Coordination Chemistry Reviews, 9 (1972–1973) 219–274

LIGAND DESIGN AND SYNTHESIS

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(Received February 1st, 1972)

CONTENTS

A. INTRODUCTION

Metal complexes are made up of a metal ion, the acceptor, and one or more ligands containing the donor atoms. A ligand may be attached to a metal ion by more than one donor atom, thus forming a heterocyclic ring called a chelate[1] ring. In such a case, the ligand may be termed a chelating agent and the resulting complex a metal chelate. The properties of a metal complex are dependent on the nature of the metal ion and also of the ligands. The variation in metal ions is considerable; on the other hand, the variation in

ligands is virtually limitless because of the extent of organic chemistry available for the synthesis of suitable molecules. Many types of ligands are known and the properties of their derived metal complexes have been investigated. However, as a result of this information, there is now a need for the synthesis of new ligands of specific design which could lead to metal complexes with special and possibly predictable properties.

The design of a ligand must take into account the factors affecting the stability of metal complexes and also the geometrical considerations of molecular construction. Some ligands are, of course, easier to synthesise than others and a good design should produce a structure which can be synthesised fairly readily. In this context, a number of reaction types are especially applicable to ligand synthesis, although in principle all organic reactions are available for use.

These features of ligand design and synthesis will be dealt with in Sects. B, C and D. Section E will further illustrate these general features by way of selected examples ranging mainly from bidentate to sexadentate chelating agents; brief discussions of possible higher multidentate chelating agents and chelating agents which form binuclear metal complexes are also included.

Because of the extent of this area of coordination chemistry the discussion is restricted to ligands containing nitrogen, oxygen, sulphur, phosphorus and arsenic donor atoms. Aspects of the design and synthesis of ligands which form σ or π carbon–metal bonds in their complexes are excluded, as this area is almost as extensive as organic synthesis itself.

In this review, emphasis is placed on the nature of the ligands, often at the expense of the nature of the metal complexes which they form. It should be pointed out that not all ligands can be isolated as such and some only exist in their metal complexes. However, for the sake of clarity and simplification, structural diagrams of free ligands predominate in Sect. E. The structures are often drawn in a way which emphasises the donor atom sites and hints at the type of coordination involved in their complexes; such diagrams would not necessarily reflect the geometry of the ligand itself.

B. FACTORS AFFECTING THE STABILITY OF METAL COMPLEXES

The design of ligands is usually directed towards the production of stable metal complexes. This need not always be so, and the specific design and synthesis of "unfavourable" ligands, giving rise to complexes of poor stability, presents a virgin area for future research. The formation and dissociation of relatively weak metal complexes is relevant to the chemistry[2] of metal–enzyme systems.

(i) Relative strength of donor and acceptor atoms

Since metal ions are Lewis acids the basic strength of a donor atom is relevant[3] to the metal–donor atom bond. However, the donor atom must be considered together with the metal ion. Ahrland et al.[4] divided the acceptor metal ions into two classes depending

on whether they form their more stable complexes with (*a*) the smaller donor atoms such as nitrogen, oxygen and fluorine or (*b*) the larger ones, including phosphorus, sulphur and chlorine. This classification has proved to be very useful, but there is considerable overlap between the two classes and some of the most interesting metal ions lie in the borderline region. In a ligand containing several different donor atoms, the situation becomes rather complicated and a simple classification is not very meaningful. The oxidation state of a metal also helps to determine its classification.

There is a strong tendency for π-bonding to occur[5] in coordination of a metal atom with phosphorus and arsenic donor atoms, but not with thioether sulphur atoms[6, 7].

(ii) The chelate effect

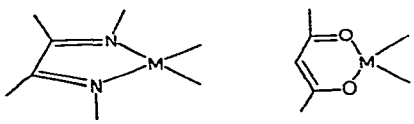
Many quantitative studies[8] have confirmed that metal chelate complexes are more stable than those of related unidentate ligands. An entropy effect is at least partly[9] responsible for this phenomenon. One of the main reasons for the synthesis of multidentate chelating agents is provided by the increased stability of the derived metal complexes, by virtue of the chelate effect. The number of chelate rings is important and for two similar metal chelates, that which contains the greater number of stable chelate rings will generally be the more stable.

Chelate rings play an important part in reducing the lability of metal complexes with respect to simple substitution. Although cobalt(III) ammine complexes are inert, the corresponding cobalt(II) and nickel(II) complexes are labile. Thus, the use of polyamine chelating agents allows the formation of cobalt(II) and nickel(II) complexes with reduced lability.

The formation of new chelate rings is also a major feature of metal template reactions (see Sect. D (iv)).

(iii) Size and shape of chelate rings

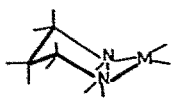
The factors governing the stability of chelate rings are essentially the same as those that apply to heterocyclic rings[10, 11]. However, different constraints are placed on some bond angles and bond lengths by the presence of a metal ion. Five- and six-membered chelate rings are by far the most common[12] and are in general the most stable. In the case of unsaturated five- and six-membered rings in which resonance occurs[13, 14], all the atoms in the ring are approximately coplanar. This is illustrated by the partial structures shown below, for instance.



For fully unsaturated chelate rings, the angle strain is less for those with six members that for those with five. Also, unsaturated six-membered chelate rings are less strained[15] than saturated ones.

In saturated chelate rings, some deviation from coplanarity results in a reduction of angle strain. Corey and Bailar[16] have treated the conformational aspects of chelate rings derived from 1, 2-diaminoethane and 1, 3-diaminopropane, by relating them to cyclopentane and cyclohexane respectively. Their conformational analysis led to an accurate prediction of the shape of the chelate rings in the tris(1, 2-diaminoethane) cobalt(III) ion[17]. These chelate rings were found to have the staggered conformation illustrated.

Similarly, the six-membered chelate ring in a 1, 3-diaminopropane complex would be expected to adopt an approximate chair conformation as shown[18].

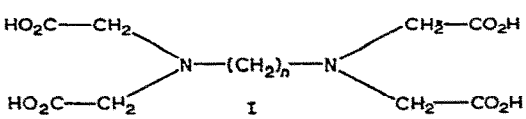


However, the ring is more sharply folded than cyclohexane, because of the constraints imposed by metal–nitrogen bond lengths of ~2 Å and a nitrogen–metal–nitrogen bond angle of approximately 90°. Thus the interaction between axial substituents is significantly increased.

Consequently, some destabilisation of the six-membered chelate ring is observed relative to the similar five-membered one. Complexes of 1, 2-diaminoethane have been found[19, 20] to be more stable than those of 1, 3-diaminopropane, despite the greater base strength of the latter diamine.

Four-membered chelate rings are now fairly common and include complexes of the carbonate ion[21, 22], the dithiocarbamates[23, 24] and 1, 8-naphthyridine[25]. An increasing number of four-membered chelate rings containing two metal atoms[24, 26] has been detected; usually the other atoms in the ring are sulphur or oxygen.

Medium and large chelate rings[27] have been postulated in a variety of structures. Their effect on the stability of a complex depends on the flexibility of the ring and the presence or otherwise of other chelate rings. The stability constants of metal complexes derived[28] from the tetracarboxylic acids I decrease along the series $n = 2 > 3 > 4 > 5$.



I

However, large chelate rings are not necessarily detrimental to the stability of metal complexes, but are usually part of a highly stable multidentate chelate structure. For example, the cobalt complex vitamin B_{12} contains[29] a nineteen-membered chelate ring, and the

iron hydroxamates, the mycobactins and ferrioxamines[30] also contain large chelate rings.

C. GEOMETRICAL CONSIDERATIONS OF LIGAND DESIGN

In addition to the factors affecting the stability of metal complexes, various considerations of geometry must be borne in mind when designing a multidentate ligand. Various stereochemical features influence the shape and flexibility of organic compounds in general. Steric interactions may result in a loss of molecular flexibility through the restriction of bond rotation. Conformational preferences can also affect the particular shape of a molecule. Where these stereochemical features occur in ligands they may influence the geometrical arrangement of donor atoms in a derived metal complex or the precise configuration of such a complex.

Apart from these normal stereochemical effects of organic molecules, there are in metal complexes additional geometrical consequences of the metal ion and of the donor atoms, and these are now considered further.

(i) Geometrical consequences of the metal ion

In four-coordinate metal complexes, the distribution of bonds about the metal ion is such that the donor atoms lie at the corners of a square or at the apices of a tetrahedron, with the metal ion at the centre of that square or tetrahedron. Similarly the donor atoms surrounding a six-coordinate metal ion are usually situated at the apices of an octahedron or trigonal prism and those about a five-coordinate metal ion lie at the corners of a square pyramid or trigonal bipyramid. Thus the metal ion exerts a preference for a particular kind of environment and some ligands are better able to conform to that environment than others. Also, each ligand has its own preference for a particular geometrical configuration. Ligand design is important because of the possible conflict between these two effects. If the aim is to produce a highly stable metal chelate, then the ligand should be designed so as best to suit one of the geometrical preferences of the metal ion. On the other hand, if new and unusual properties are being sought in the resulting metal complex, a strong and rigid ligand may force a metal ion to form a complex of non-ideal geometry.

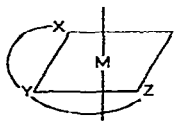
The size of the metal ion is also important. For instance, the conformational strain in five-membered chelate rings is increased with an increase in size of the metal ion. In general, bond lengths and bond angles in chelate rings depend on the size of the metal ion.

(ii) Geometrical consequences of the donor atoms

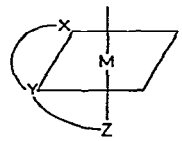
Donor atoms can be present in ligands in a number of different functional groups. The most common for nitrogen atoms are primary, secondary and tertiary amino, imino, azo or oximino groups. Oxygen atoms can act as donor atoms in carboxylate, phenolate, carbonyl, alkoxide, *N*-oxide or ether groups; sulphur atoms can act in thiocarboxylate, xan-

thate, dithiocarbamate, thiolate or thioether groups and phosphorus and arsenic atoms can act in phosphino or arsino groups. Most of the following discussion will centre on the use of nitrogen, oxygen and sulphur donor atoms.

In multidentate chelating agents the bond distribution about the non-terminal donor atoms influences the geometry of the ligand in the metal complex and consequently the configuration of the metal complex itself. In the case of a tridentate chelating agent co-ordinated to a metal ion M two general configurations, IIa and IIb, where X, Y and Z are donor atoms, are possible.

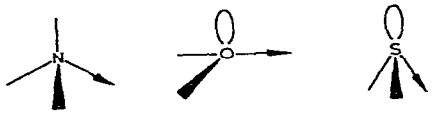


IIa

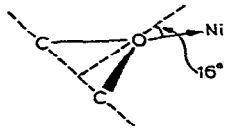


IIb

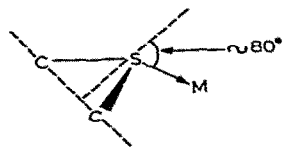
In configuration IIa there is an equatorial arrangement of donor atoms X, Y and Z and these are coplanar with the metal M, whereas in configuration IIb there is a vicinal arrangement of X, Y and Z because X, Y and M are coplanar and Y, Z and M are coplanar and these two planes are orthogonal. The nature of the central donor atom Y can influence the preference for one or other configuration. If Y is part of an unsaturated group, such as an imine, then the distribution of bonds about Y would tend to be coplanar and therefore configuration IIa would be less strained than configuration IIb. On the other hand, there would be a pyramidal distribution of bonds about a coordinated saturated nitrogen, ether oxygen or thioether sulphur atom.



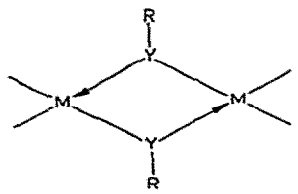
Because of this there is greater flexibility in the ligand, and complexes with both configurations IIa and IIb are possible. Where Y is a pyramidal nitrogen atom, both equatorial and vicinal arrangements of the three donor atoms about the metal ion are relatively free of strain. However, where Y is an ether oxygen atom, an equatorial arrangement of donor atoms is preferred to a vicinal one. In contrast, a vicinal arrangement of donor atoms is preferred when Y is a thioether sulphur atom. These configurational preferences are a consequence of the different bond angles about the coordinated oxygen and sulphur atoms. For example, an X-ray crystal structure determination[31] of dibromo-[1-(*o*-methoxyphenyl)-2, 6-diazaoctane]-nickel(II) reveals that the oxygen–nickel bond deviates from the plane of the two carbon–oxygen bonds by approximately 16°, as shown.



However, X-ray crystal structure analyses[6, 7, 32] of a number of coordinated thioethers show that the sulphur–metal bond normally deviates from the carbon–sulphur–carbon plane by an angle as large as 80°, as shown.



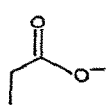
Similar variations in bond angles are apparent from studies of the structures of oxygen-bridged[33–35] and sulphur-bridged[36] compounds incorporating four-membered chelate rings of the following type, where Y is oxygen or sulphur.



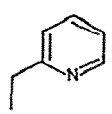
The above configurational preferences hold only for the metal complexes of ligands which contain ethano bridges between donor atoms and consequently contain five-membered chelate rings. Larger saturated chelate rings have greater flexibility which considerably reduces the effects of the bond geometry of a central donor atom.

