The effect of phenyl substituents on supramolecular assemblies containing directly linked bis-pyridylimine ligands: synthesis and structural characterisation of mononuclear nickel(II) and dinuclear silver(I) and cobalt(III) complexes of (2-pyridyl)phenylketazine

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The effects of phenyl substituents introduced at the imine carbon of directly-linked bis-pyridylimine ligands is investigated. With octahedral metals the (2-pyridyl)phenylketazine ligand acts as an N_3 donor ligand with a non-coordinated imine unit. The triple-helical $[M_2L_3]^{4+}$ complexes (observed with the unsubstituted ligand and in which the ligand uses all four nitrogen atoms) are not observed. A mononuclear $[NiL_2]^{2+}$ complex containing *mer*-coordinated N_3 ligands and a dinuclear $[Co_2L_2(OAc)(OH)_2]^{3+}$ containing *fac*-coordinated ligands are structurally characterised. With silver(I) the library of supramolecular architectures observed for the unsubstituted ligand is driven to a single double-helical architecture by the presence of the phenyl substituents. A dimeric $[Ag_2L_2]^{2+}$ double-helical cation is structurally characterised. In addition to the N_4 coordination afforded by the ligands, one of the silver centres in each helicate forms a short contact to a methanol solvent or a tetrafluoroborate anion. Although the double-helical structure can support the addition of four phenyl substituents, it appears that the triple-helical structure is unable to accommodate the steric requirements of six phenyl substituents. Thus in this system, the phenyl substituents destabilise the *triple*-helical architectures but stabilise *double*-helical architectures (relative to the alternative competing structures).

Introduction

We have been investigating synthetic routes that will allow sophisticated metallo-supramolecular architectures[1–4] to be constructed quickly and simply from commercial reagents.[5–11] In particular we have developed a range of simple imine-based ligand systems which are readily prepared and allow access to a range of different structures.[5–11] Using our approach we have designed double-, triple- and circular- helicates, grids, metallo-cyclophanes and helical and non-helical polymers from bis-pyridylimine ligands and explored routes to encode additional information into the array such as strand directionality, groove size and chirality.

We have explored the chemistry of pyridylazines which are the simplest class of bis-pyridylimine ligands and in which the two pyridylimine binding units are linked directly (no spacer unit) through the imine nitrogen atoms (see Fig. 1). These ligand systems not only allow access to a fascinating range of supramolecular architectures but are of historic importance to the field of metallo-supramolecular chemistry; In the late 1950s, Stratton and Busch[12] described the reaction of L^1 with octahedral transition metal ions to give $[M_2(L^1)_3]^{4+}$ tetracations. The graphical illustration of their proposed "spiral" cation structure is clearly that of a triple helix and we have confirmed this triple-helical architecture through X-ray crystallography.[6] We have also explored the chemistry of these systems with d^{10} monocations and demonstrated the formation of triple helicates, polymers, dimers, double helicates, grids and trinuclear circular helicates.[6,11] A particular focus has been to probe how different metal ions affect the architecture and the extent to which substituents (introduced at the imine carbon) can also influence the architecture adopted. To this end we studied the

copper(I) chemistry of the ligands L^1, L^2 and L^3.[11] While the chemistry of the ligands L^1 and L^2 with other metal ions is well established,[12–15] the chemistry of L^3 has been the subject of just a single report.[16] We have therefore undertaken a more detailed study of the chemistry of this ligand and report that study herein.

Results and discussion

Octahedral metal ions

The reaction of L^1 with octahedral metal ions was investigated originally by Stratton and Busch.[12] They reported that the ligand could coordinate in two distinct fashions: In the first, the ligand can act as a dinucleating ligand employing all four nitrogen atoms (Fig. 2(a)). When acting in this coordination mode, dinuclear $[M_2(L^1)_3]^{4+}$ triple-helicates result. In the second coordination mode, the ligand acts as a monucleating tridentate ligand and one of the imine nitrogens does not coordinate (Fig. 2(b)). In this coordination mode $[M(L^1)_2]^{2+}$ species result. The interconversion between these modes can be followed spectroscopically and Stratton and Busch reported that over time in aqueous solution the iron(II) triple-helical complexes
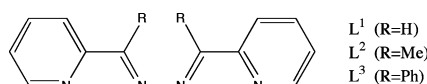

Fig. 1 Ligands L^1, L^2 and L^3.

L^1 (R=H)
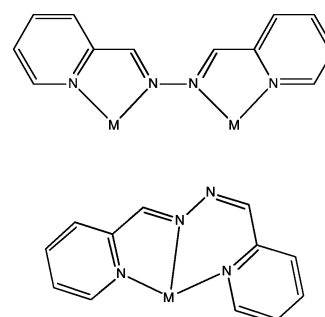L^2 (R=Me)
L^3 (R=Ph)

Fig. 2 The two coordination modes adopted by L^1.

were converted to the simple mononuclear species (with liberation of iron(II)). They proposed the term 'flexidentate' to describe the coordination behaviour of the ligand.[12]

Octahedral $[M_2L_3]^{4+}$ metal complexes containing L^1, L^2 or a related ligand (R = NH$_2$) have been structurally characterised and are of triple-helical structure and contain the ligand acting in the first coordination mode.[6,15] The introduction of methyl groups in L^2 enhances the twisting about the central N–N bond (inherent in the helical structures) but also enhances the aqueous stability of the triple-helicates. $[ML_2]^{2+}$ species have not previously been crystallographically characterised, however, the structures of the 1 : 1 complexes $[Zn(L^1)Cl_2]$ and $[Cu(L^2)-(NO_3)_2]$ have been reported.[13,14] In both complexes the geometry is a distorted trigonal bipyramid and contains an approximately planar ligand coordinated in the second, mononucleating N$_3$ coordination mode. In each structure the pyridine nitrogens occupy the apical positions of the trigonal bipyramid. The only previous L^3 complex to be characterised by X-ray diffraction, $[Zn(L^3)Cl_2]$, is also distorted trigonal biyramidal,[16] however, the pyridine nitrogens occupy two equatorial positions, with the imine in an axial position. This necessitates ligand distortion from planarity, and this occurs primarily within the monodentate pyridylimine unit (dihedral angle ~45°).

