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Coordination and supramolecular chemistry of multinucleating ligands containing two or more pyrazolyl-pyridine ‘arms’

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Abstract

A wide variety of new ligands has been prepared in which two or three bidentate or terdentate chelating units, based on pyrazolyl-pyridine (bidentate) or pyrazolyl-bipyridine

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(terdentate) fragments, have been attached to a central spacer. This may be a borohydride unit to give bis- or tris(pyrazolyl)borate derivatives, or an aromatic (phenyl or biphenyl) unit. A general characteristic of these ligands is that they can coordinate all of their binding 'arms' to a single metal ion, giving mononuclear complexes, or they can coordinate each separate 'arm' to a different metal ion to give assembly of polynuclear species of occasionally quite unexpected structural complexity. We have observed self-assembly of helicates, helical rings, and tetrahedral cages, in some cases with non-coordinated anions playing a crucial templating role in the assembly process. The tetrahedral cages in particular, which have been prepared with both $M_4(\mu^3\text{-}L)_4$ and $M_4(\mu^2\text{-}L)_6$ stoichiometries, provide elegant examples of how high-symmetry structures can assemble from simple components. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Self-assembly; Tris(pyrazolyl)borate; Bis(pyrazolyl)borate; Helicate; Cage; Bridging ligand; Lanthanide

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1. Introduction

In the last 20 years or so, 'self-assembly' has changed from being a process of interest only to biochemists to one of the most exciting areas of modern synthetic chemistry. It allows the preparation of elaborate molecules whose size and complexity can, in some cases, begin to match that of biological assemblies and which can be prepared simply by mixing together some carefully-designed component parts in the correct proportions. From the first examples of double helicates in the mid-1980's [1–3], the complexity of self-assembled systems has grown rapidly and now includes architectures such as triple helicates [4], molecular cylinders [5], rings [6], grids [7], polyhedra such as the cube [8], tetrahedron [9], octahedron [10] and dodecahedron [11], and elaborate assemblies containing several of these components which defy description in simple terms [12].

In the realm of metal complexes based on self-assembly, it is clear that the process relies on two factors which may be at odds with each other: the geometric preference of the metal ion for a particular geometry, and the number, type and arrangement of the ligand binding sites. The properties of particular metal ions are inherent and reasonably predictable [e.g. Cu(I) likes to be four-coordinate, whereas Fe(II) likes to be octahedral]. It is the design of the ligand that is the key to new self-assembly processes and which is where the variety (and unpredictability, in some cases) of self-assembly comes from.

This review summarises our work over the last 5 years or so in which we have prepared a wide variety of new multinucleating ligands, all of which are based on two or three pyrazolyl-pyridine chelating units linked to a central head-group of some sort. These ligands have proven to be a fertile source of interesting new metal complexes which encompass a wide range of structural types, and which have made a significant contribution to coordination and supramolecular chemistry in areas as diverse as self-assembly of cages and photophysics of lanthanide complexes. The emphasis in this article is towards the former area, on the self-assembly of unusual molecular architectures with these multinucleating ligands, and the discussion centres primarily on crystallographic results. It is therefore worth emphasising the important difference between the process of self-assembly in solution, which is under thermodynamic control if the metal ions are kinetically labile; and the process of crystallisation, in which the additional so-called 'crystal-packing effects' can result in one minor (in solution) component of an equilibrium distribution being amplified — i.e. a kinetic effect. Where possible we have used studies on solutions (NMR and electrospray mass spectrometry) to support the crystallographic measurements.

2. Complexes of ligands based on bis- and tris-(pyrazolyl)borates

2.1. Ligand syntheses

This programme of research started with our desire to extend the chemistry of the well-know tris(pyrazolyl)borate ligand, first introduced by Trofimenko [13]. This terdentate face-capping ligand has been derivatised in many ways, largely with the aim of making a sterically protected binding pocket by using bulky (but chemically inert) substituents at the C^3 position of the pyrazolyl rings [14]. It occurred to us that it would be just as easy to attach a 2-pyridyl substituent to each of the pyrazolyl rings, and thereby convert the terdentate face-capping ligand to a hexadentate 'podand' ligand which could completely encapsulate a large metal ion. The ligand Tp^{Py} (following Trofimenko's nomenclature) was readily prepared following the usual method for tris(pyrazolyl)borates, from reaction of 3-(2-pyridyl)pyrazole (Hpzpy) with KBH_4 in a melt [15].[1] By adjusting the stoichiometry appropriately and reducing the temperature, we could also prepare the tetradentate bis(pyrazolyl)borate ligand Bp^{Py} with two bidentate arms [16]. An obvious extension of this was to attach chelating 2,2′-bipyridyl units to each pyrazolyl arm, such that each arm of the ligand became a *ter*dentate chelating pyrazolyl-bipyridine unit. Reaction of 6-(3-pyrazolyl)-2,2′-bipyridine (Hpzbipy) with KBH_4 in the usual way afforded the hexadentate bis(pyrazolyl)borate ligand Bp^{bipy} (Scheme 1) [17]; we have not yet been able to isolate the nonadentate tris(pyrazolyl)borate analogue Tp^{bipy}. An alternative route into polynucleating ligands based on tris(pyrazolyl)borates is to use $B_2(NMe_2)_4$ as the starting material for reaction with a substituted pyrazole [18], which affords B–B linked 'back-to-back' dimers such as hexadentate Tp–Tp and the 12-dentate two-compartment ligand Tp^{Py}–Tp^{Py} [19].

2.2. Complexes of Tp^{Py} with Tl(I), lanthanides and actinides having a 1:1 metal:Tp^{Py} ratio

Tp^{Py} was designed to act as a hexadentate 'podand' ligand for encapsulation of large metal ions, and in many cases it behaves in this way. For example, Fig. 1

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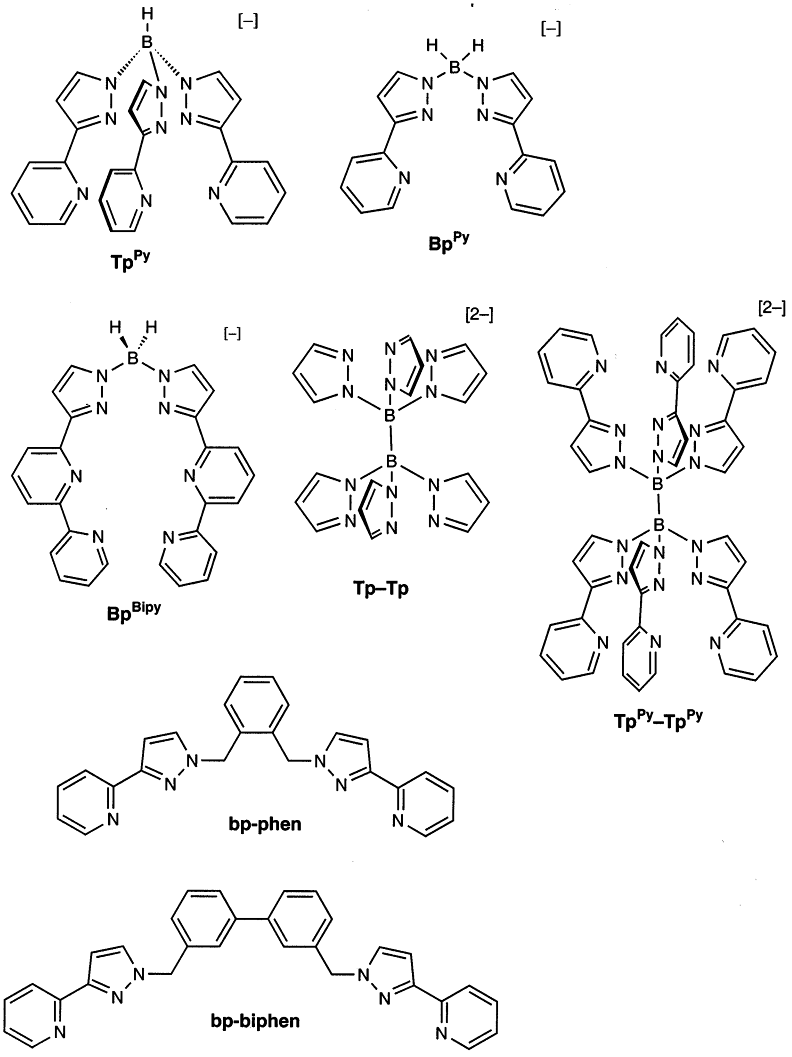
[1] The ligand Tp^{Py} was also prepared independently at about the same time: see Ref. [52].