(iii) Concept of spatial equivalence of groups

This concept has been advanced by Lions[10] as an aid in the design of new chelating agents. Different donor atoms may be incorporated into structural fragments of similar atomic dimensions, thereby allowing a variation in ligand types without a change in the geometrical arrangement of donor atoms about a metal ion. For example, the acetate group III is spatially equivalent to the α-pyridylmethylene fragment IV.



III



IV

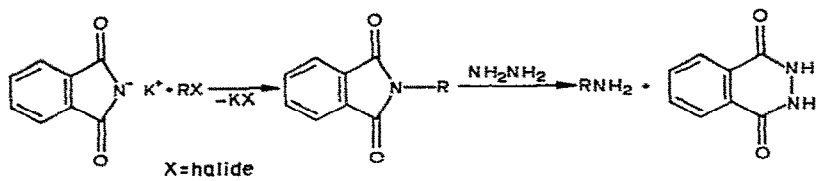
However, an interchanging of these two fragments would affect the charge on metal complexes of the resulting ligands. Clearly, spatially equivalent groups are incorporated in chelate rings of the same size. However, most manipulation of such groups has an effect[37, 38] on the rigidity of the ligand. Thus the replacement of an ethano bridge by an *ortho*-disubstituted benzene ring would result in a chelate ring of reduced flexibility.

D. BOND FORMATION AND LIGAND SYNTHESIS

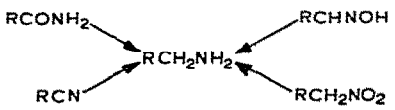
(i) Direct synthesis of amines and thiols

The starting materials for the synthesis of ligands are usually alcohols, amines or thiols.

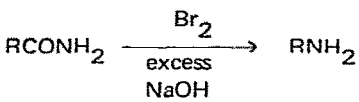
Primary amines are commonly prepared by a number of methods. Controlled alkylation of ammonia is achieved by the use of potassium phthalimide, as in the Gabriel synthesis[39].



Primary amines can also be formed readily by the reduction[40] of amides, nitriles, nitrocompounds and oximes.

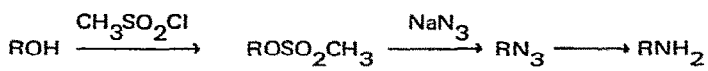


The reaction of amides with bromine and sodium hydroxide (the Hofmann reaction)[41] leads to primary amines with one less carbon atom.



Primary amines can also be formed by the related molecular rearrangement of carboxylic acid derivatives, namely carbonyl azides (Curtius[42] and Schmidt[43] rearrangements) and hydroxamic acids (Lossen[44] rearrangement).

A very useful sequence for the conversion of hydroxyl groups to amino groups has recently been applied[45] to the synthesis of amine ligands. The readily available alcohol is first converted to its methanesulphonate derivative which is in turn transformed to an azide by nucleophilic displacement; the azide is then reduced[46] to a primary amine by lithium aluminium hydride.



Alkyl or aryl thiols are most conveniently prepared from halides by reaction with sodium hydrosulphide[47] or thiourea and alkali[48]. A synthetically useful modification[49] involves the reaction of alcohols with thiourea in the presence of hydrobromic acid.

(ii) Extension of ligand coordination by reaction at donor atoms

The extension of ligand coordination has been discussed recently by Lions[50]. The most general method for the amplification of donor atoms is provided by alkylation. This process is applicable to amines, thiols, alcohols, phosphines and arsines and provides ethers, thioethers, tertiary amines, phosphines and arsines. It is of most use in the preparation[51] of thioethers.

$$RSH \xrightarrow{NaOH} RSNa \xrightarrow{R'X} RSR'$$

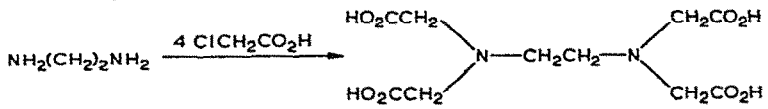
The dialkylation of sodium sulphide similarly leads[51] to symmetrical thioethers.

$$2\,RX \xrightarrow{Na_2S} RSR$$

Thiols can thus be converted into a variety of bidentate ligands, by alkylation with bifunctional alkyl halides, such as chloroacetic acid or 1, 2-dibromoethane.

$$RSCH_2CO_2H \xleftarrow{ClCH_2CO_2H} RSH \xrightarrow{BrCH_2CH_2Br} RSCH_2CH_2SR$$

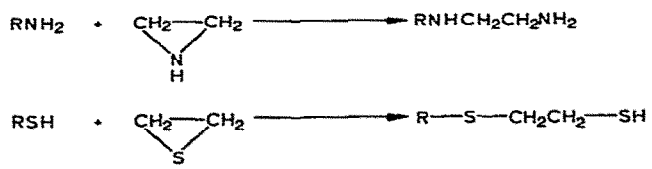
The alkylation of amines with chloroacetic acid has found wide applicability in the synthesis[52] of tertiary amine chelating agents, such as those of the ethylenediamine tetraacetic acid (EDTA) group, e.g.



A similar transformation[53, 54] can be effected by reaction of an amine with formaldehyde and sodium cyanide.

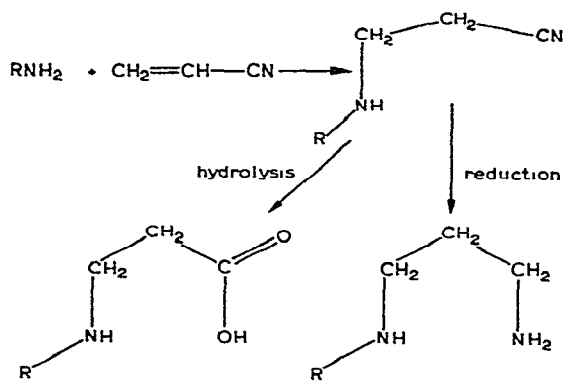
$$RNH_2 + HCHO + NaCN \xrightarrow[\text{base}]{\text{aqueous}} RNHCH_2CO_2H$$

A particularly useful nucleophilic substitution reaction is that of amines and thiols with ethylenimine[55] or ethylene-sulphide[56].

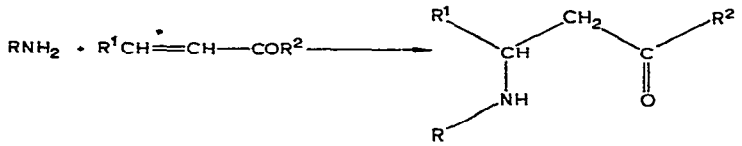


Aluminium chloride is used [57] as a catalyst in the addition of amines to ethylenimine.

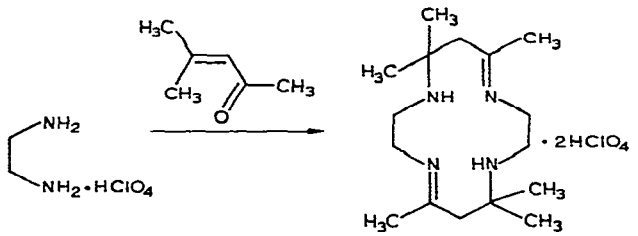
The addition of amines to electrophilic alkenes takes place readily and provides a variety of opportunities for ligand development. The products of addition[58] of amines to acrylonitrile can be easily converted to a number of useful ligand types, viz.



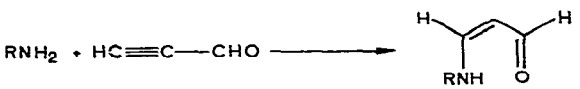
A wide variety of β-aminoketones can be readily prepared by the addition[59] of amines to α, β-unsaturated ketones.



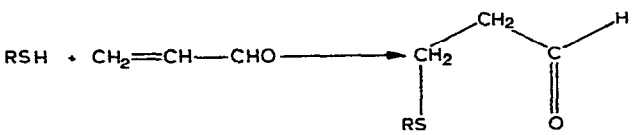
The use of diamines in this type of reaction can lead to the synthesis of macrocyclic quadridentate ligands[60–62], e.g.



Similar addition of an amine to formyl acetylene has been used[63] as an initial step in the synthesis of a ligand.



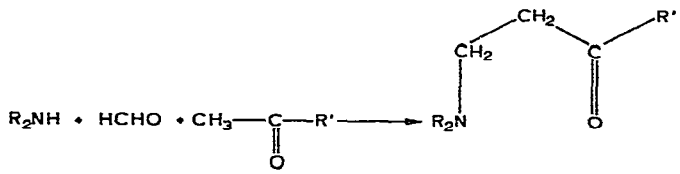
Thiols also add to electrophilic alkenes[64–66] in good yield, e.g.



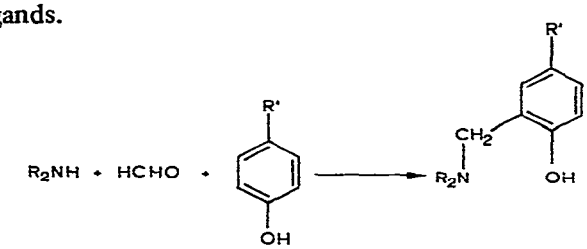
The base-catalysed addition of phosphines and arsines to vinyl phosphines has been developed[67, 68] as a general preparative method for polytertiary phosphine and arsine ligands.

The Mannich reaction provides a further approach to the extension of a sequence of

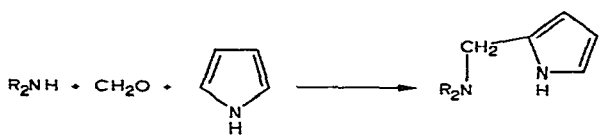
donor atoms. This process is most applicable to the synthesis of tertiary amines from secondary ones and yields a wide variety[69, 70] of β-aminoethyl derivatives. Methylene ketones, formaldehyde and secondary amines react[71, 72] to form β-aminoethylketones.



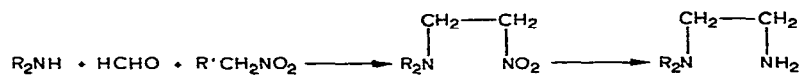
Similarly *para*-substituted phenols may be used to give products[73] which are potential ligands.



Other compounds such as pyrroles[74] undergo the Mannich reaction and afford useful products.

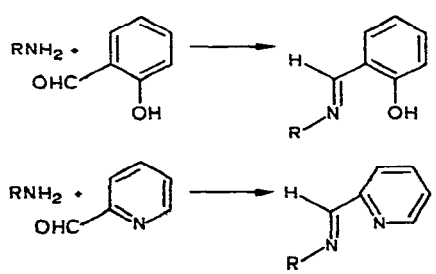


The nitroamines formed in the Mannich reaction of nitroalkanes[75] can be reduced to 1, 2-diamines.

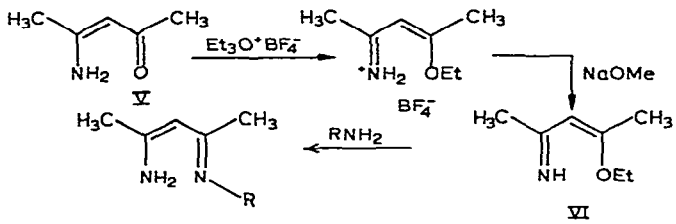


Some Mannich bases undergo ready elimination of an amine and steps need to be taken to prevent the occurrence of this reaction.

The most valuable reaction for the extension of donor atom sequences from primary amines is condensation with aldehydes to form imines (or Schiff bases)[76]; salicylaldehyde and pyridine-2-aldehyde are most commonly used.

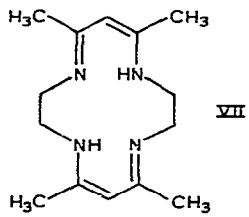


Extensions of this reaction to include other related aldehydes[50, 77, 78] have not been numerous. In many cases it is preferable to prepare metal complexes directly[79] by reaction of the amine and aldehyde in the presence of the metal salt rather than preform the imine. Where the carbonyl group is part of a vinylogous amide such as V, its normal electrophilic properties are diminished. However, condensation with amines can be achieved[80, 81] by reaction with an intermediate iminoester such as VI.



V VI

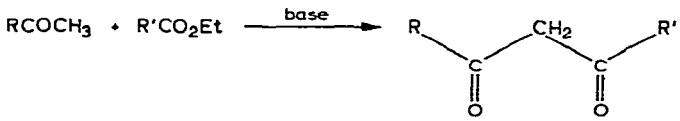
A sequence of such reactions has been recently applied to the synthesis[82] of the macrocyclic ligand VII from the vinylogous amide V by combination with 1, 2-diaminoethane.



VII

(iii) Extension of ligand coordination by reaction at non-donor atoms

In principle this presents a wide area of possibilities, but they have not received much attention. These possibilities include the formation of β-diketones by acylation[83] of methylene ketones or their enamines[84].



The formation of a new carbon–carbon bond often takes place at a carbon atom which is activated by a carbonyl or nitro group; in such cases, carbanion reactivity is important.

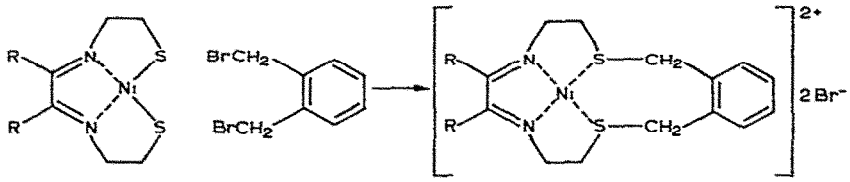
Nitroalkanes are useful synthetic intermediates and undergo addition to carbonyl groups. The nitro group can then be reduced to an amino group or modified in other ways. Nitro groups are themselves[85–87] capable of coordination to metal ions.