In introducing phenyl substituents we expect some changes to the chemistry with octahedral metal ions. While methyl groups stabilise the $[M_2L_3]^{4+}$ triple-helical structure, the larger phenyl groups in L^3 will not only induce introduce twisting about the N–N bond but are also expected to introduce greater steric crowding into the structure. By contrast, the second (mononucleating) coordination mode places the imine substituents far apart and so should not be disrupted by the presence of the phenyl groups. The phenyl groups will however induce some small ligand twistings to relieve steric clashes (e.g. between the pyridine H^3 and the phenyl ring) and this will cause some deviation from ligand planarity.

To investigate these steric effects we have studied the complexation of L^3 with nickel(II), cobalt(II) and iron(II) salts. In none of the cases have we been able to observe formation of triple-helical $[M_2L_3]^{4+}$ complexes, regardless of stoichiometries of metal and ligand used. Although double-helical structures can support the addition of four phenyl substituents, it appears that the triple-helical structure is unable to accommodate the steric requirements of six phenyl substituents.

Nickel(II) complex of L^3. Coordination of L^3 to nickel(II) was achieved by stirring one equivalent of nickel(II) acetate with one equivalent of L^3 in methanol for 3 h. The same complex was also obtained on mixing the metal salt and ligand in 1 : 2 and 2 : 3 stoichiometries. Treatment with ammonium hexafluorophosphate resulted in the formation of an orange solution from which orange crystals formed within 24 h. Microanalytical data support the formulation $[Ni(L^3)_2][PF_6]_2$ **1** and the FAB mass spectrum shows peaks (with the correct isotopic distributions) corresponding to $[Ni(L^3)_2(PF_6)]^+$ (*m/z* 927), $[Ni(L^3)_2(F)]^+$ (*m/z* 801), $[Ni(L^3)(F)]^+$ (*m/z* 439) and $[Ni(L^3)]^+$ (*m/z* 420). Similarly the ESI mass spectrum shows peaks corresponding to $[Ni(L^3)_2(PF_6)]^+$ and $[Ni(L^3)_2]^{2+}$. These data are consistent with formation of a mononuclear $[Ni(L^3)_2]^{2+}$ cation containing two ligands coordinated in an N$_3$ fashion and this has been confirmed by X-ray crystallography.

Orange crystals of **1**, suitable for X-ray analysis, were isolated from the filtrate after standing for 3 days at 4 °C. The crystal structure (Fig. 3) reveals a mononuclear $[ML_2]^{2+}$ cation with the nickel(II) center in a pseudo-octahedral environment, surrounded by six nitrogen atoms from two distinct ligand units. Both ligands use only three donor atoms, coordinating through one didentate pyridylimine unit and one monodentate pyridyl residue. The Ni–N bond distances and angles (Table 1) are unremarkable. As anticipated, the ligand is not planar: the didentate pyridylimine units are twisted slightly (imine–pyridine

Table 1 Selected bond lengths (Å) and bond angles (°) for complex **1**

Ni1–N101 (pyridine)	2.080(4)	Ni1–N218 (pyridine)	2.072(4)
Ni1–N114 (imine)	2.037(4)	Ni1–N215 (imine)	2.032(4)
Ni1–N118 (pyridine)	2.134(4)	Ni1–N201 (pyridine)	2.090(4)
N114–Ni1–N101	78.86(17)	N215–Ni1–N218	78.92(17)
N114–Ni1–N118	87.95(17)	N215–Ni1–N201	88.15(18)
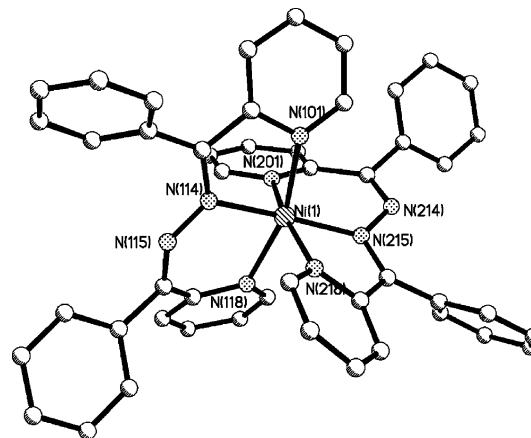
Fig. 3 The structure of the mononuclear cation in **1**. Hydrogens are omitted for clarity.

dihedral angles: 18°), while the monodentate units exhibit a greater deviation from planarity (imine–pyridine dihedral angles: 22, 38°). Twisting about the central N–N bond (14, 15°) is considerably less than that observed in the helical structures supported by this ligand class. The phenyl groups twist about the aryl–imine bond (torsion angles: 39–49°) to relieve steric interactions with the pyridine groups (particularly H^3). Despite the twistings in the ligand backbone (induced by the presence of the phenyl substituents) the two ligands are coordinated in a *mer* fashion in the solid state. The asymmetry of the co-ordinated ligand renders the complex chiral and equal amounts of both enantiomers are present in the crystal. Despite the many aromatic rings present, no intra- or inter-molecular face–face π-stacking interactions are observed in the structure. The hexafluorophosphate anions make a number of short contacts to phenyl and pyridyl protons.

