PAPER

NJC
www.rsc.org/njc

Homo- and heteropolynuclear helicates with a '2 + 3 + 2'-dentate compartmental ligand

Stephen P. Argent,[a] Harry Adams,[a] Lindsay P. Harding,[b] T. Riis-Johannessen,[c] John C. Jeffery[c] and Michael D. Ward*[a]

[a] *Department of Chemistry, University of Sheffield, Sheffield, UK S3 7HF. E-mail: m.d.ward@sheffield.ac.uk; Fax: 0114 2229346; Tel: 0114 2229484*
[b] *Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield, UK HD1 3DH*
[c] *School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS*

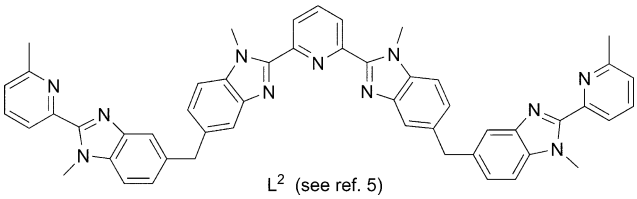
Received (in Durham, UK) 16th February 2005, Accepted 12th April 2005
First published as an Advance Article on the web 18th May 2005

An octadentate ligand L has been prepared which contains a sequence of bidentate (pyrazolyl-pyridine), terdentate [bis(pyrazolyl)pyridine] and bidentate (pyrazolyl-pyridine) binding sites separated by *p*-xylyl spacers. This forms a range of double helical complexes in which the two ligands define 4-, 6-, and 4-coordinate binding sites, and there is substantial π-stacking between overlapping parallel areas of the ligands. In $[Cu_3L_2][PF_6]_4$ the sequence of oxidation states for the copper ions is +1, +2, +1 with the Cu(I) ions being four-coordinate at the terminal sites and Cu(II) being in the central six-coordinate site. In $[Cu_3(OAc)_2L_2][PF_6]_4$ all copper centres are in oxidation state +2, with the terminal ions having an additional monodentate acetate ligand giving them a five-coordinate geometry. The 4 + 6 + 4 arrangement of coordination numbers means that reaction of L with a mixture of Fe(II) and Ag(I) results in high yield formation of $[Ag_2FeL_2][BF_4]_4$ in which Ag(I) ions occupy the terminal 4-coordinate sites and Fe(II) occupies the central pseudo-octahedral site. Reaction of L with Ag(I) produced a mixture of $[Ag_3L_2][BF_4]_3$ (major product) and $[Ag_4L_2][BF_4]_4$ (minor product). In $[Ag_3L_2][BF_4]_3$ the central Ag(I) ion is, unusually, in a pseudo-octahedral coordination environment from the two meridional, terdentate bis(pyrazolyl)pyridine donors. In $[Ag_4L_2][BF_4]_4$ in contrast the central 6-coordinate cavity is occupied by two Ag(I) ions separated by 2.85 Å. The terdentate chelating bis(pyrazolyl)pyridine units at the centre of the helicate are now substantially twisted such that each donates a bidentate pyrazolyl-pyridine to one Ag(I) centre and a monodentate pyrazole unit to the other. In solution, ^{1}H NMR and mass spectroscopic evidence indicates that the fourth Ag(I) ion is lost and $[Ag_3L_2][BF_4]_3$ forms, unless a large excess of Ag(I) is present in which case traces of $[Ag_4L_2][BF_4]_4$ can be detected by mass spectrometry.

Introduction

Complexes with double or triple helical structures ('helicates') have been of interest in the field of coordination chemistry for many years, and have elegantly demonstrated how the formation of architecturally complex systems is directed by the interplay between simple parameters such as the stereoelectronic preference of the metal ions and the disposition of the binding sites in the ligand.[1,2] In addition to the interest in their structures and the mechanisms by which they assemble, they can also provide a convenient way for assembling a collection of different metal ions in heteronuclear arrays, as illustrated by Piguet's helicates containing both d-block and lanthanide metal ions which are of interest for their inter-metallic photo-induced energy-transfer.[3] To assemble a selection of different ions in such a helical array requires either ligands which contain two distinct binding sites (*e.g.* bidentate and terdentate, which give 6- and 9-coordinate sites in triple helical arrays),[3] or the use of ligands which partition into inequivalent domains, as in 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine which partitions into terdentate and bidentate domains, resulting in 6-coordinate and 4-coordinate sites in its double helicates [Cu(II)/Cu(I) or Co(II)/Ag(I)].[4]

In this paper we describe the synthesis and coordination chemistry of the ligand L (below) which contains a sequence of bidentate, terdentate and bidentate binding sites, which we expect to result in 4-, 6- and 4-coordinate sites in a double helical array. This has been exploited to prepare and structurally characterise a range of helicates in which the presence of different binding sites leads to the formation of heteronuclear complexes, as well as some unexpected homonuclear complexes. We note that Piguet and co-workers described heteronuclear helicates with a related 2 + 3 + 2 compartmental ligand L^2 some years ago, although this paper concentrated on solution rather than structural properties, providing a detailed NMR analysis of the complexes and a discussion of the thermodynamic and structural factors required for the helicates to form.[5]



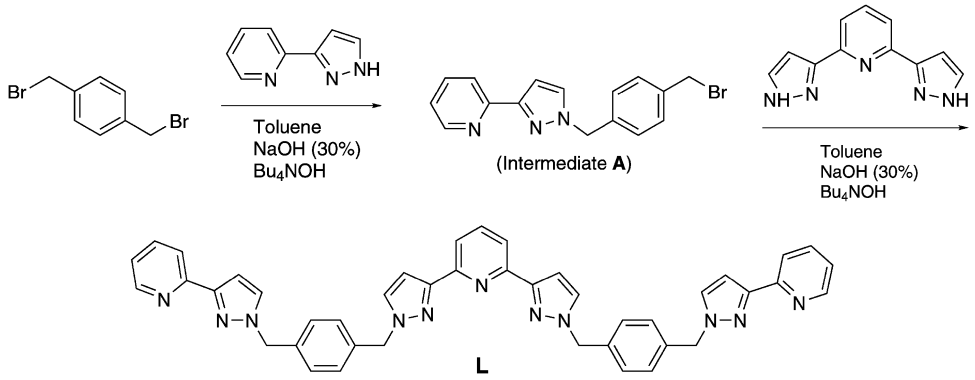
L^2 (see ref. 5)

Results and discussion

Ligand synthesis

The new ligand L was prepared according to the route in Scheme 1. Reaction of 3-(2-pyridyl)pyrazole with excess

DOI: 10.1039/b502423d



Scheme 1

1,4-bis(bromomethyl)benzene under phase-transfer conditions gave intermediate **A** in 62% yield; it is necessary to use a considerable excess of 1,2-bis(bromomethyl)benzene to prevent substitution at both bromomethyl sites. Reaction of intermediate **A**, having one reactive bromomethyl site, with half an equivalent of 2,6-bis(3-pyrazolyl)pyridine[6] under the same phase-transfer conditions, afforded the desired ligand L in 72% yield following chromatographic purification. ^{1}H NMR spectroscopy, electrospray mass spectrometry and elemental analysis confirmed the identity of the ligand. The *para* phenylene linkage separating the binding sites was used to ensure that each binding site had, for steric reasons, to bind a separate metal ion. We accordingly prepared a series of complexes which are sketched in Fig. 1; all were characterised on the basis of electrospray mass spectra and elemental analyses, as well as by X-ray crystallography.