The alkylation reactions described in the previous section can be viewed as nucleophilic substitution of alkyl halides and in this respect can be thought of as reactions at a non-donor atom. Similarly, the preparation of imines from the chelating agent salicylaldehyde involves reaction at a carbon atom adjacent to a donor atom. The addition of water or alcohols to coordinated imines[88, 89] or ketones[90–92] has also been observed and this will be discussed later in specific examples.

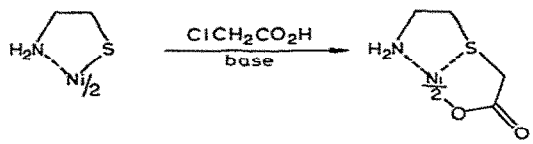
(iv) Development of new chelate rings by metal template methods

Metal template reactions[93–95] are ligand reactions which are dependent on, or can be significantly enhanced by, a particular geometrical orientation imposed by metal coordination. One of the driving forces for such reactions is the achievement of stable metal complexes, either by the formation of new chelate rings or the modification of existing ones.

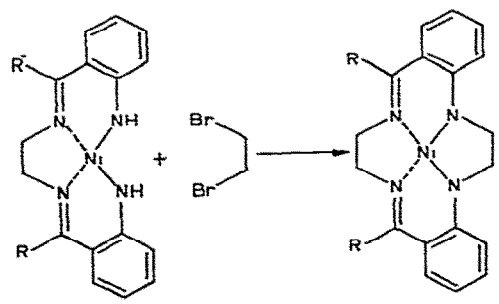
New chelate rings can be formed by the alkylation of coordinated sulphur[96–99] or nitrogen atoms[100]. Busch developed[98, 101] the construction of macrocyclic metal complexes through difunctional alkylation of *cis*-coordinated sulphur atoms, e.g.



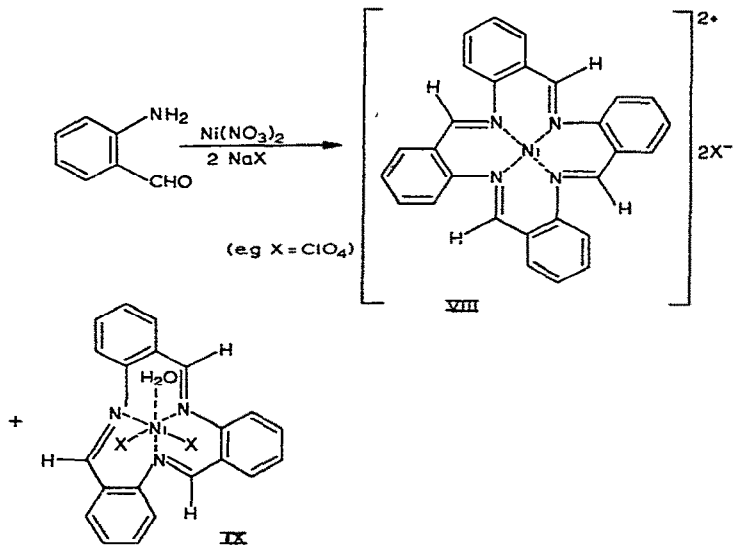
A new chelate ring can also be formed by the alkylation of a coordinated sulphur atom with chloroacetic acid[99].



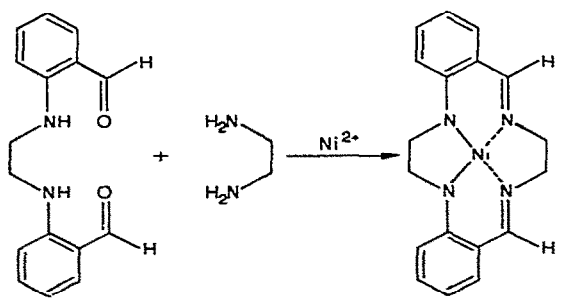
Alkylation of coordinated nitrogen atoms can only be achieved if these atoms retain a non-bonding pair of electrons and are not quaternary ammonium salts. Formation of a series of macrocyclic metal complexes has been achieved[100] by the alkylation of quadridentate chelates with 1, 2-dibromoethane.



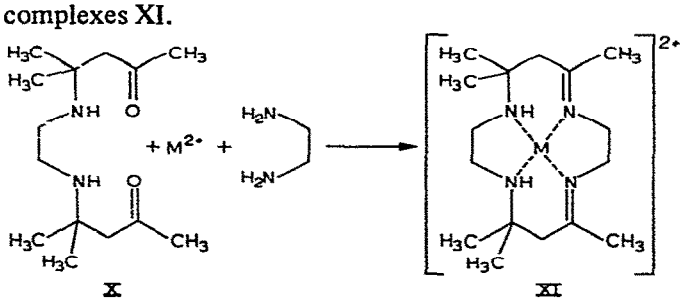
Metal template reactions very often lead to products in which new imine groups have been constructed. Indeed, metal ions can play a crucial role in the formation of imines and certain aspects of metal-ion control in these reactions have been reviewed[79] recently. Such control is clearly exemplified in the polymerization of *o*-amino-benzaldehyde in the presence of nickel ions to give predominantly the macrocyclic complex VIII[102–104] and the tridentate chelate IX[105].



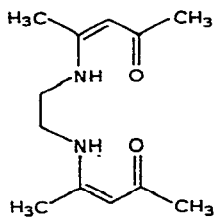
The construction of new chelate rings by the condensation of amines with aldehydes has led to the preparation of other macrocyclic chelates of the quadridentate[106–109], quinquedentate[110] and sexadentate[111–113] types. One example[106, 107] is shown below, and others will be discussed later (see Sect. E).



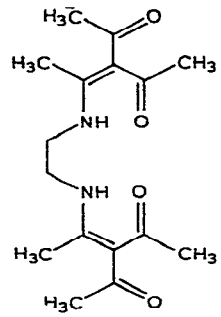
Imines can also be derived from ketones, but less readily than from aldehydes. Reactions of this type have also given rise to the preparation of macrocyclic metal complexes. For example, the carbonyl group of the aminoketone X has normal electrophilic properties and condenses[114] with 1, 2-diaminoethane in the presence of metal ions to give metal complexes XI.



Such a reaction cannot proceed[115] with a related vinylogous amide system such as XII, but can occur[116–118] if a second carbonyl group is provided, as in the compound XIII[117].

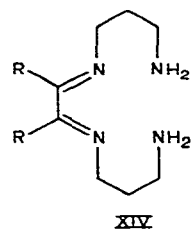


XII

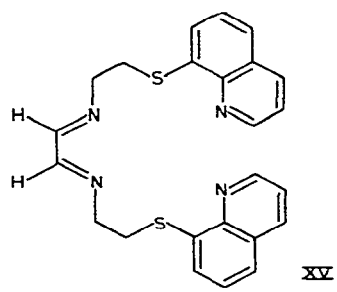


XIII

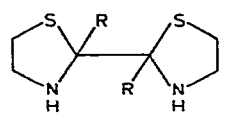
α-Diimines can be stabilised[119, 120] as metal complexes by virtue of the formation of stable five-membered chelate rings. Consequently, metal template reactions of glyoxal or α-diketones with amines afford metal complexes of multidentate chelating agents, such as XIV[121, 122], XV[123] and XVII[124, 125].



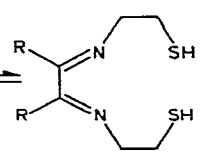
XIV



XV



XVI



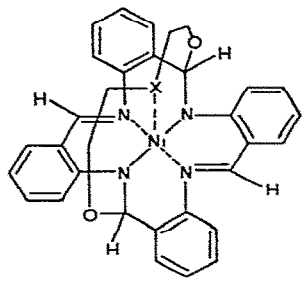
XVII

β-Mercapto amines normally react with α-diketones to yield bis-thiazolidines, such as XVI. However, in the presence of suitable metal ions, stable metal complexes[126] of the diimine (e.g. XVII) are produced; the equilibrium between XVI and XVII is influenced by the precipitation of the quadridentate metal chelates. This kind of metal-induced rearrangement was originally observed[127, 128] in the reaction of *o*-aminophenol with glyoxal and then extended to other examples[129, 130], including those of sulphur analogues[131–133].

Although most imine metal complexes are quite stable and can be isolated as the end-products of reactions, some special types are sufficiently reactive to yield products of further reaction. Coordinated imines are iminium ions and show similar chemical reactivity to aldehydes and ketones. Thus, nucleophilic attack at the imine carbon atom is characteristic for imine hydrolysis[134–136] (where water is the nucleophile) or amine exchange[137]

(where a primary amine is the nucleophile).

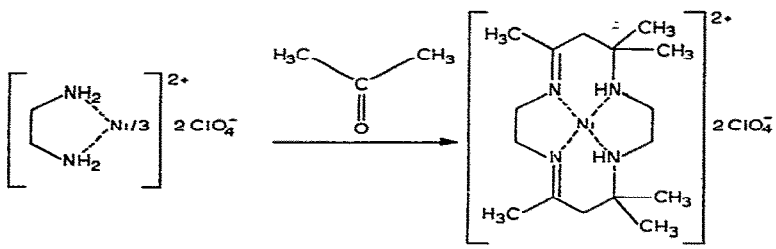
Alcohols can also add as nucleophiles to coordinated imines. For instance, addition of the disodium salts of two 1, 5-glycols to the macrocyclic complex VIII yields[89] the quinquedentate chelates XVIII, where X is either S or NCH_3.



XVIII

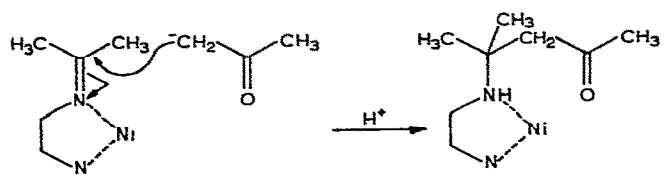
There is apparently a certain amount of strain in the cyclic ligand of the complex VIII, despite the ease with which the complex is formed.

It is also possible for carbanions to act as nucleophiles in reactions with coordinated imines. This occurs in the reaction[138] of tris(1, 2-diaminoethane) nickel(II) perchlorate with acetone to form the macrocyclic nickel complex XIX[139].



XIX

Isopropylidene imines are intermediates in the reaction, where the bridging process is a base-catalysed aldol-type addition. Circumstantial evidence suggests that the nucleophile is an acetonyl carbanion which adds to a coordinated imine to yield a coordinated aminoketone.



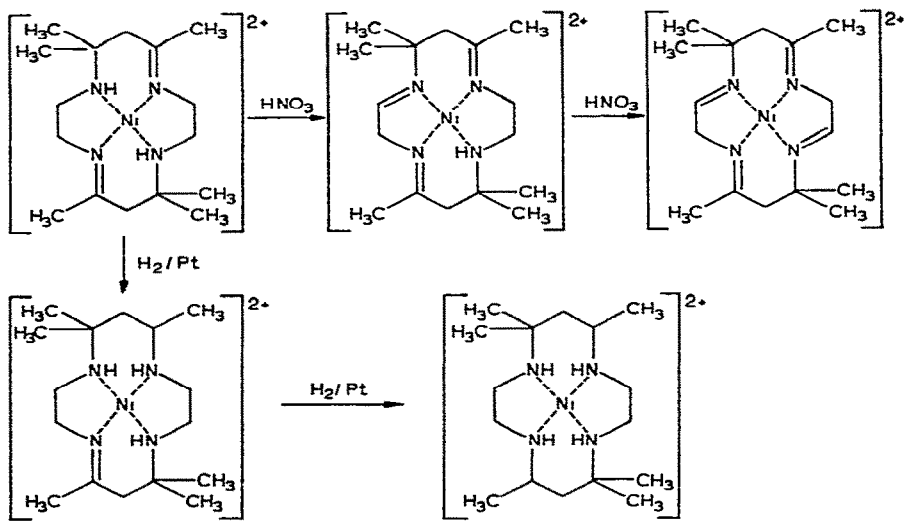
The final macrocyclic product arises from further condensation of this intermediate aminoketone with 1, 2-diaminoethane, followed by metal coordination. Many examples of this and related[140–143] reactions have been investigated and the subject has been reviewed[144] by Curtis.

Metal template reactions which result in the formation of new chelate rings are particularly useful for the preparation of macrocyclic metal complexes. However, it is also possible that the modification of an existing chelate ring could occur, provided that a more stable chelate is produced.

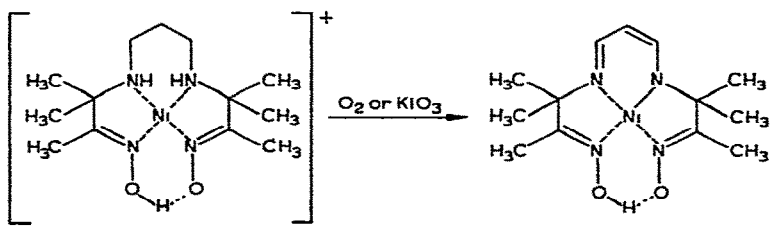
(v) Modification of existing chelate rings

Some aspects of the relationship between the size, shape and stability of chelate rings have been discussed earlier. Chelate rings, like carbocyclic and other heterocyclic rings should be capable of undergoing reactions which involve oxidation, reduction, ring-expansion or contraction. The initial chelate ring must incorporate the necessary functional group or groups to allow such reaction processes to occur. The initial chelate ring must also be sufficiently stable to allow the initial metal complex to form, but it must not be so stable as to be resistant to further reaction.