Cobalt(III) complex of L^3. Stirring one equivalent of L^3 with one equivalent of cobalt(II) acetate in methanol for 2 h gave an orange solution from which orange crystals were isolated on treatment with ammonium hexafluorophosphate. The same complex was also obtained from solutions of 1 : 2 and 2 : 3 stoichiometries. Stratton and Busch have previously noted that preparation of $[Co_2(L^1)_3]^{4+}$ requires an inert atmosphere because of facile oxidation of the cobalt centres. Indeed they were unable to isolate complexes of ML$_2$ stoichiometry because of concomitant damage to the ligand. We also observe oxidation of the cobalt centres, however the ligand is retained intact and a dinuclear cobalt(III) complex of stoichiometry $[Co_2(L^3)_2-(OH)_2(CH_3CO_2)][PF_6]_3$ **2** is formed. The FAB mass spectrum shows peaks corresponding to $[Co_2(L^3)_2(OH)_2(CH_3CO_2)-(PF_6)_2]^+$ (*m/z* 1225), $[Co_2(L^3)_2(OH)_2(CH_3CO_2)(PF_6)]^+$ (*m/z* 1080) and $[Co_2(L^3)_2(OH)_2(CH_3CO_2)]^+$ (*m/z* 937) consistent with this dinuclear formulation. Similarly, the ESI mass spectrum shows peaks corresponding to $[Co_2(L^3)_2(CH_3COO)(OH)_2-(PF_6)_n]^{(3-n)+}$. Peaks corresponding to species of higher nuclearity are not observed. The infrared spectrum reveals bands corresponding to ligand stretches, coordinated acetate and the hexafluorophosphate anion. The complex is diamagnetic and soluble in methanol and acetonitrile. The electronic spectrum in methanol shows three intense bands at 205, 252 and 317 nm due to the intraligand transitions, along with a weak peak at 453 nm assigned to the $^1T_{1g}(F) \leftarrow {}^1A_{1g}$ spin-allowed d–d transition of

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **2**

Co1–N115 (imine)	1.886(5)	Co2–N215 (imine)	1.881(5)
Co1–N11 (pyridine)	1.919(6)	Co2–N21 (pyridine)	1.906(6)
Co1–N118 (pyridine)	1.924(6)	Co2–N218 (pyridine)	1.909(6)
Co1–O1 (hydroxy)	1.913(5)	Co2–O1 (hydroxy)	1.901(5)
Co1–O2 (hydroxy)	1.898(5)	Co2–O2 (hydroxy)	1.922(5)
Co1–O31 (acetate)	1.913(4)	Co2–O32 (acetate)	1.904(4)
N115–Co1–N11	84.7(2)	N215–Co2–N21	84.2(2)
N115–Co1–N118	82.1(3)	N215–Co2–N218	81.8(3)
Co1–O1–Co2	95.7(2)	Co1–O2–Co2	95.5(2)

the cobalt(III) ion (assuming an ideal octahedral geometry). The ^1H NMR spectra of the complex in both deuterated acetonitrile and methanol solutions, are well resolved and reveal the solution to contain primarily a single solution species in which the ligand is not symmetrical on the NMR timescale. Such asymmetry is consistent with the ligand adopting the mononucleating N_3 coordination mode. The structure of the complex was confirmed by an X-ray crystal analysis.

Orange crystals suitable for X-ray analysis were obtained from the filtrate by slow evaporation of the solvent at 4 °C. The X-ray structural analysis confirms that the cation has a dinuclear structure (Fig. 4). However rather than a dinuclear system with L^3 bridging the metal centres (as seen in the helical complexes) each L^3 ligand is bound to just one metal centre and the dinuclear structure is supported by a triple-bridge formed by one acetate ligand and two hydroxide ligands. As in the nickel(II) structure, the ligand is coordinated in a tridentate manner through one didentate pyridylimine unit and one mondentate pyridine. While in the nickel(II) structure the ligand coordinates in a *mer* fashion, in this cobalt(II) complex the ligand coordinates *fac* which facilitates the formation of the bridged structure. As in the nickel(II) structure, the didentate pyridylimine units of each ligand are slightly twisted from planarity (imine–pyridine dihedral angles: 14, 15°) by the presence of the phenyl substituents on the imine bonds. The twisting required to afford the *fac* coordination takes place primarily about the central N–N bonds (dihedral angles: 42°) and within the mondentate pyridylimine units (dihedral angles: 26, 28°). The Co–N bond distances and angles are presented in Table 2. Each cobalt centre is in a pseudo-octahedral environment coordinated to one N_3 ligand and three oxygen donors afforded by two bridging hydroxy groups and one bridging acetate. The Co $\cdots$ Co separation is 2.8255(14) Å. The phenyl groups are again twisted around the aryl–imine bond (torsion angles in the range 45–57°). The bridging hydroxy groups would be expected to be quite acidic and, consistent with this, both groups form hydrogen-bonding interactions, one with the oxygen of a methanol solvent molecule (O $\cdots$ H 1.65 Å) and the other with the fluorine of a hexafluorophosphate counter-anion (F $\cdots$ H
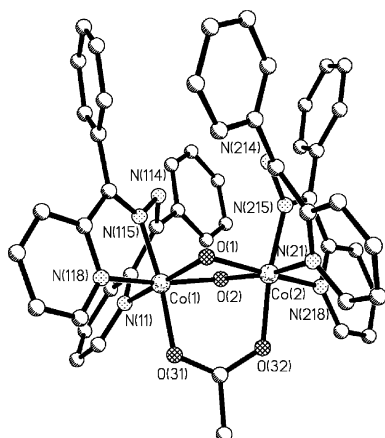
Fig. 4 The structure of the dinuclear cation in **2**. Hydrogens are omitted for clarity.