shows the crystal structures of [Tl(Tp^{Py})], [Eu(Tp^{Py})(NO$_3$)$_2$] and [Th(Tp^{Py})(NO$_3$)$_3$] which all have 1:1 metal:Tp^{Py} stoichiometries. The Tl(I) complex is basically three-coordinate, with the metal ion bound to the three pyrazolyl donors [20]; in this pyramidal three-coordinate geometry the lone pair of the Tl(I) ion is assumed to occupy the fourth coordination site, cf. the structure of NH$_3$. The coordination geometry of the metal ion is similar to that seen for complexes of simpler alkyl-substituted tris(pyrazolyl)borates [21], i.e. the three pyridyl donors are not



Scheme 1.

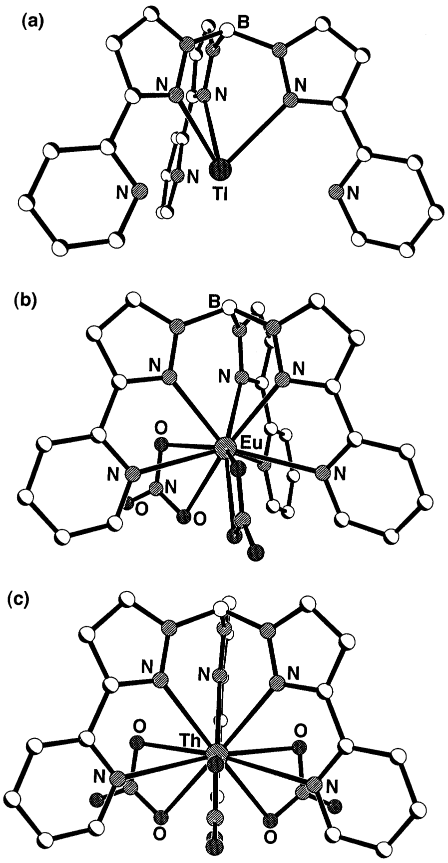


Fig. 1. Structures of (a) [Tl(Tp^{Py})], (b) [Eu(Tp^{Py})(NO$_3$)$_2$] and (c) [Th(Tp^{Py})(NO$_3$)$_3$].

coordinated. However a slight displacement of the Tl(I) ion towards the 'remote' pyridyl N atoms, manifested in a lengthening of the Tl–N(pyrazolyl) bonds by about 0.09 Å compared to the structure of (for example) [Tl(Tp^{t}Bu)], suggests a weak interaction between Tl(I) and the pyridyl donors despite the separation of ca. 3.2 Å between them.

In the structures of [Eu(Tp^{Py})(NO$_3$)$_2$] [22] and [Th(Tp^{Py})(NO$_3$)$_3$] [23], the Tp^{Py} ligand is acting as a hexadentate ligand with the three bidentate arms fully coordinated to the metal centre. In each case the charge balance is provided by coordinated bidentate nitrate ligands, resulting in ten-coordinate Eu(III) and 12-coordinate Th(IV). The Tp^{Py} in these cases does not completely encapsulate the metal ions, but leaves enough space in the coordination sphere for other ligands to bind, and we have found that for lanthanide complexes of Tp^{Py} a variety of ancillary monodentate or bidentate ligands may be attached at the vacant coordination site [15,24].

An interesting variant on the same basic coordination mode (i.e. all six donor atoms coordinated to the same metal ion) is provided by the 12-coordinate complexes $[\mathrm{Ln(Tp^{Py})_2}]^+$ [Ln = a lanthanide(III) ion] (Fig. 2) [22,25]. In cases where there are no other good ligands available to complete the coordination sphere of the lanthanide ion, two $\mathrm{Tp^{Py}}$ ligands can coordinate such that they are interleaved between one another. The result is a slightly distorted icosahedral coordination sphere, compressed along the B–B axis, with metal–N bond lengths being rather long to provide room for all 12 donor atoms in the coordination sphere. Although 12 coordination is well-known in lanthanide(III) complexes, it is largely confined to complexes containing several bidentate oxyanion ligands such as nitrates in which the two donor atoms are very close together. The only 12-coordinate lanthanide complexes with solely N-donor ligands are $[\mathrm{M(napy)_6}][\mathrm{ClO_4}]_3$ (napy = 1,8-naphthyridine; M = La, Ce, Pr) [26] and $[\mathrm{La(ctthb)_4}][\mathrm{ClO_4}]_3$ (ctthb = *cis*-triaza-tris-σ-homobenzene) [27], in both of which the high coordination number was ascribed to the unusual proximity of the N-donor atoms within each ligand. With more conventional N-donor ligands such as polypyridines, coordination numbers of 8 or 9 are more common.[2]

Detailed photophysical studies have been carried out on the luminescent lanthanide complexes (of Tb and Eu) of both structural types (1:1 and 1:2 metal:$\mathrm{Tp^{Py}}$ ratio). Although this aspect of the work is not directly relevant to this review, the results were of interest and it was found that ligand-to-metal energy-transfer following excitation of fully-allowed ligand-centred electronic transitions provide effective sensitisation of the metal emission, especially from Tb(III), resulting in emission quantum yields of *e.g.* 0.41 in $\mathrm{CH_2Cl_2}$ and 0.13 in $\mathrm{H_2O}$ [28].

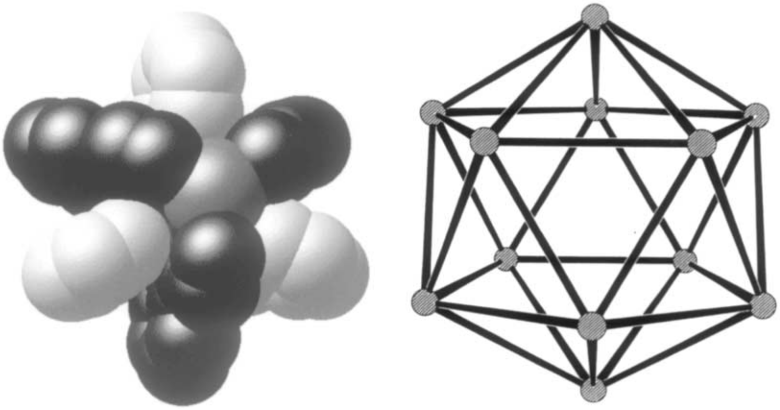


Fig. 2. Structure of $[\mathrm{Sm(Tp^{Py})_2}]^+$, showing (left) interpenetration of the two ligands, and (right) the near-perfect icosahedral coordination geometry.

