Coordination Chemistry Reviews, 106 (1990) 227–265
Elsevier Science Publishers B.V., Amsterdam

AROMATIC NITROGEN HETEROCYCLES AS BRIDGING LIGANDS; A SURVEY

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(Received 6 March 1990)

CONTENTS

A. INTRODUCTION: PURPOSE AND SCOPE OF THE SURVEY

Aromatic nitrogen heterocycles represent an important class of ligands in coordination chemistry [1]. Monodentate ligands, such as pyridine, and chelating ligands, such as 2,2′-bipyridine, readily form stable complexes with most transition metal ions and have long been extensively used in both analytical and preparative coordination chemistry. Six-membered aromatic nitrogen heterocycles (azines) have relatively low energy π^* orbitals which act as good acceptors of metal *d*-orbital electron density in metal–ligand backbonding. In contrast, the π-excessive five-membered aromatic nitrogen heterocycles (azoles) are good π-donors and can also exist as anionic ligands by deprotonation of acidic N–H groups in the free ligand. Thus metal–ligand interactions are governed by the specific metal and ligand involved and many such ligands are available [1,2].

Binuclear and multinuclear transition metal complexes comprising two or more metal centres bridged by multidentate ligands have been the subject of an enormous amount of work, particularly in recent years. Such complexes

0010-8545/90/$13.65

can exhibit metal–metal interactions, such as energy or electron transfer, magnetic coupling and intervalence transfer [3]. These interactions are mediated by the bridging ligand, and where this is a multidentate aromatic nitrogen heterocycle, communication between the metal centres generally takes place via the π system of the ligand. It is possible to control the extent of such interactions by varying the metal–metal distance, the extent of conjugation between the coordination sites and the charge and π-donor/acceptor properties of the ligand used to bridge the metals. The study of such complexes has been important in developing our understanding of the theory of electron transfer processes, of mixed-valence compounds and of magnetic coupling interactions. Such compounds are also used to model important bio-inorganic systems such as some metalloproteins and are finding applications as photosensitizers, catalysts and in low dimensional conducting coordination polymers.

The present report surveys the available ligands, L, which are capable of forming $M(\mu\text{-}L)M'$ complexes wherein both M and M′ are coordinated to nitrogen atoms contained in a five- or six-membered aromatic nitrogen heterocycle. Such bimetallic complexes may be homonuclear ($M = M'$) or heteronuclear ($M \neq M'$). The survey is restricted to ligands wherein all donors are heteroaromatic nitrogen atoms and therefore excludes many excellent bridging ligands, including many macrocyclic ligands, that comprise nitrogen heterocycles with pendent coordination groups such as amine or imine [1]. Other bridging ligands containing coordinating oxygen, sulphur or phosphorus are similarly excluded. Aromatic macrocycles such as porphyrins and phthalocyanins are also excluded, although it should be noted that covalently linked bis and oligo porphyrins are well known [4] and that covalently linked binuclear, trinuclear and tetranuclear phthalocyanines have recently been prepared [5–7]. Also excluded are polymers containing nitrogen heterocycles which can act as polynucleating ligands and function as ion exchange resins [8–10]. Ligands containing saturated (non-aromatic) heterocycles are also not considered. The ligands are classified according to the number of donor nitrogen atoms at each metal site (non-chelating, bidentate, tridentate, mixed) with further subdivisions according to the types of heterocycle involved. The present survey concentrates on recent work, with coverage until the end of 1989, and it is hoped that it will make workers in this area aware of a wider range of available ligands and aid them in selecting appropriate ligands for their specific requirements.

B. NON-CHELATING LIGANDS

(i) Azines

Figure 1 shows the ligands discussed in this section. Of the three diazines **1–3**, pyridazine (**1**) has been least frequently employed as a bridging ligand.

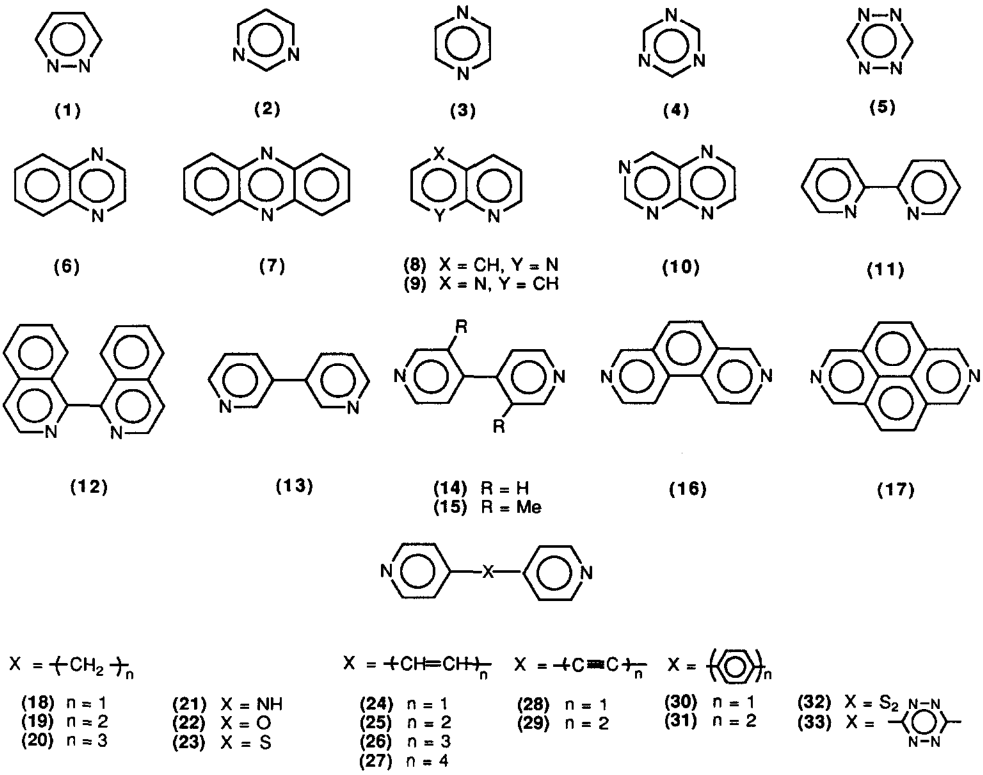


Fig. 1. Bridging azines.

Like the more well-studied pyrazolate anion discussed below, pyridazine is a relatively versatile ligand in that it is able to bridge a wide range of intermetallic separations through its two adjacent nitrogen donors. For example, the X-ray structure of the polymeric complex of **1** with CuCN shows the pyridazine-bridged copper atoms to be separated by 3.68 Å [11]. More recent structures of complexes containing pyridazine bridging two rhodium(III) centres [12] and two copper(I) atoms held within a macrocycle [13] showed intermetallic separations of 3.397 Å and 3.150 Å respectively. Shorter separations exist in complexes in which **1** bridges across metal–metal bonds, as in the structures of pyridazine-bridged iron [14] and ruthenium [15–17] carbonyl clusters (Fe···Fe, 2.573 Å; Ru···Ru, 2.743 Å).

Binuclear complexes of pyrimidine (**2**) are also not common, although many reported polymeric complexes of **2** undoubtedly involve bridging by the ligand [18–20]. Several mixed-valence diruthenium complexes have been studied in some detail [21,22] and a diplatinum complex has recently been studied in solution [23]. Pyrimidine is a poorer π-acceptor than the other two diazines but is still better than pyridine [24], in line with the relative energies of the LUMO π^* orbitals [25]. π-mediated metal–metal interactions are also weaker in pyrimidine than in pyrazine-bridged complexes [22] despite the fact that the metals are closer in space in binuclear complexes of **2** (about 6.0 Å [21,26]) than in complexes of **3** (about 6.9 Å [27]). Although pyrimidine itself has not been extensively studied as a ligand, the coordination chemistry of substituted derivatives has been the subject of much work because of the biological importance of the pyrimidine nucleosides [28,29].

In contrast with the relatively uncommon use of **1** and **2** as binucleating ligands, the literature contains an enormous number of reports of complexes incorporating metal centres bridged by pyrazine (**3**). Many homobimetallic and heterobimetallic binuclear complexes as well as oligomeric and polymeric species incorporating pyrazine bridges, far too numerous to catalogue here, have been reported. An excellent review of all aspects of the chemistry of pyrazine has been published [30]. Pyrazine has relatively low energy π^* orbitals [25,31] and hence is an excellent π-acceptor of metal *d*-orbital electron density. This in turn facilitates electron or energy transfer between metals bridged by **3**, and this has been the basis of most of the work on pyrazine-bridged complexes. The most well-studied such complex is the mixed-valence Creutz–Taube complex, $[(NH_3)_5Ru(\mathbf{3})Ru(NH_3)_5]^{5+}$, which over the last two decades has been the subject of much study and controversy, principally centred on whether this ion exists as a symmetrical (valence delocalized) or unsymmetrical (valence localized) species [27,32–38]. The study of inner-sphere electron transfer between two different metals bridged by pyrazine has also been the subject of much study [30,39]. Accordingly, many heterobimetallic pyrazine-bridged complexes have been prepared [40–43]. Magnetic interactions between two paramagnetic ions bridged by pyrazine can result in ferromagnetic or antiferromagnetic coupling and this has also been the subject of much study [18,44–46]. All the above processes involve interactions between the two metals by way of the pyrazine π-system.