1.70 Å). Two of the phenyl groups are approximately co-planar with a centroid–centroid separation of 6.7 Å. They define an aromatic cleft above the two hydroxy bridges. In the crystal, the cations pair with their clefts interdigitated such that one phenyl ring from each cation is partially inserted into the cleft of the other cation, forming short C $\cdots$ C contacts in the range 3.5–3.7 Å and which may represent weak face–face π-stacking interactions (Fig. 5).
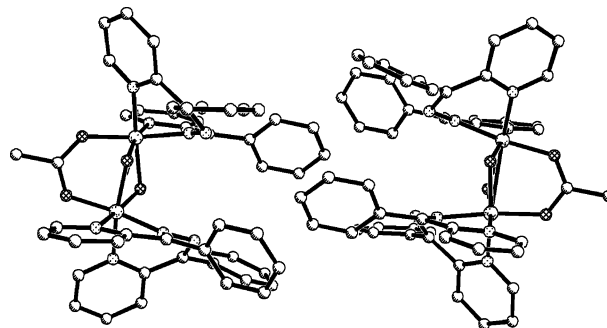
Fig. 5 Interdigitation of the phenyl rings of two dinuclear cations in **2**. Hydrogens are omitted for clarity.

Acetate bridged dinuclear centres play diverse and crucial roles in biological systems, and are found at the active sites of some metallohydrolases, oxygen-binding proteins (*e.g.* hemerythrin), purple acid phospatases, ribonucleotide reductases and methanemonoxygenase hydroxylase (MMOH).[17] In particular MMOH contains an $[M_2(\mu\text{-OAc})(\mu\text{-OH})_2]^{3+}$ core.[17,18] Such cores remain relatively unusual in synthetic compounds[18] and for cobalt(III) are usually associated with facially arranged amine co-ligands (rather than imines) or with a mixture of O and N donor co-ligands.[19] Moreover in the structure described herein the motif is located beneath an aromatic cleft. Catalytic bio-coordination motifs are frequently located at the foot of hydrophobic clefts in the protein structure and there is much current interest in design of synthetic agents that combine both a biological coordination motif and a hydrophobic cavity.[20,21]

Although there are many possible isomers of this formulation, a single one is observed in the crystal structure and this is consistent with the ^1H NMR spectrum which indicates that >95% of the material is a single isomer. There are some trace peaks just visible in the baseline which may indicate that traces (<5%) of other isomers are present in solution.

Iron(II) complex of L^3. Coordination of L^3 to iron(II) was achieved by stirring one equivalent of FeX_2 (X = Cl, CH_3CO_2 or $X_2 = SO_4$) with one equivalent of L^3 in methanol for 2 h. The resulting green solution was filtered and further treated with methanolic ammonium hexafluorophosphate. A green precipitate was formed, which was isolated by filtration. The same complex was also obtained from solutions of 1 : 2 and 2 : 3 stoichiometries and no intermediates of different colour were observed during the reactions. This contrast with the chemistry of L^1 for which a red, triple-helical species forms first, and again supports our assertion that the phenyl rings prevent formation of the triple-helicate. Microanalytical data is consistent with a formulation $[Fe(L^3)_2][PF_6]_2$ **3** and the FAB mass spectrum shows peaks (with the correct isotopic distributions) corresponding to $[Fe(L^3)_2(PF_6)]^+$ (*m/z* 925), $[Fe(L^3)_2(F)]^+$ (*m/z* 799) and $[Fe(L^3)(F)]^+$ (*m/z* 437). Peaks corresponding to species of higher nuclearity are not observed.

The complex is diamagnetic, indicating a d^6 low spin configuration and confirming that (in contrast to the cobalt chemistry) the iron remains in the +2 oxidation state. The ^1H NMR spectra of the complex in deuterated acetonitrile has been recorded and reveals that the ligand is not symmetrical on the NMR timescale. Such asymmetry indicates that the ligand has again adopted the mononucleating N_3 coordination mode. The

Table 3 Selected bond lengths (Å) and bond angles (°) for complex **4**

Metal center	M–N$_{pyridyl}$	M–N$_{imine}$	Bite angle
Ag1	2.199(5)	2.446(5)	70.82(19)
	2.189(5)	2.485(5)	70.39(18)
Ag2	2.249(5)	2.484(5)	69.15(18)
	2.227(5)	2.559(5)	69.10(18)
Ag3	2.222(5)	2.420(5)	70.58(19)
	2.189(5)	2.538(5)	69.89(18)
Ag4	2.227(5)	2.521(5)	69.67(19)
	2.233(5)	2.481(5)	69.22(18)

NMR spectrum reveals a principal species (~90%) and a smaller amount of a minor species. While many of the peaks corresponding to the minor species lie underneath those of the principal component it appears that the ligand is also asymmetrically arranged in this species again indicating N$_3$ coordination. Given the plethora of potential geometric isomers (particularly *fac*-isomers) for an [Fe(L^3)$_2$]$^{2+}$ cation it is impossible to predict the structures of these principal and minor solution species with confidence.