Syntheses and structures of copper complexes

Reaction of $[Cu(MeCN)_4]PF_6$ with L in air afforded an orange precipitate of $[Cu_3L_2][PF_6]_4$ [denoted **Cu(121)**] in which the oxidation state distribution of +1, +2, +1 for the Cu ions is indicated by the presence of four counter ions and is consistent with the expected stereoelectronic preferences of Cu(I) and Cu(II) for four- and six-coordinate sites, respectively. The crystal structure (Fig. 2) confirms this and also confirms the

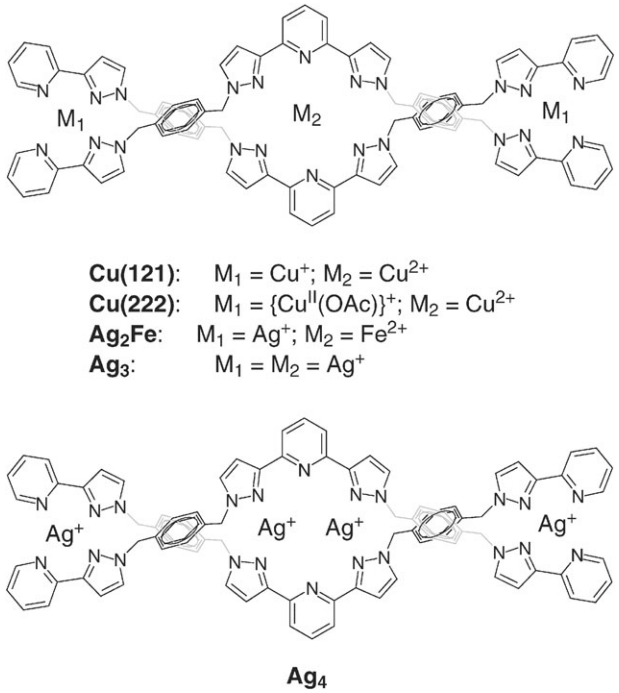


Fig. 1 Sketches of the structures of the complexes described in this paper, and the nomenclature used.

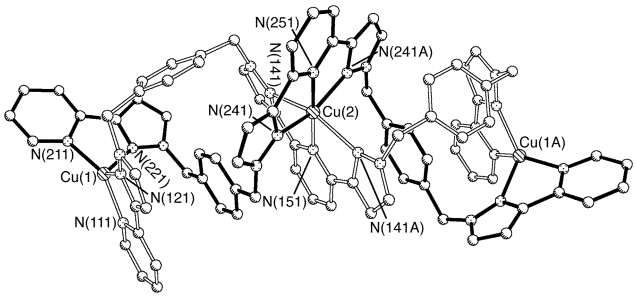


Fig. 2 The complex cation of $[Cu_3L_2][PF_6]_4 \cdot 4MeCN$ with the ligands shaded differently for clarity.

double helical arrangement of ligands about the three metal ions. The central six-coordinate Cu(II) ion [Cu(2)] lies on a twofold axis and has short, medium and long N–Cu–N axes with Cu–N distances on these axes of 1.95, 2.16 and 2.35 Å, with the shortest axis involving the central pyridyl donors, which is usual in terdentate chelates containing five-membered chelating rings.[7] The fact that one of the two axes involving the pyrazolyl donors is substantially longer than the other is consistent with the presence of Jahn–Teller distortion.[8] The four-coordinate Cu(I) ions are in irregular geometries that are a long way removed from the D_{2d} symmetry of 'ideal' bis-chelates, with Cu(1)–N separations in the range 1.99–2.16 Å and an angle between the two CuNN planes of 71° (see Table 1). The Cu(1)···Cu(2) separations are 8.46 Å.

A particularly striking feature of this structure is the series of π-stacking interactions along the long axis of the helicate between overlapping and essentially parallel aromatic units (Fig. 3). From the left of the figure working to the right, these domains comprise (i) the terminal pyridyl ring of one ligand (ligand A, pale grey); (ii) a phenylene spacer group from the alternate ligand (ligand B, dark grey); (iii) the central pyridyl ring from ligand A; (iv) the second phenylene spacer from ligand B; and (v) the terminal pyridyl ring of ligand A. The average inter-planar separations along the stack are 3.4–3.5 Å. It will be apparent from this that the two ligands are in quite different environments in the solid state, with the phenylene groups of ligand B being interleaved between terminal and central pyridyl rings of ligand A. In contrast, the phenylene units of ligand A and the pyridyl rings of ligand B are not involved in any significant intramolecular stacking interactions. Aromatic stacking interactions between ligands in helical structures is common, but is by no means essential for their formation, as shown by examples of helicate structures in which there is no significant inter-strand stacking.[9]

Reaction of L with copper(II) acetate in MeOH (2 : 3 ratio), followed by precipitation of the complex as its hexafluorophosphate salt, afforded $[Cu_3L_2(OAc)_2][PF_6]_4$ [denoted **Cu(222)**] in which all three sites are occupied by Cu(II) ions. The crystal structure (Fig. 4) confirms the expected double helical arrange-

Table 1 Selected bond lengths (Å) and angles (°) for $[Cu_3L_2][PF_6]_4 \cdot 4MeCN$

Cu(1)–N(211)	1.987(4)	Cu(2)–N(251)	1.951(5)
Cu(1)–N(111)	2.008(4)	Cu(2)–N(151)	1.952(5)
Cu(1)–N(121)	2.140(4)	Cu(2)–N(241)	2.157(4)
Cu(1)–N(221)	2.158(4)	Cu(2)–N(141)	2.349(4)
N(211)–Cu(1)–N(111)	149.55(19)	N(251)–Cu(2)–N(151)	180
N(211)–Cu(1)–N(121)	121.43(17)	N(251)–Cu(2)–N(241)	78.26(11)
N(111)–Cu(1)–N(121)	80.28(16)	N(151)–Cu(2)–N(241)	101.74(11)
N(211)–Cu(1)–N(221)	79.58(17)	N(241A)–Cu(2)–N(241)	156.5(2)
N(111)–Cu(1)–N(221)	107.62(17)	N(241)–Cu(2)–N(141A)	85.91(13)
N(121)–Cu(1)–N(221)	122.98(15)	N(251)–Cu(2)–N(141)	102.77(10)
N(241)–Cu(2)–N(141)	99.29(13)	N(151)–Cu(2)–N(141)	77.23(10)
N(141A)–Cu(2)–N(141)	154.46(19)		

Symmetry operation for generating equivalent atoms: $-x, y, -z + 0.5$.