Polymeric structures incorporating bridging pyrazines have long been known [47] and various one-, two- or three-dimensional arrays exist in structures with pyrazine bridges [30,48]. Some interesting pyrazine-bridged linear oligomers have also been studied [49]. Many X-ray structures of pyrazine-bridged complexes [50–68], including the Creutz–Taube complex [50,51], have been described. Several substituted pyrazines have also been used as bridging ligands [69] and several of the ligands discussed later in this section have been studied for comparison of the properties of their complexes with that of the corresponding complexes of **3**.

The coordination chemistry of the higher azabenzenes (triazines, tetrazines etc.) as bridging ligands is relatively unexplored. A recent study [23] of the $PtCl_2(PEt_3)$ complexes of 1,3,5-triazine (**4**) revealed that coordination at one nitrogen atom does not significantly affect the donor capacity of the other nitrogen atoms. The complexes were, however, more labile than the corresponding pyrimidine complexes. The X-ray structure of a triplatinum(II) complex of **4** was also described [23]. Although the ligand itself is unstable, *s*-tetrazine (**5**) has been used to bridge phthalocyaninato ruthenium(II) and phthalocyaninato iron(II) complexes [70]. Indeed, several of the ligands described in this section have been used for this purpose [71].

Of the diazanaphthalenes, quinoxaline (**6**) has frequently been employed as a bridging ligand in both homobimetallic and heterobimetallic complexes [30]. In general it behaves in a similar manner to pyrazine to which it is structurally related. The X-ray structures of polymeric copper [72] and silver [73] complexes containing bridging quinoxalines have been reported. The dibenzo analogue phenazine (**7**) has also been used to bridge homobinuclear complexes of rhodium [74,75], iridium [75] and platinum [76]. The crystal structure of a linear polymeric chain rhodium(II) complex of **7** has also been reported [77]. Of the six naphthyridines the 1,8 isomer **8** is the most well studied. This ligand can act as a monodentate or chelating ligand in addition to acting in a binucleating mode. X-ray structures have been reported for complexes in which 1,8-naphthyridine (**8**) bridges two copper [78], nickel [79], silver [73], rhodium [80] and ruthenium [81] atoms. A complex in which 1,5-naphthyridine (**9**) bridges two tungsten pentacarbonyl groups has recently been reported [82]. The same paper described binuclear complexes of pteridine (**10**) and NMR studies revealed the fluxional behaviour shown in Fig. 2 in which competition between coordination to the more basic pyrimidine nitrogen of **10** and the better π-backdonating pyrazine nitrogen slightly favours the latter [82].

Only the symmetrical isomers of the six bipyridines have been employed as binucleating ligands. Although 2,2′-bipyridine (**11**) has been extensively used as a chelating ligand for over a century [83], there have also been occasional reports of 2,2′-bipyridines acting in a non-chelating bridging mode. However, no such complexes had been structurally characterized until a recent report [84] described the X-ray structure of a diplatinum

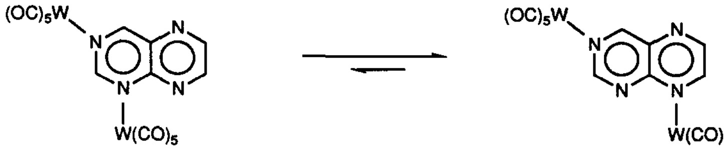


Fig. 2. Fluxional pteridine ditungsten complex.

complex containing a bridging **11**, in which the two pyridine rings are mutually inclined at an angle of 42°. Binuclear chromium pentacarbonyl complexes with 4,4′-dimethyl-2,2′-bipyridine bridges have also been recently reported [85] and an X-ray structure determined [86]. In this case the two pyridine rings were found to be approximately orthogonal. In a similar manner, 1,1-biisoquinoline (**12**), which for steric reasons is unable to attain the planar conformation required for bidentate chelation, has been shown to bridge two palladium atoms [87]. In such a complex the two isoquinoline rings are approximately orthogonal, which renders the complex chiral. Resolution (of the ligand) was achieved as a result of high chiral recognition on reaction with a homochiral palladium complex [87]. 3,3′-Bipyridine (**13**) has been used as a bridging ligand in diindium [88], diruthenium [89] and heterobimetallic Ru–Co complexes [89]. The intermetallic separation in complexes of **13** will be dependent on the specific conformation of the ligand and can vary between about 7.5 Å (for a syn-coplanar conformation) and about 9.8 Å (for an anti-coplanar conformation).

In contrast with the other bipyridines, 4,4′-bipyridine (**14**) has been extensively employed as a bridging ligand. The majority of this work is an extension of the studies described above of pyrazine-bridged complexes. Replacement of a bridging pyrazine by 4,4′-bipyridine increases the metal–metal separation from about 6.9 Å to about 11.2 Å. Since the metal–metal interactions discussed above occur through the π system of the ligand, an important feature of the binuclear complexes of **14** is the coplanarity or otherwise of the two pyridine rings, since in order for the metals to interact there must be some overlap of the two separate pyridine π systems. X-ray crystal structures have shown that in its complexes, **14** can be either planar [90–93] or non-planar [94,95]. By changing substituents on the ligand it is possible to control the relative orientations of the two rings and hence the interactions between coordinated metals. For example, in binuclear complexes of 3,3′-dimethyl-4,4′-bipyridine (**15**) the methyl substituents impose steric interactions which prevent the two pyridine rings from being coplanar [95–97]. In contrast, coplanarity can be imposed on the two pyridine rings by ring fusion as is the case in the benzo-fused ligands 3,8-phenanthroline (**16**) and 2,7-diazapyrene (**17**) [27,97].

Many other ligands have been studied which contain two 4-pyridyl groups joined to a common linking group. In binuclear complexes of the bipyridylmethane **18** the two metal centres are closer (about 10.5 Å) than in complexes of **14** but intermetallic interactions, such as electron transfer, are reduced since there is no longer conjugation between the two pyridine rings [39,89]. For the dipyridylethane **19** and dipyridylpropane **20** there is no conjugation between the pyridine rings and through-ligand interactions are weak. Nevertheless, electron transfer between metals in complexes of **19** is often facile [39,98], particularly when the two halves of the molecule have high and opposite charges. This has been attributed to the complex existing in a conformation having a ‘closed’ structure which facilitates direct electron transfer between the metals [39].

When the two pyridine rings are separated by heteroatoms as in the ligands **21**–**23**, interactions between metals can be relayed via the heteroatom non-bonding orbitals [33,96]. Separation of the pyridine rings by unsaturated spacer groups, as in the olefinic ligands **24**–**27**, the acetylenic ligands **28** and **29**, and the aromatic ligands **30** and **31**, preserves the conjugation between the pyridine rings whilst increasing the intermetallic separation [96,97]. A recent study of the mixed-valence pentaammineruthenium complexes of the polyenes **25**–**27** showed [99] that there is only a modest decrease in the electronic interaction between the metals despite the large increase in intermetal separation (greater than 20 Å for **27**). Intermetallic interactions are weaker, however, in the corresponding complexes of the ligands **30** and **31** with *para*-phenylene spacers, probably owing to weak π-overlap between adjacent rings which are likely to be non-coplanar [100].

Several of the ligands discussed above have been extensively employed as bridging ligands to various transition metals, including heterobimetallic examples, as probes into the origins of intermetallic interactions [43,55,97,101–110]. Such ligands have also been used to bridge metalloporphyrins [111,112], metallophthalocyanins [71] and tetrapyrazolic macrocycles [113] and the ligand **18** has been used to bridge the two metal centres of gable metalloporphyrins [114,115]. A recent report described the synthesis of a bis(4-pyridyl)porphyrin which was shown to bridge two metalloporphyrins and to bind within the cavity of a host metalloporphyrin–pyromellitide dimer [116]. Similarly, a tri(4-pyridyl)-*s*-triazine has recently been shown to bind strongly within the cavity of a cyclic trinuclear porphyrin host [117]. The disulphide **32** and the tetrazine **33** have also recently been employed as bridging ligands [118–120]. However, apart from the 4,4′-isomers the other bipyridines [121] and bipyridyl methanes, ethers [122], sulphides [122], amines and ketones have not as yet been systematically studied as bridging ligands.

(ii) Azoles

The ligands discussed in this section are shown in Fig. 3. Compared with the π-deficient azines discussed above, the π-excessive azoles are π donors rather than π acceptors and are relatively strong σ-donors. In most cases in order to act as bridging ligands the free N–H heterocycles must be deprotonated, such that the bridging species is in fact the anionic azolate.

By far the most well-studied bridging azolate is the pyrazolate anion (**34**).

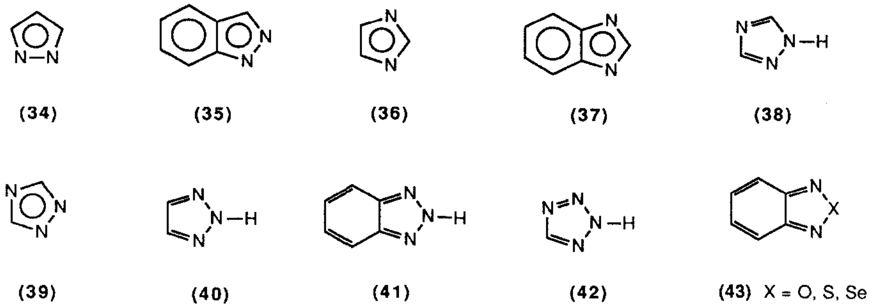


Fig. 3. Bridging azoles and azolates.

