Tetrahedron Vol. 48, No. 46, pp. 10013-10059, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00
Pergamon Press Ltd

TETRAHEDRON REPORT NUMBER 325

OLIGOPYRIDINES AS HELICATING LIGANDS

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(*Received* 4 *September* 1992)

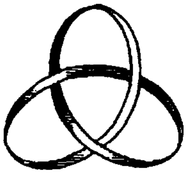
Contents

1. INTRODUCTION

Chemists have been concerned with the third dimension ever since the recognition of the tetrahedral character of the sp^3 carbon centre by van't Hoff and Le Bel[1]. Their adventures in three dimensional space have been many and varied, and have culminated in today's detailed understanding of chiral molecular species. A recurrent theme in organic chemistry has been the quest for molecules which resemble familiar macroscopic objects or geometries, as the successful or attempted syntheses of compounds such as tetrahedrane[2] or dodecahedrane[3] and the characterisation of the fullerenes bears witness[4]. A common motif in art, both primitive and modern, is the twisting or inter-lacing of threads[5], a theme which is more formally developed in chemical topology[6]. One of the more arcane activities which have occupied chemists in recent years is the design of molecular threads which may be twisted or inter-twisted in a controlled manner[5,7]. The controlled and sequential twisting of molecular threads allows the development of helical molecular systems[8,9]. The frequent occurrence of such systems in molecular and macroscopic biology renders such compounds irresistible targets for the synthetic chemist. A helix is necessarily chiral, and the challenge of accessing novel chiral systems has appealed to chemists. The subject of this review is the use of metal ions to control the twisting of oligopyridines into helical or multiple-helical arrays.

2. THE CONTROL OF MOLECULAR TOPOLOGY

It is apparent that relying upon statistics and chance for molecular threads to adopt the correct conformations for the formation of systems such as a trefoil knot **1**[10-11] or a triple-helix **2**[12] would not be a fruitful approach.



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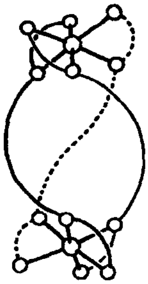

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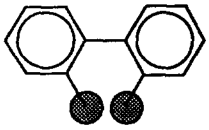
How could one approach such controlled twisting at a molecular level? We have sought to reduce the problem to a simple rotational process involving an inter-annular C-C bond between two aromatic rings. The simplicity of this process avoids the myriad possibilities associated with conformational changes involving tetrahedral sp^3 carbon atoms. We may consider two limiting conformations for two directly bonded aromatic rings.

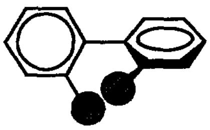


Coplanar

Electronically favoured
Maximum conjugation

Sterically disfavoured
Maximum ortho-ortho interaction

3



Orthogonal

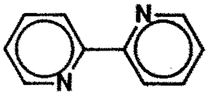
Electronically disfavoured
Minimum conjugation

Sterically favoured
Minimum ortho-ortho interaction

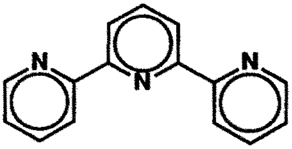
4

If the two rings are coplanar, 3, the conformation is *favoured* by the maximum conjugation of the π systems of the two rings, but is *disfavoured* by the maximum steric interactions between any groups which are attached *ortho* to the C-C bond. In contrast, the limiting alternative conformation with the two rings orthogonal, 4, is electronically *disfavoured* by the complete loss of conjugation, but is sterically *favoured*. The inter-annular angle which is adopted will depend in practice upon the balance of these steric and electronic effects. If we can introduce other constraints into the systems, we should be able to selectively control the inter-annular angle, and hence the degree of twisting in a molecular thread which incorporates two directly linked aromatic rings.

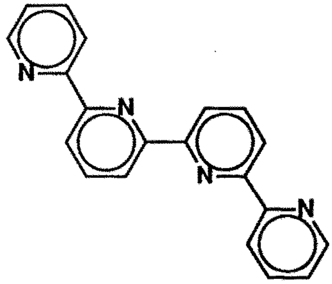
The introduction of donor atoms into the aromatic rings should allow the conformation of the two rings about the inter-annular C-C bond to be controlled by their interactions with metal ions. The simplest such hetero-biaryl is 2,2'-bipyridine (bpy, 5), which is the first of a series of oligopyridines linked through the 2-positions of the pyridine rings.



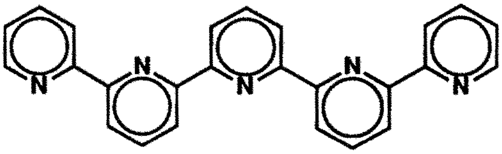
2,2′-bipyridine, bpy **5**



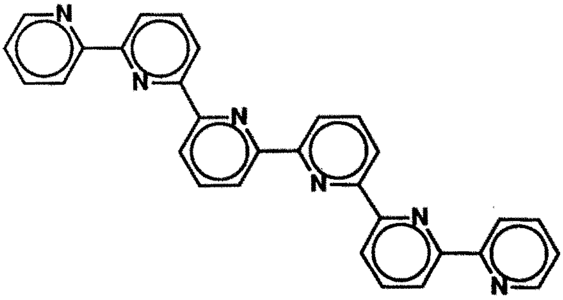
2,2′:6′,2″-terpyridine, tpy **6**



2,2′:6′,2″:6″,2‴-quaterpyridine, qtpy **7**

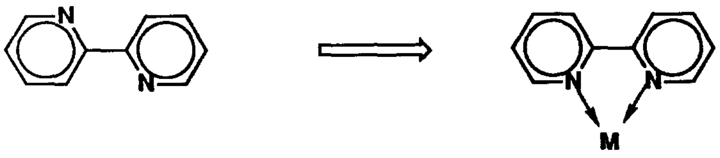


2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine, qpy **8**



2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2′′′′′-sexipyridine, spy **9**

In the solid state, bpy (and higher oligopyridines) adopt a near-planar conformation with a *trans* arrangement of the pyridyl rings about the inter-annular bond[13]. In solution, the situation is more complex, with free rotation about the inter-annular bond resulting in an *average* approximately orthogonal conformation[14]. Whatever the solution conformation of the bpy, a profound change occurs upon coordination to a metal centre. The adoption of the bidentate mode with both nitrogen atoms coordinated to the metal is strongly favoured by the thermodynamic chelate effect[15]. The adoption of this bonding mode results in the formation of an approximately planar *cis* conformation about the C-C bond **10**.

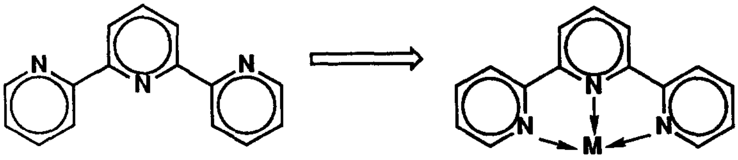


***cis* coplanar**

10

Additional small changes occur in the bond lengths and bond angles within the bpy ligand, but these do not need to be further considered here[14,16]. Whilst the interaction of the archetypal oligopyridine, bpy, with a metal ion supports our ideas of coordination-induced conformational change, the imposition of a planar *cis* conformation does not suggest that it will necessarily allow us to access the orthogonal or near-orthogonal arrangements needed for the formation of helically twisted systems.

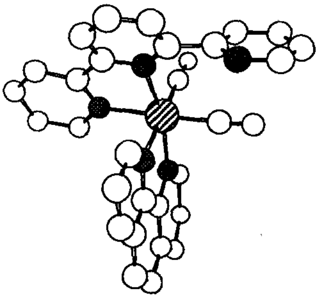
The situation is very similar when we consider the next higher oligopyridine, tpy. In the solid state, tpy and its derivatives exist in the planar *trans, trans* conformation[17], but upon coordination to a metal ion the majority of complexes contain a terdentate planar *cis,cis* ligand **11**[18]. Once again, the conformational change resulting from coordination is profound, but this is not useful in inducing adjacent rings to adopt an orthogonal conformation.



***cis, cis* coplanar**

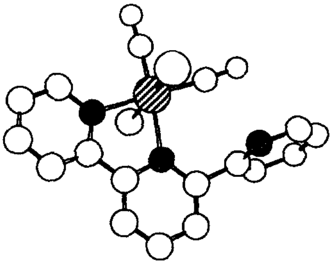
11

The situation is very different, however, if it is possible to force a tpy ligand into a bidentate mode. Although a number of compounds have been reported which are thought to contain bidentate tpy ligands[19], the first structurally characterised examples were [Ru(tpy)(CO)Br_2] **12** and [Ru(Htpy)(phen)$(CO)_2$]$^{3+}$ **13**[20,21]. The two rings of the tpy which are coordinated to the ruthenium are in a near-planar *cis* conformation; however, the non-coordinated ring is now no longer coplanar with the other two.



$[Ru(Htpy)(phen)(CO)_2]^{3+}$

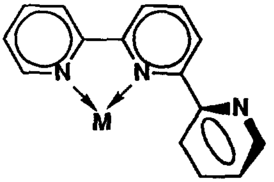
12



$[Ru(tpy)(CO)Br_2]$

13

This is a crucial observation. ***In general, if we only coordinate some of the potential donor atoms of an oligopyridine to a metal, there will be a non-planar arrangement about the C-C bond between coordinated and noncoordinated rings*** **14**. This is the vital principle which have used for the assembly of multiple-helical systems. There is a simple extension of this principle to polynuclear systems in which oligopyridines act as bridging ligands between two or more metal centres. ***In such a system there will again be a non-planar arrangement between rings coordinated to different metal centres*** **15**.



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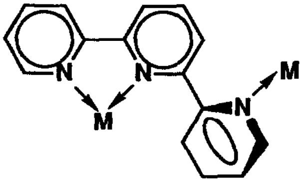

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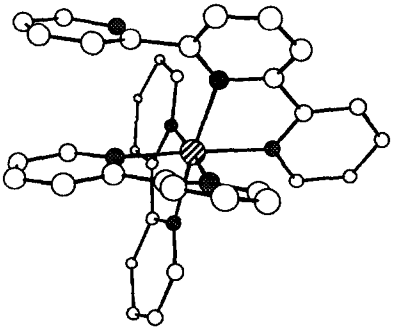
We now know all that is needed for the development of twisting in an oligopyridine, but we do not yet know how to control the coordination of some, but not all, of the donor atoms to a given metal centre. This is achieved by a consideration of the acceptor properties of transition metal ions, and a number of approaches may be utilised. In general, we may subdivide the two approaches into those involving labile metal ions, and those involving kinetically inert metal ions. To all intents and purposes, the latter may be limited to chromium(III), cobalt(III) and certain second and third row transition metal ions such as ruthenium(II).

2.1 Mismatches involving kinetically inert or kinetically labile metal ions

The use of kinetically inert metal ions is the simplest way to deliberately induce partial coordination of an oligopyridine ligand. The majority of examples of this type have involved the use of inert low spin d^6 ruthenium(II) centres, which have a strong crystal field dictated preference for six-coordinate octahedral or near-octahedral geometry. Let us consider the specific example of the reaction of $[Ru(bpy)_2Cl_2]$ with tpy. The two bpy and one tpy ligands present a total of seven nitrogen donor atoms. The ruthenium(II) centre will remain six-coordinate, and the bpy ligands are essentially non-labile. The result is that the tpy ligand is forced to adopt a bidentate bonding mode **16**[22].



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This cation also illustrates a number of other features which are a result of coordinating some, but not all, of the potential donor atoms of an oligopyridine. Firstly, as expected, the non-coordinated pyridine ring is not coplanar with the remaining 'bpy' position of the tpy ligand; in fact, the two planes are twisted at approximately 50° with respect to one another. A second feature, which will recur many times, is the approximately coplanar arrangement adopted between the non-coordinated ring and one of the other aromatic rings in the cation. In this case, the non-coordinated ring lies approximately coplanar with and about 3.5Å from one of the rings of a bpy ligand. This graphitic type of arrangement is a feature which is found in many helical systems derived from oligopyridine ligands.