Tetrahedral metal ions

Silver(I) complex of L^3. We have shown that the ligand L^3 forms dinuclear double-helical complexes with the d^{10} metal ion copper(I).[11] However the coordination environment at the copper centres was not ideal. Due to the constraints of the ligand, the Cu–imine bonds were considerably longer than those to the pyridines. Silver(I) has a much lower preference for four-coordinate pseudo-tetrahedral geometries and indeed we have characterised complexes with ligands L^1 and L^2 in which the silver(I) centre is three- or five-coordinate. Consequently we were intrigued to explore the silver(I) chemistry of L^3.

Complex formation was achieved by stirring one equivalent of L^3 with one equivalent of silver(I) acetate in methanol with the exclusion of light for 2 h. The resulting yellow solution was filtered through Celite and treated with methanolic ammonium tetrafluoroborate. Yellow crystals formed and were collected by vacuum filtration. The infrared spectrum of the complex shows absorptions characteristic of the coordinated ligand and also peaks corresponding to the tetrafluoroborate counter ion. Partial microanalytical data are consistent with a formulation [Ag$_n$(L^3)$_n$][BF$_4$]$_n$. and the FAB mass spectrum displays peaks (with the correct isotopic distributions) corresponding to [Ag$_2$(L^3)$_2$(BF$_4$)] (*m/z* 1027), [Ag$_2$(L^3)$_2$] (*m/z* 940), [Ag(L^3)$_2$] (*m/z* 833), [Ag$_2$(L^3)(F)] (*m/z* 597), [Ag$_2$(L^3)] (*m/z* 577) and [Ag(L^3)] (*m/z* 469), suggesting a dinuclear structure. The ^{1}H NMR spectra of **4** in deuterated acetonitrile, acetone and dichloromethane solutions are sharp at room temperature and indicate the presence of one solution species of high symmetry. These data are consistent with the formation of a dinuclear double-helical species, similar to that observed with copper(I). The structure has been confirmed by X-ray crystallography.

X-Ray quality, yellow crystals of **4** formed from the filtrate after standing for 2 days at 4 °C. The X-ray structural analysis indicated that **4** is indeed a dinuclear double-helicate similar to that observed for copper(I). The structure contains two crystallographically independent, but quite similar, complex cations and these are illustrated in Fig. 6. Bond distances and angles relevant to the silver(I) coordination spheres are given in Table 3.

Each silver(I) center binds to two ligand strands thereby attaining a pseudo-tetrahedral coordination geometry. The bond lengths to the pyridine groups (2.188–2.333 Å; average Ag–N distance: 2.217 Å) are significantly shorter than those to the imine units (2.420–2.559 Å; average Ag–N distance: 2.481 Å) as observed in the copper(I) structure. The silver centres within the cations are separated by 4.86 and 4.89 Å. The twisting of the ligand strands (which is essential for helicate
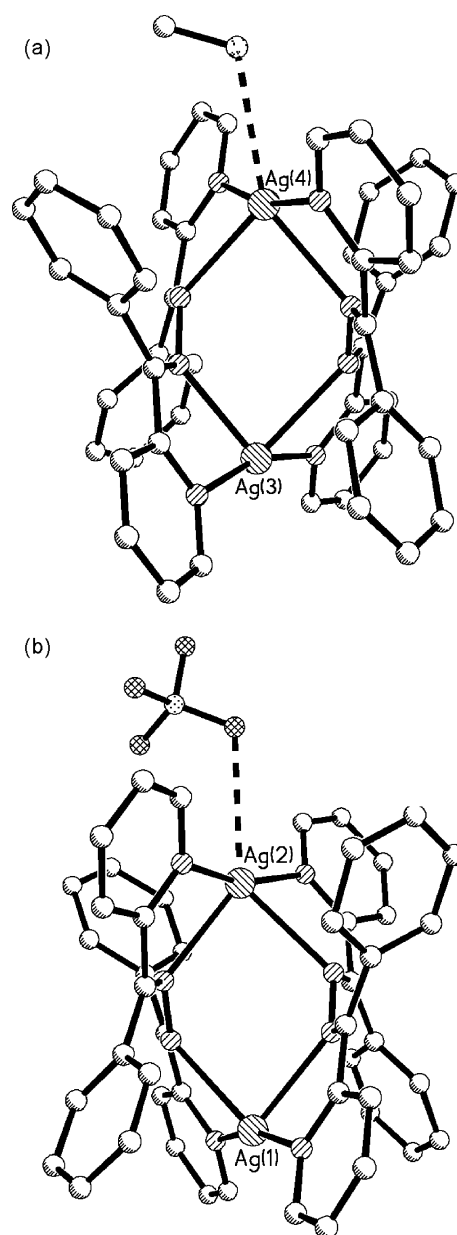
Fig. 6 The structures of the two distinct but similar double-helical cations in **4**. Hydrogen are omitted for clarity.

formation) takes place primarily about the N–N bond between the binding units (torsion angles in the range 22–34°), but also between the pyridyl and imine units (dihedral angles in the range 10–30°). The phenyl units are again twisted about the aryl–imine bond (dihedral angles 44–59°) and this facilitates the formation of face–face π-stacking interactions with the coordinated pyridyl groups. As in the copper(I) structure the connectivity constraints prevent idealised π-stacking by all four phenyl rings, and although the interplanar distances are around 3.5 Å, the rings are quite substantially offset, and at one end of each helix, the overlap is essentially restricted to the edge of the rings.