The coordination chemistry of pyrazole and pyrazole-derived ligands has been the subject of an excellent review by Trofimenko [123]. Numerous complexes have been reported which contain two metal centres bridged by one, two or three pyrazolate groups (Fig. 4). Usually the two metals are identical although several heterobinuclear complexes bridged by **34** have been reported in recent years.

Complexes bridged by a single pyrazolate group often contain other bridging ligands; for example, **34** has often been used to bridge two copper atoms held within macrocycle ligands as metalloprotein models [124]. Several group 11 metal cyclic pyrazolate-bridged trimers, which contain a nine-membered $[M-N-N]_3$ ring (Fig. 4(a)), have been prepared and X-ray structures reported for several examples [125–130], including a mixed-valence $Au(I)_2$–Au(III) complex [129] and a tricopper(II) complex containing a central capping μ_3-hydroxo group [125]. Also recently described [127,128] is the X-ray structure of a novel hexameric gold(I) complex possessing an 18-membered inorganic ring in the shape of a two-bladed propeller with the six gold atoms arranged about an edge-sharing bitetrahedron. Several heterobimetallic complexes containing a single pyrazolate

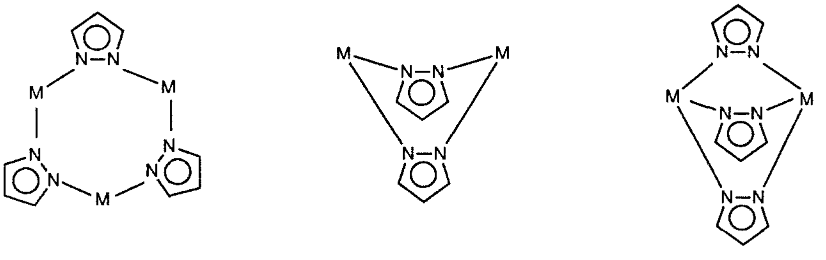

(a) (b) (c)

Fig. 4. Pyrazolate-bridged complexes.

bridge have been prepared [131–136] and X-ray structures of mixed Ru–Rh [134], Ru–Pd [135] and Pd–Rh [136] complexes determined.

Complexes containing two metals bridged by two pyrazolate groups have been extensively studied [123]. Such compounds generally exist in boat conformations (Fig. 4(b)), which thereby facilitates interactions between the two metal centres, a factor which has important consequences on the catalytic activity of such compounds [137]. In fact, **34** is an extremely versatile ligand in that it is able to bridge an unusually wide range of intermetallic separations [138–146]. For example, X-ray structures containing bis pyrazolate bridges across metal–metal bonds (M–M separation, less than 2.6 Å) and non-interacting metal centres (M–M separation, greater than 3.5 Å) have been reported. Again, several heterobimetallic species have been prepared [147–154] and X-ray structures of a Cr–Pt complex [150] and a mixed-valence Rh(I)–Rh(III) complex [151] reported. Also noteworthy are the X-ray structures of two linear trinuclear nickel complexes [152,153] of the type $LNi(\mathbf{34})_2Ni(\mathbf{34})NiL$ and the recently reported [154] heterotrinuclear structure of $[(OC)_2Rh(\mathbf{34})_2Pd(\mathbf{34})_2Rh(CO)_2]$. 3,5-Dimethyl substitution of a bridging pyrazolate ring has been shown to induce conformational changes through steric interactions and also significant changes to metal–ligand electronic interactions as a result of the methyl group inductive effect [137]. Magnetic interactions between pyrazolate-bridged copper atoms have been correlated to structural factors [155]. Various substituted pyrazolates (most notably 3,5-dimethyl) [123] and the benzo-annelated indazolate anion (**35**) [140,156] have also been used as bridging anions.

Bimetallic complexes of the type in Fig. 4(c), bridged by three pyrazolate groups, are much less common with transition metals. The X-ray structure of an anion comprising two nickel nitrosyls bridged by three pyrazolates has been reported [157]. The very well studied metal complexes of tris(pyrazolyl)borates and tris(pyrazolyl)gallates are formally of this type but are considered outside the scope of the present review and have been the subject of excellent recent reviews elsewhere [123,158]. However, worthy of mention is the crystal structure of a novel tris(pyrazolyl) borate complex of copper(I) wherein two copper atoms are bridged by one of the three pyrazole rings through a single nitrogen atom [159].

The imidazolate anion (**36**), obtained by deprotonation of imidazole, is also capable of acting as a bridging ligand. However, the 1,3-arrangement of the nitrogen atoms imposes geometrical constraints such that, unlike pyrazolate, only one imidazolate bridge is possible between two metal centres. Accordingly, imidazolate-bridged transition metal complexes show higher linearity than the pyrazolate-bridged complexes discussed above. Indeed, many oligomeric and polymeric complexes have been known for some time to contain imidazolate bridges [160,161].

Because of the importance of histidine involvement in enzymic catalysis, much of the interest in imidazolate bridging has been in a bio-inorganic context and particularly in the chemistry of the metalloprotein superoxide dismutases. An X-ray crystal structure of the biologically important enzyme bovine erythrocyte superoxide dismutase has shown [162] the active site to consist of a Zn–Cu bimetallic pair bridged by the imidazolate group of a histidine residue. Many models of the active site have been synthesized which incorporate an imidazolate bridge usually between two copper ions, since the catalytic activity of the enzyme is unaffected by replacement of the zinc with copper. The stability of an imidazolate bridge is increased by additional bridging between the copper atoms and hence many binuclear copper models have been prepared wherein the imidazolate ring is incorporated into a multidentate ligand or where the two copper atoms are held within a macrocyclic ligand [163–174]. X-ray crystal structures have also been reported for two heterobimetallic model complexes containing Cu–Co [175] and Cu–Ni [176] pairs bridged by imidazolate. Several imidazolate-bridged Fe–Cu binuclear complexes were also prepared as models to test an earlier suggestion that the active site of cytochrome c oxidase might also incorporate an imidazolate bridge [177–179]. Imidazolate bridging has also recently been shown to exist in the cobalt(III) complexes of a synthetic analogue of the important antitumour drug bleomycin [180].

Much of the interest in imidazolate bridging has centred on the ability of the ligand to mediate magnetic coupling between the coordinated metals [181,182]. Other imidazole-bridged complexes include homobimetallic complexes of ruthenium [183], mercury [184], nickel [185] and rhodium [186,187]. The rhodium complexes form cyclic trimers similar to the pyrazolate-bridged trimers discussed above. A cyclic tetramer of rhodium has also been characterized by X-ray crystallography [188]. Imidazolate has also been used to bridge iron and manganese porphyrins [189]. Other imidazolate-bridged heterobimetallic complexes include Co–Ru [183], Cu–Ni [190], Rh–Au [147,186] and Rh–Pt [147] examples. Several 2-substituted imidazolates and the benzo-annelated derivative, benzimidazolate (**37**), have also been used as binucleating ligands.

The higher azoles (triazoles, tetrazoles) are extremely versatile ligands which exhibit a variety of bridging modes of coordination. 1,2,4-Triazole (**38**) is a well-studied ligand which is capable of acting as a bridging ligand either with or without deprotonation. As shown in Fig. 5 the neutral ligand can coordinate as the 4-H tautomer through N1 and N2 in a manner analogous to that of the pyrazolate anion, or as the 1-H tautomer through N2 and N4 in a configuration similar to that of the imidazolate anion. Similarly the deprotonated 1,2,4-triazolate anion can be involved in N1,N2

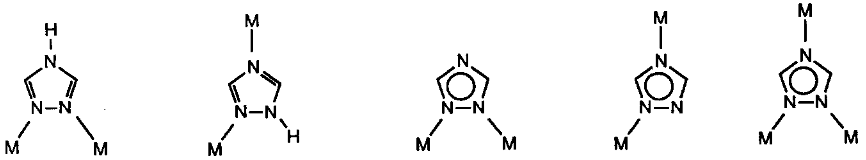


Fig. 5. Bridging modes of 1,2,4-triazole (**38**) and 1,2,4-triazolate (**39**).

or N2,N4 bridging or even act as a tridentate ligand with coordination to all three nitrogen atoms. All these possibilities are known.

In the same way that two metal centres can be bridged by one, two, or three pyrazolate anions (see above), 4-H or 4-substituted 1,2,4-triazoles can form single or multiple bridges. Single bridging is exemplified by the long-established [191] polymeric structure for dichloro(1,2,4-triazole)copper(II) which consists of chains of copper atoms bridged by two chlorides and a 4-H triazole (bridged through N1 and N2). N1,N2 bridging by two 4H-triazoles is exemplified by the polymeric and linear trimeric structures of 3,5-disubstituted triazoles. X-ray crystal structures have been reported for nickel [192] and cobalt [193] trimers possessing double triazolate bridges with additional bridging thiocyanato and fluoro groups respectively. N1,N2 bridging by three triazoles is relatively common. X-ray crystal structures of such compounds include a linear trinuclear nickel compex of 4H-1,2,4-triazole [194] and binuclear manganese [195] and cobalt [196] complexes, trinuclear iron [197], cobalt [198] and manganese [199] complexes and a polymeric cadmium complex [200], all containing triple bridges of 4-substituted triazoles. N2,N4 bridging by **38** is less common, although X-ray crystal structures have been reported for cobalt, copper, zinc [201] and iron [202] complexes, all of which exhibit extended two-dimensional polymeric structures with 2,4-bridging triazoles.