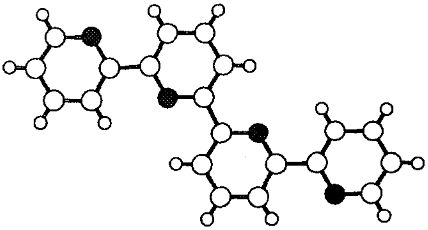
This principle may now be applied to the use of non-labile metal centres to selectively control the coordination of varying numbers of pyridine rings in oligopyridines. For example, the reaction of $[Ru(tpy)Cl_3]$ with qtpy under reducing conditions gives $[Ru(tpy)(qtpy)]^{2+}$ with a terdentate qtpy ligand bearing a non-coordinated pyridyl ring, whilst reaction with qpy under similar conditions yields

$[Ru(tpy)(qpy)]^{2+}$ with a terdentate qpy bearing a non-coordinated 2,2'-bipyridyl group[22]. We shall return to the consequences of non-coordinated multidentate groups and the use of labile metal centres shortly.

Labile metal ions undergo facile ligand replacement processes. Although the formation of complexes with multidentate ligands is driven by the chelate effect, it is no longer possible to rely upon the use of other multidentate ligands to 'block' coordination sites. However, this is not to say that labile metal ions do not exhibit favoured geometries, and the ease of ligand displacement may be utilised in allowing a given metal-ligand system to reach a thermodynamically favourable (or at least a compromise) minimum.

3. 2,2':6',2":6",2"'-QUATERPYRIDINE (QTPY)

The ligand qtpy is planar with a *trans, trans, trans* conformation in the solid state **17**[23] and could act as a planar quaterdentate **18**, a terdentate with a non-coordinated pyridine **19**, or as a bidentate with either two non-coordinated pyridines **20** or a non-coordinated bipyridine **21**.



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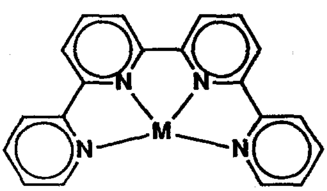
The planar quaterdentate mode will be favoured by a metal ion which has a preference for octahedral or square-planar geometry. In the case of an octahedral centre, the ligand will occupy the four equatorial sites. This is indeed the case, and the majority of complexes of qtpy contain a near-planar ligand in such an environment. This is found for the complex cations $[Ni(qtpy)(MeCN)_2]^{2+}$ **22** and $[Pd(qtpy)]^{2+}$ **23**[23,24] When a metal ion has a preference for square-planar or octahedral geometries, complexes with qtpy almost invariably contain an approximately planar quaterdentate ligand. This over-rides any effects associated with ionic radius, and such a mode is observed with copper(II) (r = 0.73Å)[25], cobalt(III) (r = 0.61Å)[26], cobalt(II) (r = 0.745Å)[26], nickel(II) (r = 0.69Å)[17], chromium(III) (r = 0.615Å)[27] and palladium(II) (r = 0.64Å)[24].



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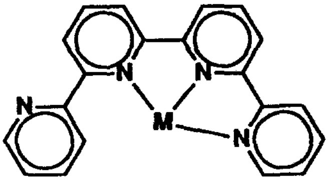

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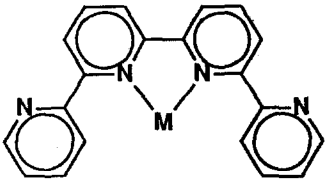

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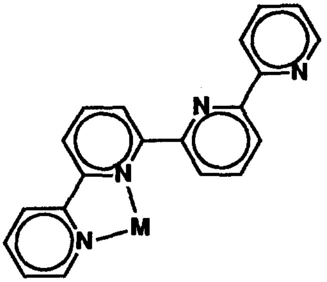

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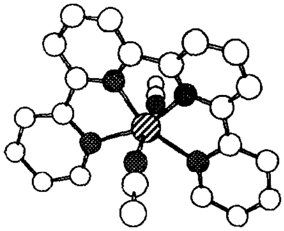

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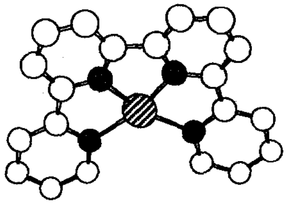

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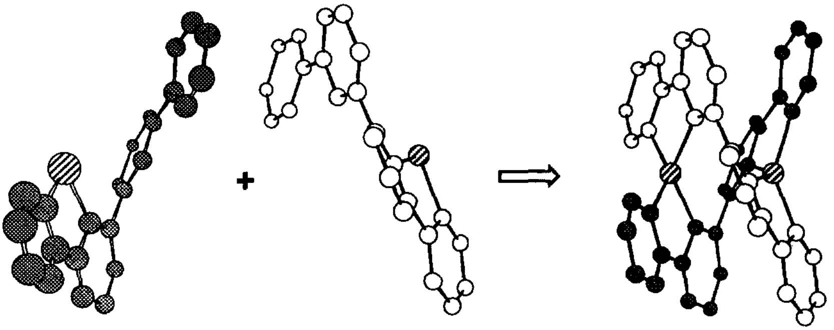
If a metal ion is too small for the coordination cavity resulting from the all *cis* conformation of the ligand it is expected to coordinate to only some, but not all, of the donor atoms. Similarly, if a metal ion is too large for the coordination cavity in the all *cis* conformation, twisting should occur to minimise unfavourable steric interactions. Clearly the range of ionic radii accessed above with first and second row transition metal ions is insufficient to induce anything other than a quaterdentate coordination mode. Coordination of qtpy to a larger metal ion with a preference for a high coordination number also results in the formation of a complex containing a planar quaterdentate qtpy ligand, as seen in the complex cation $[Y(qtpy)(NO_3)_2(H_2O)]^+$ in which the yttrium(III) centre (r = 1.075Å) has no ligand field imposed geometries, but has a charge-imposed preference for higher coordination numbers. The qtpy and the water ligand form a pentagonal planar arrangement about the metal centre[28].

The situation is rather different if we consider relatively large metal ions of low charge. In these cases, the steric constraints may favour the formation of complexes in which only some of the donor atoms are coordinated. If no ligand field effects are operative, as with main group metal ions, or transition metal ions with d^0, d^5 or d^{10} configurations, the disposition of the donor atoms about the metal centre should be according to VSEPR rules[29]. A d^{10} metal ion such as copper(I) (r = 0.60Å) has a sterically imposed preference for a tetrahedral arrangement of four ligands. If such a metal ion coordinated to the terminal two rings of a qtpy ligand the coordination of the remaining two to the same metal ion in a planar manner is disfavoured. Furthermore, inter-annular twisting will not allow the qtpy ligand to distribute the donor atoms to the vertices of a tetrahedron about a single metal centre. Accordingly, a structure in which the qtpy is bidentate with a non-coordinated bpy group is anticipated and in which there is a major twisting between the two bpy portions of the ligand. Whereas there is a steric restriction upon the non-coordinated bpy coordinating to the *same* metal as the remainder of the ligand, there is, however, *no* restriction upon its coordinating to a second metal, or indeed to a second {Cu(qtpy)} fragment. It is now possible for the metal ion to achieve a *pseudo-tetrahedral* arrangement, with the coordination sphere consisting of two bidentate bpy groups from each of two qtpy ligands. *The natural and unavoidable consequence is the formation of a dinuclear double-helical complex* **24**.



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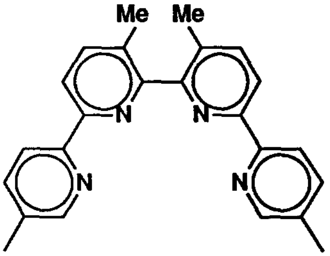
The difficulty lies in judging the magnitude of the *steric* preference of the copper(I) centre for the tetrahedral arrangement; there is no *electronic* preference for any geometry, and a planar arrangement about the metal is possible. The first example of this deliberate strategy was applied by Lehn and co-workers, who argued that the possibility of a planar arrangement could be precluded by the introduction of sterically demanding substituents at the junction between the two bpy ligands. They achieved this with the ligand **25** which forms a double-helical complex cation $[Cu_2(\mathbf{25})_2]^{2+}$ upon reaction with copper(I)[30-32]. It was suggested that the assembly of the helix was a consequence of the steric interactions between the methyl groups in the 5' and 3" positions. Support for this came from the observation that although the copper(II) complex of **25** was mononuclear, there was a considerable distortion from planarity within the ligand, which exhibited an inter-annular twist of 31° between the two central rings. Electrochemical investigations have established that the mononuclear copper(II) and dinuclear copper(I) complexes may be inter-converted.



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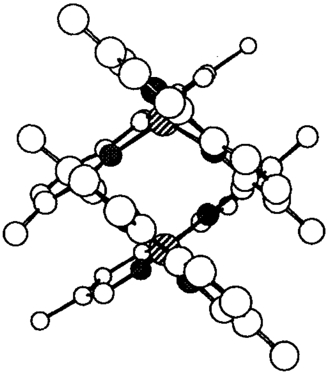

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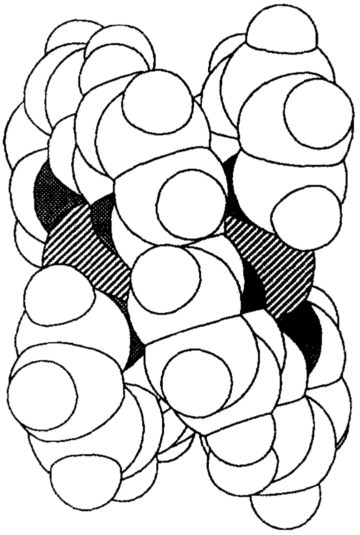
More recently, we have shown that the methyl substituents are not essential for the formation of the double-helix, and the reaction of qtpy with $[Cu(MeCN)_4]^+$ results in the formation of the double-helical cation $[Cu_2(qtpy)_2]^{2+}$ **27**[33]. The role of the substituents is to control the pitch of the helix and the metal-metal distance; in **27** the Cu...Cu distance is 3.17Å whereas in **26** it is 3.90Å. These differences arise from the steric repulsions between the methyl groups increasing the twisting about the central inter-annular bond of each ligand; in **27** this angle is between 35° and 40°, whereas it increases to 75° in **26**. Interestingly, the larger silver(I) cation (r = 1.00Å) also reacts with qtpy to form a dinuclear double-helical cation **28**. Most remarkably, the Ag...Ag distance of 3.107Å is actually shorter than the Cu...Cu distance in **27**. This is a consequence of a subtle series of interactions. The larger silver(I) cation leads to longer Ag-N distances of 2.2-2.4Å (*c.f.* Cu-N, 1.97-2.1Å). The consequence of this is a larger twisting about the central inter-annular bond than in **27** (45°)[33].



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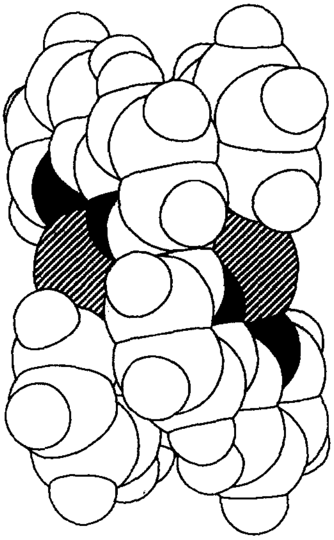

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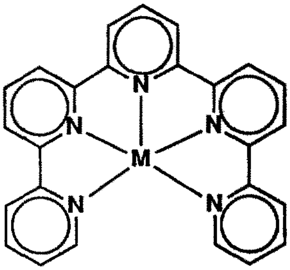
These complexes also exhibit approximately coplanar arrangements of pyridine rings from the two different ligands. In the cases of **26** and **27** the centroid-centroid distances are in the range 3.6-3.9Å and are short enough to be viewed as graphitic, but in **28** the shortest such contact is 4.5Å, although there is a short edge-edge contact of 3.5Å. The importance of such stacking interactions is unclear, and we are uncertain whether the interaction is a key feature in the assembly of the double-helix, or whether it is merely a natural consequence of the adoption of such a structure.