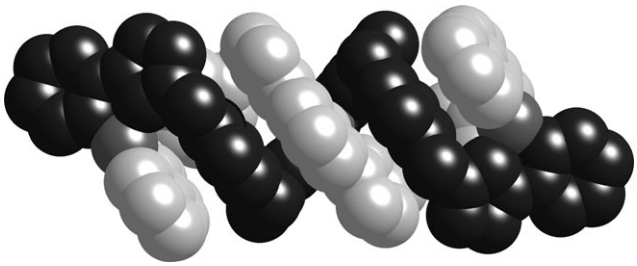


Fig. 3 Space-filling depiction of the complex cation of $[Cu_3L_2][PF_6]_4 \cdot 4MeCN$, emphasising the aromatic π-stacking between the interpenetrating ligands.

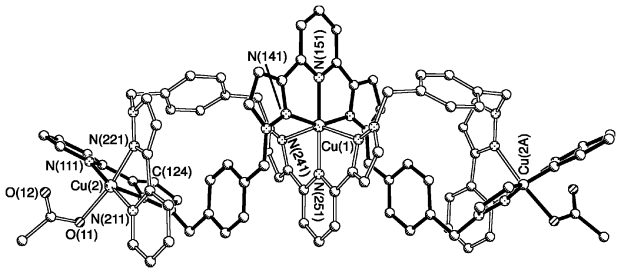


Fig. 4 The complex cation of $[Cu_3L_2(OAc)_2][PF_6]_4 \cdot 2MeCN$ with the ligands shaded differently for clarity.

ment of ligands about the three metal ions. The central metal ion Cu(1) is in an irregular 6-coordinate geometry and lies on a C_2 axis, with the same pattern of bond lengths as seen above—*viz.* the shortest axis involves the Cu–N(pyridyl) bonds (*ca.* 1.98 Å, see Table 2). In addition, one of the other two axes is considerably elongated, with the bonds to N(241) and N(241A) being 2.394(5) Å, in contrast to the bonds to the alternate pair of pyrazolyl donors N(141) and N(141A), which are 2.123(5) Å—clear evidence for a Jahn–Teller elongation along one axis.[8] The bite angles between the terminal pyrazolyl donors of each terdentate unit are both $<160°$, reflecting the usual steric limitations of such ligands which cannot stretch to give a bite angle of 180° between the termini.[7] The Cu(II) centres at the termini of the helicate, which are crystallographically equivalent, are ligated by two bidentate pyrazolyl-pyridine units, as well as a monodentate acetate ligand which allows them to attain a five-coordinate geometry. The coordination environment of these is closer to a square-based pyramid than a trigonal bipyramid, with the τ parameter [on a scale of 0 (perfect square pyramid) to 1 (perfect trigonal bipyramid)][10] being 0.30; the axial ligand is N(121) which, in keeping with the Jahn–Teller effect, has a longer bond to Cu(2) [2.282(5) Å] than the other four donors (average 2.01 Å). The Cu(1)···Cu(2) separations are 8.78 Å. The conformation of the two ligands is generally similar to what was observed in **Cu(121)**, with the phenylene spacers of one ligand (black) interleaved between the pyridyl rings of the other (hollow bonds) to give a five-component π-stack.

Synthesis and structure of a mixed-metal Ag_2Fe complex

The successful isolation of a Cu(I)–Cu(II)–Cu(I) system **[Cu(121)]** suggested that a mixed-metal complex, containing Ag(I) for the tetrahedral sites and Fe(II) for the octahedral sites, should be possible. Reaction of L with a mixture of $[Ag(MeCN)_4]BF_4$ and $Fe(BF_4)_2 \cdot 6H_2O$ (2 : 2 : 1 ratio) in MeCN

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_3L_2(OAc)_2][PF_6]_4 \cdot 2MeCN$

Cu(1)–N(151)	1.978(7)	Cu(2)–O(11)	1.958(4)
Cu(1)–N(251)	1.987(7)	Cu(2)–N(211)	2.002(5)
Cu(1)–N(141)	2.123(5)	Cu(2)–N(111)	2.011(5)
Cu(1)–N(241)	2.394(5)	Cu(2)–N(221)	2.068(5)
		Cu(2)–N(121)	2.282(5)
N(151)–Cu(1)–N(251)	180	O(11)–Cu(2)–N(211)	92.6(2)
N(151)–Cu(1)–N(141)	78.12(14)	O(11)–Cu(2)–N(111)	88.2(2)
N(251)–Cu(1)–N(141)	101.88(14)	N(211)–Cu(2)–N(111)	178.2(2)
N(141A)–Cu(1)–N(141)	156.2(3)	O(11)–Cu(2)–N(221)	160.05(19)
N(151)–Cu(1)–N(241)	103.88(14)	N(211)–Cu(2)–N(221)	80.0(2)
N(251)–Cu(1)–N(241)	76.12(13)	N(111)–Cu(2)–N(221)	98.8(2)
N(141A)–Cu(1)–N(241)	84.28(18)	O(11)–Cu(2)–N(121)	93.57(18)
N(141)–Cu(1)–N(241)	101.45(18)	N(211)–Cu(2)–N(121)	103.72(19)
N(241)–Cu(1)–N(241A)	152.2(3)	N(111)–Cu(2)–N(121)	77.83(19)
		N(221)–Cu(2)–N(121)	106.15(19)

Symmetry operation for generating equivalent atoms: $-x + 1, y, -z + 1.5$.

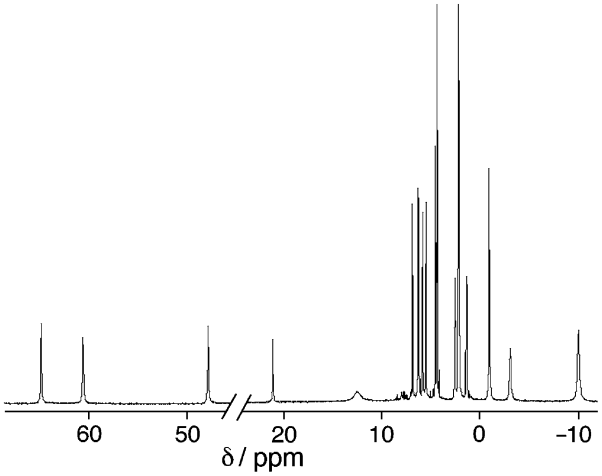


Fig. 5 Room-temperature ^{1}H NMR spectrum (300 MHz, CD_3CN) of **Ag_2Fe**.

afforded in high yield a yellow solid whose ES mass spectrum and elemental analysis were consistent with the formulation $[Ag_2FeL_2][BF_4]_4$ (denoted **Ag_2Fe**). The proton ^{1}H NMR spectrum (Fig. 5) was highly paramagnetically shifted, with peaks appearing in the range *ca.* −10 to +65 ppm, indicating a high-spin configuration for the Fe(II) centre. However the number of signals is that expected for a complex in which both ligands are equivalent and have two-fold symmetry, *i.e.* 16 peaks (assuming that the CH_2 protons are independent in the chiral environment, but the four protons on each phenyl ring split into two sets of two equivalent protons).