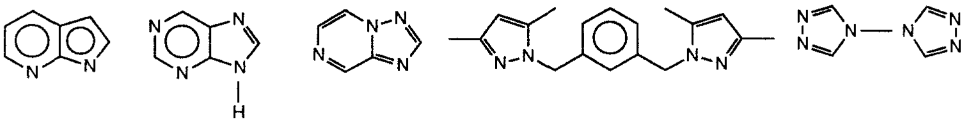
All three possible bridging modes of the deprotonated triazolate anion (**39**) are known. For example, N1,N2 bridging was used to link two copper atoms within a macrocycle [203], whereas N2,N4 bridging was observed in cyclic rhodium trimers, an example of which was characterized crystallographically [187] and X-ray crystal structures have been reported for trinuclear rhodium complexes [204,205], a tetranuclear mixed Rh–Pd complex [206] and a pentanuclear copper complex [207], all of which include **39** bridging three separate metal centres.

The coordination chemistry of 1,2,3-triazole (**40**), benzotriazole (**41**), tetrazole (**42**) and their respective deprotonated azolates has been the subject of an excellent recent review [208]. These ligands, like the 1,2,4-triazoles discussed above, exhibit a variety of bridging modes. Neutral 1,2,3-triazoles can bridge as the 1-H tautomer through N2 and N3 as is found in the crystal structure of a benzotriazole-bridged dimolybdenum complex [209].

1,2,3-Triazolate bridges are well known [208] and X-ray structures of complexes with single [210,211] N1,N3 bridging as well as double [212,213] and triple [214,215] N1,N2 bridging have all been characterized. Furthermore, tridentate coordination by all three nitrogen atoms of benzotriazolate has also been osberved for tetranuclear rhodium complexes [216] and in the crystal structures of X-shaped pentanuclear copper complexes [217–219]. N2,N3-bridging tetrazolate complexes are also well known [208] and a complex involving tridentate coordination by tetrazolate to three different rhodium atoms has recently been structurally characterized [220]. Attempts to force tetrazolate to coordinate to four rhodium atoms were unsuccessful [220]. Complexes incorporating bridging 1,2,3-triazolates and tetrazolates can be prepared by reactions of coordinated azide with activated alkynes and nitriles respectively [208,221,222]. The weakly basic 1,2,3-benzochalcogenadiazoles (**43**) are structurally similar to benzotriazolate and have been used to bridge group 6 metal pentacarbonyls [223].

Numerous other heterocyclic compounds exist which contain two or more basic nitrogen atoms capable of multinuclear coordination but whose coordination chemistry is relatively unexplored. Some representative examples are shown in Fig. 6. The 7-azaindolate anion (**44**) is geometrically similar to 1,8-naphthyridine and like **8** can exhibit several modes of coordination, including bridging across metal–metal bonds or across two non-bonded metal atoms. X-ray crystal structures have been reported for dimolybdenum [224] and dirhodium complexes of both types [225,226] as well as for an interesting triruthenium cluster [81] in which the azaindolate is coordinated to all three ruthenium atoms, through the pyridine nitrogen to one metal atom and through the pyrrolic nitrogen to the other two metal atoms.

Although the coordination chemistry of the biologically important purines (**45**) is considered outside the scope of the present survey, such ligands are capable of acting as multinucleating bridges [28]. For example, several X-ray structures of methylmercury complexes of deprotonated adenine have been reported and include examples of adenine bridging two, three and four mercury atoms [227]. The X-ray structure of a polymeric iron(II) complex with N1,N3 bridging by the triazolopyrimidine ligand **46** has been reported [228]. The bis(pyrazolylmethyl)benzene **47** has been used to bridge two two-coordinate copper(I) centres to give a cyclic dimer which was structurally



(44) **(45)** **(46)** **(47)** **(48)**

Fig. 6. Other selected ligands with bridging azole groups.

characterized [229]. X-ray structures of cobalt(II) [230] and manganese(II) [231] polymers containing 4,4′-bi-1,2,4-triazole (**48**) bridges have been reported. Structurally similar 4,4′-linked bipyrazoles have also been reported to bridge two ruthenium(II) centres [232]. Much work still remains to be done in exploring the coordination chemistry of many other potentially bridging non-chelating ligands.

C. BIDENTATE CHELATING LIGANDS

In all the complexes described above the metal is bound to the ligand through one nitrogen only. In some cases that nitrogen is a poor σ-donor with reduced basicity as a result of the electron-withdrawing nature of a metal ion coordinated to another nitrogen in the complex. Accordingly such binuclear complexes are often relatively unstable. The stability of such complexes can be increased by incorporating bidentate coordination to each metal, with the chelate effect stabilizing each metal coordination site. Many such ligands exist and are the subject of this section.

(i) Dipyridyldiazines and related ligands

3,6-Bis(2′-pyridyl)pyridazine (**49**) (Fig. 7) has been extensively employed as a binucleating ligand over the past two decades [233–242]. In binuclear

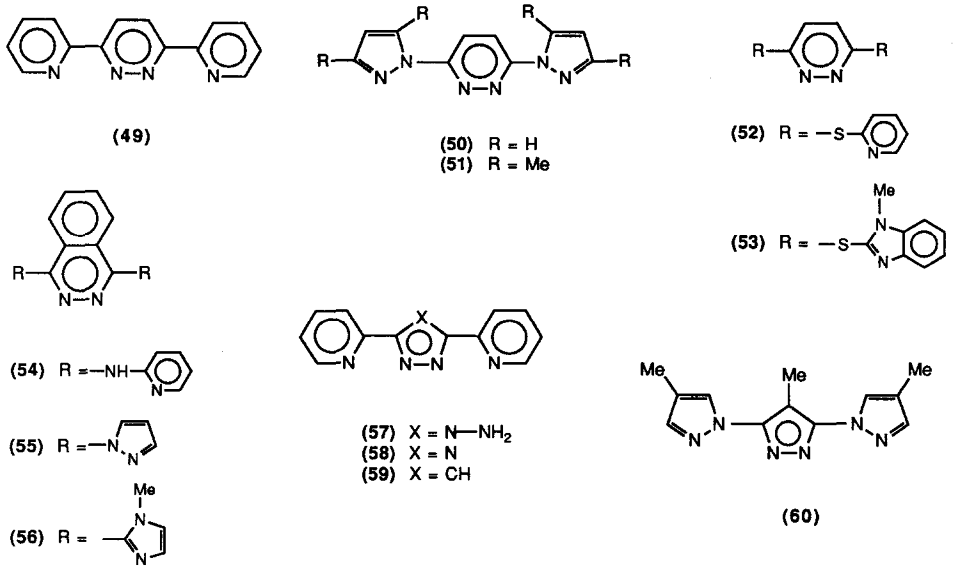
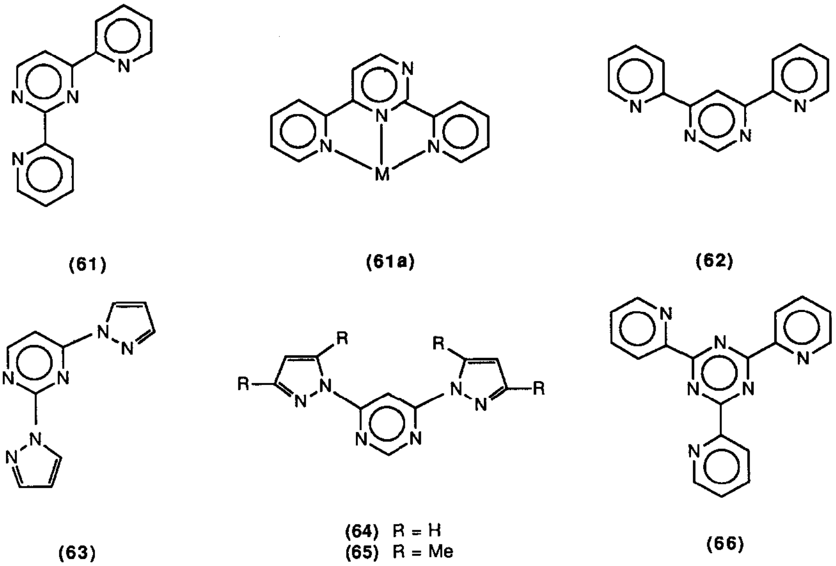


Fig. 7. 3,6-Bis(2′-pyridyl)pyridazine and related ligands.

complexes of **49** the two metal atoms are separated by approximately 3.35 Å and strong interactions, such as antiferromagnetic exchange, can exist between the two metal centres. There have been many studies of dicopper complexes of **49**, including several X-ray structure determinations [234–239]. A number of heterobimetallic complexes of **49** have also been prepared [240,241] and the X-ray structure of a mixed Cu–Ir complex determined [242]. The crystal structure analysis of a homobinuclear iridium complex of **49** showed that the ligand had undergone cyclometallation and was coordinating through three nitrogen atoms and one carbon atom [243]. Some unsymmetrically substituted derivatives of **49** have recently been prepared and their mononuclear platinum(II) complexes studied [244].