In addition to the coordination to the pyridyl and imine units, one silver center in each dimer makes a long contact with either a methanol solvent molecule (Ag ⋯ O 2.99 Å) or a tetrafluoroborate anion (Ag ⋯ F 3.11 Å) and in this the structure differs from that of the copper(I) complex. Some double-helical silver(I) complexes of L^2 have recently been reported;[22] in these structures both silver centres in the double helical array also form long contacts to the anions. The intermetallic distance is similar to that seen in **4**, however, as would be expected, in the L^2 structures the twisting within the pyridylimine units is

less and to compensate the twist about the N–N bond is greater (~50°).

Conclusion

The results confirm that phenyl substituents attached at the imine carbon have significant effects on the supramolecular architecture of the metal complexes of these directly-linked bis-pyridylimine ligands. The phenyl groups prevent the formation of dinuclear triple-helicates which are observed for L^1 and L^2. This is presumably a steric effect (the system is unable to pack six bulky phenyl groups around the centre of the triple-helical core). The phenyl stabilise the ligand structure when acting in an N_3 coordination mode as reflected by the ability to isolate cobalt(III) complexes. This may arise both from steric protection of the imino carbon from hydrolytic attack and from enhanced conjugative stabilisation of the imine bond. With silver(I), despite the lack of a strong metal coordination preference, the phenyl substituents drive the complex solely to the double-helical architecture. This is in stark contrast to the situation with L^1 and L^2, the silver complexes of which are a diverse library of different architectures. Thus in this system, the phenyl substituents destabilise the *triple*-helical architectures but stabilise *double*-helical architectures (relative to the alternative competing structures).

Experimental

General

All reagents and solvents were purchased from commercial sources (Aldrich) and used without further purification. (2-Pyridyl)phenylketazine (L^3) was prepared according to a previously described procedure.[15] Infrared spectra (KBr pellets) were measured with a Perkin Elmer Paragon 1000 FTIR spectrometer. Electronic spectra in the UV–visible range were recorded in solution with a Perkin Elmer Unicam 8700 Spectrophotometer. NMR spectra were recorded on Brüker DPX 400 and DRX 500 instruments using standard Brüker software. FAB mass spectra were recorded by the Warwick mass spectrometry service on a Micromass AutoSpec spectrometer using 3-nitrobenzyl alcohol as matrix. Electrospray mass spectra were recorded by the EPSRC National Mass Spectrometry Service Centre, Swansea, on a Micromass Quatro (II) (low-resolution triple quadrupole mass spectrometer) at 20 V cone voltage. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by the University of Warwick Analytical service.

Complex 1. L^3 (0.127 g, 0.35 mmol) and nickel (II) acetate tetrahydrate (0.087 g, 0.35 mmol) were stirred in methanol (20 mL) for 3 h. The resulting orange solution was filtered and the filtrate treated with methanolic ammonium hexafluorophosphate. On cooling at 4 °C orange crystals formed. The product was collected by vacuum filtration, washed with small amounts of cold methanol and dried *in vacuo* under P_4O_{10} (0.103 g, 55%). Anal. Calc. for $[Ni(C_{24}H_{18}N_4)_2][PF_6]_2 \cdot 2.5H_2O$: C, 51.6; H, 3.7; N, 10.0%. Found: C, 51.7, H, 3.4; N, 9.9%. Mass spectrum (FAB): m/z 927 $[Ni(L^3)_2(PF_6)]$, 782 $[Ni(L^3)_2]$, 801 $[Ni(L^3)_2(F)]$, 439 $[Ni(L^3)(F)]$, 420 $[Ni(L^3)]$. Positive-ion ESI: m/z 927 $[Ni(L^3)_2(PF_6)]^+$, 801 $[Ni(L^3)_2(F)]^+$, 439 $[Ni(L^3)(F)]^+$, 391 $[Ni(L^3)]^{2+}$, 363 $[LH]^+$. UV–Vis (MeCN): 207 (84900), 228 (54100), 278 (29300) and 365 ($\varepsilon = 24800$ dm³ mol⁻¹ cm⁻¹) nm. IR data (KBr, cm⁻¹): 3652w, 3442br, 3079w, 1593w, 1584m, 1561m, 1550sh, 1534w, 1477w, 1467w, 1445s, 1338m, 1320m, 1296w, 1267m, 1180w, 1164w, 1111m, 1080w, 1060vw, 1019m, 1000vw, 965w, 950vw, 906vw, 838vs, 797m, 776w, 749m, 705s, 691w, 673vw, 660w, 641vw, 615vw, 604vw, 580w, 558s. X-Ray quality, orange crystals of compound **2** were obtained from the filtrate by standing for three days at 4 °C.