The crystal structure (Fig. 6) shows the complex to be essentially isostructural with **Cu(121)** apart from minor perturbations associated with the higher ionic radius of Ag(I), which results in Ag–N distances in the range 2.26–2.44 Å (see Table 3). The angle between the two AgNN planes is 70°. At the Fe(II) centre the bonds to the central pyridine rings of the terdentate chelates are again the shortest of the Fe–N bonds (average 2.11 Å), with the other two N–Fe–N axes being longer, but the substantial elongation of one of these axes with respect to the other that occurred with Cu(II) is not present. The Ag···Fe separation is 8.50 Å, almost identical to the separation between adjacent Cu centres in **Cu(121)**, and the ligand conformations and π-stacking arrangements are essentially identical.

Syntheses and structures of Ag(I) complexes

We next wanted to see what would happen if the ligand were provided only with a metal ion that is not normally found in an octahedral environment; specifically to see if an alternate self-assembly arrangement could occur which would avoid a 2 : 2 helicate which necessitates a central octahedral binding site. Accordingly we prepared complexes of L with Ag(I) alone, with some interesting results.

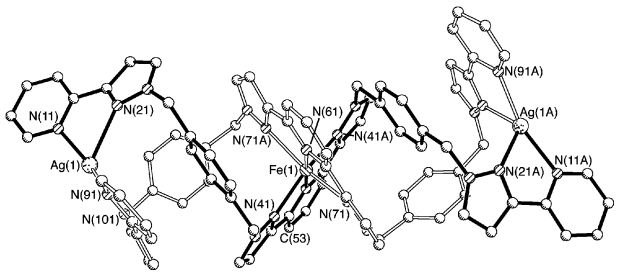


Fig. 6 The complex cation of $[Ag_2FeL_2][BF_4]_4$ with the ligands shaded differently for clarity.

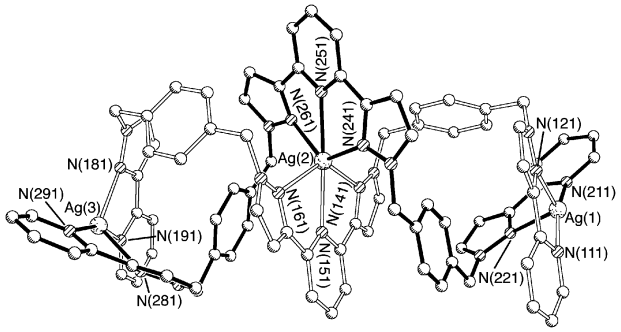


Fig. 7 The complex cation of $[Ag_3L_2][BF_4]_3 \cdot CH_3NO_2$ with the ligands shaded differently for clarity.

Reaction of L with $[Ag(MeCN)_4][BF_4]$ (2 : 3 molar ratio) in MeCN afforded a clear solution from which a white solid precipitated on addition of ether; mass spectrometry and elemental analysis indicated this to be $[Ag_3L_2][BF_4]_3$ (denoted **Ag_3**). The crystal structure (Fig. 7) shows it to be a double helicate similar to those described above, but with the central Ag(I) ion in a six-coordinate N-donor environment. This is rather unusual for Ag(I), which commonly forms complexes with N-donor ligands having a coordination number of 4, especially with bidentate chelating ligands such as diimines; indeed the tendency of Ag(I) to bind two diimines in an approximately mutually perpendicular arrangement has been used as a design principle for a wide range of helicate, grid-like and cylindrical complexes.[11] The few examples of hexadentate N-donor coordination around Ag(I)[12,13] are often imposed by a highly constrained ligand such as a macrocycle or a cryptand.[12] Surprisingly, no Ag^IN_6 complexes arise from coordination of two meridional tris-chelates, and in fact Ag(I) complexes with 2,2′:6′,2″-terpyridine are usually mononuclear four-coordinate complexes (with an additional solvent or counter-anion completing the coordination)[14] or have helical structures in which the ligand bridges two metal ions and the coordination number of the Ag(I) ions is low.[15,16] In **Ag_3**, the average Ag–N bond length about the six-coordinate ion is rather long, at 2.50 Å (see Table 3), compared to average Ag–N lengths of 2.34 Å and 2.36 Å about the four-coordinate ions Ag(1) and Ag(3), respectively, which is to be expected on electroneutrality grounds. The six Ag–N bonds all lie within the relatively narrow range of 2.40–2.59 Å such that none of them can be discounted as being anomalously long; Ag(2) is genuinely six-coordinate, presumably because of the limited flexibility and high stability of the helical structure. We note that a double helical complex of Ag(I) with a ligand containing two terpyridyl binding domains still gave only five-coordination around the Ag(I) ions, as one of the terminal pyridyl units was not coordinated and directed away from each Ag(I) ion.[17] In **Ag_3** this is not possible because of the position of the hexadentate cavity at the centre of the helical array; there is less scope for one of the terdentate units to coordinate incompletely without disrupting the rest of the structure. Conversely, binding of the two terminal Ag(I) ions in their 'ideal' four-coordinate geometry necessarily generates a hexadentate cavity at the centre of the helicate.

The metal–metal separations are 8.25 Å for Ag(1)–Ag(2) and 8.06 Å for Ag(2)–Ag(3), which are slightly smaller than seen for the other complexes, resulting in a more compact arrangement of the helical superstructure. This compression is apparent in the coordination geometry around Ag(2), where the two terdentate chelating units are not mutually perpendicular, with an angle of 75° between the two AgN_3 mean planes. It is noteworthy that whilst in the solid state the two ligands are clearly inequivalent, this is not reflected in the solution ^{1}H NMR spectrum of the complex (see Experimental section) which is consistent with four-fold symmetry, *i.e.* both ligands

Table 3 Selected bond lengths (Å) and angles (°) for $[Ag_2FeL_2][BF_4]_4$ and $[Ag_3L_2][BF_4]_3 \cdot CH_3NO_2$

$[Ag_2FeL_2][BF_4]_4$			
Ag(1)–N(11)	2.259(4)	Fe(1)–N(61)	2.107(3)
Ag(1)–N(91)	2.304(4)	Fe(1)–N(51)	2.118(6)
Ag(1)–N(101)	2.323(4)	Fe(1)–N(41)	2.214(3)
Ag(1)–N(21)	2.440(4)	Fe(1)–N(71)	2.269(4)
N(11)–Ag(1)–N(91)	157.76(16)	N(61)–Fe(1)–N(51)	180.000(1)
N(11)–Ag(1)–N(101)	128.82(16)	N(61)–Fe(1)–N(41)	105.51(11)
N(91)–Ag(1)–N(101)	72.28(16)	N(51)–Fe(1)–N(41)	74.49(11)
N(11)–Ag(1)–N(21)	71.98(15)	N(41)–Fe(1)–N(41A)	149.0(2)
N(91)–Ag(1)–N(21)	105.05(14)	N(61)–Fe(1)–N(71)	75.08(10)
N(101)–Ag(1)–N(21)	120.44(13)	N(51)–Fe(1)–N(71)	104.92(10)
		N(41)–Fe(1)–N(71)	86.27(13)
		N(41)–Fe(1)–N(71A)	101.70(13)
		N(71)–Fe(1)–N(71A)	150.2(2)

Symmetry operation for generating equivalent atoms: $-x, y, -z + 0.5$.