Many ligands that are structurally related to **49** have been used to form binuclear complexes in recent years (Fig. 7). Most of this work has been with dicopper complexes either as models for the metal centres of dicopper metalloproteins or as probes into the structural factors affecting the magnitude of antiferromagnetic exchange. By replacing either the terminal pyridine rings or the central pyridazine ring with other nitrogen heterocycles it is possible to vary the electronic and geometrical properties of the ligand. The pyrazole-containing ligands **50** and **51** form complexes similar to those of **49**, with comparable intermetallic separations. Binuclear nickel(II), cobalt(II) and copper(II) complexes of **50** and copper(II) and rhodium(I) complexes of **51** have all been prepared and several crystal structures determined [245–248]. Some homochiral derivatives of **50** have also been prepared [249]. The introduction of a heteroatom between the heterocycles, as in the ligands **52**–**54**, converts the chelate ring from a five- to a six-membered ring. This results in greater flexibility in the chelate rings and a reduction in the intermetallic separation. Thus the five-membered chelate ring systems typically form double-bridged dicopper complexes with intermetal separations between 3.29 and 3.46 Å, whereas the six-membered chelate systems usually form triply bridged complexes with Cu–Cu separations between 2.99 and 3.22 Å [250]. Dicopper complexes of the pyridyl and (benz)imidazolyl sulphides **52** and **53** have been prepared and several X-ray structures have been reported [251–255]. The bis(pyridylamino)phthalazine **54** and some methyl-substituted derivatives have been extensively employed as binucleating ligands over the past two decades [250,251,256–261]. The 1-pyrazolyl and 1-methyl-2-imidazolyl phthalazines **55** and **56** have also been used as binucleating ligands with several different metals [245,247,262]. Replacement of the central pyridazine ring of **49** by a five-membered heterocycle results in an increase in the intermetallic separation. X-ray structures of a dinickel complex of the aminotriazole **57** [263], a dicopper complex of the triazolate **58** [264] and a dinickel complex of the pyrazolate **59** [265] all showed metal–metal separations greater than 4.0 Å. In common with the simple triazolates discussed previously the ligand **58** can exhibit two different bridging modes, depending on which nitrogen atoms of the triazole ring are coordinated. In the bis(2,2′-bipyridine)ruthenium(II) complexes of **58**, steric constraints prevent N1,N2-triazolate bridging and N1,N4 coordination is observed [266–268]. A dirhodium complex of the dipyrazolylpyrazolate **60** has recently been prepared [269].

The two dipyridylpyrimidines **61** and **62** (Fig. 8) are each capable of acting as binucleating ligands with two bidentate chelate rings. Although both ligands have been known for over 20 years the only mention of their coordination chemistry is in the original report of their preparations, where iron(II) complexes were studied in solution [270]. It was proposed that the 2,4-isomer **61** forms mononuclear complexes **61a** with tridentate coordination analogous to that of 2,2′,6′,2″-terpyridine. The related ligand 2,4-bis(1′-pyrazolyl)pyrimidine **63** and some complexes have recently been prepared [271]. The 4,6-isomer **62** should readily act as a bridging ligand and form binuclear complexes. On the basis of the recent X-ray structure of a cyclopalladated analogue [272], two metals coordinated to **62** would be separated by about 5.9 Å. The dipyrazolyl and the 3,5-dimethylpyrazolyl analogues **64** and **65** have, however, been used as bridging ligands [248,271]. The well-studied, commercially available ligand 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (**66**) exhibits a variety of bonding modes. Like **61** this ligand normally forms mononuclear complexes with tridentate coordination [273–275]. However, there have been recent reports of **66** forming a



(61) (61a) (62)

(63) (64) R = H (65) R = Me (66)

Fig. 8. Dipyridylpyrimidine and related ligands.

binuclear ruthenium(II) complex with bis-bidentate chelation in a manner analogous to that of **62** [276] and a trinuclear rhodium(I) complex, presumably with tris-bidentate chelation [277].

The binucleating ligand 2,3-bis(2′-pyridyl)pyrazine (**67**) (Fig. 9) was first prepared over 30 years ago [278], but only recently has it become a popular doubly chelating ligand. Diruthenium complexes have been the most well studied [279–282], and excellent intermetal communication has been demonstrated in diruthenium(II) [281] and diiron(II) [283] complexes of **67**. Bridging by **67** has been reported in studies of diplatinum(II) [284], mixed Ru–Pt and Ru–Pd [285] and several group 6 metal carbonyl complexes [286–289], including heterobinuclear examples [289]. Some interesting tetranuclear complexes have recently been described which contain a central metal core (ruthenium(II) [290] or osmium(II) [291]) bridged by three **67** ligands to bis(2,2′-bipyridine)ruthenium(II) groups.

A number of structurally related ligands exist which are capable of acting as bridging ligands. The most well studied of these is the corresponding quinoxaline **68** [280,292–295], which forms both binuclear and mononuclear complexes. The crystal structure of a mononuclear ruthenium(II) complex of this ligand has been determined [293]. Many substituted deriva-

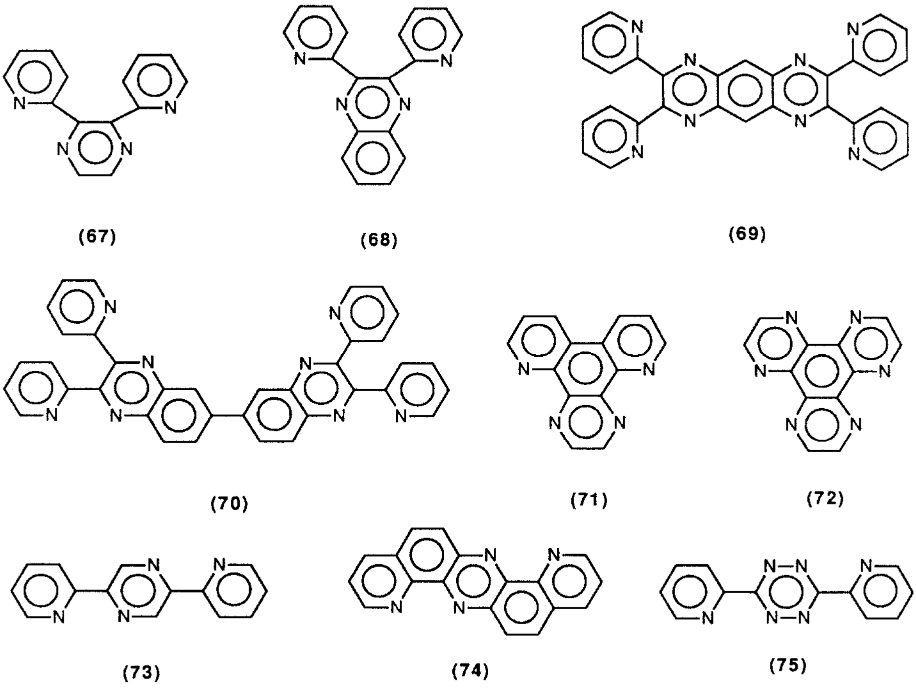

(67) (68) (69)
(70) (71) (72)
(73) (74) (75)

Fig. 9. Dipyridylpyrazines and related ligands.

tives of **68** are known [296] and the coordination chemistry of some of these has recently been investigated [297]. The X-ray structure of a copper (II) complex of the 6,7-dimethyl derivative showed an unusual mode of coordination by the ligand wherein the metal was bound to the two pyridine ring nitrogen atoms with the quinoxaline nitrogen atoms non-coordinating [297]. Two structurally related ligands, **69** and **70**, which are potentially capable of acting as tetranucleating ligands, have been studied [292,298]. The biquinoxaline **70** has been shown to bridge up to four bis(2,2′-bipyridine)ruthenium(II) units [298].

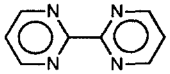
There has been considerable discussion in the literature about the structure of binuclear complexes of the above ligands [279,284,293,297,299]. Originally it was thought that these ligands would be incapable of acting as bridging ligands since steric interactions between the two pyridine rings in **67** were expected to prevent the coplanar conformation required for this ligand to act in a bridging mode. As described above, several binuclear complexes of **67** have now been reported and, although no X-ray structures of binuclear complexes of **67** have been reported, the crystal structure of a doubly cyclopalladated complex, incorporating a ligand isoelectronic with **67**, has recently shown that the steric interaction between the pyridine rings is relieved by severe twisting within the ligand [300]. Such twisting has also been detected by variable-temperature NMR studies of diplatinum(IV) complexes of **67** [284]. The intermetal separation in such complexes is about 6.7 Å [300].

The steric interaction between the pyridine rings and the consequential twisting of the ligand in the complexes are absent in the planar ligand **71**, which readily forms binuclear complexes [280,301]. Similarly the planar hexaazatriphenylene **72** [302] forms complexes with the ligand bridging three metal centres. Trichromium(0) [303], triruthenium(II) [304,305] and mixed Ru(II)–Rh(I) [306] complexes of **72** have all recently been reported. Substituted derivatives of **72** are also known [307].

2,5-Bis(2′-pyridyl)pyrazine (**73**), which has no steric hindrance to coplanarity of the rings and has relatively low lying π^* orbitals, is a better π-acceptor than its isomer **67** and readily forms binuclear complexes. Several theoretical and experimental studies have been recently reported for complexes in which **73** bridges group 6 metal carbonyls [308–310] or two ruthenium atoms [282,311,312], including mixed-valence examples [311]. The related doubly fused planar ligand **74** has been known for some time but its coordination chemistry is unexplored [313]. The tetrazine **75** is also a well-studied ligand which could, in principle, bridge either through two adjacent nitrogen atoms, in a manner analogous to the pyridazine **49**, or through two opposite nitrogen atoms, similar to **73**. In practice, only the latter mode of coordination has been observed, presumably since this minimizes steric interactions between the metals. Binuclear complexes of **75** with group 6 metal carbonyls [308–310,314,315], copper [316] and ruthenium [311,312,317] have all been reported. The ligand **75** has very low lying π^* orbitals which make it an excellent π acceptor, although this is counteracted by the fact that it is a relatively weak σ-donor [309].