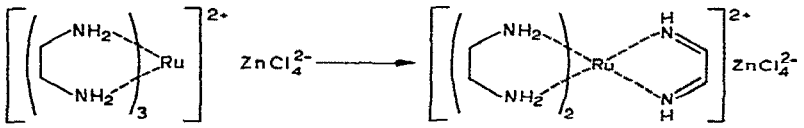
Chelate rings can be modified by both oxidation and reduction to produce complexes of ligands which may be difficult to synthesise in their free, uncoordinated state. Such reaction sequences have been developed by Curtis and lead to a range of macrocyclic complexes[144, 145].



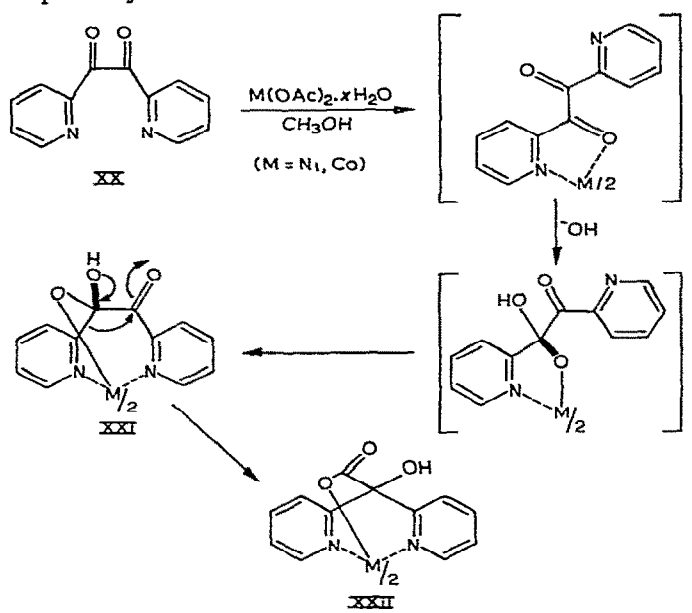
An interesting vinylogous amidine system has been developed[146] as part of a quadridentate chelate by the oxidation of the related tetrahydro compound.



Although substituted α-diimine complexes can be prepared directly, a chelate ring incorporating the parent α-diimine is formed[147] by the oxidation of tris(1, 2-diaminoethane)-ruthenium(II) tetrachlorozincate by air or iodine.



A metal template rearrangement is observed in the metal-promoted conversion[90, 91] of 2, 2′-pyridil, XX, to metal complexes XXII of 2, 2′-pyridilic acid. This is an example of the benzilic acid rearrangement[148], which is a base-catalysed hydration reaction. Some details of the metal-promoted rearrangement have been elucidated. The tridentate chelate XXI has been shown to be an intermediate in the rearrangement and the proposed mechanistic pathway is



The intermediate tridentate chelates XXI are relatively stable and can be isolated at low temperatures, despite the fact that they contain seven-membered chelate rings. However, each seven-membered chelate ring is fused to two six-membered ones and the latter presumably add to the overall stability of the complex. However, molecular rearrangement leads to the significantly more stable chelate XXII, which contains three fused six-membered rings. The exact nature of the rearrangement process is not known, but it is reasonable to suppose that a coordinated pyridyl group undergoes migration and that ligand dissociation is not required for the rearrangement to occur.

E. SELECTED EXAMPLES OF LIGAND TYPES

(i) Bidentate chelating agents

There is only one fundamental way of arranging two donor atoms in a bidentate chelating agent and this can be subdivided into the two patterns* [2.1] and [2.2].

2.1 2.2

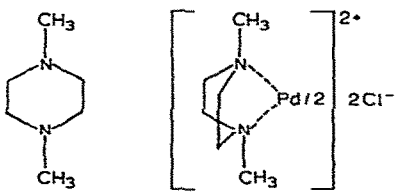
There is a vast array of bidentate chelating agents, mainly because of their simplicity and their ready availability. The metal chelates derived from ligands of pattern [2.1] contain only one chelate ring, whilst those derived from ligands of pattern [2.2] contain two.

A review[24] of bidentate chelating agents has dealt with most examples, from the point of view of the donor atoms, the functional groups and the properties of their metal complexes.

The most important bidentate chelating agents are 1, 2-diaminoethane, 2, 2′-dipyridyl and 1, 10-phenanthroline.

Other common bidentate chelates are those of β-diketones, α-amino acids, α-diimines and imines derived from diamines, salicylaldehyde or pyridine-2-aldehyde. These fragments with two donor atoms are repeated in the structures of the higher multidentate chelating agents, where they will be dealt with in more detail. The ligands in all these metal complexes are of pattern [2.1] and in all cases the two donor atoms occupy adjacent positions in their arrangement around metal ions.

Ligands of pattern [2.2] are quite rare. However, 1, 4-dimethylpiperazine, XXIII, forms[149] bidentate chelates of palladium(II), platinum(II) and iridium(II) in which the ligand is present[150] in a boat conformation, as shown for the complex XXIV.



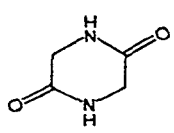
XXIII XXIV

This type of conformation is already built into the less strained 3, 7-diazabicyclo [3:3:1] nonanes, such as XXV, which form[151] stable copper(II) complexes.

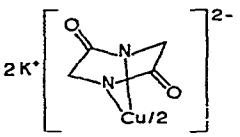
* The numbering system for ligand patterns uses arabic numerals: the first denotes the number of donor atoms present and the second is an identification number. The patterns themselves are topological tree-diagrams of donor atom arrangements.

XXV

It has also been reported[152] that diketopiperazine, XXVI, can act as a bidentate chelating agent by loss of the amide protons and that the ligand displays an "open-book" shape in its anionic complexes (e.g. the copper(II) complex XXVII).



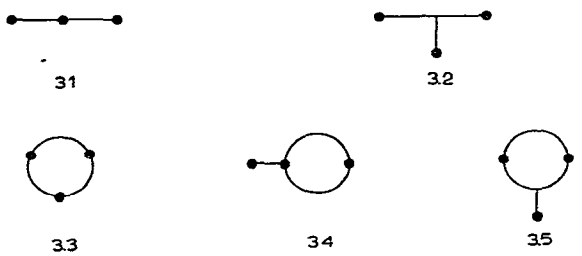
XXVI



XXVII

(ii) Tridentate chelating agents

The donor atoms in tridentate chelating agents can be arranged in linear or branched (bifurcated) patterns as shown.



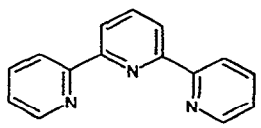
Patterns [3.3] and [3.4] are special examples of the linear pattern [3.1], and pattern [3.5] is a special example of both the linear pattern [3.1] and the branched pattern [3.2].

Goodwin[153] has discussed multidentate chelating agents which contain three or more donor atoms. At that time, only linear tridentate chelating agents of pattern [3.1] were known and these were sub-divided into "planar" and "non-planar" types. A "planar" type is one in which two molecules of the ligand are arranged in equatorial planes at right angles to each other, when coordinated to an octahedral metal ion. Thus the complex has the pictorial configuration XXVIIIa. On the other hand, a "non-planar" type of ligand gives rise to a metal complex with configuration XXVIIIb. These situations have been described earlier with respect to configurations IIa and IIb.

XXVIII a XXVIII b

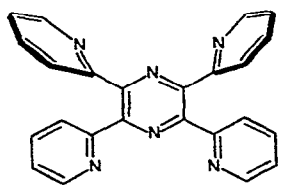
It is clear that linear tridentate chelating agents of pattern [3.1] can give rise to either configuration, depending on a suitable choice of the central donor atom (see Sect. C(ii)). However, five-coordination[5, 154–156] is common in metal complexes containing tridentate chelating agents and a number of distorted configurations are observed. Therefore it is more meaningful to use the terms "planar" and "vicinal", as defined in Sect. C(ii), to describe ligands containing three donor atoms.

2, 6-Bis(α-pyridyl)pyridine (terpyridine), XXIX, is a symmetrical, planar ligand[157, 158] which yields complexes of configuration [3.1].



XXIX

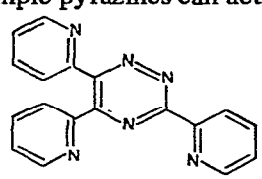
This planarity is a consequence of electron delocalization throughout the three pyridine rings. A similar ligand is 2, 3, 5, 6-tetrakis (α-pyridyl) pyrazine, XXX, which acts only[159] as a tridentate chelating agent, despite the presence of six basic nitrogen atoms.



XXX

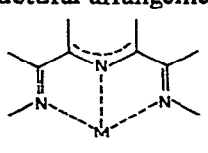
The reason for this is that only two of the four pyridine rings can be coplanar with the pyrazine ring at any one time. Thus, when a tridentate chelate is formed, the two non-coordinated pyridine rings cannot lie in the plane of the pyrazine ring and consequently further chelation cannot occur.

For similar reasons, 3, 5, 6-tri(α-pyridyl)-1, 2, 4-triazine, XXXI, also acts[160] only as a tridentate chelating agent. It has been shown[161], however, that both nitrogen atoms in simple pyrazines can act as donor atoms.



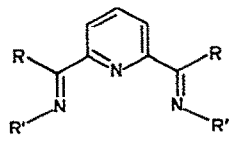
XXXI

On the assumption that the stability of terpyridine complexes is a consequence of the structural arrangement XXXII

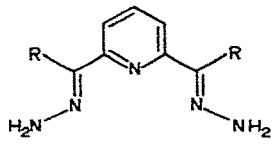


XXXII

a large number of ligands containing this structural fragment has been investigated. The design of these ligands is based on the idea of spatial equivalence of groups (see Sect. C(iii)). The simplest variation is provided by the bis-imines XXXIII[162–165] and bis-hydrazones XXXIV[166] derived from pyridine-2, 6-dialdehyde and 2, 6-diacetylpyridine.

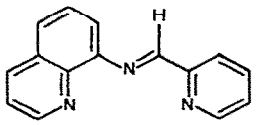


XXXIII



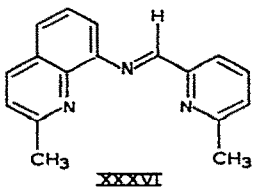
XXXIV

Most other direct analogues of the terpyridine structure are simple imines. For example, 8-(α-pyridylmethyleneamino)-quinoline, XXXV, can be readily prepared[167] by condensation of pyridine-2-aldehyde and 8-aminoquinoline.



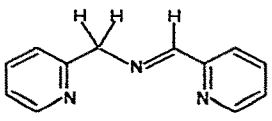
XXXV

The dimethyl analogue XXXVI has also been studied[168].

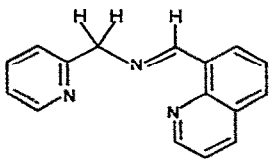


XXXVI

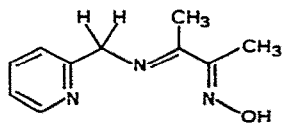
The condensation of 2-aminomethylpyridine with pyridine-2-aldehyde, quinoline-8-aldehyde and the monoxime of diacetyl has yielded respectively the tridentate chelating agents XXXVII[162, 169], XXXVIII[162] and XXXIX[162], viz.



XXXVII



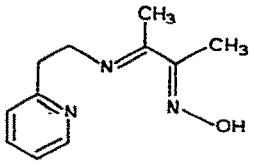
XXXVIII



XXXIX

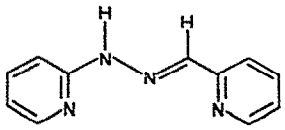
The structural variations of these ligands from terpyridine are of interest. The presence of a methylene group adds flexibility to the ligand structure and also forces a break in the

conjugated system. Also, the ligand XXXVIII forms metal complexes with fused five- and six-membered chelate rings, in contrast to the two five-membered ones in terpyridine metal chelates. The 2-aminoethyl homologue XL[170] of XXXIX acts as a more flexible tridentate chelating agent.



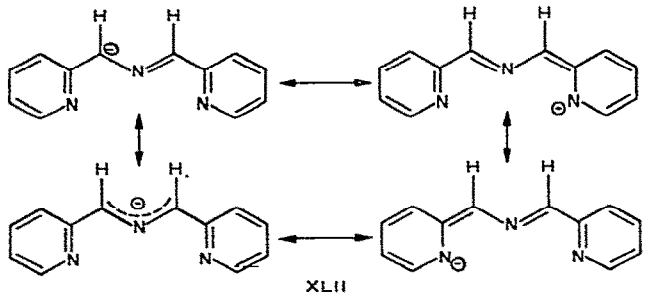
XL

Nitrogen analogues of the above structures can be obtained[171] by replacing 2-aminomethylpyridine with 2-pyridylhydrazine. The most important of these ligands is the pyridylhydrazone XLI of pyridine-2-aldehyde, which forms similar complexes to those of ligand XXXVII.