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[2] At the same time, the group of J. Takats prepared the 12-coordinate complex $[\mathrm{U^{III}(Tp^{Py})_2}]^+$ which has essentially the same structure as the lanthanide analogues. The structure of this uranium complex is included with our lanthanide complex in Ref. [25].

2.3. Complexes of Tp^{Py} with Co(II), Mn(II) and Zn(II): assembly of tetrahedral $M_4(Tp^{Py})_4$ cages

The arrangement of the three bidentate arms in Tp^{Py} is such that it naturally tends to impose a trigonal prismatic donor set if there are no other donor atoms present. The only way for one Tp^{Py} ligand to present an approximately octahedral donor set to one metal ion would be to have a strong trigonal twist, such that the triangle described by the three pyrazolyl donors and the triangle described by the three pyridyl donors become staggered, which would result in substantial steric strain. The imposition of trigonal prismatic geometry is generally inconsistent with the stereoelectronic preferences of metal ions in the d-block: not only is it less favoured than octahedral geometry on steric grounds, but in addition LFSE effects favour octahedral geometries over trigonal prismatic for most d-electron configurations (obvious exceptions being d^0, high-spin d^5 and d^{10}, where LFSE is zero in all geometries) [29,30]. It is accordingly relatively rare, and tends to occur only when there is an element of rigidity in the ligand donor set which imposes trigonal pyramidal geometry.

Reaction of Tp^{Py} with Co(II) salts resulted in formation of mononuclear $[Co(Tp^{Py})][PF_6]$, in which the Co(II) centre is in a trigonal prismatic environment clearly imposed by the steric limitations of the ligand (Fig. 3), despite the electronic preference for octahedral geometry [31]. The three Co–N(pyrazolyl) bonds (average 2.06 Å) are significantly shorter than the three Co–N(pyridyl) bonds (average 2.27 Å) because of the divergent geometry of the three arms. In remarkable contrast to this, reaction of Tp^{Py} with Mn(II) or Zn(II) salts produced tetrameric complexes $[M_4(Tp^{Py})_4][PF_6]_4$ (Fig. 4) [31,32]. Each ligand is spread out such that it coordinates each of its three bidentate arms to a different metal ion, i.e. it caps one triangular face of the metal tetrahedron (Fig. 4). In order to do this, the tris(pyrazolyl)borate fragment adopts an unusual 'inverted' geometry such that the apical hydride is directed inwards, towards the centre of the triangular face. This conformation appears to be necessary for all three pyrazolyl donors to coordinate to different atoms, rather than converging on one atom. Each metal ion is therefore in a pseudo-octahedral coordination geometry, arising from three bidentate pyrazolyl-

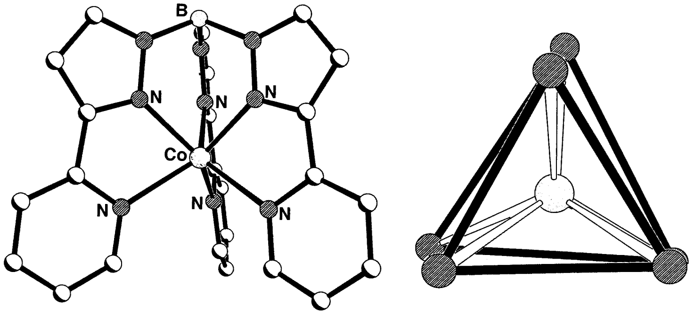

Fig. 3. Structure of $[Co(Tp^{Py})]^+$, emphasising (right) the trigonal prismatic coordination geometry.

pyridine groups provided by three different ligands, in contrast to the trigonal prismatic coordination geometry seen for [Co(Tp^{Py})][PF$_6$]. It is not obvious why the Co(II) complex should be trigonal prismatic whereas Mn(II) and Zn(II) should both be octahedral; if anything, the lack of stereoelectronic preferences for Mn(II) and Zn(II) should lead to these ions being more likely to be trigonal prismatic. We could find no evidence for monomer/tetramer equilibrium in solution, with the ^{1}H-NMR spectrum of the Zn(II) tetramer showing the presence of only one product.

A space-filling picture of the tetrameric complexes (Fig. 4) shows how the intermeshing of the four ligands leads to numerous aromatic π-stacking interactions between overlapping sections of different ligands. All four metal ions have the same chirality, which is essential for steric reasons; the four ligands could not interlock without interference between them if any one of the metals had a different configuration from the others. It is apparent that formation of the tetramer structure is the only way in which an octahedral geometry can be attained with Tp^{Py}: since it is not possible for the three arms of one ligand to provide an octahedral donor set to one encapsulated metal ion, it is necessary to use three independent bidentate fragments, one from each of three different ligands. With the benefit of hindsight we can see how this necessarily leads to formation of a tetrahedron. Each ligand, because it binds to three different metals, can be considered to cap a triangular face of a polyhedron which has metal ions at its vertices. Each vertex is likewise connected to three faces (i.e. each metal interacts with three bidentate ligand arms to give the required octahedral geometry). Given a 1:1 metal:ligand stoichiometry, because each ligand has six donor atoms and each metal requires six donors, we require a polyhedron having the same number of (three-connected) vertices as (triangular) faces, i.e. a tetrahedron having four vertices and four faces. This symmetry-based argument has recently been exploited by Raymond for the planned synthesis of topologically similar tetrahedral complexes with a 4:4 metal:ligand ratio [33].

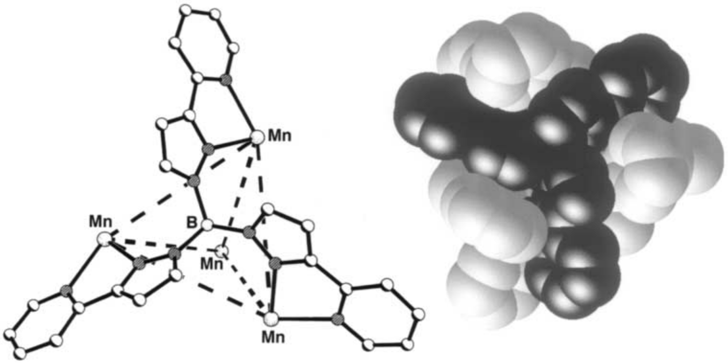

Fig. 4. Structure of [Mn$_4$(Tp^{Py})$_4$]$^{4+}$, showing (left) the coordination mode of each individual ligand, and (right) a space-filling picture showing how the ligands intermesh.