(ii) 2.2′-Bipyrimidine and related ligands

The commercially available ligand 2,2′-bipyrimidine (**76**) (Fig. 10) is the most well studied of the doubly bidentate chelating bridging ligands. Numerous homobinuclear complexes have been described in which **76** bridges two metals, mainly of groups 6, 8 or 10 [283,284,292,295,307–312,317–326]. Ruthenium complexes have been particularly well studied [292,295,311,312,318–321], including mixed-valence examples [311] and a tetranuclear complex with a central ruthenium core bridged by three **76** ligands [295,318]. A number of heterobimetallic complexes of **76** have also been prepared [277,285,306,320,323,327–332]. In a cytochrome c oxidase model, which was originally proposed to contain a **76** bridge between iron(II) and copper(II) [333], it has since been shown that this is not the case [334]. X-ray crystal structures of a dicobalt(II) [335], a diiron(II) [336], a distannacarborane [337] and several dicopper(II) [338–340] complexes with bridging **76** have been reported. The metal–metal separation in such complexes is typically about 5.5 Å and this facilitates relatively strong metal–metal interactions mediated by the ligand. Despite the extensive work on binuclear commplexes of **76**, there have been no reports of bridging by the benzo-annelated analogue 2,2′-biquinazoline (**77**), which was first prepared 25 years ago [341]. Interestingly, however, a 2,2′-biquinazoline fragment has recently been incorporated into a macrocyclic ligand synthesized as a dicyanocobalamin analogue [342].



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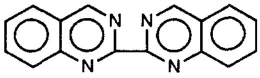

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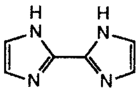

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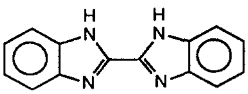

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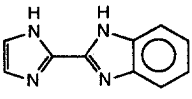

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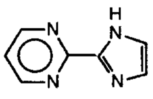

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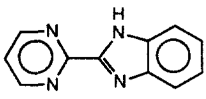


(82)

Fig. 10. 2,2′-Bipyrimidine and related ligands.

The 2,2′-biimidazolate dianion (**78**), obtained by double deprotonation of the readily prepared [343–345] ligand 2,2′-biimidazole, and the corresponding bibenzimidazolate **79** have both been extensively employed as bridging ligands. A wide range of metals have been bridged by **78** and **79** in both homobinuclear [167,187,345–356] and heterobinuclear [357–360] complexes. Crystal structures have been reported for both the free ligands [361,362] and binuclear complexes [355,356] in which **78** acts in a doubly chelating mode (other bridging modes will be discussed below). The coordination geometry of such complexes is similar to those of **76** with metal–metal separations of about 5.5 Å. However, unlike **76**, which is a π acceptor, these ligands are π donors and this is manifested in the physicochemical properties of the complexes. A recent study [353] of the spectroscopic and electrochemical properties of homobimetallic and heterobimetallic ruthenium, osmium, cobalt and nickel complexes of **79**, in combination with molecular orbital calculations, showed that these complexes are considerably more stable than the corresponding complexes of **76**. This was attributed to a combination of the superior donor properties of the ligand and a reduction in electrostatic repulsion between the two positively charged metal centres when bridged by the dianionic ligand. Binuclear complexes of the tetramethyl [350,363] and π-deficient tetracyano [364–367] derivatives of **78** have been described and the 2,2′-biimidazole unit has recently been incorporated into macrocycles [368] and cryptands [369]. Despite the interest in these ligands, no reports have appeared of bridging by the monobenzo analogue **80**, which has been known for over 20 years [370]. Similarly the coordination chemistries of the pyrimidyl imidazolate **81** and known [371] benzimidazolate **82** have not been studied. These unsymmetrical monoanionic ligands would be expected to bridge with properties intermediate between those of the ligands **76**, **78** and **79**.

(iii) Ligands with isolated 2,2′-bipyridine-like units

A number of ligands exist which are capable of acting as doubly bidentate bridging ligands through two 2,2′-bipyridine-like units and which vary in the extent of interactions between the two chelating units. For example, the fusion of two 2,2′-bipyridine units as in 2,7-bis(2′-pyridyl)-1,8-naphthyridine (**83**) [372] (Fig. 11) incorporates the bridging properties of **8**. The X-ray structure has been reported of a dirhodium(II) complex of **83**, in which the naphthyridine unit bridges a Rh–Rh bond with chelation by the pendent pyridine rings [373]. A dirhodium(II) complex of the corresponding fused dihydrophenanthroline **84** has also been reported [374].

Direct linking of two 2,2′-bipyridine units exists in the various quaterpyridines of which the 2,2′:6′,2″:6″,2‴-isomer **85** is the only one to have been

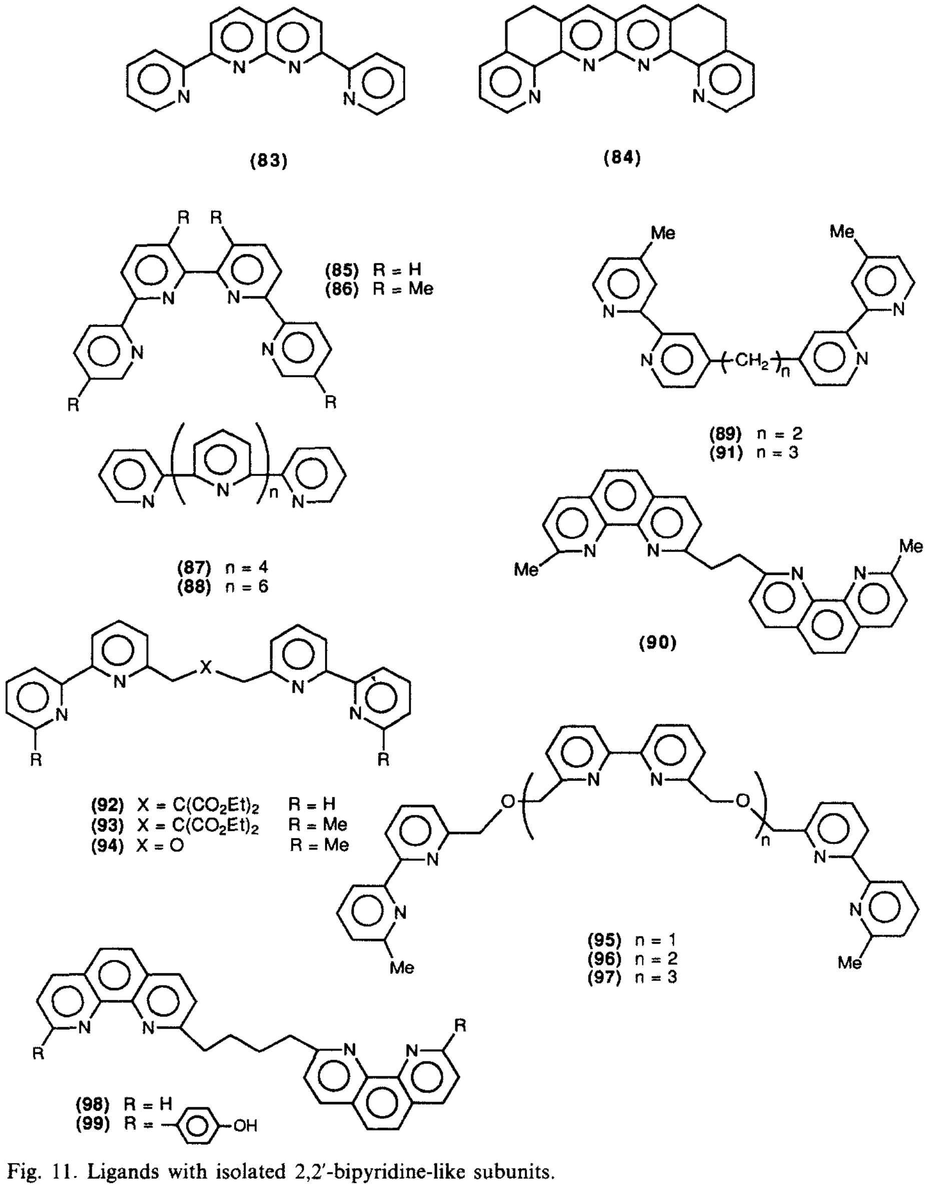


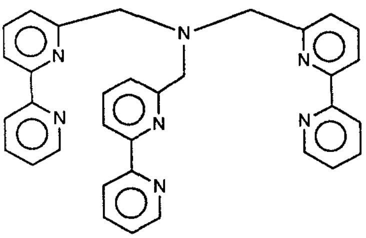
Fig. 11. Ligands with isolated 2,2′-bipyridine-like subunits.

employed as a ligand. This ligand normally forms mononuclear complexes with planar quadridentate coordination to the metal ion [375]. However, the tetramethyl-substituted derivative **86** forms both mononuclear [376] and binuclear [377,378] complexes. Interactions between the methyl groups act to twist the ligand about the central bond thereby favouring bis-bidentate bridging. The X-ray crystal structure of a dicopper(I) complex of **86** has been reported [377]. Directly linked bis-1,10-phenanthrolines are also known [379]. The higher linear oligopyridines **87** and **88** are potentially capable of acting as tris-bidentate and tetrakis-bidentate polynucleating ligands respectively. As described below, a complex of **87** in which the ligand acts in a bis-tridentate mode has very recently been structurally characterized [380].