XLI

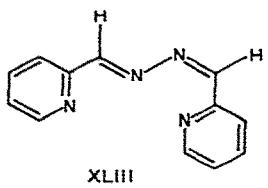
A consideration of the design of these ligands, particularly XXXVII, reveals that a rigid, planar, fully conjugated ligand containing the structural arrangement XXXII could be achieved by deprotonation to give the delocalised anion XLII, viz.



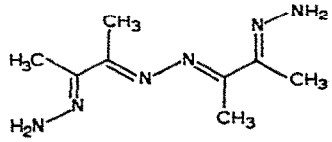
XLII

This idea has been exploited by Lions and his co-workers[172–174], who showed that the highly stable neutral complexes derived from ligands XXXVII and XLI could be prepared directly by deprotonation of ionic complexes.

The formation of the azines XLIII and XLIV can be readily achieved[175, 176] by reaction of hydrazine with pyridine-2-aldehyde and the monohydrazone of diacetyl respectively.



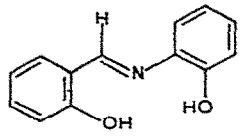
XLIII



XLIV

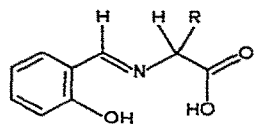
The azine XLIII functions as a tridentate chelating agent with a planar, fully-conjugated structure; it is also capable[177] of coordinating with two metal ions as a bis-bidentate chelate. However, the azine XLIV functions only[176] as a bis-bidentate chelate.

Oxygen donor atoms can be introduced into the terminal positions of planar tridentate chelating agents by the construction of imines derived from *o*-aminophenol and/or salicylaldehyde. Tridentate chelates of salicylideneamino-*o*-hydroxybenzene, XLV, have been studied by Pfeiffer et al.[178].

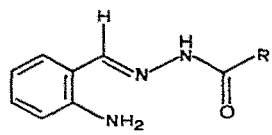


XLV

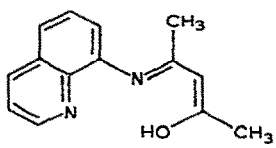
A selection of other related imine ligands, XLVI–XLIX, is shown below; references are given in parentheses after the structure numbers.



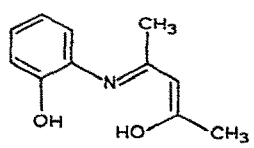
XLVI (179)



XLVII (180,181)



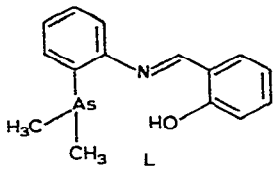
XLVIII (171)



XLIX (182—184)

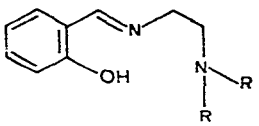
The formation of dimeric chelates from these ligands is possible and has been proven, for example, in the case of the copper(II) complex of ligand XLIX[185, 186]. In this complex there is distortion from a square arrangement of donor atoms about the copper atom, because of the non-planarity of the ligand. The cause of this non-planarity is a steric interaction between the methyl group attached to the imine bond and the *ortho* hydrogen atom of the benzene ring.

The preparation and coordination properties of the ligand L, incorporating an arsenic donor atom, have been reported[187] recently.



L

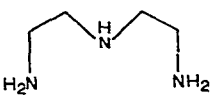
Sacconi et al.[188–190] have studied a series of more flexible salicylaldimine ligands LI. The presence of the central imine linkage is responsible for the preferred equatorial configuration XXVIIIa of the derived metal chelates.



LI

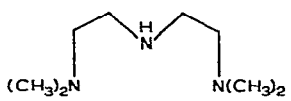
Fully-saturated linear tridentate chelating agents have sufficient flexibility to make vicinal attachment to a metal ion possible. However, the central donor atom is responsible for any preference towards a vicinal or planar arrangement of the ligand (see Sect. C(ii)).

1, 5-Diamino-3-azapentane (diethylene triamine), LII, should be capable[191] of behaving as either a planar or vicinal ligand.

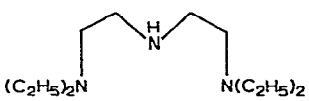


LII

Indeed, the ligand has been found to be planar[192] in a nickel(II) complex and vicinal[193, 194] in some molybdenum(VI) complexes. The derived alkylated ligands LIII and LIV are respectively planar and vicinal in comparable cobalt complexes[195].

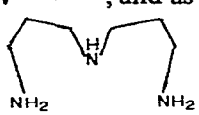


LIII



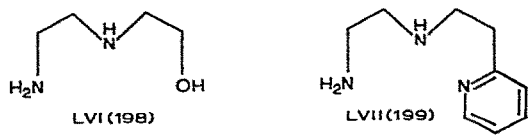
LIV

There is more flexibility in the ligand 1, 7-diamino-4-azaheptane (dipropylenetriamine), LV[196, 197], and as a result, the planar arrangement is preferred[192] to the vicinal one.

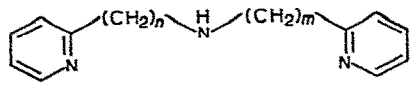


LV

Many other linear tridentate chelating agents contain central nitrogen donor atoms, but their geometrical arrangements are not known. Some further examples LVI–LX are shown below, with references in parentheses.

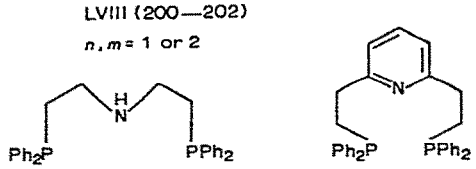


LVI (198) LVII (199)



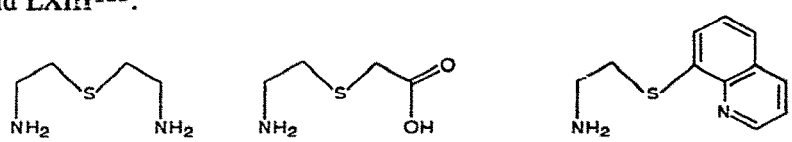
LVIII (200—202)

$n, m = 1$ or 2



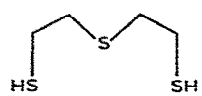
LIX (203) LX (204)

The base 1, 5-diamino-3-thiapentane (β, β'-diamino-diethylsulphide), LXI, could possibly[205] coordinate with a metal ion in either a planar or vicinal arrangement, but the vicinal one should be preferred. The same situation should hold for the ligands LXII[99] and LXIII[123].



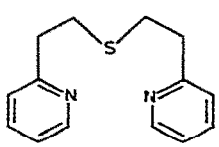
LXI LXII LXIII

The related ligand 3-thiapentane-1, 5-dithiol, LXIV, acts as a planar tridentate chelating agent[36, 206] in some highly strained polymeric nickel(II) and palladium(II) complexes.



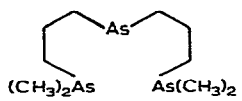
LXIV

There should be some relief of strain associated with planar geometry in the ligand LXV[200] which would form six-membered chelate rings.

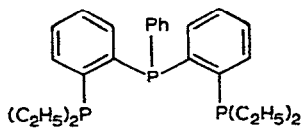


LXV

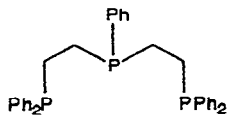
Evidence has been advanced for the planar coordination of the triarsine LXVI[207, 208] and the vicinal coordination of the phosphines[209, 210] LXVII and LXVIII.



LXVI

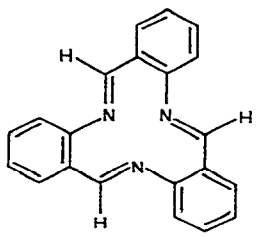


LXVII

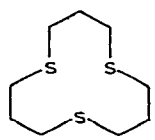


LXVIII

Linear tridentate chelating agents whose donor atoms are arranged in the cyclic pattern [3.3] could theoretically be planar or vicinal. However, the only known[105, 211–214] examples LXIX and LXX[215] of ligands of this type are vicinal (see Sect. D(iv)).

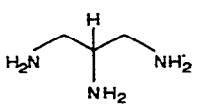


LXIX

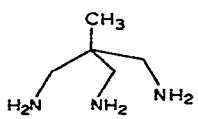


LXX

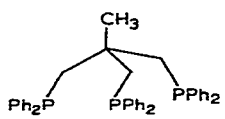
Tridentate chelating agents which contain a bifurcated arrangement of their donor atoms (i.e. pattern [3.2]) are not common. The triamines LXXI[216] and LXXII[217] and the phosphine LXXIII[210] all form tridentate chelates in which the ligands should be vicinal.



LXXI

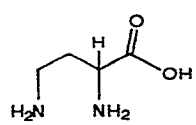


LXXII



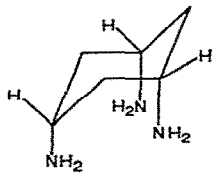
LXXIII

This kind of coordination has been detected[218] in complexes of a variety of substituted aminoacids, e.g. LXXIV.

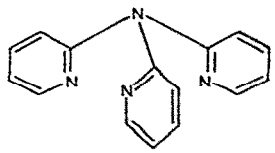


LXXIV

A very good example of a vicinal ligand is provided by *cis, cis*-1, 3, 5-triaminocyclohexane when it coordinates[219, 220] with its three amino groups in axial positions (LXXV).

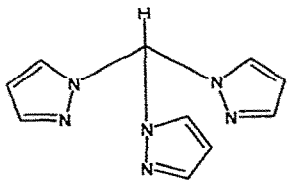


LXXV



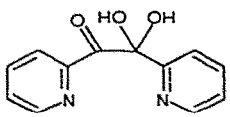
LXXVI

Tri-2-pyridylamine, LXXVI, also acts[221, 222] as a vicinal tridentate chelating agent, as does tri(*N*-pyrazolyl)methane, LXXVII[223]

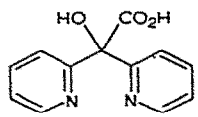


LXXVII

As mentioned earlier (see Sect. D(v)), the metal-promoted rearrangement of 2, 2′-pyridil yields[90, 91] metal complexes containing the vicinal ligands LXXVIII and LXXIX.

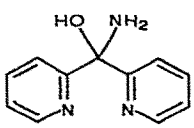


LXXVIII



LXXIX

The free ligand LXXIX undergoes spontaneous decarboxylation, but is stabilized by metal coordination. An important aspect of the formation of the metal complex of LXXVIII is the relief of strain by the addition of a nucleophile to a carbonyl group of 2, 2′-pyridil, to form a tetrahedral carbon atom. A similar phenomenon occurs with metal complexes of di-2-pyridyl ketone[224, 225] and various nucleophiles (e.g. ammonia) readily add[226] to the carbonyl group to afford complexes of vicinal ligands, e.g. LXXX.

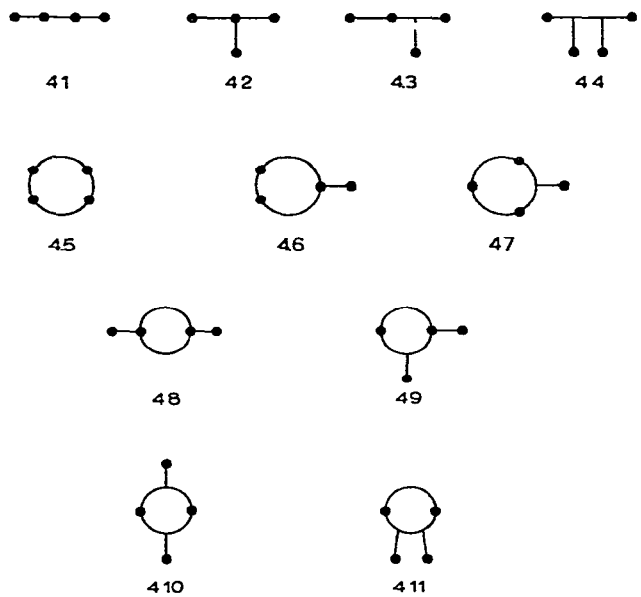


LXXX

Ligands with donor atom patterns [3.4] and [3.5] have not been reported.

(iii) Quadridentate chelating agents

The following patterns are possible for the arrangement of donor atoms in quadridentate chelating agents.



Except for pattern [4.10], the cyclic patterns are special cases of the linear pattern [4.1], although pattern [4.6] is also an example of the branched pattern [4.2] and patterns [4.7], [4.9], [4.10] and [4.11] are also examples of the branched pattern [4.3].

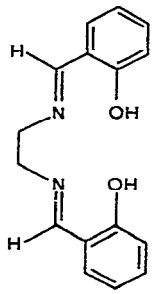
Most of the known quadridentate chelating agents have the linear arrangement of donor atoms depicted by pattern [4.1]. However, these linear ligands can be subdivided into three stereochemical types, which have been defined by Goodwin[153] as follows.

(*a*) Planar ligands are those which are constrained to coordinate with a metal ion in such a way that the donor atoms lie in a plane.

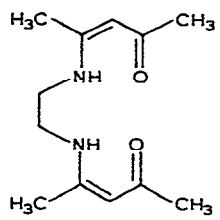
(*b*) Tetrahedral ligands are constructed so that the donor atoms cannot lie in a plane, but may be arranged tetrahedrally about a metal ion.

(*c*) Facultative ligands are flexible so that the donor atoms can coordinate from either a planar or non-planar arrangement.