2.4. Complexes of Tp^{Py} with Cu(I) and Ag(I): assembly of triangular $M_3(Tp^{Py})_2$ complexes

Given the obvious importance of the role of the geometric preference of the metal ion in directing the course of the metal–ligand assembly process, we also investigated the coordination of Tp^{Py} to Cu(I) and Ag(I) which usually adopt a four-coordinate, pseudo-tetrahedral geometry. Following the arguments above, assuming that Cu(I) and Ag(I) will be four-coordinate, we expect 1.5 metal ions per hexadentate ligand, i.e. the stoichiometry $\{M_3(Tp^{Py})_2\}^+$ (or some multiple thereof).

Reaction of Tp^{Py} with $[Cu(MeCN)_4][PF_6]$ afforded $[Cu_3(Tp^{Py})_2][PF_6]$, whose structure is in Fig. 5 [34]. The normal pseudo-tetrahedral bis-diimine coordination environment around each Cu(I) is provided by two bidentate arms, one from each of the two ligands; as in the tetrahedral complexes above, each ligand is spread out such that it binds each bidentate arm to a separate metal ion. The result is a triangle of Cu(I) centres, with each face of the triangle ‘capped’ by a Tp^{Py} ligand. This triangle is not however equilateral but is strongly isosceles, with one short Cu···Cu separation (2.915 Å) and two much longer ones (3.500 and 3.614 Å); the short Cu···Cu separation is associated with π-stacking interactions between ligand fragments attached to the two metal ions involved.

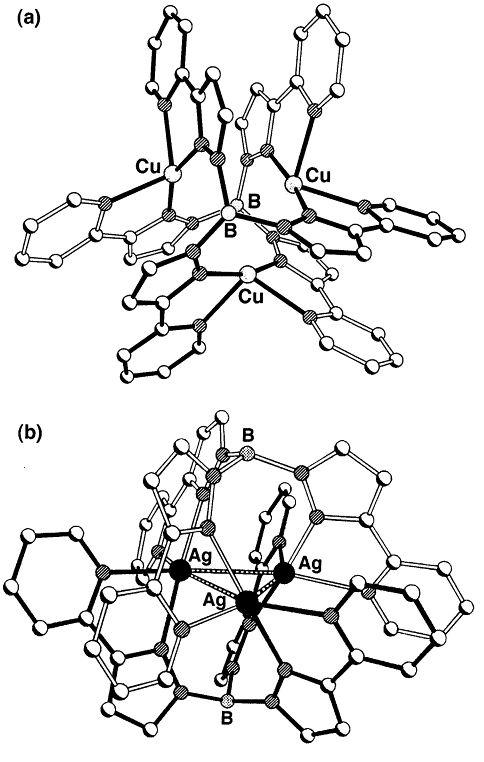

Fig. 5. Structure of (a) $[Cu_3(Tp^{Py})_2]^+$ and (b) $[Ag_3(Tp^{Py})_2]^+$ with the two ligands coloured differently for clarity in each case. For (b) the Ag···Ag bonds are shown by dotted lines.

A particularly interesting feature of $[Cu_3(Tp^{Py})_2][PF_6]$ is that it undergoes a fully reversible one-electron oxidation to the $Cu(I)_2/Cu(II)$ form, which remains intact as $[Cu_3(Tp^{Py})_2]^{2+}$ [34]. In this form EPR spectroscopic data clearly show that at low temperatures (below 120 K) the unpaired electron from the Cu(II) centre is delocalised over *two* copper centres, giving a characteristic seven-line spectrum from coupling to two nuclei with $I = 3/2$. This is in agreement with the solid-state structure which showed one short Cu···Cu bond, such that in the oxidised form there is a delocalised pair of $Cu^{1.5+}$ ions and a more remote valence-trapped Cu^+ ion. As the complex is warmed up, the unpaired electron becomes localised at 160 K and above giving a valence-trapped $Cu(I)_2/Cu(II)$ complex, possibly because increased thermal motion disrupts the close Cu···Cu contact that was responsible for the delocalisation. This structural and spectroscopic behaviour of a trinuclear copper complex is relevant to attempts to model the properties of trinuclear copper metalloproteins such as ascorbate oxidase, which also contain an 'isosceles' arrangement of copper ions which includes a strongly-interacting Cu_2 pair and a more remote metal site [35].

Reaction of Tp^{Py} with $Ag(ClO_4)$ afforded $[Ag_3(Tp^{Py})_2][ClO_4]$, with a 3:2 metal:Tp^{Py} ratio for the same reasons that applied to the Cu(I) complex, giving superficially a very similar structure [20]. However, the crystal structure shows one important difference compared to the Cu(I) analogue: in the Ag(I) complex, there are clearly Ag···Ag bonds (length 2.977 Å) along each edge of the equilateral Ag_3 triangle (Fig. 5). Rather than a complex of three metal ions, it is more appropriate to regard this as an $\{Ag_3\}^{3+}$ triangular cluster which is accommodated inside the cavities of the two Tp^{Py} ligands. To accommodate the large Ag_3 unit, the arms of each ligand are 'splayed out' such that the apical N–B–N angles are 114.1°, in contrast to 109–110° in $[Tl(Tp^{Py})]$. If the Ag···Ag contacts are taken into account, the metal ions are in highly distorted six-coordinate geometries which may loosely be considered as based on 'octahedral' given the constraints due to the bite angles of the *N*,*N*-chelating groups (ca. 71°) and the 60° angles within the Ag_3 cluster.

2.5. Complexes of Bp^{Py}, and a mixed Bp^{Py}/Tp^{Py} complex

As with Tp^{Py}, the coordination properties of the bis(pyrazolyl)borate ligand Bp^{Py} can be split into two categories: either all donor atoms coordinate to the same metal ion, to give in this case a tetradentate chelate; or the two bidentate arms attach to different metal ions, in which case more elaborate polynuclear complexes may assemble.

The simple mononucleating coordination mode of Bp^{Py} is exemplified by the structures of $[Tl(Bp^{Py})]$ and $[Ln(Bp^{Py})_2(NO_3)]$ (Ln = a lanthanide + 3 ion) (Fig. 6). In $[Tl(Bp^{Py})]$ the Tl(I) ion has two short, strong interactions with the pyrazolyl N donors (between 2.61 and 2.69 Å), and two much more tenuous ones with the pyridyl N donors (between 2.96 and 3.17 Å), cf. the structure of $[Tl(Tp^{Py})]$ described earlier. The four N donor atoms are approximately coplanar, with the Tl atom lying ca. 1.4 Å out of the plane and the metal lone pair presumably directed to the vacant axial coordination site of the square pyramid [36]. In

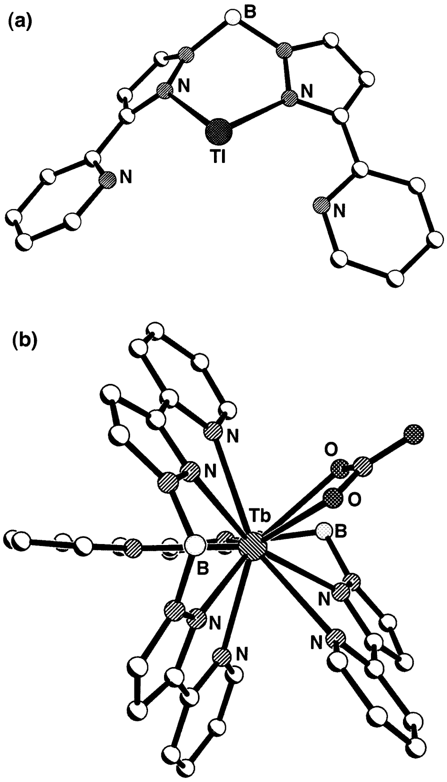

Fig. 6. Structures of (a) $[Tl(Bp^{Py})]$, and (b) $[Tb(Bp^{Py})_2(NO_3)]$.