We have now seen the important feature of self-assembly. The formation of the double-helical complex is a natural consequence of the correct matching of coordination properties, and no other external factors are involved. A helix is, of course, chiral, but the self-assembly in an achiral environment necessarily gives rise to equal amounts of both enantiomers.

4. 2,2':6',2":6",2"':6"',2""-QUINQUEPYRIDINE (QPY)

The ligand qpy differs from qtpy in that if it uses all of its donor atoms, it cannot be accommodated in any of the regular metal ion geometries (tetrahedral, square-planar or octahedral). The ligand could coordinate to a metal ion as a near-planar quinquedentate, **29**, as a quaterdentate with one non-coordinated pyridine, **30**, as a terdentate with two non-coordinated pyridines, **31** or as a terdentate with a non-coordinated bpy, **32**. Each of these coordination modes might be favoured by differing metal ions. The quinquedentate mode **29** will be favoured by metal ions which have no ligand field imposed preference for a particular geometry, whereas the quaterdentate mode **30** will be associated with square-planar or octahedral centres. The two terdentate modes **31** and **32** will also be associated with octahedral or square-planar centres, with **32** being favoured upon steric grounds.



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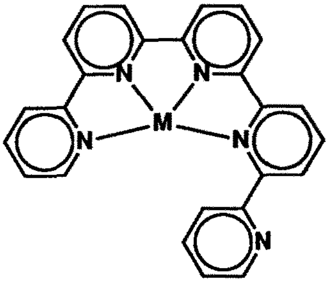

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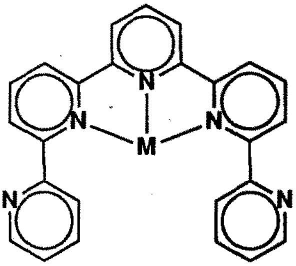

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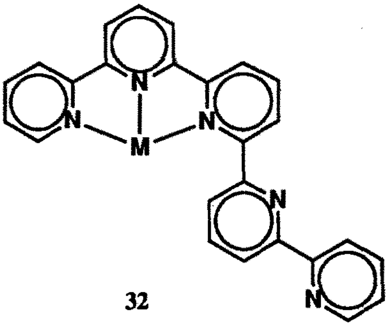

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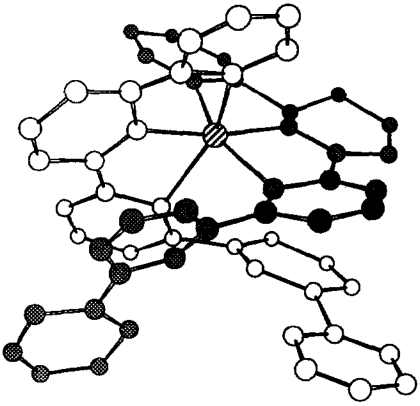
The bonding mode indicated in **32** is crucial to the formation of double-helical complexes. If the metal ion in **32** has a preference for an octahedral geometry, a second qpy ligand could act as a terdentate to complete the coordination requirement, **33**. Once the octahedral centre has coordinated to the qpy, two non-coordinated bpy groups are left correctly oriented for coordination to a metal ion with a requirement for a coordination number of four (or more if other ancillary ligands are involved) **34**. The coordination of the bpy groups to the second metal ion is driven by the chelate effect and is highly favourable. Once again, the inescapable effect is the formation of a dinuclear double-helical complex. There are some significant differences in the behaviour of qpy and qtpy. In the formation of double-helical complexes with qtpy, the two metal centres were in identical environments and no metal-ligand recognition imposed selectivity could be envisaged. In contrast, the two binding sites in a double-helix derived from two qpy ligands as described above differ; one will favour a six-coordinate metal ion, the other will favour a four-, five- or six-coordinate centre. This ultimately allows the selective synthesis of heterometallic systems.



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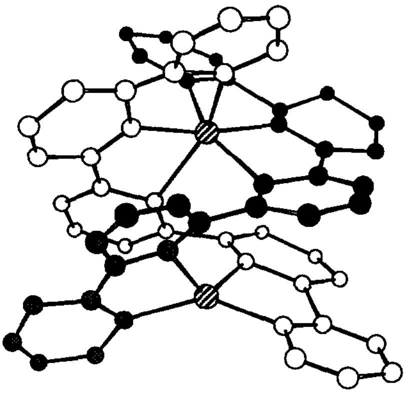

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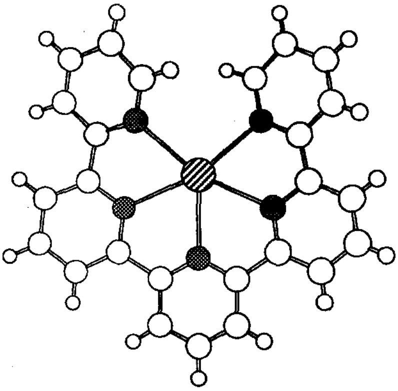
One of the beauties of working with qpy and the higher oligopyridines is the insolubility of the free ligands in most solvents. It is very easy to determine whether the ligand is successfully coordinating to a metal by simply stirring a suspension of the ligand with a solution of an appropriate metal salt. If the ligand dissolves, reaction has occurred. To all intents and purposes, the inorganic chemist is a passive observer of this process - all of the information required for the assembly of the complexes lies in the coordination preferences of the metal ions and the ligands. This is the essence of a self-assembly process, as seen in the formation of the double-helical complexes with qtpy.

4.1 Helical and non-helical complexes

We shall initially consider the quinquedentate bonding mode **29**. This will occur with a metal ion which has no strong geometrical preference and which is the correct size for the cavity formed by the all-*cis* conformation of the pyridine rings. The radius of this cavity is about 1Å. These requirements are met by the d^{10} silver(I) cation, and upon stirring a suspension of qpy with a solution of silver(I) hexafluorophosphate a clear solution is obtained. In the solid state the cation contains a quinquedentate ligand **35**[34]. In fact, the silver(I) ion is slightly too small for the cavity and the formation of the optimal Ag-N distances results in a steric interaction between H_6 and $H_{6''''}$. The effect is the development of a slight twisting of the ligand, **36**, to give what we term a mono-helical complex. Interestingly, there are no stacking interactions between the approximately planar cations in the solid state. The ^1H n.m.r. spectrum of a solution of this complex indicates that the ligand is in a highly symmetric environment, and suggests that the structure is maintained.



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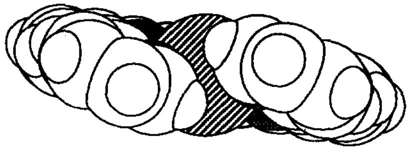

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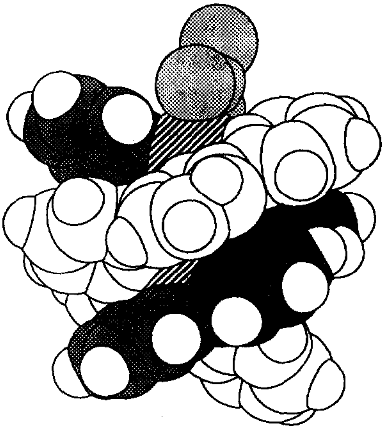
The formation of double-helical complexes will be favoured by the use of metal ions which have a preference for a six-coordinate geometry. First row transition metal dications exhibit such a preference, and it is generally observed that the reaction of qpy with such ions leads to the formation of double-helical complexes. Suspensions of qpy dissolve upon warming with methanolic solutions of nickel(II) or cobalt(II) acetate to give green-brown or orange solutions respectively[35-37]. Crystalline products from these reactions exhibit fast atom bombardment spectra containing ions corresponding to $[M_2(qpy)_2(OAc)]$, suggesting structures in which a double-helix is formed with one six-coordinate metal ion coordinated to a tpy portion of each ligand and a second metal ion coordinated to the two bpy parts and also to an acetate group. This is indeed the structure adopted, **37**, with a bidentate acetate ligand completing the coordination sphere at a second six-coordinate site. In each case the metal ions are 4.4-4.5Å apart and the double-helical ligand array is achieved by a series of twists about inter-annular C-C bonds within each ligand. As expected, the major twists of 58-60° occur between the bpy and tpy portions of each ligand with smaller deviations from planarity between other rings. Approximately parallel arrangements of rings of the two ligands lying 3.2-3.4Å apart are a feature in both complexes.



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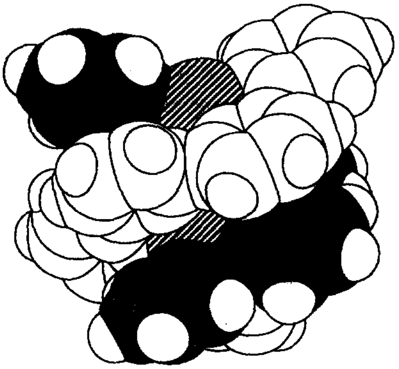

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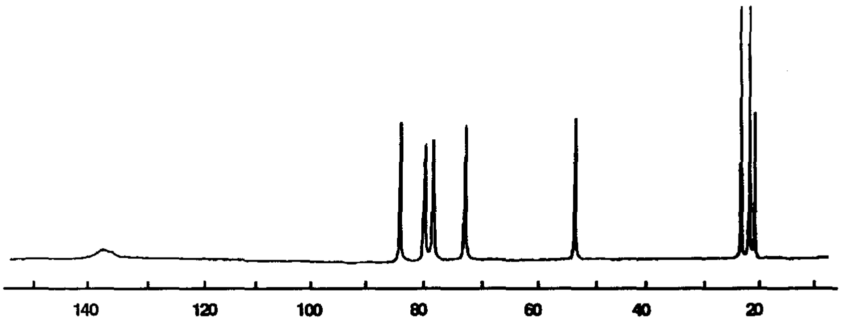
A very similar complex is formed with copper(II), and the only significant difference from those formed with cobalt(II) and nickel(II) is in the presence of a monodentate acetate ligand in the solid state[35,38]. The metal-metal distance of 4.50Å and other stacking and intra-ligand twisting features are essentially similar. Fast atom bombardment mass spectroscopy provides very strong evidence that cadmium and zinc also form 2:2 complexes with qpy.

These complexes contain double-helical cations in the solid state, but this does not necessarily mean that such a structure will persist in solution. A solution containing $[Cu_2(qpy)_2(OAc)]^{3+}$ exhibits two reversible metal-centred redox processes at modest potential, suggesting that the solution species is also dinuclear. This also indicates that, on the electrochemical time-scale at least, double-helical complexes containing one copper(I) and one copper(II) centre, or two copper(I) centres are also stable. In the preparation of $[Cu_2(qpy)_2(OAc)]^{3+}$ brown complexes were sometimes obtained, and these were found to be identical to the mono-reduced species obtained electrochemically. Mass spectroscopy confirmed the presence of the $[Cu_2(qpy)_2]$ structural unit, and the solid state structure established the formation of a double-helical cation in which the copper(II) centre was six-coordinate (with two tpy units) and the copper(I) was four coordinate, with two bpy units, **38**. This is exactly the structure we predicted earlier. The facile reduction of $[Cu_2(qpy)_2(OAc)]^{3+}$ is undoubtedly associated with the distorted tetrahedral arrangement of the two bpy ligands around the five-coordinate copper(II) centre[35,38]. Although copper(I) is a larger ion than copper(II), the increased Cu-N distances are accommodated by a change in the twisting between the bpy and tpy parts of each ligand; in the {Cu(II),Cu(II)} complex these angles are 51-55°, whereas they reduce to ≈48° in the mixed oxidation state compound. This is associated with a reduction in Cu...Cu distance from 4.50Å to 3.96Å. Once again, stacked aromatic rings are a feature of this complex. Clearly, in the case of the copper complexes the double-helical structure persists in solution and over a range of oxidation states.