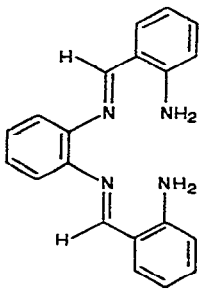
The presence of unsaturation is typical of planar quadridentate chelating agents, and this unsaturation is most commonly provided by imine bonds. Whereas planar tridentate chelating agents are often formed by the condensation of amines with aldehydes, the corresponding planar quadridentate chelating agents can similarly arise from the condensation of two molecules of an aldehyde with a diamine. Some of the best-known examples, LXXXI–LXXXVIII, are shown below, with references given in parentheses.



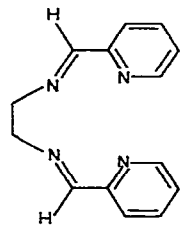
LXXXI (227, 228)



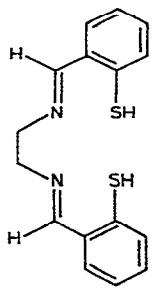
LXXXII (229—231)



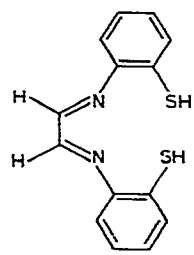
LXXXIII (178, 232)



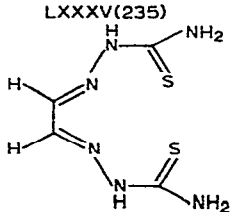
LXXXIV (233, 234)



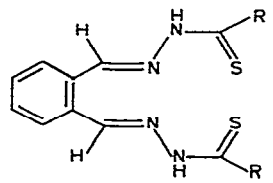
LXXXV (235)



LXXXVI (126, 131—133, 236)



LXXXVII (237—240)



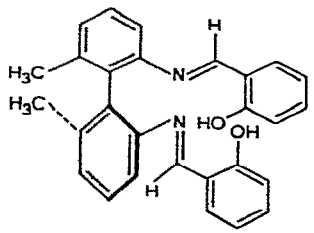
LXXXVIII (241)

In the case of quadridentate chelates[233] of 1, 2-bis-(α-pyridylmethyleneamino)ethane, LXXXIV, some distortion of the bond angles in the chelate rings is necessary. This strain can be relieved either by hydrolysis or reduction of the imine bonds, or by the alternative action[234] of the ligand as a bis-bidentate chelating agent.

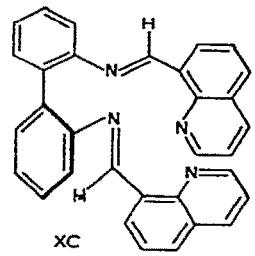
Ligands of the type LXXXVI have been discussed earlier (see Sect. D(iv)).

Ligands of pattern [4.1] can be designed in such a way that they cannot be planar, but fit strainlessly into a tetrahedral arrangement. Lions and co-workers have made use of

the phenomenon of restricted rotation in the hindered diphenyl compounds LXXXIX[242] and XC[233], which function as non-planar quadridentate chelating agents.



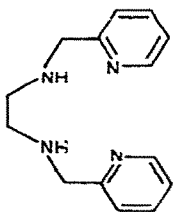
LXXXIX



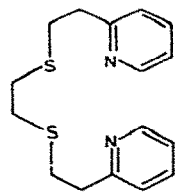
XC

More flexible ligands of the facultative type can be obtained by variation of the structural features of planar ligands. For instance, the extension of the ethano bridges of imines such as LXXXI reduces any strain which might arise from a non-planar arrangement of the ligand in a metal complex. Flexibility can also be introduced easily, by the reduction[243] of imine bonds, as in the preparation[233] of the ligand XCI from LXXXIV.

Another general method for the synthesis of facultative ligands is alkylation, particularly of thiolate anions, as in the preparation of the ligand XCII[233, 244].

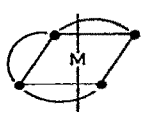


XCI

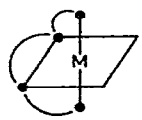


XCII

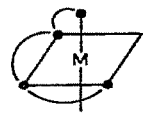
When facultative quadridentate chelating agents are involved in coordination with octahedral metal ions, three configurations (XCIIIa, b and c) are possible.



XCIIIa

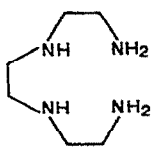


XCIIIb

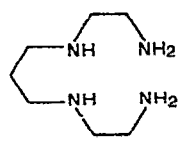


XCIIIc

1, 8-Diamino-3, 6-diazaoctane (triethylene tetramine), XCIV[245, 246], is the simplest facultative ligand with four nitrogen donor atoms and the steric constraints on its complexing behaviour have been discussed in comparison[247] with the more flexible homologue 1, 9-diamino-3, 7-diazanonane, XCV.

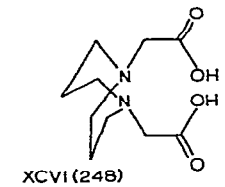


XCIV

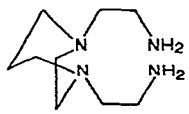


XCV

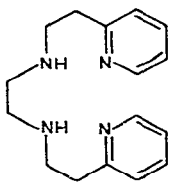
Some related facultative ligands XCVI–XCIX are shown below with references in parentheses.



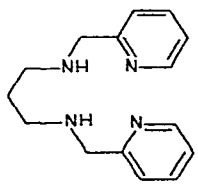
XCVI (248)



XCVII (249)



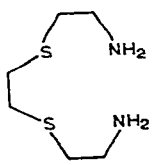
XCVIII (250)



XCIX (251)

The ligands XCVI and XCVII, while essentially linear, are examples of pattern [4.8]. The nickel(II) complex of the ligand XCVI is five-coordinate and an X-ray crystal structure determination shows that the complex has a square-pyramidal configuration in which the sixth coordination site is blocked by a central methylene group of the diazacylooctane ring, as a consequence of the conformational preference of that ring. In contrast, the nickel(II) complex of the ligand XCVII has a square planar configuration.

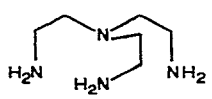
The geometry of metal chelates containing sulphur donor atoms is more predictable (see Sect. C(ii)). It is known that 1, 8-diamino-3, 6-dithiaoctane[252, 253], C, and related ligands[254–256], which contain only ethano bridges, exhibit the non-planar configuration XCIIIb in their complexes.



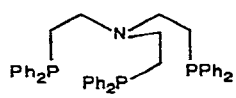
C

However, greater flexibility enables the thioether XCII to behave as a facultative ligand[244].

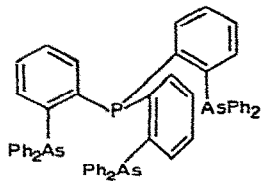
The most common branched quadridentate chelating agents have the pattern [4.2]. In these structures branching occurs at a donor atom and consequently non-planar ligands result. In some cases these function as tetrahedral ligands; in other cases they force a distorted trigonal bipyramidal or octahedral geometry on their complexes. Some examples, CI–CVI, of these "tripod" ligands[257] are shown below, with references in parentheses.



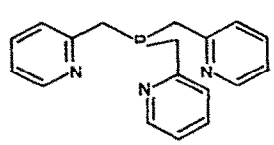
CI (258,259)



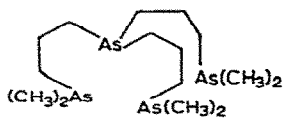
CII (260)



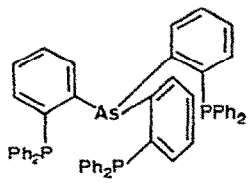
CIII(261,262)



CIV(263)



CV(264)

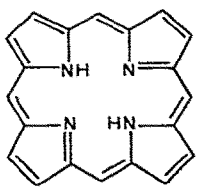


CVI(262)

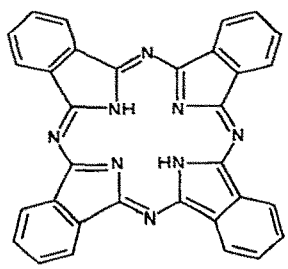
Branched ligands displaying the patterns [4.3] and [4.4] are rare and their synthesis requires systematic study.

Cyclic ligands of pattern [4.5] are very common, but none with patterns [4.6], [4.7], [4.9], [4.10] or [4.11] is known.

The oldest classes of cyclic quadridentate chelating agents are the porphyrins, e.g. CVII, and phthalocyanines, e.g. CVIII, which have been reviewed[94, 265] elsewhere.

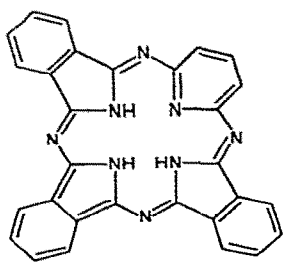


CVII

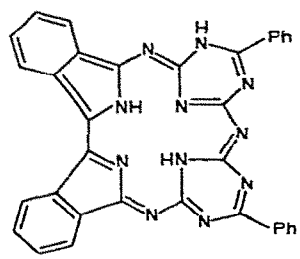


CVIII

The preparation[266, 267] of phthalocyanine analogues, e.g. CIX and CX, is still an active area of research.

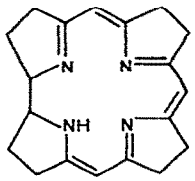


CIX



CX

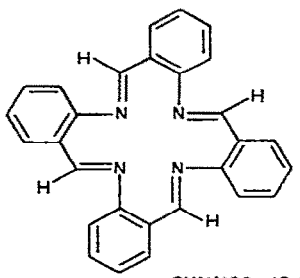
Porphyrin structures are of interest because of their presence in a number of natural products and the corrins, e.g. CXI, have received much attention for the same reason.



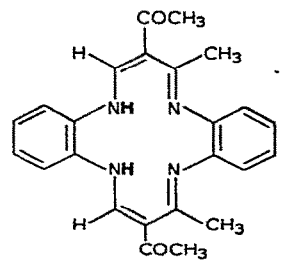
CXI

Many corrin metal complexes have now been synthesised[268] by intricate and ingenious sequences of organic reactions, in which metal template effects are sometimes important.

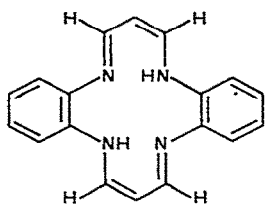
The development of metal template reactions has led to the synthesis of many planar macrocyclic quadridentate chelating agents, some of which have been described in Sect. D(iv). The nature of these reactions usually encourages the formation of macrocyclic ligands with some unsaturation. Some examples (CXII–CXXI) of these are shown below, with references in parentheses.



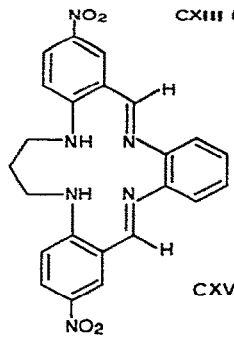
CXII(102–104)



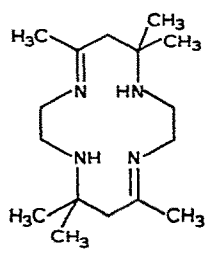
CXIII (116,117)



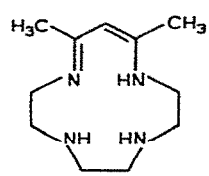
CXIV(269)



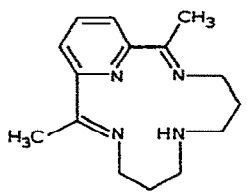
CXV(109)



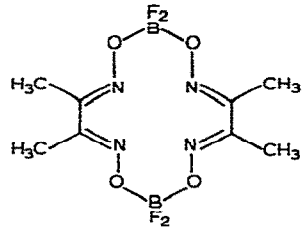
CXVI(144)



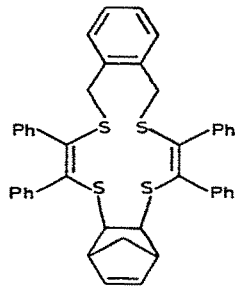
CXVII(270)



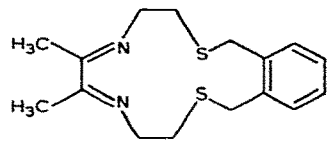
CXVIII(271—274)



CXIX(275,276)

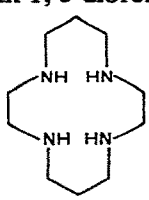


CXX(277)

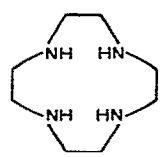


CXXI(98,101)

The macrocyclic rings of planar ligands with four nitrogen donor atoms are ideally fourteen-, fifteen- or sixteen-membered. Some variation occurs with saturated, flexible macrocyclic ligands, which can be obtained by the reduction of unsaturated ligands, or by direct synthesis involving the high dilution technique[278]. The tetramine CXXII was prepared[279, 280] in low yield by the high dilution alkylation of 1, 4, 8, 11-tetraazaundecane with 1, 3-dibromopropane; a similar process yielded[281] the lower homologue CXXIII.

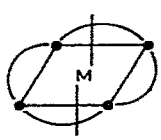


CXXII

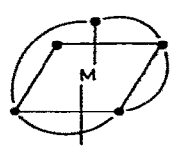


CXXIII

The amine CXXII is flexible or facultative in its coordination behaviour[282] and complexes of both configurations CXXIVa and CXXIVb are formed, although the latter are thermodynamically unstable with respect to the former.