$[Ln(Bp^{Py})_2(NO_3)]$ the two Bp^{Py} ligands are coordinated as conventional tetradentate chelates, with the lanthanide ion being ten-coordinate from two such ligands and a bidentate nitrate [16,37]. The photophysical properties of the Eu and Tb members of this series proved to be interesting, with emission quantum yields for $[Tb(Bp^{Py})_2(NO_3)]$ being 0.33 in CH_2Cl_2 and 0.36 in MeOH [37].

As with Tp^{Py}, it is the bridging coordination mode of Bp^{Py} which provides the more unexpected and interesting structures from the point of view of self-assembly. Reaction of Bp^{Py} with Co(II) salts, followed by precipitation with hexafluorophosphate as the anion, afforded a material whose electrospray mass spectrum contained a peak corresponding to the fragment $[Co_8(Bp^{Py})_{12}(PF_6)]^{3+}$ at m/z 1410 [38]. Given that Bp^{Py} is tetradentate, and assuming a six-coordinate geometry for Co(II), we expected 1.5 ligands per metal ion (i.e. a 2:3 metal:Bp^{Py} ratio) if no other ligands are present; such a proportion could be provided, for example, by a dinuclear triple helicate. A combination of eight metal ions and 12 ligands is in agreement with this ratio but seems unnecessarily large: also, it was not clear why the complex cation should be only associated with *one* anion. These puzzles were resolved by the crystal structure (of the perchlorate salt), which is in Fig. 7. The eight metal ions and

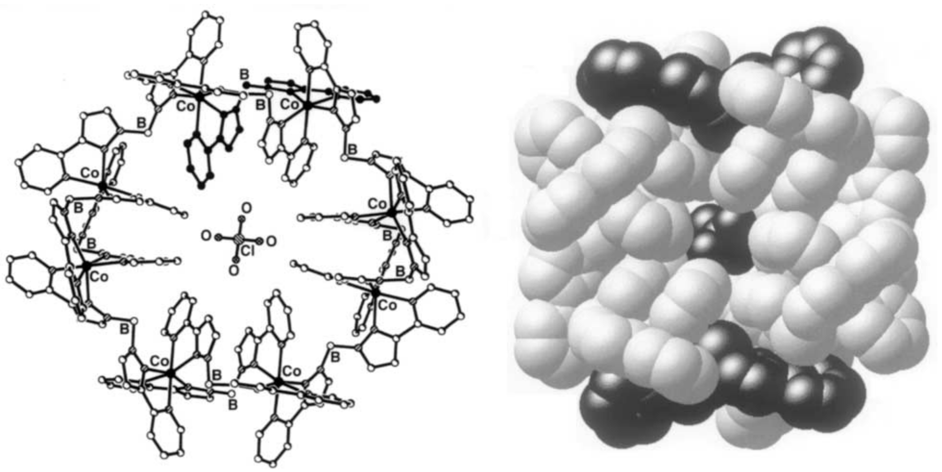

Fig. 7. Structure of $[Co_8(Bp^{Py})_{12}(ClO_4)]^{3+}$, showing (left) a conventional depiction of the structure, with three of the bridging ligands coloured to emphasise their arrangement, and (right) a space filling picture emphasising the good fit of the central perchlorate anion for the cavity.

twelve bridging ligands form a closed ring, with the perchlorate ion bound in the centre of the cavity. Each ligand Bp^{Py} acts as a bridge between two adjacent metal ions, with an alternating pattern of one and then two bridging ligands between each adjacent pair of metals. Each metal is therefore six-coordinate (pseudo-octahedral) by three bidentate chelating fragments, each from a different ligand. The complex cation is chiral, with all eight metal centres having the same absolute chirality and it is therefore a helical ring. The space-filling picture shows how the anion is a good fit for the central cavity, and the obvious conclusion to draw is that a template effect is operative such that the metal/ligand assembly is directed along one particular path because the components assemble around the central anion. There is an obvious similarity between this and an example from Lehn's group in which a chloride ion templates the assembly of a helical cyclic complex around it [39]. The significance of this observation is that the course of a self-assembly does not depend on the nature of the metal ion and the ligand alone: it may be that there are several possible outcomes of similar energy, such that a relatively minor perturbation from some other source (e.g. electrostatic interactions with a non-coordinating anion) can tip the balance one way. In this case it is likely that there are many smaller species present in solution and the crystal structure is not wholly representative.

Another interesting (and fortuitous!) example of self-assembly was provided by reaction of a Mn(II) salt with a mixture of Tp^{Py} and Bp^{Py}. We had been attempting to prepare more of the $[Mn_4(Tp^{Py})_4]^{4+}$ tetramer (see Section 2.3), but partial decomposition of the Tp^{Py} ligand liberated some Bp^{Py} into the reaction, and small amounts of a crystalline product were obtained which proved to be $[Mn_3(Tp^{Py})(Bp^{Py})_3](ClO_4)_2$ (Fig. 8) [40]. The central Tp^{Py} ligand bridges the Mn_3 triangle, by donating one bidentate arm to each of the three metal ions, as in the

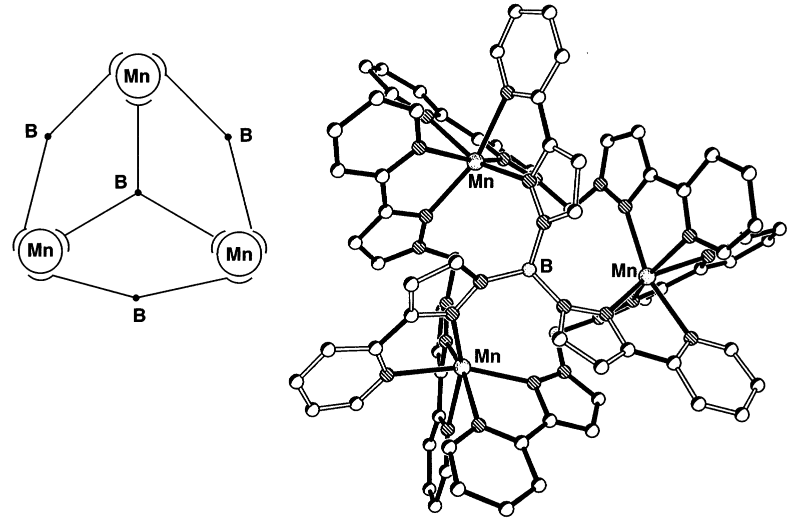

Fig. 8. Structure of $[Mn_3(Tp^{Py})(Bp^{Py})_3]^{2+}$, with the two different types of ligand coloured differently for clarity; inset is a schematic diagram of how the ligands are arranged.

tetrahedral complexes of Section 2.3. Each edge of the Mn_3 triangle is then spanned by a bridging Bp^{Py} ligand, such that each Mn(II) ion is octahedrally coordinated by bidentate arms from one Tp^{Py} and two Bp^{Py} ligands. Since there is mixture of Tp^{Py} and Bp^{Py} in solution, we would expect that a mixture of homoleptic complexes form, such as $[Mn_4(Tp^{Py})_4]^{4+}$ and $[Mn_8(Bp^{Py})_{12}(ClO_4)]^{3+}$. However it is apparent that mixtures of ligands can also be used to satisfy the coordination demands of the metal ions in unexpected ways. With a little ingenuity it is possible to imagine many other combinations: for example, a cluster of four Mn^{2+} ions could have the necessary 24 donor atoms (12 bidentate arms) provided by a mixture of two Tp^{Py} and three Bp^{Py} ligands. It is very likely that the solution behaviour is complex, with many species present, and the X-ray crystallography alone does not give the whole story. Further studies on mixtures of this type are in progress.