Several ligands exist which consist of two 2,2′-bipyridine units joined through a bridging group. The most common bridge is an ethylene group since such compounds can conveniently be synthesized by oxidative coupling of methylene carbanions derived from methyl precursors [381,382]. Binuclear complexes bridged by the 4,4′-substituted ligand **89** have been reported with several transition metals [383–386], including a heterobinuclear Ru(II)–Pt(II) example [384]. The crystal structure has been reported of a diiron(II) complex which has triple bridging by three units of **89** across the two metal centres [385]. The corresponding 5,5′- and 6,6′-isomers, as well as several ethylene-linked bis(1,10-phenanthrolines) such as **90**, have also been prepared for study as binucleating ligands [381].

Three-atom bridges between two 2,2′-bipyridine units are also known. For example, a diruthenium(II) complex which involves bridging by the 4,4-propylene-linked ligand **91** has been reported [383]. In contrast, the 6,6-linked ligands **92** and **93** failed to form binuclear complexes on reaction with two equivalents of copper(I) ions, but gave instead a mononuclear tweezer-type complex, with **92** and **93** having quadridentate coordination to a single metal ion [387]. The 2-oxapropylene-linked ligand **94** does, however, form binuclear copper(I) complexes with two bis-bidentate ligands bridging the two metals [388]. Indeed, **94** and the higher homologues **95**–**97** all form self-organized double-stranded helicates on reaction with copper(I) ions [388,389]. X-ray structures of the binuclear and trinuclear species have been determined and the pentanuclear complex of **97** is estimated to be about 27 Å in length and as such represents an example of a functional nanoscale species [390]. The butylene-linked bis(1,10-phenanthroline) **98** has recently been synthesized and a dicopper(I) complex bridged by the substituted derivative **99** prepared [391]. This structural unit was also incorporated into several macrocyclic ligands, including the first synthetic molecular trefoil knot [391].

Several polybipyridine ligands derived from acyclic and monocyclic polyamines have been synthesized which contain three, four or six isolated 2,2′-bipyridine units [392]. For example, the tripodal ligand **100** (Fig. 12) forms both mononuclear and trinuclear complexes, the latter of which has **100** acting as a tris-bidentate bridge [392]. Similarly the three-armed mesitylene ligand **101** has recently been synthesized and shown to form a mononuclear capped hemicage ruthenium(II) complex [393]. Trinuclear complexes bridged by **101** are undoubtedly accessible. The potentially bridging ligand



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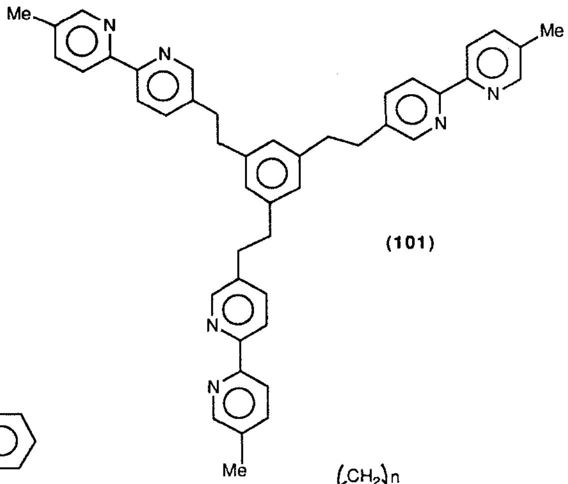

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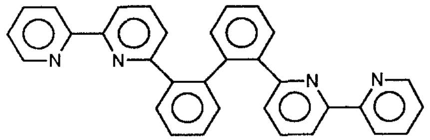

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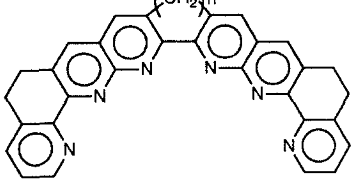

(104) n = 2
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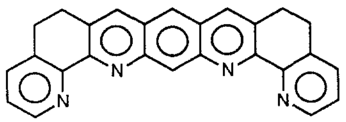

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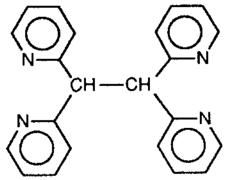

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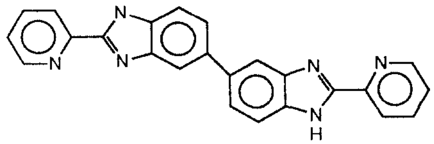

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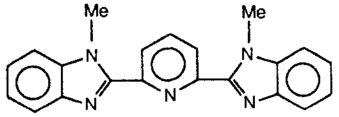


(109)

Fig. 12. Some other bidentate chelating bridging ligands.

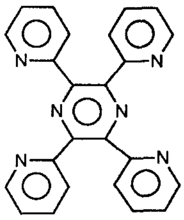
102 has been shown to form mononuclear complexes with copper(I) and copper(II) [394]. A number of polyaza cavity-shaped molecules which might act as bridging chelating ligands have been synthesized in recent years. For example, **103** represents the common fusion of two dihydrophenanthroline units to a single benzene ring and, as such, is potentially capable of acting as a bis-bidentate bridge [395]. Similarly the three ligands **104**–**106** may be considered to comprise three 5,6-fused 3,3′-annelated 2,2′-bipyridine subunits. Studies of the bis(2,2′-bipyridine)ruthenium(II) complexes of these ligands have shown that coordination occurs to the distal rather than central bipyridine subunits and an X-ray crystal structure was described of a binuclear complex of **106** [396].

Doubly chelating bridging ligands containing subunits other than 2,2′-bipyridine or 1,10-phenanthroline also exist. For example, just as di(2-pyridyl)methane is an excellent chelating ligand, so the related dimeric tetrapyridylethane **107** is an excellent bridging ligand which forms two six-membered chelate rings [397,398]. Likewise, binuclear ruthenium and osmium complexes of the bibenzimidazole **108** have recently been described [399], in accord with the excellent chelating ability of the component monomer 2-(2-pyridyl)benzimidazole [2]. Similarly the related ligand **109**, which normally forms mononuclear complexes with tridentate chelation [400–402], has recently been shown to bridge two copper(I) centres in an unusual manner wherein the central pyridyl nitrogen is coordinated to both metals. The structure of this double-helical complex was confirmed by X-ray crystallography [403]. This bridging mode is similar to that previously mentioned [159] for a dicopper(I) complex of a tris(pyrazolyl)borate. A crystal structure has recently been reported of a dicopper(II) complex of a hexaimidazole-containing ligand in which each metal is bound to two imidazole donors [404]. Many other ligands incorporating other common biheteroaromatic chelating subunits [2] are expected to be synthesized and studied in the future.

D. TRIDENTATE CHELATING LIGANDS

In contrast with the many bidentate chelating bridging ligands discussed above, there are relatively few bridging ligands which have tridentate chelation at each metal centre (Fig. 13). 2,3,5,6-Tetra(2-pyridyl)pyrazine (**110**) has been known for over 30 years [278] but was originally thought to be incapable of acting as a bis-tridentate bridge because of steric repulsions between coplanar pyridine rings, similar to those discussed above for **67**. Recently, however, this has been shown not to be so, and binuclear complexes have now been prepared in which **110** bridges two ruthenium(II) [405,406], copper(II) [297] and rhodium(III) [407] centres. Indeed, this is an excellent binucleating ligand which has been shown to facilitate effective communication between the metal centres [406]. The closely related ligands **111** and **112** have also been known for some time [313,408], but their coordination chemistry remains unexplored.

The linear sexipyridine **87** has recently been shown to form binuclear complexes with several different metal ions, and an X-ray crystal structure was reported of an interesting double-helical dicadmium(II) complex in which each metal is coordinated to two terpyridine subunits of two different



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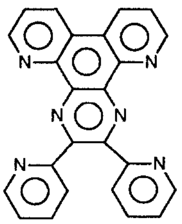

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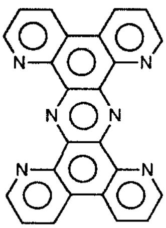

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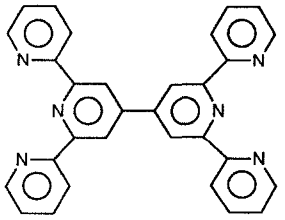

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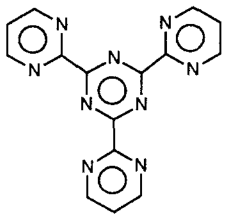

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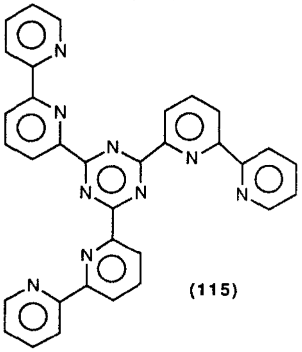


(115)

Fig. 13. Some tridentate chelating ligands.