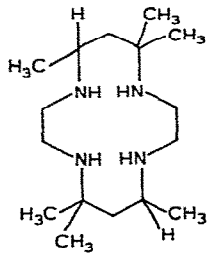
CXXIVa



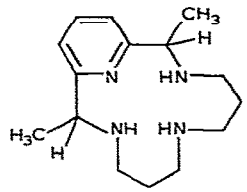
CXXIVb

On the other hand, the ethano bridges of the amine CXXIII make its ring size too small for it to act as a planar ligand and only complexes of configuration CXXIVb have been re-

ported[283, 284]. The two macrocyclic amines CXXV[285] and CXXVI[274] can be prepared by reduction of related unsaturated ligands CXVI and CXVIII respectively. Their behaviour in the formation of metal complexes is facultative[284–288], analogous to that of CXXII.

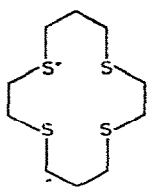


CXXV

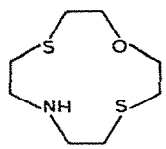


CXXVI

Several similar macrocyclic ligands such as CXXVII[215, 289, 290] and CXXVIII[291] contain sulphur donor atoms, which undoubtedly have a major influence on the configuration of their complexes.



CXXVII

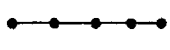


CXXVIII

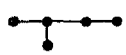
(iv) Quinquedentate chelating agents

Quinquedentate chelating agents have received relatively little study, in view of their wide range of possible structural variation. Lions[50] has attempted to remedy this situation by laying down synthetic guidelines and by suggesting the structural features of numerous potential ligands.

The donor atoms in quinquedentate chelating agents can be arranged in the following patterns; cyclic structures with fewer than three donor atoms in the ring are not considered.



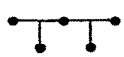
5.1



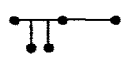
5.2

5.3

5.4

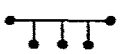


5.5

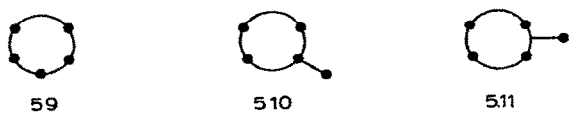


5.6

5.7



5.8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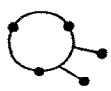
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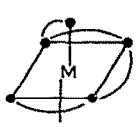
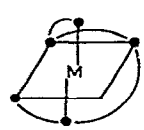
Of all these structural patterns, only four are represented among the ligands known to date: these patterns are [5.1], [5.2], [5.9] and [5.11].

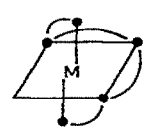
The linear quinquedentate chelating agents (pattern [5.1]) are certainly the most common and four possible configurations, CXXIXa–CXXIXd, are available for their coordination to octahedral metal ions, viz.



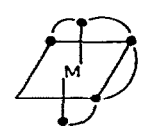
CXXIXa



CXXIXb



CXXIXc



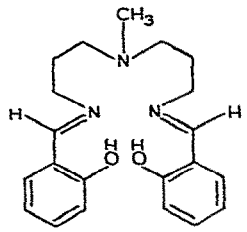
CXXIXd

The main feature of all these configurations is that the ligand arrangement of donor atoms must be non-planar and must accommodate a twist at one or more donor atoms. If only one twist occurs then it must be at the second donor atom of the sequence, as in configuration CXXIXa. If two twists occur, these can be either at the second and third donor atoms as in configuration CXXIXb or at the second and fourth donor atoms, as in configuration CXXIXc. Twist at three donor atoms leads to configuration CXXIXd. In the design of linear quinquedentate chelating agents, a careful selection of donor atoms can offer a preference for one or other of the above configurations. However, the situation is complicated by the occurrence of five-coordinate complexes with trigonal-bipyramidal or square-pyramidal configurations[292, 293].

The condensation[294, 295] of α, ω-diamines with aromatic aldehydes gives quinquedentate chelating agents of the general structure CXXX, where X and Y may be nitrogen, oxygen or sulphur donor atoms.

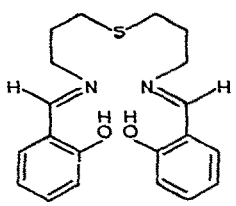
CXXX

Ligands such as CXXXI, prepared by Sacconi and Bertini[292], form five-coordinate complexes with structures intermediate between square-pyramidal and trigonal-bipyramidal geometry.



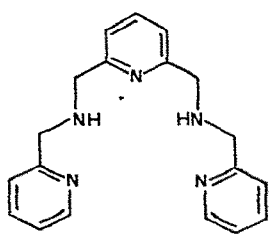
CXXXI

Similar ligands[293] such as CXXXII, with central sulphur donor atoms also form five-coordinate metal complexes.

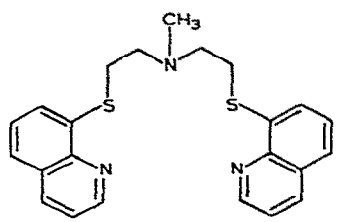


CXXXII

Fully-saturated ligands such as CXXXIII and CXXXIV offer more flexibility and generally form six-coordinate metal complexes[296–300].



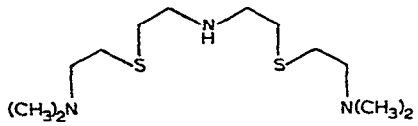
CXXXIII



CXXXIV

Because of the large bulk of the quinoline ring the metal complexes formed[300] by the ligand CXXXIV would be likely to have the configuration CXXIXc, in which there would be no crowding of the sixth coordination position. Such crowding was postulated[300] for

the complexes of the related ligand 1, 11-bis(dimethylamino)-3, 9-dithia-6-azaundecane, CXXXV, and five-coordination is a possible consequence.

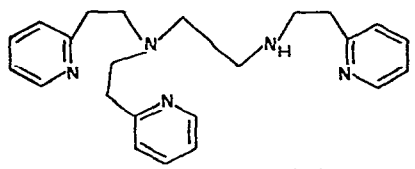


CXXXV

Several branched quinquedentate chelating agents with the donor atom pattern [5.2] have been investigated. These are all based on the EDTA structure, with one donor atom omitted. EDTA itself[301–303] acts as a quinquedentate chelating agent in some of its complexes, and the triacetic acid CXXXVI[304] functions in a similar way[305].

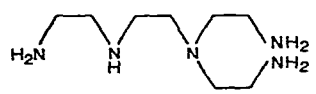
CXXXVI

Two similar ligands[306, 307] which contain five nitrogen donor atoms also form quinquedentate chelates. One of these ligands, the tripyridyl compound CXXXVII forms a nickel(II) complex[308] with a distorted square-pyramidal configuration.



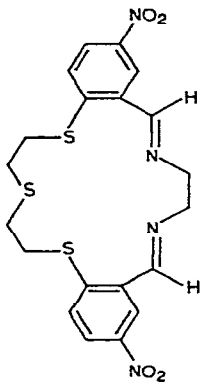
CXXXVII

The other ligand, 4-(2-aminoethyl)-1, 4, 7, 10-tetraazadecane, CXXXVIII[306], forms an octahedral cobalt(III) complex.

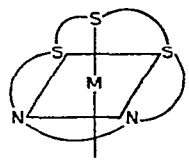


CXXXVIII

Ligands with the cyclic donor atom pattern [5.9] would be expected to take up an octahedral configuration if possible in their metal complexes. One example of such a ligand is the thioether CXXXIX, whose iron(II) complex was formed[110] by a metal template condensation. Evidence suggests that the complex has the configuration CXL.

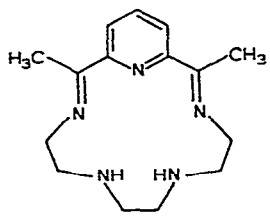


CXXXIX



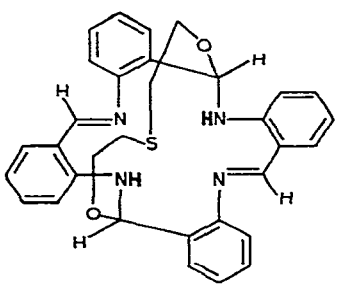
CXL

However, the cyclic imine CXLI[309] has been shown to act as a planar quinquedentate chelating agent in the formation of a seven-coordinate iron(III) complex[310].



CXLI

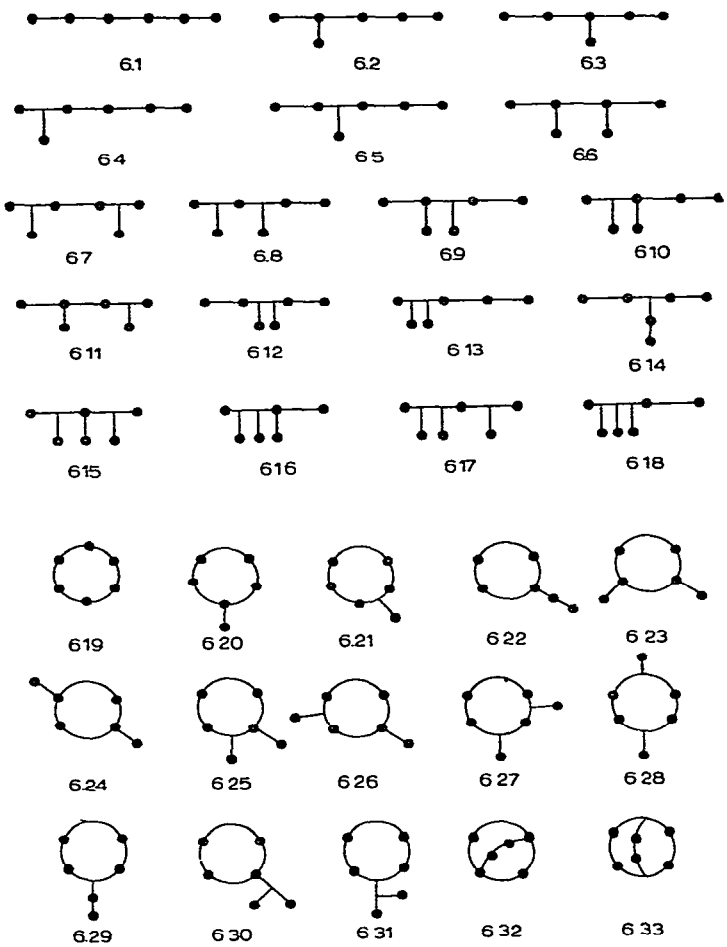
The ligand present[29] in the quinquedentate chelate vitamin B_{12} is representative of the branched cyclic pattern [5.11]. The only synthetic examples are those[89] such as CXLII, which were discussed in Sect. D(iv).



CXLII

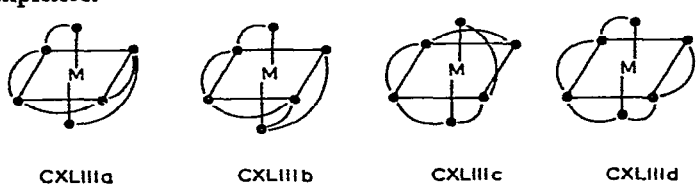
(v) Sexadentate chelating agents

There are many possible donor atom patterns available for sexadentate chelating agents. Some are shown below, but the list excludes those cyclic structures with fewer than four donor atoms in the ring.

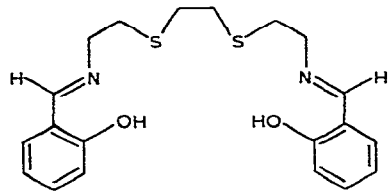


Many more patterns with three donor atoms in the ring are possible, but no corresponding compounds are known. Bicyclic patterns are also possible and sexadentate chelating agents with the donor atom pattern [6.33] are known. This pattern is a special case of the pattern [6.14].

The principles for the construction of sexadentate chelating agents have been discussed by Lions[10], and are the same as those mentioned earlier for the lower multidentate chelating agents. Many linear ligands of donor atom pattern [6.1] have been studied. Such ligands may adopt any of four configurations CXLIIIa–d in the formation of octahedral complexes.



The bis-imine, 1, 8-bis-(salicylidenamino)-3, 6-dithiaoctane, CXLIV[252], is typical of linear sexadentate chelating agents and was the first known example.



CXLIV

This ligand can only form metal complexes[311, 312] of configuration CXLIIIc because each set of O, N and S donor atoms must be coplanar. Many related ligands have since been studied and their structures incorporate variation in the donor atoms and the bridges between them. The sulphur donor atoms can be replaced by nitrogen[313] or oxygen[314], the *o*-hydroxyphenyl fragment can be replaced by the α-pyridyl group[37, 315] and the ethano bridges can be replaced by propano or longer bridges[37, 311, 312, 316, 317] or by benzene rings[37, 38].

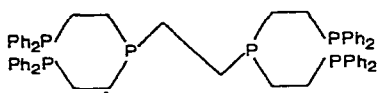
The iron(II) complex[123] of the α-diimine XV (see Sect. D(iv)) must have the configuration CXLIIIa in which the four central donor atoms are coplanar.

The most important sexadentate chelating agent is undoubtedly EDTA (CXLV)[318], which exhibits the branched pattern [6.6] in the arrangement of its donor atoms.

CXLV

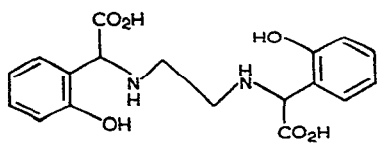
Metal chelates of EDTA and related ligands have been studied in great detail and the area has been thoroughly reviewed[319]. Analogous ligands (CXLVI and CXLVII) with six nitrogen[320] or phosphorus[67] donor atoms have also been studied.