2.6. Complexes of Bp^{bipy}

Applying the same rules as above, we can differentiate between complexes of Bp^{bipy} in which it chelates to a single metal ion, and polynuclear complexes arising from coordination of each terdentate ion to a different metal. The former category is exemplified by $[Tl(Bp^{bipy})]$ and the lanthanide complexes $[Ln(Bp^{bipy})(NO_3)_2]$ (Fig. 9) [41]. The structural features of these are in accord with the behaviour of the related ligands Tp^{Py} and Bp^{Py}. For the Tl(I) complex there are strong Tl–N interactions with the pyrazolyl donors and one of the pyridyl donors, which between them describe the approximate base of a pyramid whose fourth vertex is assumed to be occupied by the lone pair of Tl(I). The remaining three pyridyl donors interact with the Tl(I) either weakly or not at all. In contrast, for the

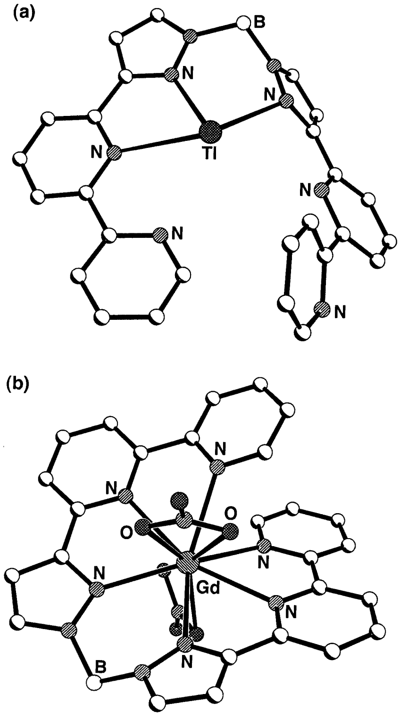

Fig. 9. Structures of (a) [Tl(Bp^{bipy})] and (b) [Gd(Bp^{bipy})(NO$_3$)$_2$].

lanthanide complexes [Ln(Bp^{bipy})(NO$_3$)$_2$] the preference for a higher coordination number means that Bp^{bipy} is coordinated as an approximately equatorial hexadentate chelate, with a slight helical twist; the 'axial' positions are occupied by bidentate nitrate ligands. Again, the photophysical studies of some of the lanthanide complexes have been studied in some detail [37].

Bridging behaviour of Bp^{bipy} results in formation of dinuclear double helicates, with both d- and s-block metals (Fig. 10). Thus [Cu$_2^{II}$(Bp^{bipy})$_2$]$^{2+}$ and [K$_2$(Bp^{bipy})$_2$] are both double helicates, with each metal ion in a distorted six-coordinate geometry arising from two terdentate fragments [17,41]. Other complexes with first-row transition metal dications having a 2:2 metal:Bp^{Bpy} stoichiometry (by mass spectroscopy) are also assumed to be helicates. Whilst double helical complexes of transition-metal ions are now quite common, those of alkali metals are very rare and at the time of writing [K$_2$(Bp^{bipy})$_2$] remains the only structurally characterised double helicate of a group 1A metal ion. It is interesting to see that the K···K distance in [K$_2$(Bp^{bipy})$_2$] of 3.954(2) Å is considerably less than the Cu···Cu separation of 5.388(2) Å in [Cu$_2^{II}$(Bp^{bipy})$_2$]$^{2+}$, despite the greater ionic radius of K$^+$. This presumably reflects the increased inter-metal electrostatic repulsion between two dipositive metal ions which will, to a first approximation, be four times greater than that between two monopositive metal ions for a given separation. Comparison

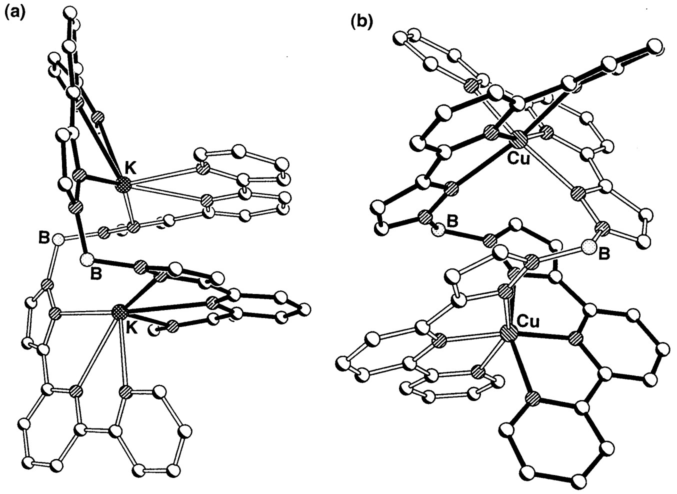

Fig. 10. Structures of the double helicates (a) $[K_2(Bp^{bipy})_2]$ and (b) $[Cu_2(Bp^{bipy})_2]^{2+}$.

of the two structures shows how the 'pitch' of the helical array can be controlled by this electrostatic effect; the assembly is acting like a 'spring' which can be opened out or compressed. The increase in the metal–metal separation in the copper(II) complex is reflected in the increased N–B–N angles [113.4(3) and 112.9(3)° at B(1) and B(2), respectively] which allow the two terdentate fragments within each ligand to stretch further apart from one another at the expense of some additional strain at the bridgehead $-BH_2-$ groups. The effects of electrostatic repulsion on the metal-metal separation in a helicate system are also apparent in the structures of the Cu(I)/Cu(II) and Cu(II)/Cu(II) double helical complexes with quinquepyridine (metal-metal separations 3.96 and 4.50 Å, respectively) [42].