In the case of the double-helical complexes with other metal ions, the situation is by no means so clear. The bulk of the data available refers to the cobalt(II), nickel(II) and iron(II) complexes. Solutions of $[Co_2(qpy)_2(OAc)]^{3+}$ show a series of ligand-centred reductive processes, but do not exhibit the facile oxidation of the six-coordinate centre to cobalt(III) which might be expected upon ligand field grounds. However, the *paramagnetic* solutions of $[Co_2(qpy)_2(OAc)]^{3+}$ salts exhibit well-resolved paramagnetically shifted ^1H n.m.r. spectra in which only nine resonances are observed in the range 20 to 140 ppm **39**. The ligand is in a highly symmetric environment, and in fact the solution species is a mononuclear seven-coordinate species with two axial solvent molecules **40**[39,40]. It is this seven-coordinate species which is resistant to oxidation. In the presence of chloride ion, the solution species is $[Co(qpy)Cl_2]^+$, and this illustrates the need for innocent anions in the case of systems which show dynamic mono-helix double-helix interconversions[37].



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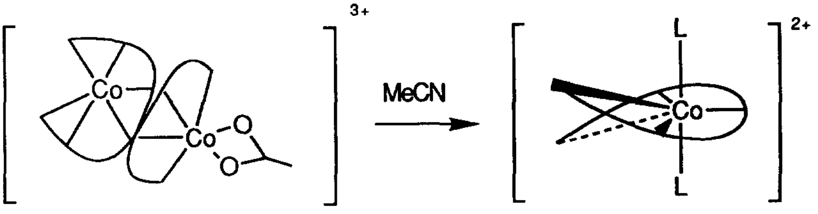

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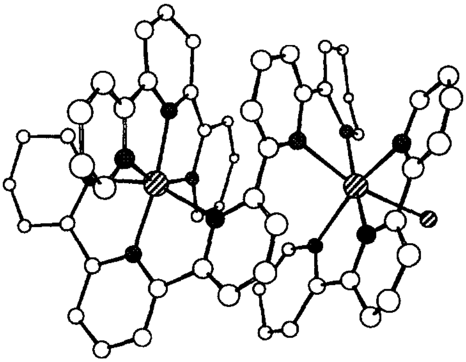
Solutions of iron(II) complexes of qpy also exhibit paramagnetically shifted ^{1}H n.m.r. spectra with only nine resonances, suggesting a similar seven-coordinate solution species might be present[41]. In contrast, solutions of $[Ni_2(qpy)_2(OAc)]^{3+}$ salts exhibit a larger number of resonances, indicating that the dinuclear structure is maintained in solution[41,42]. In conclusion, the double-helical structure of the $[M_2(qpy)_2X]^{n+}$ cations appears to persist in solution for M = Cu or Ni, but mono-helical solution species are formed with M = Fe or Co.

It is also possible to develop other types of dinuclear helical systems by matching up the number of available coordination sites at a metal with the donor properties of the ligand. An example of this is seen in the reaction of $[Ru(tpy)Cl_3]$ with qpy in reducing conditions. At a 1:1 stoichiometry, the product of this reaction is $[Ru(tpy)(qpy)]^{2+}$, in which the qpy ligand acts as a terdentate with a non-coordinated bpy group[22]. Reaction of $[Ru(tpy)(qpy)]^{2+}$ with a further equivalent of $[Ru(tpy)Cl_3]$ or the direct reaction of qpy with two equivalents of $[Ru(tpy)Cl_3]$ results in the formation of the dinuclear complex $[(tpy)Ru(qpy)Ru(tpy)Cl]^{3+}$, **41**[22,43].



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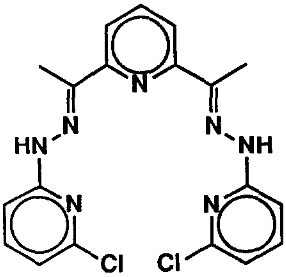
The qpy ligand acts as a bidentate bpy donor to one metal, and as a terdentate tpy donor to the other. The two metal centres are 5.38Å apart and do not interact significantly; the complex shows two reversible ruthenium(II) oxidation processes corresponding to the *RuN_6* and *RuN_5Cl* centres. There is the expected twisting (of 24°) between the tpy and bpy parts of the qpy ligand, which results in the development of a helical twist within this cation. The tpy ligands exhibit stacking interactions with the qpy ligand. This complex might be described as containing a dinuclear mono-helical cation.

4.2 Features controlling the assembly of helicates with *N*$_5$ donors

The considerable amount of data available for the qpy ligand allows us to probe the features leading to helication in some detail. We shall consider here the importance of metal-ion/cavity size, charge, substituents and preferred metal ion geometry.

We have shown that a metal ion which is the correct size for the cavity of qpy in the all-*cis* conformation and has no strong geometrical preference for a particular geometry, such as silver(I), gives rise to near-planar mononuclear complexes. If the cavity is made larger, or the metal ion is made smaller, we would expect some, but not all, of the donor atoms to be coordinated. This results in the development of interannular twisting in the ligand, and is the situation which leads to the formation of the double-helical $[Ag_2(qtpy)_2]^{2+}$ cations. We may probe this a little further, by increasing the coordination cavity of a qpy-type ligand by the introduction of sterically hindering substituents. The ligand that we chose was the hydrazone, **42** which acts as a *N*$_5$ donor comparable to qpy.



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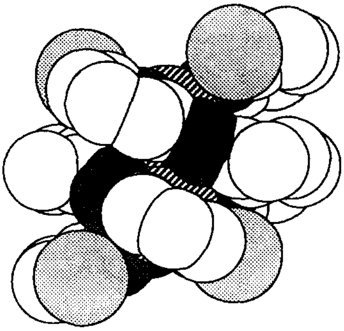

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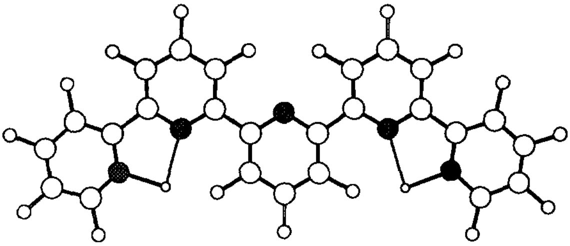
The repulsion between the chlorine substituents results in an opening out of the ligand and an increase in the effective coordination cavity in the all-*cis* conformation. Less-hindered ligands related to **42** have been shown to give rise to helical complexes with first row transition metal-ions,[44] and we considered that the interaction of **42** with silver(I) would provide a good test for our models of helication. The reaction of **42** with silver(I) results in the formation of a double-helical complex $[Ag_2(\mathbf{42})_2]^{2+}$ (**43**) in which each silver is in a distorted four-coordinate environment[45]. The helication results from the opening of the cavity and the subsequent coordination of each metal to only two of the nitrogen donor atoms available from each ligand. The metals lie 3.142Å apart, and short distances between planar aromatic rings are a noticeable feature of the cation.

These observations raise an interesting point regarding the use of sterically hindering substituents in the design of helicates. We saw earlier that the introduction of methyl groups at the central inter-annular bond of qtpy accentuated the twisting of the ligand; we now see that the introduction of substituents at sites *remote* from the site of twisting may also be involved in the helication of suitable ligands.

There is a close relationship between the charge and the ionic size of a metal ion. We have seen that it is possible to obtain helical complexes with unipositive and dipositive ions, and that the helication is a function of the coordination requirements and the ionic size of the metal ion. Simply bonding a qpy ligand to a charged centre is not sufficient to cause it to twist. This is seen in the formation of the dicationic species $[H_2qpy]^{2+}$ from the reaction of qpy with protic acids. The ^1H n.m.r. spectrum of this species indicates that it is highly symmetrical. In the solid state a number of interesting features are evident. Firstly, the cation, **44**, is planar, with a sequential *cis,trans,trans,cis* conformation about the inter-annular bonds[46]. The ligand splits into two Hbpy parts, with a central 'innocent' pyridine ring, rather than into a Htpy and a Hbpy part. The *cis* conformation is charge controlled, and reflects the 'chelation' of each of the two terminal bpy groups to a proton. The inter-annular bonds to the central ring are not affected by the proton, and adopt the expected *trans* conformation.



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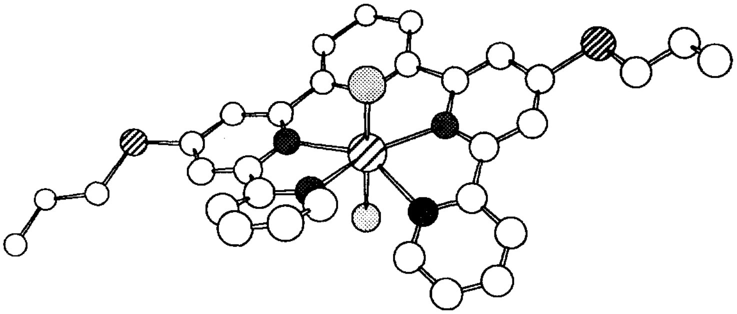
A second feature to note is that the cations $[H_2qpy]^{2+}$ form coplanar stacks within the crystal lattice, with the interplanar contacts lying within the range 3.51-3.69Å. It is significant to note that the bonding of the ligand to the proton results in a closing up of the interplanar contacts to distances typical of π-stacking interactions, and in very marked contrast to the longer distances (> 6Å) observed in the free ligand qtpy[23]. These results indicate that the development of an inter-annular twist within the ligand is not purely related to the charge build-up resulting from coordination. Similarly, if we regard the proton as the smallest possible metal ion, then they also suggest that the development of such a twist between coordinated and non-coordinated rings has a steric component.

Does the introduction of substituents onto the qpy ligand have any effect upon the formation of helicates? We saw earlier that the cobalt(II) qpy system was finely balanced regarding the formation of double- or mono-helical complexes, and that in solution the double-helical solid-state species was converted to a mono-helical one. The introduction of substituents remote from the cobalt(II) centre or the perceived site of helication has a similar effect. This was first observed in 1:1 adduct of cobalt(II) chloride with a qpy ligand bearing *n*-propylthio substituents in the 4' and 4''' positions[47]. The complex that was isolated was a *mononuclear* mono-helix with a seven-coordinate cobalt(II) centre in the solid state **45**. In this case, however, it is not clear whether the change to the mononuclear structure is a result of the introduction of the substituents, or the presence of the strongly coordinating counter-ion. We have previously shown that the presence of chloride ion is sufficient to transform double-helical cobalt(II) complexes of qpy to the mono-helical [$CoCl_2(qpy)$] species[37].



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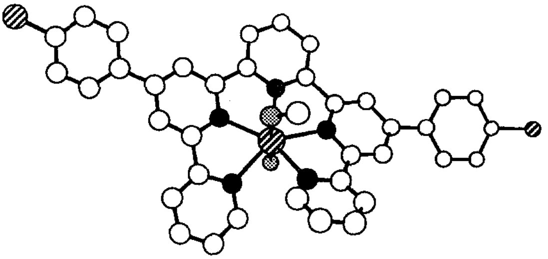
The reaction of cobalt(II) acetate with a series of 4',4'''-diaryl substituted qpy ligands (Ar_2qpy) in methanol provides a suitable reference point, as reaction with qpy under identical conditions yields the double-helical cations [$Co_2(qpy)_2(OAc)]^{3+}$. The products of the reactions with Ar = C_6H_5, 4-MeC_6H_4 or 4-ClC_6H_4 are all orange-yellow solids which only exhibit peaks assigned to mononuclear complexes in their fast atom bombardment mass spectra. This is strong evidence that these complexes are mononuclear in the solid state, and indeed, the solid state structure of the complex cation [$Co\{(4\text{-}ClC_6H_4)_2qpy\}(H_2O)(MeOH)]^{2+}$, **46**, confirms this[39]. The mononuclear complex exhibits a marked helical twisting of the quinquedentate ligand about the mean equatorial plane of the seven-coordinate cobalt(II) centre. In solution, all of these Ar_2qpy complexes retain the mononuclear structure. A number of cobalt(II) complexes of vinyl-substituted qpy ligands have been reported, but there are no convincing data regarding their constitution[47,48].