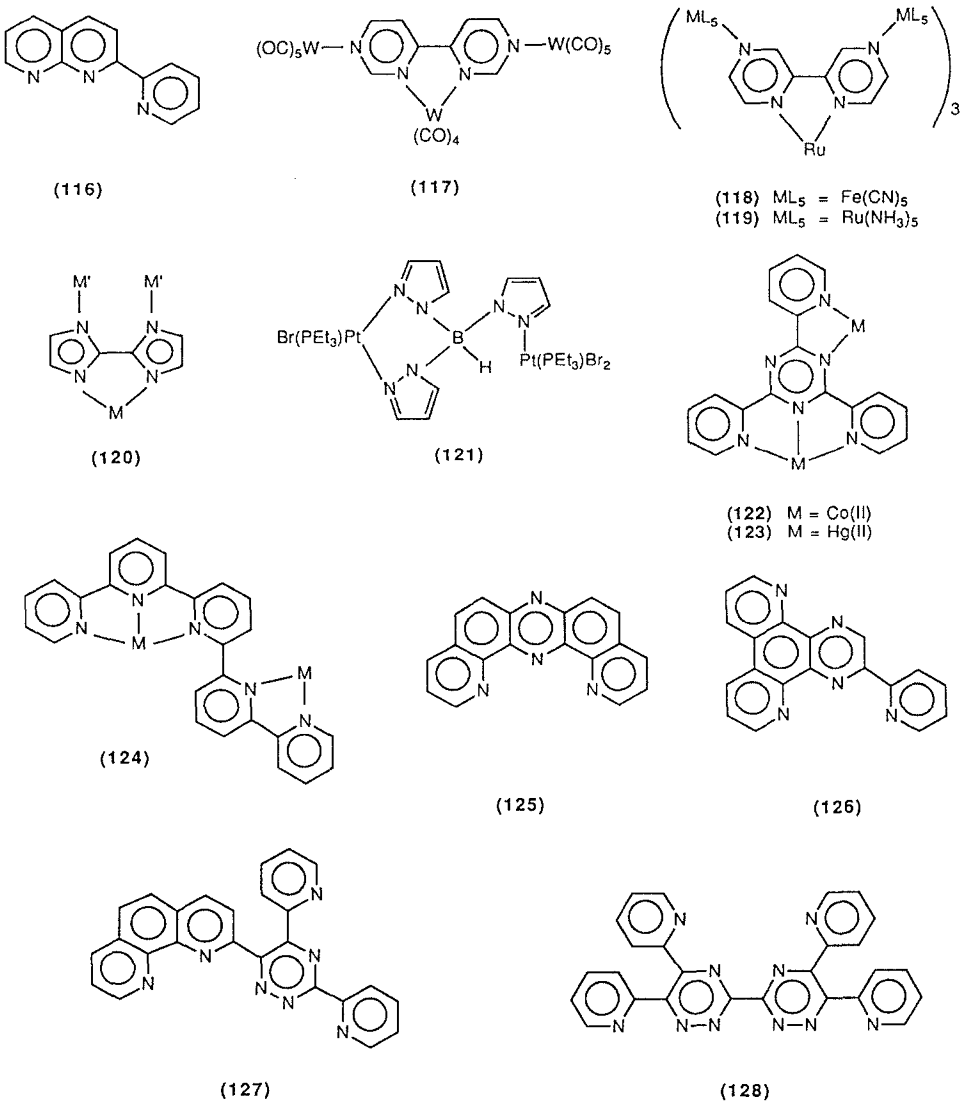
molecules of **87** [380]. The same authors recently reported the synthesis of the non-linear sexipyridine **113** [409]. This ligand, which represents the back-to-back linking of two terpyridines, was used to bridge two Ru(II)–terpyridine groups which were shown to be non-interacting [409]. From this it was concluded that for steric reasons the binuclear complex adopts a conformation in which the two terpyridine subunits in **113** are mutually perpendicular; this in turn prevents the π overlap necessary for intermetal communication, such as is observed in the complexes of **110**. A dipalladium(II) complex of **113** was also described [409]. The diosmium(II) complex of a ligand that has two terpyridine subunits bonded to a cyclohexanediol has been shown to have potent curariform activity [410]. The two triazines **114** and **115** have been known for some time [411] and each has the potential to coordinate three metal ions in terpyridine-like tridentate modes. 2,4,6-Tri-(2-pyrimidyl)-1,3,5-triazine (**114**) has been shown to coordinate up to three metal ions and the X-ray crystal structure has been reported of a dilead(II) complex in which **114** acts as a bis-tridentate ligand [412]. On reaction with copper(II) ions, **114** undergoes hydrolysis of the triazine ring to give a bis(2-pyrimidyl)carboximidato chelate complex which was structurally characterized [413,414]. There has been only one brief report of coordination by the ligand **115** [415]. In view of the importance of complexes of the tridentate ligand 2,2′:6′,2″-terpyridine [375], it is likely that many more bis-tridentate ligands will be synthesized in the near future for use as bridging ligands.

E. LIGANDS OF MIXED DENTICITY

Many ligands exist which are potentially capable of acting as binucleating or polynucleating ligands and which have two or more non-equivalent sites for metal coordination. Such ligands offer great potential, particularly for the preparation of heteronuclear complexes, since different metals can selectively complex at the different coordination sites. Surprisingly little effort has thus far been directed towards the study of such complexes. Figure 14 shows some representative ligands and complexes of this type. Various different mixes of non-chelating, bidentate and tridentate coordination are possible at each metal centre and the extent of interaction between the metals can be varied by the appropriate choice of ligand.

2-(2-Pyridyl)-1,8-naphthyridine (**116**), for example, combines the chelating properties of 2,2′-bipyridine (**11**) with the bridging properties of 1,8-naphthyridine (**8**) and readily forms dirhodium complexes, in which the naphthyridine unit bridges an Rh–Rh bond with additional chelation by the pendent pyridine at one metal centre [373,416]. One such complex has been characterized by X-ray crystallography [416]. The two symmetrical bidiazines, 4,4′-bipyrimidine and 2,2′-bipyrazine, each forms complexes with bidentate chelation to one metal and monodentate coordination to two other metals. For example the 4,4′-bipyrimidine trinuclear tungsten carbonyl complex **117** has recently been characterized and its electrochemistry and spectroscopy studied [417]. The well-known ligand 2,2′-bipyrazine [418,419] has recently been shown to bridge in an analogous manner, and spectroscopic studies have been reported on the interesting heptanuclear complexes **118** and **119**, which contain a central tris(bipyrazine)ruthenium(II) core bridging to six pentacyanoferrate(II) or pentaammineruthenium(II) residues respectively [420–422]. The structurally related ligands 1,4,5,8-tetraazaphenanthrene [423] and 2,2′-biquinoxaline [424] might also be expected to bridge in an analogous manner.

Several of the ligands previously mentioned can exhibit alternative bridging modes to those already discussed. For example, 2,2′-biimidazole and 2,2′-bibenzimidazole exhibit several other bridging modes in addition to the doubly chelating mode discussed above [358]. Bridging in a manner similar to that of bipyrazine is represented by several complexes of the type **120**, in which the ligand is chelated to one metal with monodentate bridging to two other metal centres [348,358–360,425,426]. These ligands can also bridge two or more metals with non-chelating monodentate coordination to each



(116)

(117)

(118) $ML_5 = Fe(CN)_5$
(119) $ML_5 = Ru(NH_3)_5$

(120)

(121)

(122) M = Co(II)
(123) M = Hg(II)

(124)

(125)

(126)

(127)

(128)

Fig. 14. Some mixed-denticity ligands and complexes.

metal centre [348,358,427]. An X-ray structure has recently been reported of a complex **121**, in which the normally tripodal tridentate tris(pyrazolyl) borate ligand bridges with mixed bidentate–monodentate coordination [428]. Similarly a normally tridentate chelating bis(pyrazolylmethyl)pyridine has been shown to bridge two palladium(II) atoms in an analogous manner [429].

In the above examples the ligands bridge in mixed bidentate–monodentate coordination modes. Several ligands exist which are capable of bridging in a mixed bidentate–tridentate fashion. For example, 2,4,6-tri-(2-pyridyl)-1,3,5-triazine (**66**) has long been known to form complexes in which there is mixed bidentate–tridentate chelation [430]. Crystal structures have been reported for two such complexes, **122** and **123** [431,432]. This ligand, like its pyrimidinyl analogue **114**, undergoes copper(II)-assisted hydrolysis [433,434]. Similarly, 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine has recently [435–438] been shown to form interesting helical complexes **124** with several different metals and in which the quinquepyridine coordinates with tridentate terpyridine-like chelation to one metal and bidentate bipyridine-like chelation to another. Many other ligands are known which can potentially bridge in other modes but whose coordination chemistry has not yet been investigated. For example, the ligands **125** (monodentate–tridentate) [313], **126** (bidentate–tridentate) [313], **127** (bis-bidentate–tridentate) [439] and **128** (pentakis–bidentate) [439] have all been known for some time.

F. CONCLUSION

In this review the use of aromatic nitrogen heterocycles as bridging ligands has been surveyed. Although many ligands have been discussed, only a few of them (e.g. pyrazine, pyrazolate, imidazolate, 2,2′-bipyrimidine) have been extensively employed as bridging ligands for a variety of different metals. Such studies have significantly contributed to our understanding of metal–metal interactions such as magnetic coupling and energy, intervalence or electron transfer. Many of the other ligands discussed above and many as yet unsynthesized ligands will undoubtedly be the subject of more intense study in the near future. More importantly, a number of recent studies of the physicochemical properties of transition metal complexes of nitrogen heterocycles, in combination with theoretical calculations, have greatly improved our understanding of the nature of metal–ligand interactions. Consequently it is now becoming possible to predict accurately the physical properties (spectroscopic and electrochemical) of new metal–ligand combinations and to tune these properties by subtle changes in the ligand structure. Thus many new bridging ligands are expected to be synthesized in the future which are specifically designed to impart specially desired features in the properties of their metal complexes. Such ligands offer exciting new possibilities for the preparation of new binuclear and polynuclear complexes with potential applications as catalysts, photosensitizers or low dimensional conducting polymers.

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