



(261)



(262)



(263)

sodium incorporates Na^+ into the macrocycle, and NMR evidence suggests that Na^+ interacts strongly with the acyl oxygen. Potassium does not form complexes of this type.

NO_4 macrocycles with macrocyclic pendent arms, e.g. **261**, **262** and **263**, have been described [656,663–665] and the ligand **261** has been shown to display excellent cation selectivity for sodium [664]. Structural information on these complexes would be of considerable interest but has not been reported. Finally, monoaza crown ethers have been functionalized with ethylene oligomers with M_v in the range 1000–3000 and the resulting molecules have been shown to be excellent phase transfer catalysts [666].

(v) Other compounds

Triaza macrocycles have been used to form compounds with a variety of other elements, phosphorus [95,667], sulphur [667], carbon [669–671] and boron [672]. Similar compounds have not yet been characterized with pentaaza macrocycles. Trisaminoboranes, trisaminophosphanes and trisaminomethanes have been formed with [9]aneN_3, [10]aneN_3, [11]aneN_3 and [12]aneN_3 [95,669–672]. The stability of the boron and phosphorus compounds has been shown to decrease with decreasing ring size [95,667,672]. Structural studies have shown the boron compound with [9]aneN_3 to be dimeric [672] but the phosphine sulphide compound is monomeric [95]. Similar steric effects have been observed with the trisaminomethanes in that the [9]aneN_3 derivative has the central carbon–hydrogen bond *syn* periplanar to the adjacent lone pairs and the [12]aneN_3 derivative is *anti* periplanar and different reactivities with electrophiles have been observed [669]. Tris((trifluoromethyl)sulphenyl)-1,5,9-triazacycloundecane has been prepared by reaction of the amine with CF_3SCl [668].

F. CONCLUSION

The study of macrocyclic complexes has in some ways reached a stage of maturity which is remarkable considering how short a time such complexes have been under active investigation. The elegant studies by Lindoy and coworkers on the N_3O_2 macrocycles have demonstrated how, by fine-tuning structural aspects of the macrocyclic ligand, it is possible to make profound and predictable changes in the stability of complexes with different metal ions. These differences are beginning to be exploited as a means of separation and analysis of metal ions. Synthetic techniques now exist to prepare different series of macrocyclic ligands, e.g. N_2O_3 or N_4O ligands, and much interesting work can be expected in this area in the future.

In other ways the study of these complexes is still in its infancy. With the notable exception of the [9]aneN_3 and Me_3[9]aneN_3 ligands, the ligands studied in this review have been complexed to only a small number of metal ions, usually less than five, and in a number of remarkable cases, metal complexes are unknown. For example, [15]aneN_3O_2 has been prepared but no metal complexes are known, [15]aneS_5 has only been complexed to copper, and the ligand [9]aneNS_2 has apparently not been prepared. Wieghardt and coworkers have shown that much interesting chemistry of the lighter first-row transition metals and second- and third-row transition elements can be studied using [9]aneN_3. There is no reason not to expect even more interesting and important chemistry which lies waiting to be discovered with some of the other ligands.

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