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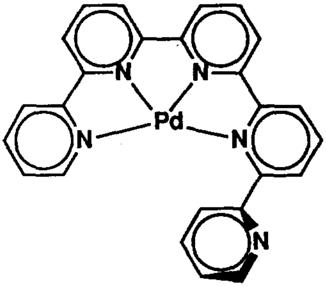
The situation is somewhat clearer with complexes of substituted qpy ligands with other metal ions. Double helical complexes are formed from Ar_2qpy and also 4',4'''-bis(methylthio) substituted ligands with copper, and both dicopper(II) and mixed oxidation state complexes may be isolated[49]. In each case fast atom bombardment mass spectra show the presence of the binuclear 2:2 species, and electrochemical studies reveal two separate redox processes. The redox potentials vary with the substitution pattern of the ligand. There is no evidence to suggest that anything other than the binuclear double-helical complexes exist in either the solution or the solid state phases.

A similar situation exists as far as the nickel(II) complexes are concerned, and all of the n.m.r. and mass spectroscopic data is consistent with the persistent presence of binuclear species in all phases. A solid state structural determination of the complex $[Ni_2\{4',4'''\text{-}(MeS)_2qpy\}_2(OAc)][PF_6]_3$ confirms the double-helical character of the cation[49].

In general, the presence of substituents in non-sterically demanding sites on qpy ligands does not appear to dramatically effect the assembly of double-helical complexes with suitable metal ions.

A final twist to the tale comes when we consider the interaction of a qpy ligand with a metal ion which has a very strong ligand-field imposed preference for a geometry which is not apparently compatible with the formation of a binuclear double-helicate. Palladium(II) is a d^8 metal ion with a very strong preference for square-planar four-coordination. We have previously seen that qtpy forms a near-planar four-coordinate complex in which the ligand acts as a quaterdentate[24]. The reaction of qpy with palladium(II) acetate gives pale yellow complexes which give ^1H n.m.r. spectra exhibiting 17 distinct resonances. The fast atom bombardment mass spectrum only exhibits peaks assigned to the 1:1 {Pd(qpy)} cation, and we took these pieces of data to be consistent with the formation of a mononuclear complex in which the qpy was quaterdentate with a non-coordinated pyridine ring **47**. However, the ^1H n.m.r. spectrum had some surprising features which were not fully compatible with this structure, the most notable being resonances assigned to H_6 of terminal pyridine rings (on the basis of coupling constants) occurring at δ 6.43 and 9.25.



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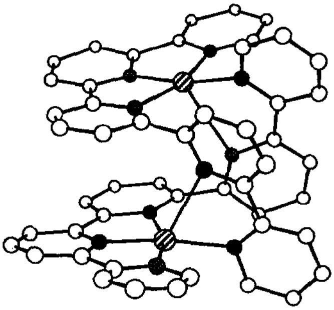

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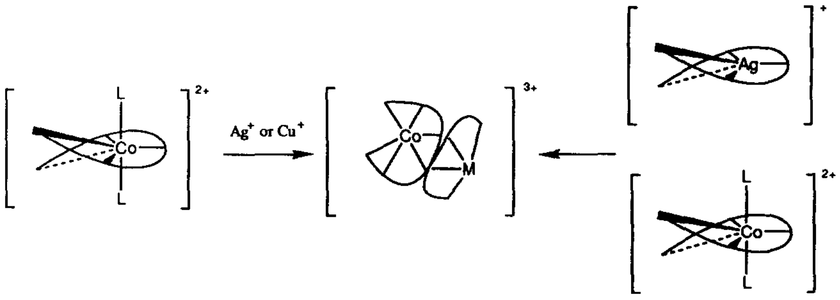
In the solid state the complex contains a binuclear double-helical cation $[Pd_2(qpy)_2]^{4+}$ **48**[24]. Each metal has an approximately planar arrangement of four nitrogen donors with Pd-N distances close to 2.0Å derived from three pyridine rings of one ligand and one terminal pyridine of the second ligand. The consequence of this is to place the remaining pyridine ring of each ligand close to the palladium which the unique terminal pyridine is coordinated to, at a Pd...N contact distance of 2.6Å. The cation could thus be regarded as a double-helix containing two five-coordinate square-based pyramidal palladium centres (with long axial distances) or two four-coordinate palladium centres with an essentially inert pyridine spacer. Whichever description is adopted, this is clearly an alternative way in which a double helix may be assembled with a metal ion with a geometrical preference which is not apparently ideally suited to helication. The Pd...Pd distance is 4.96Å, and this is achieved by a 70° twisting between the bpy and tpy parts of each ligand, and once again coplanar stacked aromatic rings at distances of 3.3-3.5Å are a feature of the structure.

4.3 Heterodinuclear and heteroleptic helicates

One of our interests has been the development of helicates in which two or more different metal ions are incorporated, or in which two different ligands selectively form complexes in which specific inter-ligand interactions may be maximised. Our initial studies rapidly convinced us that the statistical approach to the preparation of complexes of this type was unlikely to be successful. The reactions of qpy with mixtures of metal ions, or of two different qpy ligands with metal salts result in the formation of mixtures of complexes which proved to be inseparable. However, a consideration of the relative donor properties of the ligands and the acceptor properties of the metal ions proved to be more constructive.

We already knew that the total of ten donor atoms present in a double-helical array of two qpy ligands allowed the formation of mixed oxidation state complexes containing a six-coordinate copper(II) and a four-coordinate copper(I) centre. Can we use this to incorporate two *different* metal ions, one of which has a preference for six-coordination and one for four-coordination? A further constraint is that the system chosen must be relatively labile under the reaction conditions, to allow the interconversion of the various possible helical species which might be present. These conditions are met by the cobalt(II) complexes, which we have shown to be seven-coordinate mono-helical species in solution, but capable of adopting double-helical solid state structures.

Cobalt(II) is a d^7 ion with a modest ligand-field preference for octahedral geometry. Clearly the additional metal-ligand interactions combined with the relief of inter-ligand steric interactions is sufficient to allow the conversion of $[Co_2(qpy)_2(OAc)]^{3+}$, containing two six-coordinate cobalt(II) centres, to $[Co(qpy)S_2]^{2+}$, containing a seven-coordinate cobalt(II) centre, upon dissolution in a donor solvent S. We argued that it might be possible to reverse this process by the addition of a metal ion with a strong preference for four-coordination, which could occupy a site created by two bpy moieties from two qpy ligands and thus 'force' the cobalt(II) to occupy the remaining six coordinate site generated by the two tpy groups. In practice, this occurs simply by adding copper(I) or silver(I) salts to a methanolic solution of $[Co(qpy)(MeOH)_2]^{2+}$ **49**. Exactly parallel reactions occur with substituted qpy ligands. The stoichiometry of the reaction is such that the reaction with simple copper(I) or silver(I) salts results in the loss of cobalt(II)[40].



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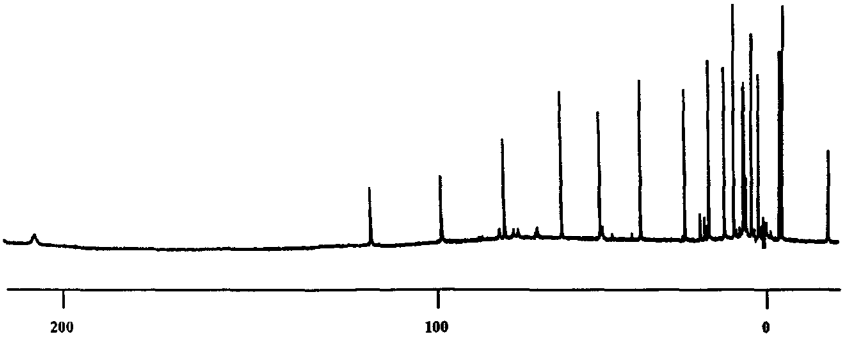
$$2[Co(qpy)(MeOH)_2]^{2+} + M^+ \rightarrow [Co(qpy)_2M]^{3+} + Co^{2+} + 2MeOH$$

However, the reaction of the seven-coordinate mononuclear cobalt(II) complex $[Co(qpy)(MeOH)_2]^{2+}$ with the five-coordinate mononuclear complex $[Ag(qpy)]^+$ is even more efficient, and results in the quantitative formation of the hetero-bimetallic double-helical complex $[CoAg(qpy)_2]^{3+}$ **50**. These new bimetallic complexes are readily characterised by fast atom bombardment mass spectroscopy and exhibit intense parent ions corresponding to the species $\{CoM(qpy)_2(PF_6)\}$. However, in the absence of a solid state structural determination, the most convincing confirmation of the formation of the mixed metal complexes comes from their paramagnetically shifted ^1H n.m.r. spectra. Whereas solutions of $[Co(qpy)(MeCN)_2]^{2+}$ in acetonitrile exhibit nine resonances in their ^1H n.m.r. spectra, those of $[CoAg(qpy)_2]^{3+}$ or $[CoCu(qpy)_2]^{3+}$ exhibit a total of 17 resonances, none of which correspond to those of the parent mononuclear cobalt(II) complexes nor to those of any copper(I), copper(II) or silver(I) solution species. The lowest field ^1H n.m.r. signals are now shifted downfield to below δ 200!



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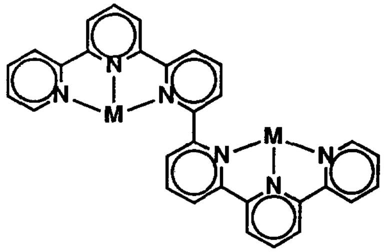
These represent the first systematic approaches to the synthesis of hetero-bimetallic double-helical species, and clearly indicate that the approach is a powerful one, and is capable of extension to the preparation of complexes incorporating a variety of other metal ions.

Attempts to prepare heteroleptic complexes by this approach have not yet been successful. In principle, the reaction of the two cobalt solution species $[Co(qpy)(MeOH)_2]^{2+}$ and $[Co(Xqpy)(MeOH)_2]^{2+}$ (where Xqpy is a substituted qpy ligand) could result in the formation of the double-helical solid state species $[Co_2(qpy)(Xqpy)(OAc)]^{3+}$. To date, we have not yet discovered a system which gives rise to such a solid state species[49]. In a similar manner, the reaction of the mononuclear complexes $[Co(qpy)(MeOH)_2]^{2+}$ and $[Ag(Xqpy)]^+$ might be expected to give the bimetallic species $[CoAg(qpy)(Xqpy)]^{3+}$. Once again, we have not yet succeeded in isolating such compounds as the clean products of such reactions. The hetero-dinuclear systems appear to be sufficiently labile that statistical mixtures of $[CoAg(qpy)(Xqpy)]^{3+}$, $[CoAg(qpy)_2]^{3+}$ and $[CoAg(Xqpy)_2]^{3+}$ are obtained.

5. 2,2':6',2":6",2"':6"',2"":6"",2""'-SEXIPYRIDINE (SPY)

When we consider the next oligopyridine, 2,2':6',2":6",2"':6"',2"":6"",2""'-sexipyridine (spy), the number of potential bonding modes increases considerably. However, a number of constraints restrict those actually observed. A completely planar *cis,cis,cis,cis,cis* sexidentate conformation is sterically disfavoured as it would result in significant interactions between the 6-positions of the terminal rings. Indeed, the consequence of these interactions is to force the spy ligand into a helical conformation reminiscent of a helicene. We originally envisaged that spy would act as a binucleating ligand with a twist about the central inter-annular bond to generate two tpy metal-binding sites, **51**.