3. Complexes of ligands based on pyrazolyl-pyridine arms linked by aromatic spacers

3.1. Ligand syntheses

Following our initial investigations into the coordination behaviour of the poly(pyrazolyl)borate ligands described above, it became clear that it would be valuable to extend this class of bridging ligand by using other spacer groups, not least because of the hydrolytic instability of pyrazolyl(borates) which led on occasion to decomposition of the ligands and the release of free pyrazole units into the reaction. Use of aromatic hydrocarbon spacers has provided perfectly stable ligands in which the separation between the two binding sites can be controlled by the size of the spacer, which has proven to be a valuable tool in the design of new ligands for self-assembly. The two ligands bp-phen [43,44] and bp-biphen [45] were

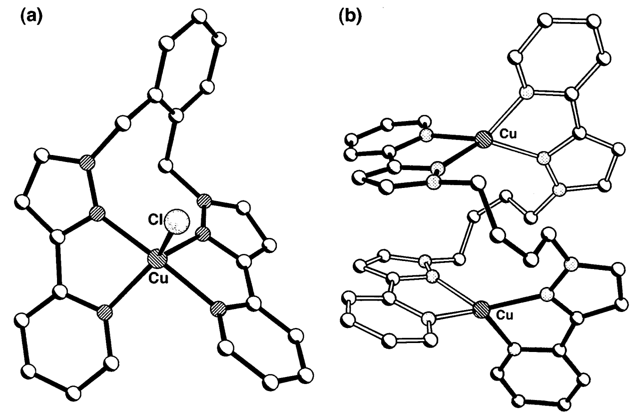

Fig. 11. Structures of (a) $[Cu(bp\text{-}phen)Cl]^+$ and (b) $[Cu_2(bp\text{-}phen)_2]^{2+}$ (with atoms C^2–C^5 of the central phenyl rings removed for clarity).

prepared by displacement of the bromine atoms of 1,2-bis(bromomethyl)benzene or 3,3′-bis(bromomethyl)biphenyl respectively by the pyrazolyl N atoms of 3-(2-pyridyl)pyrazole under phase-transfer conditions.

Given the wide availability of dimethyl-substituted aromatic units, from which the bis(bromomethyl) derivatives are prepared by reaction with *N*-bromosuccinimide, this is a potentially general method which can be used to make bridging ligands having a wide variety of spacers between the binding sites.

3.2. Coordination chemistry of bp-phen: anion-templated assembly of a tetrahedral cage

As we emphasised earlier for all of the poly(pyrazolyl)borate-derived ligands, the key point in determining the complexity of the structures of their metal complexes is whether the ligands chelate to one metal ion, or act as bridging ligands to two or more. Tp^{Py}, Bp^{Py} and Bp^{bipy} were all capable of acting either way, leading to a highly varied coordination chemistry.

Bp-phen is likewise capable of acting as either a mononucleating or a bridging ligand, as exemplified by the structures of $[Cu(bp\text{-}phen)Cl][BF_4]$, which is a trigonal bipyramidal Cu(II) complex, and $[Cu_2(bp\text{-}phen)_2][PF_6]_2$, which is a conventional dinuclear double helical complex with four-coordinate Cu(I) centres (Fig. 11) [43]. These examples show clearly the role of the stereoelectronic coordination preferences of the metal ion in dictating the course of the assembly process.

With metal ions which prefer regular octahedral coordination geometry, viz. Ni(II) and Co(II), more remarkable behaviour emerges. Given that bp-phen is tetradentate we would expect 1.5 ligands per octahedral metal ion, i.e. a 2:3 metal:ligand ratio. The structure of $[Ni_2(bp\text{-}phen)_3][BF_4]_2$ (Fig. 12) illustrates the simplest possible way to achieve this stoichiometry, which takes advantage of the fact that bp-phen can act either as a tetradentate chelate or as a bis-bidentate bridging ligand [44]. Each Ni(II) centre has one terminal tetradentate bp-phen ligand, and one additional bridging ligand donates a bidentate arm to each metal ion to complete both coordination spheres. Perhaps surprisingly this type of (LM)(μ-L)(ML) structure is very unusual [46] compared to the $[M_2(\mu\text{-}L)_3]$ triple helicate structure in which all ligands are bridging [4]; its occurrence here is presumably related to the ability of bp-phen to act as a tetradentate chelate.

We expected the Co(II) complex to have the same structure as the Ni(II) complex, but its mass spectrum showed clearly that the complex cation contained four metal ions and six ligands; the expected 2:3 proportion is maintained but in a more elaborate structure (Fig. 13) [44]. $[Co_4(\text{bp-phen})_6(BF_4)](BF_4)_7$ is a tetrahedral complex in which each metal ion occupies the vertex of the tetrahedron and each ligand, acting as a bridge between two metal ions, spans one edge of the tetrahedron. Multiple π-stacking interactions between ligands is evident (Fig. 13). Each Co(II) ion is therefore pseudo-octahedrally coordinated by one bidentate arm from each of three separate ligands, and the Co···Co separations like in the range 9.0–10.1 Å. Of the eight tetrafluoroborate anions, one is contained in the central

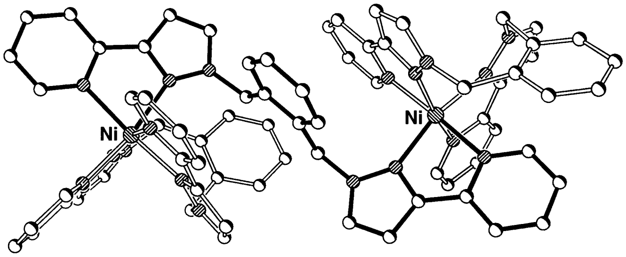

Fig. 12. Structure of $[Ni_2(\text{bp-phen})_3]^{4+}$, with the bridging ligand (dark bonds) and the terminal ligands (hollow bonds) coloured differently for clarity.

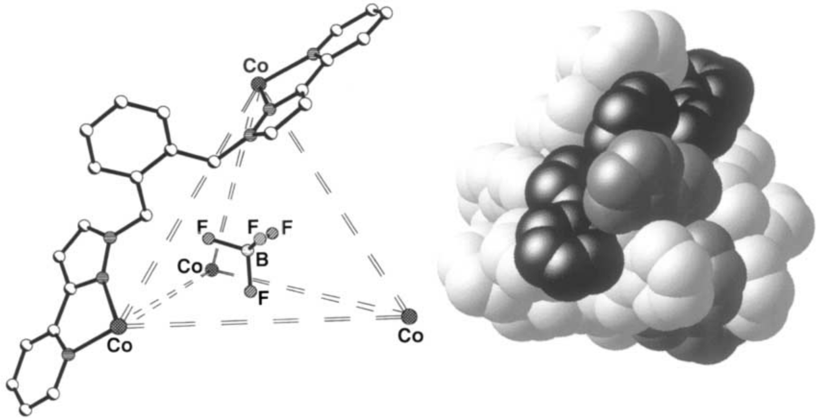

Fig. 13. Structure of $[Co_4(\text{bp-phen})_6(BF_4)]^{7+}$, emphasising (left) the arrangement of a single bridging ligand and the encapsulated anion; and (right) a space-filling view with each ligand coloured differently.

cavity for which it appears to be an ideal match on size and shape grounds; the $[BF_4]^-$ tetrahedron is inverted with respect to the Co_4 tetrahedron, such that each F atom is directed towards the space in the centre of a Co_3 triangular face. There will also be a favourable electrostatic effect arising from having an anion trapped in the central cavity of a complex cation with a charge of $+8$. The anion appears to be held tightly in place: ^{11}B- and ^{19}F-NMR spectra show two distinct signals, one for the seven free $[BF_4]^-$ anions and one (at much higher field) for the encapsulated ion. The spectra do not change at temperatures up to 70°C, indicating that exchange of free and encapsulated $[BF_4]^-$ is slow on the NMR timescale even at high temperatures. This is not surprising when one considers how many metal–ligand bonds would have to break simultaneously to open up the cavity, and suggests that this is a very stable structure which persists in solution. Other examples of this M_4L_6 tetrahedral cage topology have been reported recently [47–49].