$[Ag_3L_2][BF_4]_3 \cdot CH_3NO_2$			
Ag(1)–N(211)	2.271(3)	Ag(2)–N(241)	2.560(3)
Ag(1)–N(111)	2.289(3)	Ag(2)–N(261)	2.592(3)
Ag(1)–N(121)	2.392(4)	Ag(2)–N(161)	2.594(3)
Ag(1)–N(221)	2.412(3)	Ag(3)–N(291)	2.246(4)
Ag(2)–N(251)	2.398(3)	Ag(3)–N(191)	2.293(4)
Ag(2)–N(141)	2.416(3)	Ag(3)–N(181)	2.403(4)
Ag(2)–N(151)	2.424(3)	Ag(3)–N(281)	2.493(4)
N(211)–Ag(1)–N(111)	166.45(13)	N(151)–Ag(2)–N(261)	123.75(11)
N(211)–Ag(1)–N(121)	120.51(12)	N(241)–Ag(2)–N(261)	134.36(10)
N(111)–Ag(1)–N(121)	72.42(12)	N(251)–Ag(2)–N(161)	101.62(11)
N(211)–Ag(1)–N(221)	71.63(12)	N(141)–Ag(2)–N(161)	133.64(11)
N(111)–Ag(1)–N(221)	106.77(12)	N(151)–Ag(2)–N(161)	65.58(11)
N(121)–Ag(1)–N(221)	118.71(11)	N(241)–Ag(2)–N(161)	76.36(10)
N(251)–Ag(2)–N(141)	124.63(11)	N(261)–Ag(2)–N(161)	119.21(10)
N(251)–Ag(2)–N(151)	165.79(11)	N(291)–Ag(3)–N(191)	161.77(13)
N(141)–Ag(2)–N(151)	68.11(11)	N(291)–Ag(3)–N(181)	125.94(13)
N(251)–Ag(2)–N(241)	67.79(11)	N(191)–Ag(3)–N(181)	72.22(13)
N(141)–Ag(2)–N(241)	115.79(10)	N(291)–Ag(3)–N(281)	71.63(13)
N(151)–Ag(2)–N(241)	101.88(11)	N(191)–Ag(3)–N(281)	99.83(13)
N(251)–Ag(2)–N(261)	67.07(11)	N(181)–Ag(3)–N(281)	125.67(12)
N(141)–Ag(2)–N(261)	85.24(11)		

equivalent and each ligand having two-fold symmetry, indicating dynamic behaviour which interchanges the two ligand environments quickly on the NMR timescale.

When growing crystals of **Ag_3** we occasionally noticed the appearance of a small number of crystals with a distinctly different habit and appearance from those of the bulk of the product. These could be separated manually, and the elemental analysis was clearly inconsistent **Ag_3** but suggested the formulation $[Ag_4L_2][BF_4]_4$. An X-ray crystallographic investigation confirmed formation of a tetranuclear helicate $[Ag_4L_2][BF_4]_4$ (**Ag_4**, Fig. 8). The small size and poor crystallinity of these crystals, and extensive disorder of anions and solvent molecules, meant that the structure is of poor quality (R_1 = 16%) and no detailed discussion of structural parameters is appropriate. However, we obtained the same picture from several independent crystals that were examined and are happy that the gross structure as shown in Fig. 8 is correct. In this complex the central six-coordinate cavity of the helical structure is occupied by two Ag(I) ions, separated by 2.85 Å, each coordinated by three N atoms. The terdentate chelating bis(pyrazolyl)pyridine units at the centre of the helicate are now substantially twisted such that each donates a bidentate pyrazolyl-pyridine to one Ag(I) centre and a monodentate pyrazole unit to the other; this bridging mode of the bis(pyrazolyl)pyridine unit is similar to that shown by terpyridine in some polynuclear complexes with Ag(I),[15] and has been seen in other dinuclear helical complexes of both Ag(I)[16] and Cu(I)[18] in which a pair of metal ions is coordinated by two terdentate ligands. The Ag–N(pyridyl) distances (≈2.5 Å) are clearly much longer than the Ag–N(pyrazolyl) distances (≈2.2 Å), so the coordination geometry around Ag(1) and Ag(2) can be considered as approximately linear two-coordinate, with an additional weaker interaction with a pyridyl donor. The 'terminal' Ag(I) ions Ag(3) and Ag(4) are in their usual irregular four-coordinate geometry from two bidentate chelating units.

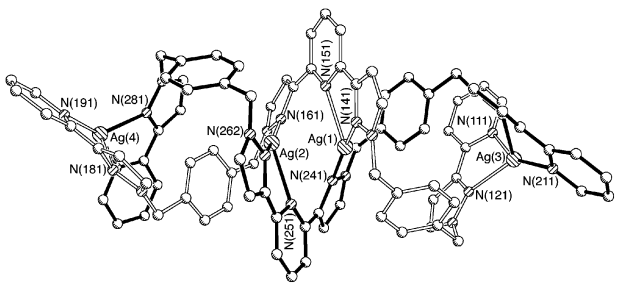


Fig. 8 The complex cation of $[Ag_4L_2][BF_4]_4 \cdot 3MeCN$ with the ligands shaded differently for clarity.

Attempts to characterize this species in solution were largely unsuccessful. The ^1H NMR spectrum and ES mass spectrum of redissolved crystals of **Ag_4** were both identical to those obtained for **Ag_3**. The implication is that the cation $[Ag_4L_2]^{4+}$ exists only in the solid state, and loses one Ag^+ ion to give $[Ag_3L_2]^{3+}$ when dissolved in good donor solvents. To push this equilibrium towards **Ag_4** we added a large excess of

$[Ag(MeCN)_4][BF_4]$ to a solution of redissolved crystals of **Ag_4** in MeCN, and under these conditions the ES mass spectrum showed, in addition to several peaks arising from **Ag_3**, a weak peak at m/z 2101 which can be assigned to the tetranuclear species $[Ag_4L_2(BF_4)_3]^+$. It clearly exists to only a very small extent in solution and its presence in the mix of crystalline products suggests that it is largely a kinetic artefact of crystallisation.

Experimental

General details

The following instruments were used for standard spectroscopic and analytical studies. For ^{1}H NMR spectra, Bruker AC 250 or Bruker AMX 400 spectrometers; FAB mass spectra, a VG AutoSpec spectrometer; electrospray mass spectra, a Waters LCT spectrometer (University of Sheffield) or a VG Quattro II triple-quadrupole instrument (University of Huddersfield); UV/Vis spectra, a Cary-50 spectrophotometer.

3-(2-Pyridyl)pyrazole[19] and 2,6-bis(3-pyrazolyl)pyridine[6] were prepared according to the published methods.