Complex 2. L^3 (0.200 g, 0.55 mmol) and cobalt(II) acetate tetrahydrate (0.137 g, 0.55 mmol) were stirred in methanol (25 mL) for 2 h and the resulting orange solution was then treated with methanolic ammonium hexafluorophosphate. Slow evaporation of the solvent at room temperature yielded an orange microcrystalline product (0.230 g, 61%), which was collected by filtration, washed with cold methanol and dried *in vacuo* over P_4O_{10}. Anal. Calc. for $[Co_2(C_{24}H_{18}N_4)_2(CH_3COO)(OH)_2][PF_6]_3 \cdot 3.5H_2O$: C, 41.8; H, 3.3; N, 7.8%. Found: C, 41.7, H, 3.1; N, 7.7%. Mass spectrum (FAB): m/z 1225 $[Co_2(L^3)_2(CH_3COO)(OH)_2(PF_6)_2]$, 1080 $[Co_2(L^3)_2(CH_3COO)(OH)_2(PF_6)]$, 937 $[Co_2(L^3)_2(CH_3COO)(OH)_2]$. Positive-ion ESI: m/z 1225 $[Co_2(L^3)_2(CH_3COO)(OH)_2(PF_6)_2]^+$, 1079 $[Co_2(L^3)_2(CH_3COO)(OH)(O)(PF_6)]^+$, 933 $[Co_2(L^3)_2(CH_3COO)(O)_2]^+$, 540 $[Co_2(L^3)_2(CH_3COO)(OH)_2(PF_6)]^{2+}$, 467 $[Co_2(L^3)_2(CH_3COO)(OH)(O)]^{2+}$, 311 $[Co_2(L^3)_2(CH_3COO)(OH)_2]^+$. ¹H NMR (MeOD, 400 MHz, 300 K): δ 9.47 (1H, d, $J = 5.3$ Hz, H⁶), 9.38 (1H, d, $J = 5.3$, H⁶′), 8.34 (1H, t, $J = 7.4$ Hz, H⁴), 8.17 (1H, t, $J = 7.8$ Hz, H⁴′), 8.02 (1H, br t, $J = 6.0$ Hz, H⁵), 7.86 (1H, br t, $J = 6.8$ Hz, H⁵′), 7.71 (4H, m, H³, H³′, H_{para}, H_{para}'), 7.54 (4H, m, H_{meta}, H_{meta}'), 7.44 (2H, d, H_{ortho}), 7.28 (2H, d, H_{ortho}'), 3.18 (1.5H, s, CH_3COO). ¹H NMR (MeCN, 400 MHz, 300 K): δ 9.29 (1H, d, $J = 4.8$ Hz, H⁶), 9.17 (1H, d, $J = 4.8$, H⁶′), 8.22 (1H, t, $J = 7.3$ Hz, H⁴), 8.11 (1H, t, $J = 7.8$ Hz, H⁴′), 7.92 (1H, br t, $J = 6.1$ Hz, H⁵′), 7.83 (1H, t, $J = 7.5$ Hz, H_{para}), 7.78 (1H, br t, $J = 6.8$ Hz, H⁵), 7.71 (1H, t, $J = 7.5$ Hz, H_{para}'), 7.60 (4H, m, H³, H³′, H_{meta}), 7.48 (2H, t, $J = 7.8$ Hz, H_{meta}'), 7.37 (2H, d, $J = 7.3$ Hz, H_{ortho}), 6.80 (2H, s br, H_{ortho}'), 3.08 (1.5 H, s, CH_3COO). UV–Vis (MeOH): 205 (86000), 252 (41600), 317 (18600) and 453 ($\varepsilon = 8000$ dm³ mol⁻¹ cm⁻¹) nm. IR data (KBr, cm⁻¹): 3453w, 3124s br, 1624w, 1598m, 1576w, 1522s, 1472m, 1400w, 1329m, 1264w, 1164w, 1035w, 1000m, 831vs, 698w, 650w, 559s. Orange crystals suitable for X-ray analysis were grown from the filtrate by slow evaporation of the solvent at 4 °C.

Complex 3. L^3 (0.072 g, 0.2 mmol) and iron(II) chloride tetradydrate (0.040 g, 0.2 mmol) were stirred in methanol (15 mL) for 2 h. The resulting green solution was filtered and the filtrate treated with methanolic ammonium hexafluorophosphate. A green precipitate formed (0.079 g, 74%) within a few minutes. This was collected by filtration, washed with small amounts of cold methanol and dried *in vacuo* under P_4O_{10}. Anal. Calc. for $\{Fe(C_{24}H_{18}N_4)_2][PF_6]_2 \cdot 2H_2O$: C, 52.5; H, 3.6; N, 10.2%. Found: C, 52.6; H, 3.3; N, 10.0%. Mass spectrum (FAB): m/z 925 $[Fe(L^3)_2(PF_6)]$, 799 $[Fe(L^3)_2(F)]$, 780 $[Fe(L^3)_2]$, 437 $[Fe(L^3)(F)]$. ¹H NMR (CD₃CN, 400 MHz, 300 K): δ 8.61 (1H, d, $J = 5.3$ Hz, H⁶), 8.14 (1H, d, $J = 5.5$ Hz, H⁶′), 7.75 (4H, m, H³, H_{ortho}, H_{meta}), 7.70 (1H, td, $J = 7.8$, 1.5 Hz, H⁴), 7.63 (1H, br d, H_{para}), 7.57 (1H, td, $J = 7.8$, 1.2 Hz, H₄′), 7.48 (1H, t, $J = 7.0$ Hz, H_{para}'), 7.36 (6H, m, H₃′, $H_{ortho'}$, H_{meta}'), 7.21 (2H, m, H⁵, H₅′). UV–Vis (MeCN): 204 (75200), 286 (25000), 323 (24200), 355 (26100), 653 (3900) and 749 ($\varepsilon = 4200$ dm³ mol⁻¹ cm⁻¹) nm. IR data (KBr, cm⁻¹): 3420br, 3092w, 1629w, 1597sh, 1584m, 1560m, 1508w, 1459m, 1444s, 1354s, 1319s, 1262w, 1184w, 1161w, 1114vw, 1062w, 1021w, 965w, 946vw, 901vw, 841vs, 790w, 775w, 753m, 702m, 658w, 614w, 558s.