CXLVI



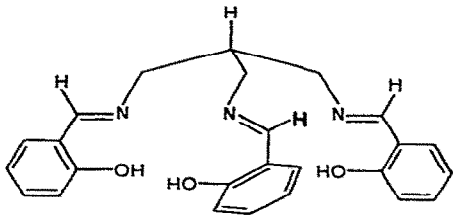
CXLVII

The donor atoms of the ligand CXLVIII[321] are arranged in the branched pattern [6.7], in which the branching occurs at non-donor atoms.

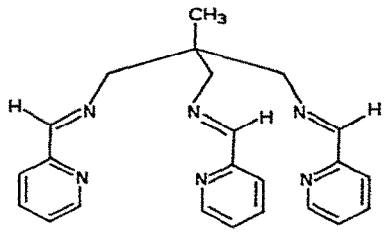


CXLVIII

The pattern [6.14] is now a relatively common one for sexadentate chelating agents, most of which are derived from tridentate chelating agents with a similar branched pattern [3.2] (see Sect. E(ii)). The tris(salicylidene) derivative CXLIX[315] of 2-aminomethyl-1, 3-diaminopropane and the tris(α-pyridylmethylene) derivative CL[322] of 2-aminomethyl-1, 3-diamino-2-methylpropane form sexadentate chelates. Distorted trigonal prismatic coordination has been established for the nickel(II) and zinc(II) complexes of the latter ligand, CL.

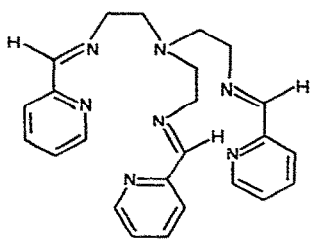


CXLIX



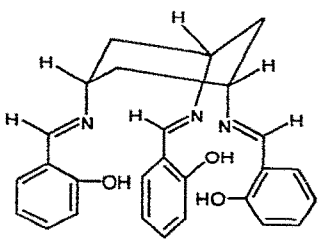
CL

However, the nickel(II) complex of the more flexible ligand CLI is octahedral[323]; the ligand acts as a sexadentate chelating agent but the lone pair of electrons on the central tertiary amino nitrogen atom is directed towards the nickel atom from a distance of 3.25 Å.



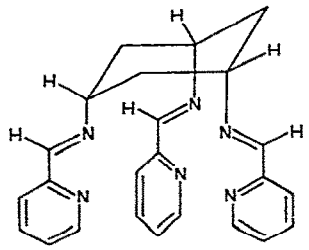
CLI

A similar donor atom pattern is exhibited by the tris(salicylidene) derivative CLII of 1,3,5-triaminocyclohexane[324], which was assumed to form octahedral metal complexes.



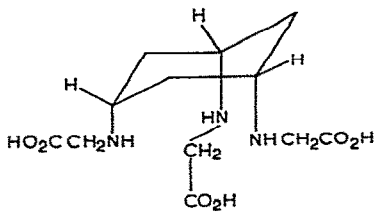
CLII

The corresponding tris(pyridine-2-aldimine) derivative CLIII[324–326] forms a trigonal prismatic zinc(II) complex[325], but its nickel(II) complex shows distorted trigonal prismatic geometry[327].



CLIII

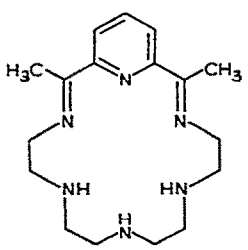
The related tris(amino acid) compound CLIV has recently been shown[328] to act as a sexadentate chelating agent.



CLIV

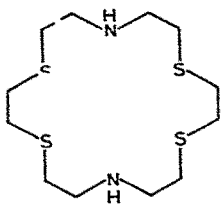
During the past few years, various series of macrocyclic sexadentate chelating agents have been synthesised and their metal chelates studied. These ligands have the donor atom patterns [6.19] and [6.33], which are special cases of the linear and branched patterns [6.1] and [6.7] respectively.

The first cyclic ligand with six donor atoms was the bis-imine CLV[329] which yielded an iron(III) complex: however, the geometry of this complex is in doubt and almost certainly octahedral six-coordination does not occur.

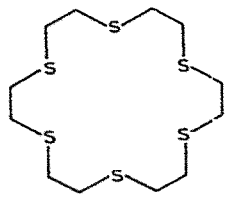


CLV

Octahedral coordination does occur in the case of nickel(II) and cobalt(II) complexes[291, 330, 331] of the macrocyclic thioethers CLVI and CLVII. The ligands themselves were prepared by alkylation reactions carried out under high dilution conditions.

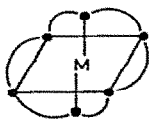


CLVI

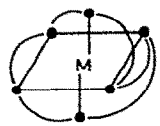


CLVII

Complexes of the ligand CLVII would be expected to have the configuration CLVIIIa, whereas both configurations CLVIIIa and CLVIIIb should be possible for complexes of the amine CLVI.



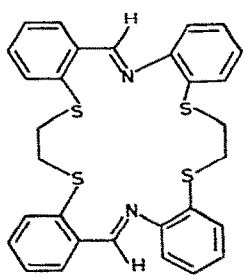
CLVIIIa



CLVIIIb

A macrocyclic ether[291, 331], similar to the amine CLVI but with the two NH groups replaced by O atoms, does not form stable metal complexes. If it were to coordinate octahedrally with a metal ion, the resulting complex would be expected to have the configuration CLVIIIb. It may be that this configuration is inherently less stable than the other and therefore the complexes of the amine CLVI could have the configuration CLVIIIa.

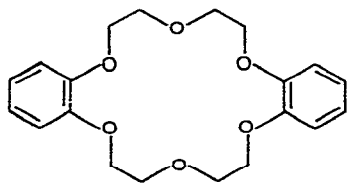
A similar macrocyclic diimine ligand CLIX[111, 332] with a twenty-membered ring would be forced to form metal complexes with the configuration CLVIIIb and it is probable that the increased ring size would reduce the strain involved in accommodating this arrangement of the ligand about the metal ion.



CLIX

Metal complexes of the diimine CLIX and a variety of related ligands[112, 113] have been prepared by metal template reactions (see Sect. D(iv)).

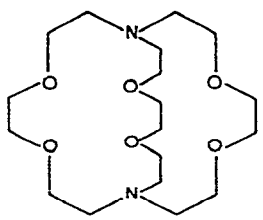
There is considerable current interest in macrocyclic polyethers[333, 334] such as CLX because of their ability to form salts[334–336] with alkali metal ions and consequently improve their solubility[337] in solvents like ether and tetrahydrofuran.



CLX

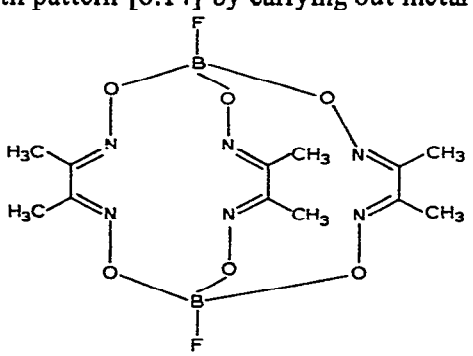
The effects of these ligands are relevant[338, 339] to the mechanism of transport of alkali metal ions through cell membranes. Although the polyether CLX does form[340] a cobalt-(II) complex, it behaves as a bis-tridentate and not a sexadentate chelating agent.

Sulphur[341] and nitrogen[342] analogues of the polyethers have been studied with respect to their ability to form alkali metal salts. The amine analogues lead with further alkylation to macrobicyclic structures[342–344] such as CLXI, known as "cryptates".

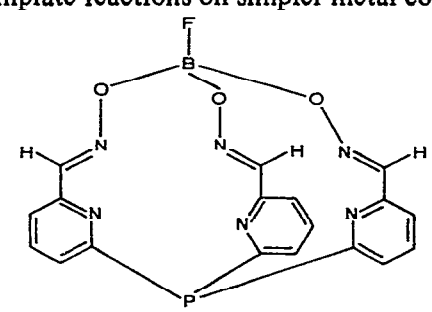


CLXI

Macrobicyclic ligands which are rather similar in structure to the cryptates, but with more specific coordination sites, occur in several sexadentate chelates. These ligands, CLXII[345] and CLXIII[346, 347], have the donor atom pattern [6.33] and are derived from the types with pattern [6.14] by carrying out metal template reactions on simpler metal complexes.



CLXII

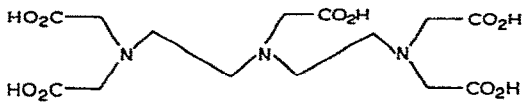


CLXIII

Trigonal-prismatic configurations have been established for the cobalt(II) complex[348] of ligand CLXII and for the nickel(II) complex[347] of the ligand CLXIII. Although the cobalt(II) and zinc(II) complexes of CLXIII are isomorphous with the nickel(II) complex, the geometry of the iron(II) complex[349] is that of a distorted trigonal prism. The cobalt-(III) complex[348] of the ligand CLXII has a configuration midway between octahedral and trigonal-prismatic.

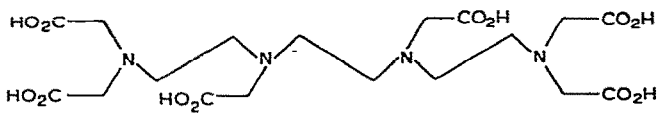
(vi) Higher multidentate chelating agents

Most systematic studies towards higher multidentate chelating agents have been based on amino acids of the EDTA type and have been carried out by Martell and his co-workers[350–356]. Solution studies indicate that the ligand CLXIV[357] acts as an octadentate chelating agent in the formation of complexes with zirconium(IV)[351] and thorium-(IV)[350].



CLXIV

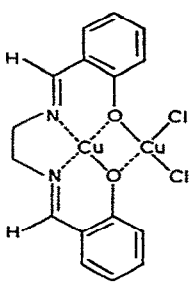
Fried and Martell[355] proposed that triethylenetetraminehexaacetic acid, CLXV, acts as a decadentate chelating agent in the formation of a thorium(IV) complex.



CLXV

(vii) Chelating agents which bind to two metal ions

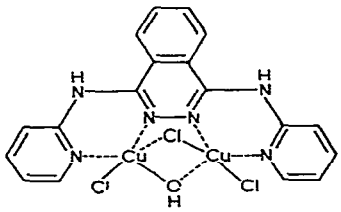
This area of coordination chemistry has become very large in recent years and has been reviewed in detail by Sinn and Harris[26]. Characteristically, four-membered chelate rings are formed in such binuclear metal complexes as the copper(II) complex CLXVI.



CLXVI

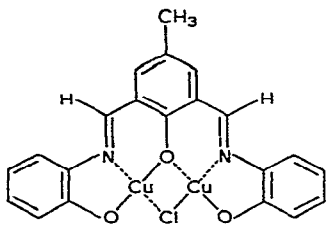
Most of the ligands which give rise to these binuclear complexes are capable of acting in other ways and generally have not been specifically designed to chelate with two metal ions. Only those recent examples of specifically designed ligands are relevant to the brief discussion here as they clearly demonstrate the value of careful ligand design.

1, 4-Di(2′-pyridyl)aminophthalazine forms binuclear copper(II) complexes[358] such as CXLVII, which contains five-coordinate copper(II) atoms in square-pyramidal configurations.

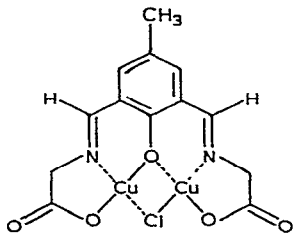


CXLVII

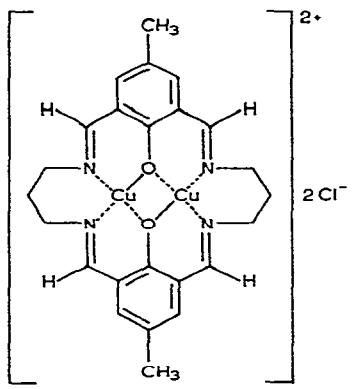
The binuclear complexes CLXVIII[359], CLXIX[360] and CLXX[361] were all derived from a phenolic dialdehyde by metal template reactions.



CLXVIII

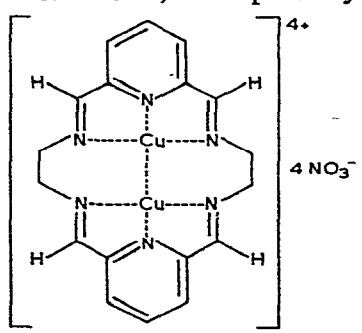


CLXIX



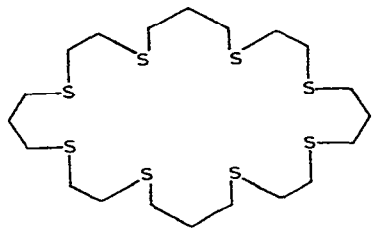
CLXX

A different type of design is illustrated by the macrocyclic binuclear copper(II) complex CLXXI[362], which probably contains a copper–copper bond.



CLXXI

The macrocyclic octathioether CLXXII has been found[363] to encompass two nickel(II) ions, but in this case there is no suggestion of a nickel–nickel bond.



CLXXII

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