Preparation of ligand L

Intermediate A. (See Scheme 1.) A mixture of 1,4-bis(bromomethyl)benzene (5.20 g, 19.8 mmol), 3-(2-pyridyl)pyrazole (1.43 g, 9.86 mmol), aqueous NaOH (10 M, 40 cm^3), toluene (130 cm^3) and Bu_4NOH (40% aqueous solution, 5 drops) was stirred at room temperature for 1 h. The mixture was diluted with H_2O (100 cm^3) before the organic layer was separated, dried over $MgSO_4$ and concentrated to a give a white solid. Purification by column chromatography on alumina using hexane–dichloromethane (1 : 4) as eluent gave the desired product as a white crystalline solid. Yield: 2.01 g, 62%. EI MS: m/z 327 (42%, M^+), 248 (100%, $\{M - Br\}^+$). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.63 (1H, ddd, $J = 0.9, 1.8, 4.9$; pyridyl H^6), 7.94 (1H, d, $J = 7.9$; pyridyl H^3), 7.71 (1H, pseudo-t; pyridyl H^4), 7.42 (1H, d, $J = 2.4$; pyrazolyl H^5), 7.41–7.34 (2H, m; phenyl), 7.26–7.17 (3H, m; 2 × phenyl, and pyridyl H^5), 6.92 (1H, d, $J = 2.4$ Hz; pyrazolyl H^4), 5.39 (2H, s; CH_2-pz), 4.47 (2H, s, CH_2Br). Found: C, 57.5; H, 4.1; N, 12.4%: $C_{16}H_{14}N_3Br \cdot 0.5\ H_2O$ requires C, 56.9; H, 4.5; N, 12.5%.

Ligand L. A mixture of **A** (1.37 g, 4.16 mmol), 2,6-bis-(3-pyrazolyl)pyridine (0.46 g, 2.18 mmol), aqueous NaOH (10 M, 40 cm^3), toluene (130 cm^3) and Bu_4NOH (40% aqueous solution, 5 drops) was stirred at 60 °C for 2 h. After cooling the mixture was diluted with H_2O (100 cm^3) before the organic layer was separated, dried over $MgSO_4$ and concentrated to a give a white solid. Purification by column chromatography on alumina using dichloromethane as eluent gave the desired product as a white crystalline solid. Yield: 1.06 g, 72%. ES MS: m/z 706 (100%, MH^+). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 8.66 (2H, ddd, $J = 0.7, 1.6, 4.4$; pyridyl H^6), 7.97 (2H, d, $J = 7.9$; pyridyl H^3), 7.91 (2H, d, $J = 7.9$; pyridyl H^3), 7.78–7.70 (3H, m; 3 × pyridyl H^4), 7.43 (4H, d, $J = 2.4$; pyrazolyl H^5), 7.28–7.17 (10H, m; 2 × pyridyl H^5 and 8 × phenyl), 7.07 (2H, d, $J = 2.4$; pyrazolyl H^4), 6.94 (2H, d, $J = 2.4$ Hz; pyrazolyl H^4), 5.41–5.38 (8 H, m; CH_2). Found: C, 72.2; H, 4.9; N, 21.3%: $C_{43}H_{35}N_{11} \cdot 0.5H_2O$ requires C, 72.3; H, 5.1; N, 21.6%.

$[Cu_3L_2(OAc)_2][PF_6]_4$

A mixture of L (100 mg, 0.14 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (37 mg, 0.17 mmol) in methanol (3 cm^3) was stirred for 5 minutes to give a clear solution, from which a precipitate appeared on addition of aqueous KPF_6. The pale green precipitate was filtered off, rinsed with H_2O and methanol before being dried *in vacuo*. Yield: 75 mg, 47%. ES MS: m/z 2153.8 ($\{Cu_3L_2(OAc)_2(PF_6)_3\}^+$), 1004.5 ($\{Cu_3L_2(OAc)_2(PF_6)_2\}^{2+}$). Found: C, 44.8; H, 3.4; N, 12.8%: $[Cu_3L_2(OAc)_2(PF_6)_4] \cdot 4H_2O$ requires C, 45.2; H, 3.6; N, 12.9%. X-Ray quality crystals were grown by diffusion of diethyl ether into a solution of the complex in acetonitrile.

$[Cu_3L_2][PF_6]_4$

$[Cu(MeCN)_4]PF_6$ (39 mg, 0.11 mmol) was added to a stirred suspension of L (50 mg, 0.07 mmol) in acetonitrile (3 cm^3) causing the ligand to dissolve. Addition of ether to the solution precipitated the product as an orange crystalline solid which was filtered off and dried *in vacuo*. Yield: 35 mg, 46%. ES MS: m/z 1891.9 ($\{Cu_3L_2(PF_6)_2\}^+$), 873.0 ($\{Cu_3L_2(PF_6)\}^{2+}$), 533.8 ($\{Cu_3L_2\}^{3+}$). Found: C, 47.0; H, 3.0; N, 13.8%: $[Cu_3L_2(PF_6)_4]$ requires C, 47.3; H, 3.2; N, 14.1%. X-Ray quality crystals were grown by slow evaporation of a solution of the complex in acetonitrile.

$[Ag_2FeL_2][BF_4]_4$

To a stirred suspension of L (350 mg, 0.50 mmol) in acetonitrile (5 cm^3) was added $Fe(BF_4)_2 \cdot 6H_2O$ (84 mg, 0.25 mmol) followed by $[Ag(MeCN)_4]BF_4$ (178 mg, 0.50 mmol); after stirring, a yellow crystalline solid precipitated which was filtered off and dried *in vacuo*. Yield: 474 mg, 93%. ES MS: m/z 1942.9 ($\{Ag_2FeL_2(BF_4)_3\}^+$). Found C, 49.0; H, 3.4; N, 14.6%: $[Ag_2FeL_2(BF_4)_4] \cdot 4H_2O$ requires C, 49.1; H, 3.7; N, 14.7%. X-Ray quality crystals were grown by diffusion of diethyl ether into a solution of the complex in nitromethane.

$[Ag_3L_2][BF_4]_3$

$[Ag(MeCN)_4]BF_4$ (76 mg, 0.21 mmol) was added to a stirred suspension of L (100 mg, 0.14 mmol) in acetonitrile (3 cm^3) causing the ligand to dissolve. Addition of ether to the reaction mixture precipitated the product as a white crystalline solid which was filtered off and dried *in vacuo*. Yield: 122 mg, 87%. ES MS: m/z 1908.0 ($\{Ag_3L_2(BF_4)_2\}^+$), 578.3 ($\{Ag_3L_2\}^{3+}$). ^{1}H NMR (270 MHz, CD_3CN) δ 8.36 (4H, ddd, $J = 0.9, 1.7, 5.0$; pyridyl H^6), 7.95–7.80 (10H, m, 6 × pyridyl H^4, 4 × pyridyl H^3), 7.73 (4H, d, $J = 2.4$, pyrazolyl), 7.66 (4H, d, $J = 7.36$, pyridyl H^3), 7.51 (4H, d, $J = 2.1$, pyrazolyl), 7.36 (4H, ddd, $J = 1.7, 5.0, 7.2$; pyridyl H^5), 6.92 (4H, d, $J = 2.4$; pyrazolyl), 6.84 (4H, d, $J = 2.4$; pyrazolyl), 5.88 (4H, d, $J = 8.2$; phenyl), 6.72 (4H, d, $J = 8.2$; phenyl) 5.05–3.85 (16H, m; CH_2). Found C, 50.7; H, 3.6; N, 15.2%: $[Ag_3L_2(BF_4)_3] \cdot 2H_2O$ requires C, 50.8; H, 3.7; N, 15.2%. X-Ray quality crystals were grown by diffusion of diethyl ether into a solution of the complex in nitromethane.