Complex 4. L^3 (0.181 g, 0.5 mmol) and silver(I) acetate (0.083, 0.5 mmol) were stirred in methanol (30 mL) with exclusion of light for 2 h, filtered through Celite and treated with methanolic ammonium tetrafluoroborate. The resulting yellow solution was filtered and the filtrate allowed to stand for 48 h at 4 °C. Yellow crystals formed (0.2 g, 68%) which were collected by filtration, washed several times with small amounts of cold methanol, and finally dried *in vacuo* over P_4O_{10}. Anal. Calc. for $[Ag_2(C_{24}H_{18}N_4)_2][BF_4]_2 \cdot 2MeOH$: C, 51.0; H, 3.7; N, 9.5%. Found: C, 51.0; H, 3.4; N, 9.5%. Mass spectrum (FAB): m/z 1027 $[Ag_2(L^3)_2(BF_4)]$, 940 $[Ag_2(L^3)_2]$, 833 $[Ag(L^3)_2]$, 597 $[Ag_2(L^3)(F)]$, 577 $[Ag_2(L^3)]$ and 469 $[Ag(L^3)]$. ¹H NMR

Table 4 Crystallographic data for complexes **1**, **2** and **4** and details of refinement

Complex	1	2	4
Empirical formula	$C_{48}H_{36}F_{12}N_8NiP_2$	$C_{53}H_{50.5}Co_2F_{18}N_8O_{8.25}P_3$	$C_{50}H_{44}Ag_2B_2F_8N_8O_2$
Formula weight	1073.50	1484.28	1178.29
Temperature/K	180(2)	180(2)	180(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	15.787(2)	12.2068(18)	20.4450(16)
b/Å	15.172(2)	13.2943(19)	15.3350(11)
c/Å	19.527(3)	21.456(3)	32.547(3)
α/°	90	80.385(3)	90
β/°	102.660(10)	82.541(3)	105.053(2)
γ/°	90	73.978(3)	90
U/Å³	4563.3(12)	3286.7(8)	9854.2(13)
Z	4	2	8
D_c/g cm^{-3}	1.563	1.500	1.588
μ/mm^{-1}	0.591	0.684	0.874
Reflections collected	20867	15747	39427
Independent reflections (R_{int})	7133 (0.1246)	10201 (0.0632)	22036 (0.0646)
Parameters	657	815	1320
Goodness-of-fit on F^2	0.998	0.962	0.984
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0706$	$R_1 = 0.0763$	$R_1 = 0.0754$
	$wR_2 = 0.1020$	$wR_2 = 0.1660$	$wR_2 = 0.1388$
(all data)	$R_1 = 0.1556$	$R_1 = 0.1671$	$R_1 = 0.1802$
	$wR_2 = 0.1254$	$wR_2 = 0.2066$	$wR_2 = 0.1758$

(CD$_3$CN, 400 MHz, 300 K): δ 8.34 (2H, dd, J = 5.0, 1.0 Hz, H^6), 7.97 (2H, td, J = 7.8, 1.7 Hz, H^4), 7.68 (2H, ddd, J = 7.8, 5.0, 1.3 Hz, H^5), 7.53 (2H, br t, J = 7.5 Hz, H$_{para}$), 7.37 (2H, d, J = 7.8 Hz, H^3), 7.26 (4H, t, J = 7.5 Hz, H$_{meta}$), 7.13 (4H, d, J = 7.3 Hz, H$_{ortho}$). UV–Vis (MeCN): 206 (86700), 228 (52200), 286 (52700) and 314 (ε = 37400 dm^3 mol^{-1} cm^{-1}) nm. IR data (KBr, cm^{-1}): 3619w, 3536w, 3059w, 1628w, 1580s, 1560s, 1491w, 1468m, 1440s, 1330s, 1283w, 1252m, 1164w, 1080sh, 1063vs, 1053sh, 1035sh, 967m, 795m, 771m, 740w, 701s, 660m, 638w, 578w, 520w. Yellow crystals suitable for X-ray analysis were formed from the filtrate by slow evaporation of the solvent at 4 °C.

The corresponding hexafluorophosphate salt was prepared in an analogous proceedure, precipitating with ammonium hexafluorophosphate. Crystals were grown from acetonitrile *via* the slow diffusion of diethyl ether.

Crystallography

Crystal data (Table 4) for compounds **1**, **2** and **4** were collected at 180 K with a Siemens-SMART-CCD diffractometer[23] equipped with an Oxford Cryosystem Cryostream Cooler.[24] Refinements used SHELXTL.[25] Systematic absences indicated the appropriate space group for **1** and **4**, while that for **2** was assumed. The structures were solved by direct methods with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. For complex **4**, there are four methanol and one water molecules in the asymmetric unit. Two molecules of methanol were modelled with partially occupancy. Additionally, one of the four BF$_4^-$ anions is disordered. For **1** one of the PF$_6^-$ anions shows disorder and this was modelled. In the case of complex **2**, several solvent molecules are present in the cell unit and a number of sites are only partially occupied. Two molecules of methanol were found to be disordered.

Crystals of the hexafluorophosphate salt corresponding to complex **4**, were also examined but were found to give poor diffraction patterns. The unit cell was established as a = 14.4117(3), b = 23.800(2), c = 33.616(3) Å, a = 100.22(1), β = 102.25(1), γ = 104.30(1)°, Space group $P\bar{1}$, Z = 8. The structure was solved from the limited difraction data but could not be fully refined. The four distinct [Ag$_2$(L^3)$_2$]$^{2+}$ cations have a double-helical structure analogous to those in **4**.

CCDC reference numbers 189697–189699.

See http://www.rsc.org/suppdata/dt/b2/b211006g/ for crystallographic data in CIF or other electronic format.

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