There are two distinct points of interest about this structure. Firstly, it is clear that a template effect is operative with the metal/ligand assembly forming around the central anion which is, fortuitously, an ideal size and shape to act in this way. Self-assembly has often been regarded as a process which relies on the interplay of metal and ligand properties, with the structure of a complex being determined by a trade-off between the stereoelectronic properties of the metal ion and the number, type and arrangement of binding sites in the ligand. It is now becoming apparent, from this example and others like it, that weak interactions involving non-coordinating counter-ions can also be pivotal in directing the self-assembly process along one particular path [39,47]. This is well illustrated by comparison of the structure of $[Co_4(\text{bp-phen})_6(BF_4)](BF_4)_7$ with that of $[Ni_2(\text{bp-phen})_3][BF_4]_2$, for which no such template effect operates and the result is consequently a quite different structure [we could find no mass spectroscopic or NMR evidence for formation of a cage complex in solution using Ni(II) in place of Co(II)]. A recent comparable example comes from the group of Raymond, in which a triple helicate M_2L_3 can convert to an edge-bridged tetrahedral cage M_4L_6 in the presence of a counter-ion which can act as a template for the conversion [47].

Secondly, the topological properties of $[Co_4(\text{bp-phen})_6(BF_4)]^{7+}$ are in interesting contrast to those of the tetrahedral cages $[M_4(Tp^{Py})_4]^{4+}$ (Section 2.3). Both structures are based on a tetrahedral array of metal ions which each require octahedral coordination from three bidentate fragments. In $[M_4(Tp^{Py})_4]^{4+}$ this is provided by four trinucleating ligands, each of which spans a triangular face of the tetrahedron and interacts with three metal ions. In $[Co_4(\text{bp-phen})_6(BF_4)]^+$ we have six binucleating bridging ligands, each spanning one edge of the tetrahedron and interacting with two metal ions. These two types of behaviour (face-capping and edge-bridging of metal polyhedra) can be seen in the assembly of other complexes: for example the cube (Thomas et al.) [8] and dodecahedron (Stang et al.) [11] mentioned in the introduction are both based on edge-bridging linear connectors, whereas assembly of the octahedral cage of Fujita et al. is based on face-capping trinucleating ligands [10]. The directed assembly of polynuclear cages using these principles has also recently been reviewed by both Raymond [9,50] and Piguet [51], and our results are generally in agreement with the principles put forward in these articles.

3.3. Coordination chemistry of bp-biphen: assembly of a tetrahedral cage without a template effect

From the above results it is clear that the ability of bp-phen to form complex structures such as cages and helicates is compromised by its ability to act as a simple tetradentate chelate to a single metal ion. We therefore prepared bp-biphen, which contains the same number and type of binding sites in the same relative arrangement, but where the additional phenyl spacer moves the two bidentate sites far enough apart that they cannot bind to the same metal ion. In this way formation of structures such as $[Ni_2(bp\text{-}phen)_3]^{4+}$ can be avoided, since only bridging behaviour of the ligands possible. This is illustrated by the dinuclear double helical structure of the copper(II) complex $[Cu_2(\mu\text{-}bp\text{-}biphen)_2(OAc)_2][BF_4]_2$ [45], which is in contrast to formation of a mononuclear complex of Cu(II) with the shorter ligand bp-phen (Fig. 11).

Reaction of bp-biphen with $Co(BF_4)_2$ afforded, after recrystallisation, a crystalline material whose structure is shown in Fig. 14 [45]. This complex is $[Co_4(bp\text{-}biphen)_6][BF_4]_8$ and has the same tetrahedral M_4L_6 core that we saw with bp-phen, i.e. a bridging ligand along each of the six edges of the Co_4 tetrahedron. However, an important difference is that the greater length of the bridging ligands means that the void in the centre of the tetrahedron is larger, such that the $[BF_4]^-$ anion is no longer an effective template. In fact the central cavity of $[Co_4(bp\text{-}biphen)_6]^{8+}$ is empty, and the complex has self-assembled without the aid of a template. This may be because the alternative tetradentate chelating coordination mode of the ligand, exemplified by $[Ni_2(bp\text{-}phen)_3]^{4+}$, has been prevented such that assembly of the cage is more likely to proceed on its own. Of course there is the possibility that a much larger tetrahedral anion could act as a template, if one can be found which is a good match for the size of the cavity.

The larger size of the bridging ligands in this complex means that the faces of the Co_4 tetrahedron are not blocked, as they are in $[Co_4(bp\text{-}phen)_6(BF_4)]^{7+}$, but have

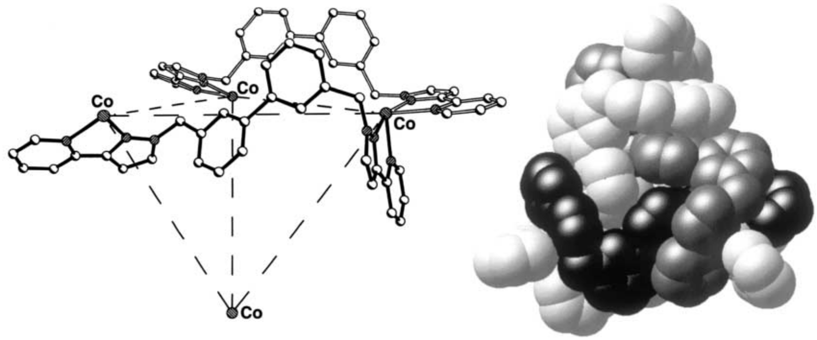

Fig. 14. Structure of $[Co_4(bp\text{-}biphen)_6]^{8+}$: (a) a view emphasising the arrangement of two of the edge-bridging ligands, and (b) a space-filling view emphasising the gap in the centre of each face through which anions can diffuse.

gaps in such that small molecules can diffuse in and out. Variable temperature ^{11}B-NMR spectroscopy of $[Co_4(\text{bp-biphen})_6][BF_4]_8$ shows just a single peak for $[BF_4]^-$ at room temperature at a position (− 5ppm) close to that expected for the free anion. As the temperature is cooled to − 40°C, a small second peak appears at − 34 ppm, a position consistent with incorporation of $[BF_4]^-$ into the cavity. It is clear from this that the anions can diffuse in and out of the cavity freely at room temperature, but at − 40°C the exchange rate becomes slow on the NMR timescale. This is in strong contrast to $[Co_4(\text{bp-phen})_6(BF_4)]^{7+}$, for which the encapsulated anion was trapped (on the NMR timescale) even on warming to 70°C. Apart from the interest in their assembly, the host-guest chemistry of cage complexes such as this is also an area of considerable promise which we are currently investigating further.

4. Conclusions

This work started from an attempt to extend the chemistry of tris(pyrazolyl)borate ligands, and has ended up in the area of host-guest chemistry and self-assembly, via areas as diverse as luminescent lanthanide complexes and a spectroscopic model for ascorbate oxidase! It is clear however that simple bridging ligands of this type can, if carefully designed and matched with a suitable metal ion, provide self-assembled structures of remarkable variety and complexity.

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