A small number of crystals of $[Ag_4L_2][BF_4]_4$ could be separated manually from the crystals of $[Ag_3L_2][BF_3]_3$ which formed the bulk of the material. Found C, 46.4; H, 3.3; N, 13.5%; $[Ag_4L_2(BF_4)_4] \cdot 3H_2O$ requires C, 46.0; H, 3.1; N, 13.7%.

X-Ray crystallography

For each complex a suitable crystal was coated with hydrocarbon oil and attached to the tip of a glass fibre, which was then transferred to a Bruker-AXS PROTEUM {for $[Ag_2FeL_2][BF_4]_4 \cdot 4MeCN$} or SMART diffractometer (for all other structures) under a stream of cold N_2. Details of the crystal parameters, data collection and refinement for each of the structures are collected in Table 4. After data collection, in each case an empirical absorption correction (SADABS), based on symmetry-equivalent and repeated reflections, was applied;[20] the structures were then solved by conventional direct methods and refined on all F^2 data using the SHELX suite of programs.[21] Except where otherwise stated, non-

Table 4 Crystal, data collection and refinement details for the crystal structures[a]

Complex	$[Cu_3L_2(OAc)_2][PF_6]_4 \cdot 2MeCN$	$[Cu_3L_2][PF_6]_4 \cdot 4(MeCN)$	$[Ag_2FeL_2][BF_4]_4$	$[Ag_3L_2][BF_4]_3 \cdot (MeNO_2)$	$[Ag_4L_2][BF_4]_4 \cdot (ca.\ 3MeCN)$
Formula	$C_{94}H_{82}N_{24}O_4P_4F_{24}Cu_3$	$C_{94}H_{82}N_{26}P_4F_{24}Cu_3$	$C_{86}H_{70}N_{22}B_4F_{16}Ag_2Fe$	$C_{87}H_{73}N_{23}B_3F_{12}O_2Ag_3$	$C_{92}H_{79}N_{25}B_4F_{16}Ag_4$
Formula weight	2382.34	2346.36	2030.47	2056.72	*ca.* 2313
T/K	150(2)	150(2)	100(2)	150(2)	150(2)
λ/Å	0.710 73	0.710 73	1.541 78	0.710 73	0.710 73
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$P2(1)/c$	$P2(1)/n$
a/Å	22.397(3)	30.388(4)	30.6701(18)	28.943(5)	19.066(3)
b/Å	15.0598(19)	14.590(2)	13.7810(8)	11.5611(19)	28.822(4)
c/Å	30.411(4)	22.348(3)	21.3348(13)	25.405(4)	19.716(3)
β/°	99.856(3)	98.943(3)	97.511(2)	100.848(3)	115.093(2)
V/Å^3	10 106(2)	9788(2)	8940.1(9)	8349(2)	9812(2)
Z	4	4	4	4	4
D_{calc}/Mg m^{-3}	1.566	1.592	1.509	1.636	1.566
μ/mm^{-1}	0.797	0.820	5.553	0.790	0.876
Crystal size/mm	0.41 × 0.34 × 0.10	0.46 × 0.32 × 0.21	0.1 × 0.1 × 0.075	0.50 × 0.40 × 0.20	0.25 × 0.20 × 0.10
Reflections collected	56 428	53 898	20 405	67 846	82 310
Independent reflections	11 549 [R(int) = 0.1498]	11 161 [R(int) = 0.0916]	7848 [R_{int} = 0.0549]	12 038 [R(int) = 0.0464]	22 151 [R(int) = 0.1060]
Data/restraints/parameters	11 549/11/687	11 161/8/684	7848/0/583	12 038/2/1172	22 151/160/522
Final R indices[b]: $R1$, $wR2$	0.085, 0.269	0.071, 0.216	0.055, 0.135	0.038, 0.106	0.162, 0.514

[a] All data sets were collected on a Bruker SMART diffractometer with Mo-Kα radiation, except for $[Ag_2FeL_2][BF_4]_4$ which was collected on a Bruker PROTEUM diffractometer with Cu-Kα radiation. [b] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters which were *ca.* 1.2 × (aromatic CH) or 1.5 × (Me) the equivalent isotropic thermal parameters of their parent carbon atoms.

In $[Cu_3L_2(OAc)_2][PF_6]_4 \cdot 2MeCN$ the central metal atom lies on a C_2 axis such that the asymmetric unit contains half of the complex cation, two anions and one solvent molecule. One hexafluorophosphate anion exhibits disorder with two of the F atoms [F(11) and F(12)] disordered over two sites (site occupancies 0.55/0.45); these F atoms were refined isotropically. The MeCN molecule was also disordered, with C(22) and N(23) split over two sites (occupancies 0.59/0.41); all three heavy atoms in this molecule were refined isotropically.

$[Cu_3L_2][PF_6]_4 \cdot 4(MeCN)$ likewise has two-fold symmetry. One of the two independent hexafluorophosphate anions shows some disorder, with atoms F(22) and F(24) disordered over two sites (occupancies 0.58/0.42); these atoms were refined isotropically.

$[Ag_2FeL_2][BF_4]_4$ also has two-fold symmetry; this structure determination presented no significant problems.

$[Ag_3L_2][BF_4]_3 \cdot (MeNO_2)$ has no internal symmetry, with all atoms being crystallographically unique. The nitromethane molecule exhibited some disorder, with O(3) being split over two sites (occupancies 0.59/0.41); this atom was refined isotropically.

$[Ag_4L_2][BF_4]_4 \cdot (ca.\ 3MeCN)$ has no internal symmetry, with all atoms being crystallographically unique. Crystals of this were very small and fragile and diffracted weakly; accordingly the structural determination is poor (R_1 = 16%) and only the gross structure should be considered to have any significance. The result given is the best of numerous attempts. Only the Ag and coordinated N atoms were refined with anisotropic thermal parameters. Extensive use of restraints was required to keep the geometries and (isotropic) thermal parameters of the fluoroborate anions reasonable. Extensive disorder of lattice solvent was apparent; numerous regions of residual electron density, which could not be made to correspond to any recognizable solvent molecules, were simply assigned as C atoms. The total of nine of these may approximately correspond to three MeCN solvent molecules, which is what has been assumed for the purposes of determining molecular weight, density *etc.* in the final refinement. There are numerous residual electron-density peaks in the range 2–3 e Å^{-3} which are close to either anions or regions of disordered solvent. The $[Ag_4L_2]^{4+}$ cation itself is reasonably well behaved, although high thermal parameters for Ag(4) and some of the pyridyl and pyrazolyl rings coordinated to it indicate unresolved disorder in these also.

CCDC reference numbers 265432–265436.

See http://www.rsc.org/suppdata/nj/b5/b502423d/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC and the University of Sheffield for financial support.