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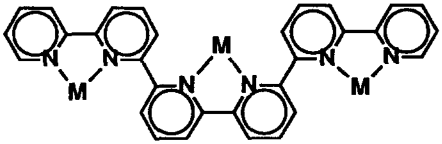
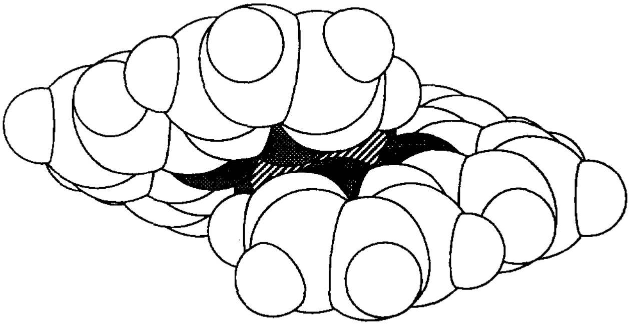


52

Such a coordination mode will result in the formation of a double-helical array in which the coordination requirements of two six-coordinate metal centres are fully satisfied by the 12 donor atoms of the ligands. It is also possible to envisage a bonding mode in which the spy acts as a trinucleating ligand, and presents three separate bpy binding sites with *two* significant inter-annular twists **52**. Such a mode will be capable of accommodating three four-coordinate centres in a double-helical array.

The coordination behaviour of spy ligands does not appear to be dependent upon the pattern of substitution, and we have demonstrated that spy, 4',4""-$(MeS)_2$spy and 4',4""-Ar_2spy behave in identical manners[50]. The free ligand spy is assumed to possess the all-*trans* conformation about each of the inter-annular C-C bonds, and this has been reported to be the case for 4',4''''-(PrS)$_2$spy in the solid state[48].

Although spy and derivatives cannot act as planar sexidentate ligands, there is no restriction to the adoption of a helically twisted sexidentate coordination mode. Such a mode will be observed with large metal ions which have no ligand field imposed geometrical preference. This is observed in the reaction of spy with europium(III) nitrate, when a complex containing the cation [Eu(spy)(NO$_3$)$_2$]$^+$ is obtained[51]. The complex only exhibits 1:1 peaks in its fast atom bombardment mass spectrum, and the ^{1}H n.m.r. spectrum is sharp and well-resolved and paramagnetically shifted by a mixture of contact and pseudo-contact mechanisms and contains ten resonances over a range from δ 24.5 to δ 0.4. This is compatible with a symmetrical average solution structure. Solutions of the complex are strongly luminescent with an intense red emission (maxima, 591, 597, 614 and 622 nm). In the solid state the mononuclear cation [Eu(spy)(NO$_3$)$_2$]$^+$ is present, which contains a ten-coordinate europium centre. The spy is sexidentate and helically wrapped around the metal centre, with the four remaining coordination sites occupied by axial bidentate nitrate ligands. The helical {Eu(spy)} core is shown in **53**. Preliminary experiments have indicated that the other lanthanide elements form similar 1:1 complexes with spy[52].



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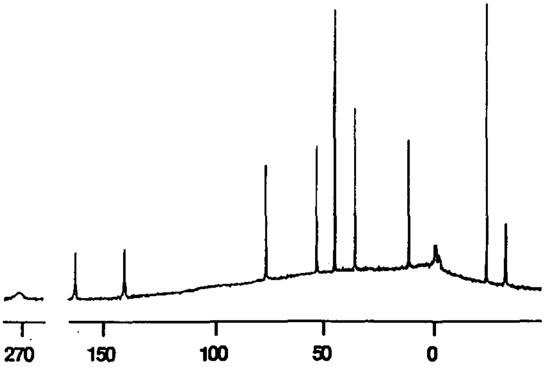
In contrast, the first row transition metal dications manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II), together with cadmium(II) and mercury(II) form double-helical 2:2 complexes with spy and substituted derivatives which contain two six-coordinate metal centres[50,52-54]. In each case, the complexes exhibit high intensity peaks assigned to the species {M$_2$(spy)$_2$(PF$_6$)$_n$} in their fast atom bombardment mass spectra. The electrochemical behaviour of the manganese, iron and cobalt complexes are fully in accord with the metal ions being in an M(tpy)$_2$ environment. The diiron(II) and dicobalt(II) complexes each exhibit two oxidation processes corresponding to the formation of mixed oxidation state and dimetal(III) complexes. The observation of the two oxidation processes provides strong support for the double-helix persisting in solution. We have never observed mononuclear-binuclear inter-conversions involving spy complexes. The zinc, cadmium and mercury complexes are diamagnetic and exhibit ^{1}H n.m.r. spectra fully in accord with the double-helical formulation. More interestingly, the paramagnetic dicobalt(II) and diiron(II) complexes exhibit well-resolved paramagnetic n.m.r. spectra; the spectra of $[Co_2(spy)_2]^{4+}$ **54** and $[Fe_2(spy)_2]^{4+}$ each exhibit ten resonances, consistent with the symmetrical double-helical structure. It is suggested that 4',4''''-(PrS)$_2$spy forms both 1:1 and 1:2 complexes with cobalt(II) chloride, although little is known about these compounds[48].



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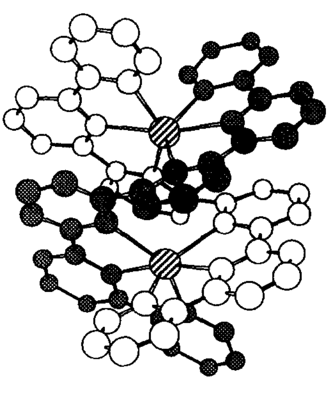
The solid state structure of the complex cation $[Cd_2(spy)_2]^{4+}$ is shown in **55** together with a space-filling representation in **56**[53,54].



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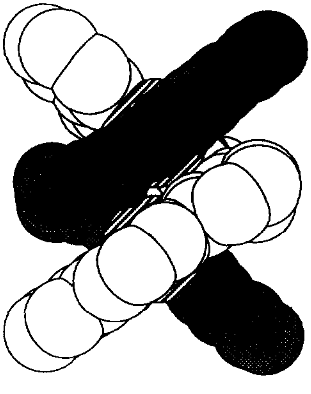
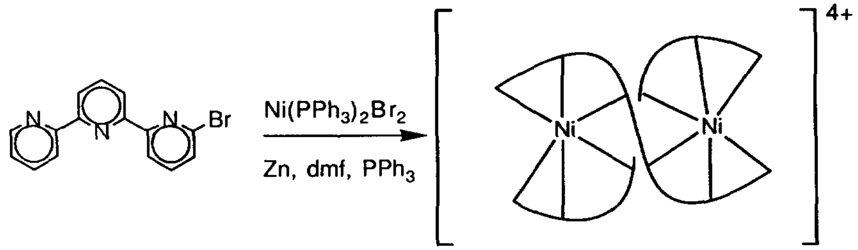


56

The cation adopts the expected binuclear double-helical structure, with each of the metal ions in a six-coordinate environment composed of a tpy fragment from each ligand. The Cd...Cd distance is 4.173Å, and the principal twisting is of 57° about the inter-annular bond connecting the two tpy portions of each ligand. There are stacking interactions between approximately coplanar portions of the two ligands in the double-helical array. The ^{1}H n.m.r. spectrum of a solution of $[Cd_2(spy)_2]^{4+}$ confirms the high symmetry of the solution species, and the upfield shifting of one of the terminal H_6 resonances which lies in the shielding region of a pyridine ring of the other ligand provides strong evidence for the maintenance of the double-helical structure in the solution phase.

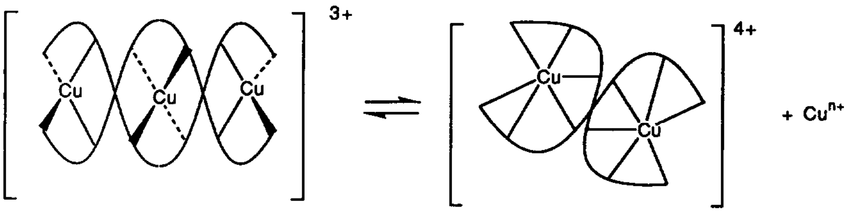
We have made many attempts to resolve the mono- or double-helical cations obtained by the coordination of oligopyridines to metal ions. In no case have we met with any success, nor have we had any marked success from the use of chiral h.p.l.c. methods. This suggested that the helical complexes might be sufficiently labile that they racemise rapidly upon the preparative chemical time-scale. The only data we have to suggest that the complexes are not racemising comes from an experiment involving solutions of racemic $[Cd_2(4',4''''\text{-}\{MeS\}_2spy)_2]^{4+}$ in the presence of the (S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol. This chiral compound forms two diastereomeric contact pairs in solution, and some of the aromatic resonances of the 4',4''''-{MeS}$_2$spy ligand were observed to split into two in its presence. Interestingly, no splitting of the methylthio resonance was observed. In no case have we observed any spontaneous resolution of helical complexes upon crystallisation.

The high stability of the double-helical complexes of spy has been utilised in the development of a high-yield synthesis of the ligand, which is isolated as the complex $[Ni_2(spy)_2]^{4+}$, which may be demetallated with NaCN to give the free ligand[55]. The reaction of 6-bromo-2,2';6',2''-terpyridine (**57**) with $[Ni(PPh_3)_n]$ in dmf results in a stoichiometric coupling to give spy and nickel(II); the latter coordinates to the spy to generate the racemic complex $[Ni_2(spy)_2]^{4+}$ (**58**) which may be readily isolated as its hexafluorophosphate, perchlorate or chloride salts. This may be regarded as a thermodynamic template effect[56].



57 58

The third bonding mode which spy may adopt involves the formation of a trinuclear complex with three four-coordinate metal centres. We first became aware of this possibility when we investigated the electrochemical behaviour of the dicopper(II) cation $[Cu_2(spy)_2]^{4+}$. Instead of observing the expected two reductions the electrochemical behaviour was complex and consistent with major structural changes upon reduction. In an attempt to understand this, we also prepared a copper(I) complex of spy and found that it was a trinuclear species of stoichiometry $[Cu_3(spy)_2]^{3+}$. In contrast to the behaviour of the copper qpy complexes, the mixed oxidation state complexes are not isolable with spy ligands. The oxidation of the first copper(I) centre in brown $[Cu_3(spy)_2]^{3+}$ results in loss of copper and the ultimate formation of the green $[Cu_2(spy)_2]^{4+}$ cation **60**[54]. The trinuclear cation $[Cu_3(spy)_2]^{3+}$ (**59**) is diamagnetic, and the ^{1}H n.m.r. spectra of its salts exhibit the expected ten environments; oxidation results in the formation of the e.s.r. active paramagnetic dicopper(II) complex. The addition of an excess of copper(I) to the dicopper(II) species **60** regenerates the tricopper(I) complex **59**.

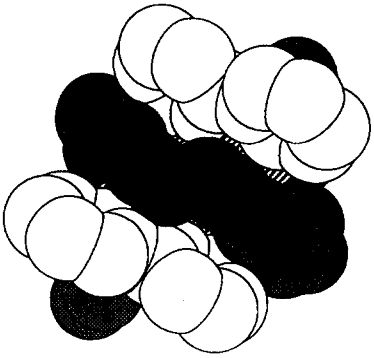


Brown diamagnetic

Green paramagnetic

59

60



60

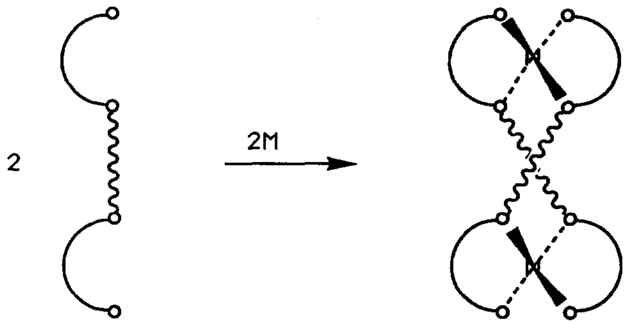
The reaction of spy with silver(I) also results in the formation of a trinuclear complex $[Ag_3(spy)_2]^{3+}$. On the basis of the differences in size between copper(I) and silver(I) we originally thought that this could not possess the double-helical structure **60**. However, in view of the formation of very similar double-helical complexes of copper(I) and silver(I) with qtpy,[33] it is possible that they possess similar structures.