References

1 Reviews: (*a*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (*b*) E. C. Constable, in *Polynuclear Transition Metal Helicates, Comprehensive Supramolecular Chemistry*, ed. J.-P. Sauvage, Elsevier, Oxford, 1996, vol. 9, pp. 213–252; (*c*) M. J. Hannon and L. J. Childs, *Supramol. Chem.*, 2004, **16**, 7; (*d*) M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281.

2 Some recent examples: (*a*) S. G. Telfer, N. Tajima, R. Kuroda, M. Cantuel and C. Piguet, *Inorg. Chem.*, 2004, **43**, 5302; (*b*) N. Ouali, J. P. Rivera, P. Y. Morgantini, J. Weber and C. Piguet, *Dalton Trans.*, 2003, 1251; (*c*) N. Fatin-Rouge, S. Blanc, A. Pfeil, A. Rigault, A. M. Albrecht-Gary and J.-M. Lehn, *Helv. Chim. Acta*, 2001, **84**, 1694; (*d*) L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. T. Zeng, *Chem. Commun.*, 2004, 654; (*e*) C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 2001, 550; (*f*) N. Yoshido, H. Oshio and T. Ito, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1674; (*g*) P. E. Kruger, N. Martin and M. Nieuwenhuyzen, *J. Chem. Soc., Dalton Trans*, 2001, 1966; (*h*) F. Tuna, J. Hamblin, A. Jackson, G. Clarkson, N. W. Alcock and M. J. Hannon, *Dalton Trans.*, 2003, 2141; (*i*) B. Quinodoz, G. Labat, H. Stoeckli-Evans and A. von Zelewsky, *Inorg. Chem.*, 2004, **43**, 7994; (*j*) A. Orita, T. Nakano, D. L. An, K. Tanikawa, K. Wakamatsu and J. Otera, *J. Am. Chem. Soc.*, 2004, **126**, 10389; (*k*) J. R. Nitscke, D. Schultz,

G. Bernardinelli and D. Gérard, *J. Am. Chem. Soc.*, 2004, **126**, 16538; (*l*) T. K. Ronson, H. Adams and M. D. Ward, *Inorg. Chim. Acta*, 2005, **358**, 1943.
3 D. Imbert, M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli and C. Piguet, *J. Am. Chem. Soc.*, 2003, **125**, 15698.
4 (*a*) M. Barley, E. C. Constable, S. A. Corr, R. C. S. McQueen, J. C. Nutkins, M. D. Ward and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1988, 2655; (*b*) E. C. Constable, A. J. Edwards, P. R. Raithby and J. V. Walker, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1465; (*c*) E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67.
5 C. Piguet, G. Hopfgartner, B. Bocquet, O. Schaad and A. F. Williams, *J. Am. Chem. Soc.*, 1994, **116**, 9092.
6 D. A. Bardwell, J. C. Jeffery, P. L. Jones, J. A. McCleverty, E. Psillakis, Z. Reeves and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1997, 2079.
7 E. C. Constable, *Adv. Inorg. Chem.*, 1986, **30**, 69.
8 M. A. Halcrow, *Dalton Trans.*, 2003, 4375.
9 E. C. Constable, M. J. Hannon and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 1883.
10 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
11 (*a*) A. Marquis, J. P. Kintzinger, R. Graff, P. N. W. Baxter and J.-M. Lehn, *Angew. Chem. Int. Ed.*, 2002, **41**, 2760; (*b*) P. N. W. Baxter, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 2000, **6**, 4510; (*c*) P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1978; (*d*) P. N. W. Baxter, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1999, **5**, 102.
12 (*a*) A. Brooker, J. D. Ewing and J. Nelson, *Inorg. Chim. Acta*, 2001, **317**, 53; (*b*) J. de Mendoza, E. Mesa, J.-C. Rodriguez-Ubis, P. Vazquez, F. Vögtle, P.-M. Windscheif, K. Rissanen, J.-M. Lehn, D. Lilienbaum and R. Ziessel, *Angew. Chem. Int. Ed.*, 1991, **30**, 1331; (*c*) H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton and G. Rossi, *J. Chem. Soc., Dalton Trans.*, 1990, 1271; (*d*) H. Adams, N. A. Bailey, M. J. S. Dwyer, D. E. Fenton, P. C. Hellier, P. D. Jempstead and J. M. Latour, *J. Chem. Soc., Dalton Trans.*, 1993, 1207.
13 (*a*) N. S. Oxtoby, A. J. Blake, N. R. Champness and C. Wilson, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4905; (*b*) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834; (*c*) C. Stockheim, K. Wieghardt, B. Nuber, J. Weiss, U. Florke and H.-J. Haupt, *J. Chem. Soc., Dalton Trans.*, 1991, 1487; (*d*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895; (*e*) D. L. Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands and G. P. A. Yap, *Organometallics*, 1997, **16**, 349; (*f*) B. F. Abrahams, P. A. Jackson and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 2656; (*g*) L. Tei, A. J. Blake, P. A. Cooke, C. Caltagirone, F. Demartin, V. Lippolis, F. Morale, C. Wilson and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 2002, 1662; (*h*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *New J. Chem.*, 2003, **27**, 483; (*i*) D. Guo, K.-L. Pang, C.-Y. Duan, Y.-G. Zhao and Q.-J. Meng, *Chem. Lett.*, 2002, 1014; (*j*) M. Pascu, F. Tuna, E. Kolodziejczyk, G. I. Pascu, G. Clarkson and M. J. Hannon, *Dalton Trans.*, 2004, 1546.
14 E. C. Constable, A. J. Edwards, G. R. Haire, M. J. Hannon and P. R. Raithby, *Polyhedron*, 1998, **17**, 243.
15 (*a*) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1998, 2659; (*b*) G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 2000, 945; (*c*) S. Binsilong, J. D. Kildea, W. C. Patalinghug, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1994, **47**, 1545; (*d*) L. Hou and D. Li, *Inorg. Chem. Commun.*, 2005, **8**, 128; (*e*) M. J. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. Alcock, *Chem. Eur. J.*, 2002, **8**, 2225.
16 C. Provent, S. Hewage, G. Brand, G. Bernardinelli, L. J. Charbonnière and A. F. Williams, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1287.
17 P. K.-K. Ho, S.-M. Peng, K.-Y. Wong and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1996, 1829.
18 (*a*) N. K. Solanki, A. E. H. Wheatley, S. Radojevic, M. McPartlin and M. A. Halcrow, *J. Chem. Soc., Dalton Trans.*, 1999, 521; (*b*) C. Piguet, G. Bernardinelli and A. F. Williams, *Inorg. Chem.*, 1989, **28**, 2920.
19 (*a*) A. J. Amoroso, A. M. W. Cargill Thompson, J. C. Jeffery, P. L. Jones, J. A. McCleverty and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1994, 2751; (*b*) H. Brunner and T. Scheck, *Chem. Ber.*, 1992, **125**, 701.
20 G. M. Sheldrick, *SADABS, A program for absorption correction with the Siemens SMART area-detector system*, University of Göttingen, Germany, 1996.
21 G. M. Sheldrick, *SHELXS-97 and SHELXL-97, programs for crystal structure solution and refinement*, University of Göttingen, Germany, 1997.