6. HIGHER OLIGOPYRIDINES

To date very little is known about the coordination chemistry of the higher oligopyridines. To a great extent this reflects the difficulties which have been associated with their synthesis. As good synthetic routes to these compounds are now becoming available, their coordination chemistry is expected to follow. To date, the only published report of a complex of a higher oligopyridine is the mention of an incompletely characterised 1:1 or 2:2 adduct of cobalt(II) chloride with 4',4",4"",4"""-tetrakis(methylthio)-2,2':6',2":6",2"':6"',2"":6"",2""':6""',2"""-septipyridine[48]. We and others are currently investigating the coordination behaviour of such ligands.

7. ALTERNATIVE APPROACHES TO MULTIPLE-HELICATING SYSTEMS

In the preceding sections we have seen the ways in which the interplay of metal-ion acceptor properties and ligand donor properties may be used to control the development of helicity within oligopyridine complexes. In the most general terms, we can identify the features in a ligand which are required for the formation of a recognisably helical complex. The basic requirement is a ligand which may be separated into two or more separate metal-binding domains, each of which is bidentate or of higher denticity[57]. The interconnection of these metal-binding domains must be such that a degree of twisting is possible, sufficient to allow the formation of the helical structure upon coordination. These requirements are illustrated in **61** in which two bidentate metal-binding features are linked; upon coordination to two four-coordinate metal ions the double-helical structure **62** is obtained. The inter-connection between the metal-binding domains may be by a direct inter-annular bond, or by a more complex spacer group. In principle, there is no restriction to the presence of polydentate binding domains, but the additional resultant kinetic and thermodynamic stability of the complexes makes this a desirable feature.

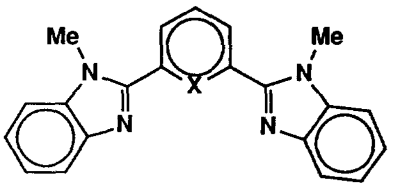


61 62

The key feature in all of the complexes discussed to date is a direct inter-annular bond between two heteroaromatic rings at the site of helication. In the following section we will discuss the extension to ligand systems in which the site of helication is at an inter-annular bond between a heteroaryl and an aryl ring, and in the final section we shall briefly consider more flexible ligands in which the twisting required for helication occurs at an sp^3 carbon or a heteroatom centre.

7.1 Aromatic and relatively rigid spacers

The concept of introducing aromatic spacer groups between metal-binding sites is a natural development of oligopyridine chemistry. The direct link is provided by the cation $[Pd_2(qpy)_2]^{4+}$ (**48**) which we could view as containing two four-coordinate palladium(II) centres with a non-coordinated pyridine spacer. Note also, that this is a rare example of the generic class in which we have terdentate and monodentate binding domains.



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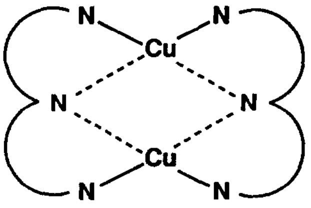

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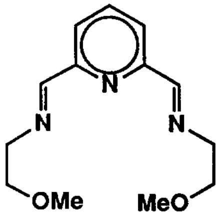
There are a very few other examples of double-helical complexes in which the helicating ligand formally acts as a monodentate donor to one site. In general, the formal description is not satisfactory, and a central pyridine donor atom is found to act as a bridging group with a M...N...M interaction. This is found with the dicopper(I) complex of the potentially terdentate ligand **63** (X = N)[58,59]. The cation $[Cu_2(63)_2]^{2+}$ is double-helical with the structure represented in **64**; the Cu...Cu distance is 2.854Å[58]. The subtlety in designing helicating ligands is well-illustrated by the observation that the analogue **63** (X = CH) forms a dicopper(I) 2:2 complex which is not double-helical, but which possesses an open structure[59]. Related ligands which incorporate more flexible spacer groups have been shown not to form double-helical complexes with copper(I)[59,60]. The use of a d^{10} metal ion is important in the assembly of these low-coordination number double-helices, since ligands related to **63** do not form double-helicates with other metal ions[61].



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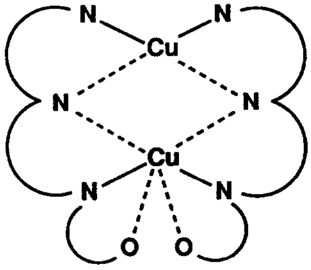
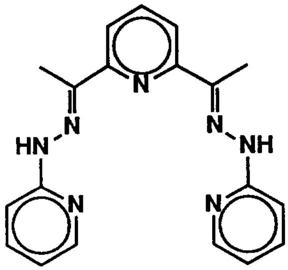


66

A slightly different approach to a double-helical complex is found with the diimine ligand **65**[62]. The reaction of **65** with copper(I) gives an asymmetrical cation $[Cu_2(65)_2]^{2+}$ in which a double-helical complex is formed together with a short Cu-Cu interaction of 2.626Å. The asymmetrical structure in which the central pyridine ring bridges the two metal centres is indicated in **66**. A final example in which a bridging pyridine is implicated, albeit one in which the ligand otherwise acts as a bis(bidentate), is found in the zinc complex formed from **67** after deprotonation. The deprotonation is essential, since the related cobalt(II) complex of the parent ligand is a mononuclear pentagonal bipyramidal species[44].



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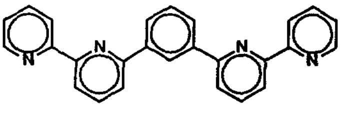

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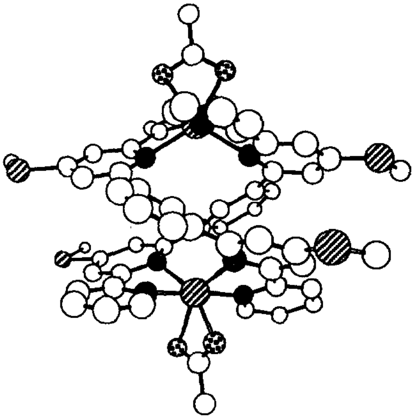
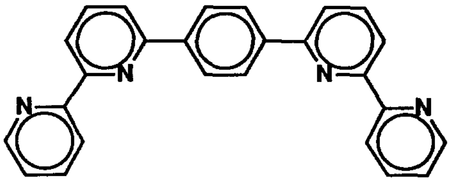


69

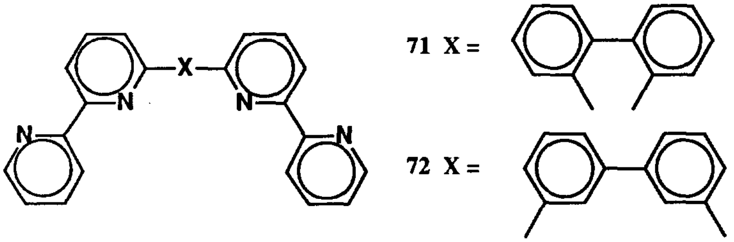
The simplest analogue of qpy is 1,3-bis(6-(2,2'-bipyridyl))benzene **68**, in which the central pyridine ring of qpy has been replaced by a 1,3-phenylene group. This ligand reacts with four-coordinate metal centres such as copper(I) or silver(I) to give dinuclear double-helical species $[M_2(\mathbf{68})_2]^{2+}$[63,64]. Metal ions which favour a six-coordinate structure also form double-helical complexes with **68**, and complete their coordination shell with additional monodentate or bidentate ligands. The structure of the double-helical complex cation obtained from the reaction of the bis(methylthio) derivative of **68** with nickel(II) acetate is shown in **69**[63]. Each nickel(II) centre is also coordinated to a bidentate acetate group, which raises the coordination number at each metal centre to six. In this cation there are no short π -stacking interactions between aromatic rings, which raises the question of how important these effects are in some of the other double-helical structures which have been discussed. The helication is now achieved by two principal twistings of 35-40° about the inter-annular bonds between the central 1,3-phenylene spacer and the two pendant 2,2'-bipyridyl groups. The dicobalt(II) complex of this ligand is thought to possess a similar structure[64]. Once again, no dependence upon the presence of substituents has been noted, and **63** and its derivatives behave in identical manners.

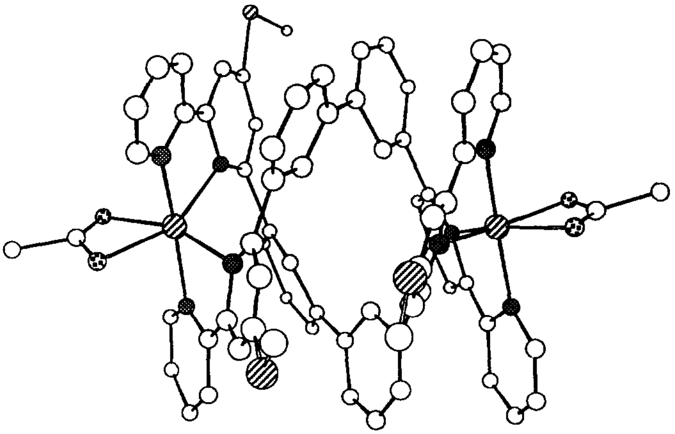
A related ligand, **70**, in which the bpy metal-binding sites are linked by a 1,4-phenylene bridge has also been investigated[64]. This may give shallow double-helical binuclear complexes upon coordination to copper(I) or silver(I).



70

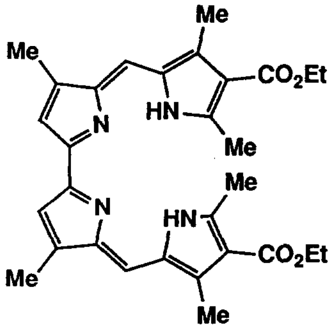
This approach may also be extended to the introduction of biphenylene or higher oligophenylene spacers between the bpy metal-binding sites. This allows additional control over the metal-metal distances within the double-helicates. In practice the steric constraints are such that the introduction of a 2,2'-biphenylene spacer in **71** does not allow the formation of double-helicates, and only mononuclear complexes are obtained from **71** with either copper(I) or copper(II)[65]. In contrast, the 3,3'-biphenylene spacer in **72** allows the formation of double-helicates with copper(I), silver(I) or nickel(II)[66]. The structure of the cation $[Ni_2(72)_2(OAc)_2]^{2+}$ is shown in **73**. The two metal centres are six-coordinate, and the helication is achieved by twisting at three sites - at the inter-annular bonds between the bpy and the biphenylene and also at the inter-annular bond within the biphenylene bridge.





73

A rather variable range of other relatively rigid ligands have also been shown to form dinuclear double-helical complexes upon coordination to appropriate metal ions. The 2,2'-bipyrrole derivative **74** forms both 1:1 and 2:2 complexes with copper(II) after the loss of two acidic pyrrole NH protons per ligand. The 2:2 complex is thought to possess a double helical structure, with the helication resulting from the development of a significant twist about the inter-annular bond between the two central pyrrole moieties[67]. After deprotonation, the related ligand **75** forms 1:1 and 2:2 complexes with zinc(II)[68]. The 1:1 complex contains a five-coordinate zinc(II) centre in which the fifth coordination site is occupied by an axial water ligand. The distortion of the ligand from planarity arises from steric interactions between the terminal carbonyl groups. The steric constraint is such that upon dehydration a 2:2 complex is formed instead of the expected planar four-coordinate mononuclear species. The structurally characterised 2:2 complex is double-helical, with each zinc coordinated to a dipyrromethene functionality from each of two ligands in a distorted tetrahedral geometry[68]. The Zn...Zn distance is 3.37Å.



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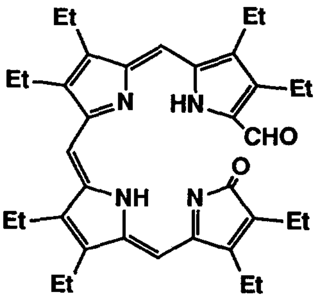

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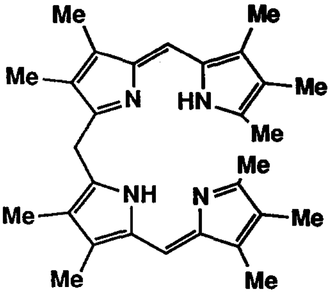
Biladienes with sterically hindering substituents on the terminal rings also form 2:2 complexes with metal ions which favour a tetrahedral geometry. It was suggested on the basis of mass spectroscopic data that the 2:2 complexes of deprotonated **76** with cobalt(II)[69] and nickel(II)[70] possessed a double-helical binuclear structure. These predictions have been confirmed by the crystallographic characterisation of the dizinc complex of the ligand[66].



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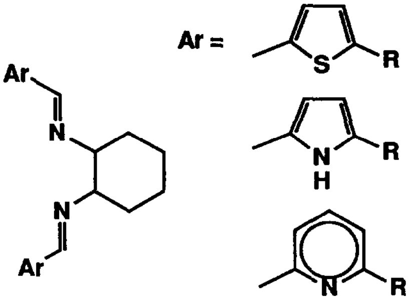
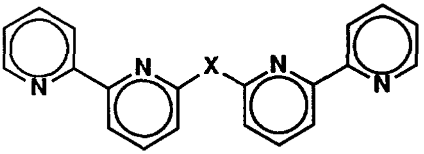


77

Another example of a relatively rigid ligand system which gives rise to double-helical dinuclear complexes is found in the diimine ligands **77**. The ligands are predisposed towards helication by the configuration at the cyclohexane ring. A variety of mononuclear 1:1 and double-helical 2:2 complexes with copper(I), zinc(II) and silver(I) have been prepared and fully characterised[71,72], together with some complexes of structurally less-developed model systems[72]. These complexes exhibit some interesting dynamic solution behaviour which is of considerable relevance to understanding the self-assembly and properties of helicates with labile metal ions.

7.2 Flexible spacers

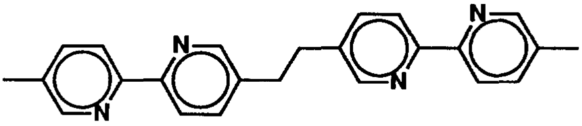
The bpy metal-binding functionality has proved to be of great facility in the design of helicating ligands and a range of polynucleating ligands incorporating two or more bpy moieties linked by more-or-less flexible groups have been investigated. The introduction of a flexible spacer means that the eventual formation of helicates upon coordination is sometimes less than predictable.



78 X = CH_2CH_2
79 X = CH=CH

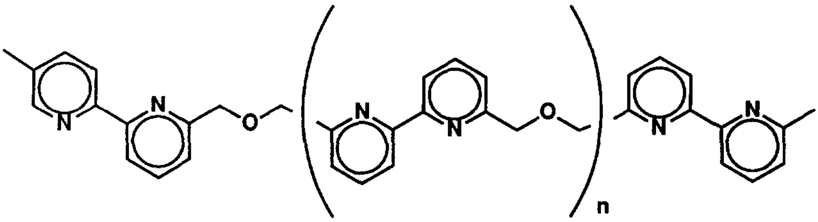
The structural requirements in the spacer group have been probed, and it is found that the ligand **78** with a unsaturated spacer, forms the double-helical cation $[Cu_2(78)_2]^{2+}$ upon reaction with copper(I). In contrast, the introduction of an unsaturated spacer in **79** results in a ligand which does not form such a double-helical complex[73]. Methyl substituted analogues of **78** and also analogues in which the bpy functionalities have been replaced by 1,10-phenanthrolines have also been shown to form double-helical dinuclear complexes with copper(I)[74]. Although cobalt(II) forms

1:1 mononuclear complexes with these substituted ligands, iron(II) forms a complex with **80** with a stoichiometry $[Fe_2(\mathbf{80})_3]^{4+}$ which almost certainly possesses a triple-helical structure.



80

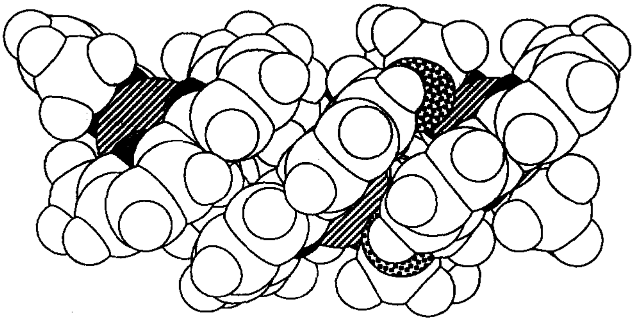
The slightly longer, more flexible, spacer CH_2OCH_2 has proved to be of more widespread application, and is relatively simple to introduce into a range of related ligands **81-84**[75]. These ligands form double-helical complexes with copper(I) and silver(I). The nuclearity of the complexes depends upon the number of metal-binding bpy units incorporated. In the double-helical ligand array, each bpy that is introduced onto an individual ligand creates a new binding site for a four-coordinate centre.



81 n = 0, **82** n = 1, **83** n = 2, **84** n = 3

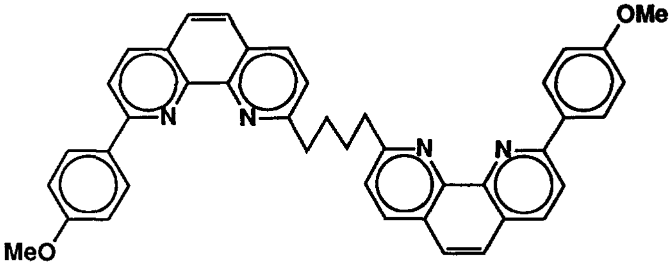
The tri-, tetra- and penta-nuclear complex cations $[M_3(\mathbf{82})_2]^{3+}$, $[M_4(\mathbf{83})_2]^{4+}$ and $[M_5(\mathbf{84})_2]^{5+}$ (M = Cu or Ag) have all been characterised[75-78], and the crystal structure of $[Ag_3(\mathbf{82})_2][CF_3SO_3]_3$ has been reported **85**[77]. Lehn has demonstrated a positive cooperativity in the self-assembly of the tricopper(I) double-helical 3:2 complexes of **84** and substituted derivatives[79]. The self assembly of polynuclear complexes of chiral analogues of the ligands **82** and **84** have also been investigated[78]

In an elegant extension of the self-assembly processes with ligands such as **81-84**, Lehn has now incorporated deoxynucleoside substituents on the *outside* of the double-helical array. This develops the potential for Watson-Crick type hydrogen bonding networks on the outer surface of the double-helicate, and raises interesting possibilities for the interaction of such complexes with nucleic acids[80].



85

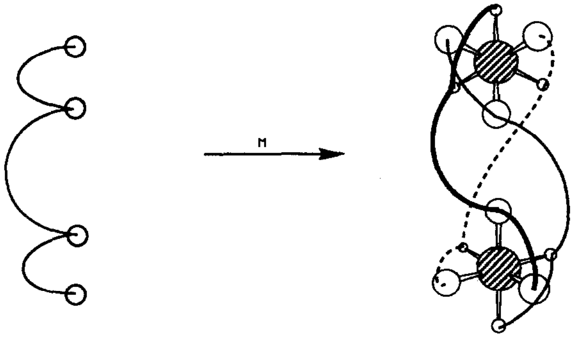
Sauvage and his co-workers have also made use of flexible spacers between 1,10-phenanthrolines in the preparation of knotted molecules. His synthetic strategy recognises that a trefoil knot (**1**) may be derived from a molecular thread which is twisted double-helically. Such an arrangement is achieved by a cyclisation reaction of open-chain precursors which are assembled into the desired double-helical conformation by coordination to transition metal centres. The key step in the synthesis of a trefoil knot is the assembly of the double-helical cation $[Cu_2(\mathbf{86})_2]^{2+}$ from the reaction of copper(I) with the flexible ligand **86**[7,11].



86

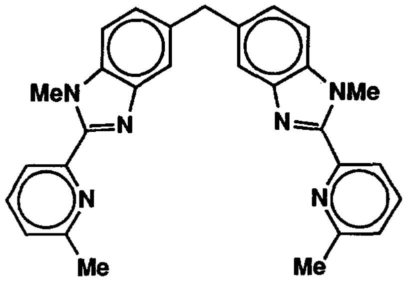
To conclude this section, it is relevant to mention the recent observations that modified peptide ligands bearing thienyl and other heteroaromatic substituents give rise to chiral, helical coordination polymers upon interaction with copper(I) and silver(I)[81].

We began this review by mentioning the difficulties involved in the preparation of a triple-helix, and the realisation of this seems an appropriate point to finish. The requirements for a ligand which will form a triple-helix are similar to those needed for double-helicates. We have seen that a ligand with two bpy metal-binding domains can give rise to a double-helical 2:2 complex with tetrahedral four-coordinate metal centres. We have also seen that these same ligands can also give 2:2 double-helical complexes with six-coordinate metal ions, in which the two remaining coordination sites per metal are occupied by ancillary ligands. However, in the absence of ancilary ligands, and if the ligand contains the correct steric features, it is possible to envisage that such a ligand could also give a 2:3 $[M_2L_3]^{n+}$ triple-helical complex **87**[57].



87

A number of examples of iron(III)[82] and iron(II)[74,83] complexes which might show this geometry have been described, but the first structurally characterised complex was obtained with the ligand **88**[12].



88

The reaction of **88** with cobalt(II) perchlorate results in the formation of the dinuclear triple-helical cation $[Co_2(\mathbf{88})_3]^{4+}$. Each cobalt centre is coordinated to a bidentate N_2 donor set from each of three ligands to give the triple-helical cation. There are some π-stacking interactions between near- (but not quite) planar aromatic rings, but these are not so pronounced as in some of the complexes discussed earlier. The subtlety of the metal-ligand interaction is admirably brought out by the observation that copper(II) complexes of **88** are *double-helical* whilst zinc(II) gives mixtures of double- and triple-helical and other species.[84] Europium(III) has been shown to form a dinuclear triple-helical complex with a bis(terdentate) analogue of **88** utilising the same spacer, in which two nine-coordinate lanthanide ions are accommodated within the ligand array. [85]

8. SUMMARY AND OUTLOOK

In this review we have concentrated upon the interplay between coordination chemistry and organic chemistry to show how metal-ligand interactions may be utilised for the assembly of a variety of novel and interesting structures. The future prospects for this area are very rosy. The formation of metal-ligand bonds is usually rapid and facile, and the bonds once formed may exhibit any desired combination of thermodynamic or kinetic stability. The knowledge of the coordination requirements of a metal ion is a prerequisite to this area of chemistry just as much is the knowledge of heterocyclic synthesis. The area we have discussed is very specialised, but the principles which are presented in this article may be adapted to the synthesis of a whole rage of novel reodx or photoactive materials. Above all, it is a fun area to work in! I hope that some of this enjoyment is apparent in the preceding pages.

It is perhaps appropriate to give the last word to Lehn, " Coordination chemistry provides supramolecular chemistry with a collection of building units, the metal ions of the periodic table, that display: - a set of interaction geometries; - a wide range of binding strengths and kinetics; - a variety of electronic, photochemical and reactional features"[9].

Acknowledgements - I should like to take this opportunity to thank some of the many people and organisations who have been involved in and supported the studies described in this review. Most of the synthetic work described has been done by a remarkable group of graduate students over the last few years; thanks especially to Rohit Chotalia, Susan Elder, Mike Hannon, Jeremy Holmes, Morag Lenman, Mike Ward, Juliet Walker and Philip Wood. The crystallographers have our profound gratitude, and I should particularly like to thank Derek Tocher for his collaboration over the years, and his unfailing good humour on being presented with some of our more amorphous pieces of chemical rubble. Finally, I should like to thank the S.E.R.C., the Royal Society of Great Britain, Ciba-Geigy, Johnson Matthey and The Isaac Newton Trust for financial support.

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