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Self-assembled dinuclear molecular box $[Ag_2L_2]^{2+}$ and triple helicates $[Co_2L_3]^{4+}$, $[Ni_2L_3]^{4+}$ {L = bis[4-(2-pyridylmethyleneamino)phenyl] ether}

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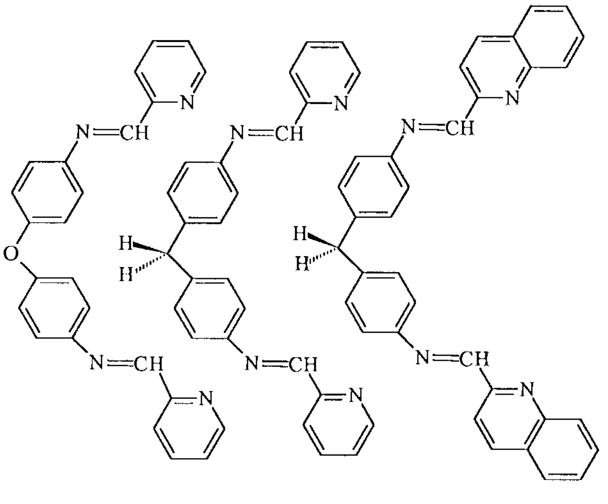
The self-assembly and structural characterization of the new silver(I) molecular box $[Ag_2L_2]^{2+}$ and cobalt(II), and nickel(II) molecular helices $[Co_2L_3]^{4+}$ and $[Ni_2L_3]^{4+}$ have been achieved. These complexes are derived from an inexpensive and easy-to-prepare bis-bidentate Schiff base ligand bis[4-(2-pyridylmethyleneamino)phenyl] ether (L). The cage-like cation $[Ag_2L_2]^{2+}$ is located at an inversion center with two tetrahedrally co-ordinated silver(I) atoms and two ether oxygen atoms in the corner of a box. The edge length Ag · · · O is *ca.* 7.1 Å. Each silver(I) center is bound to two pyridylimine units, one from each ligand. One ligand passes above the silver(I)–silver(I) axis, while the other passes beneath, giving a non-helical metallo-cyclophane with Ag · · · Ag separation *ca.* 12.3 Å. Both triple helical $[Co_2L_3]^{4+}$ and $[Ni_2L_3]^{4+}$ cations contain two metal atoms and three ligands. Each metal center is bound to three pyridylimine units to attain a pseudo-octahedral co-ordination geometry. The ligand wraps in a helical arrangement around the two metal ions. Edge-to-face and face-to-face π–π interactions play important roles in the metal-assisted self-assembling process.

Within the field of supramolecular inorganic chemistry, self-assembly provides direct access to complex architectures comprising spatially and geometrically well defined arrays of metal ions.[1,2] The application of metal–ligand interactions has proved particularly fruitful and complex molecular architectures such as helicates,[3,4] knots,[5] grids,[1,6] catenanes,[5,7] cylinders[1,8] and boxes[9,10] have all been assembled. The structure of the bridging group, the metal binding moiety, the metal co-ordination geometry as well as non-covalent interactions all dictate the architecture obtained. In order to design species presenting specific structural and functional features, it is of great importance to establish the rules by which control of the self-assembly process can be achieved through chemical programming by means of suitable components and assembling algorithms.[11]

As part of our studies of metal boxes derived from Schiff-base multidentate ligands *via* self-assembly[12] we became interested in designing new inexpensive and easy-to prepare metallo-supramolecular systems. Not only should the development of an inexpensive system enable wider access to this field, but systems which are easy to prepare and readily modified should enhance the rate at which novel molecular architectures are developed. Here we describe a new and general strategy for the construction of metal-assisted supramolecular architectures using a bis-bidentate Schiff base ligand L. The ligand, bis[4-(2-pyridylmethyleneamino)phenyl] ether contains two Schiff base chelating arms linked to a central spacer. It is postulated that the flexibility of the ligand is such that for dimeric $[M_2L_2]^{2+}$ species both double-helix and non-helical box conformations are possible.[13] To test this approach a dinuclear silver(I) molecular box was synthesized and structurally characterized. Two dinuclear triple-helical complexes of Ni^{II} and Co^{II} are also reported for comparison. These architectures are prepared readily utilizing the weak face-to-face and edge-to-face aromatic π–π interactions operating among the bridging groups of the bis-bidentate Schiff base ligand and co-ordinated pyridine rings. Related bis-bidentate Schiff bases L^1 and L^2 have been used to prepare interesting triple or double helices.[14,15]



L L¹ L²

Experimental

General

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region, ^{1}H NMR spectra on Bruker DP300 spectrometers at 298 K and electrospray mass spectra on a LCQ system (Finnigan MAT, USA) using methanol as mobile phase.

Preparations

Bis[4-(2-pyridylmethyleneamino)phenyl] ether L. Bis(4-aminophenyl) ether (1.0 g, 5.0 mmol) and 2-pyridinecarbaldehyde (1.2 g, 11 mmol) were mixed in methanol (25 mL) and

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refluxed for 2 h. The green solid (1.56 g, 4.1 mmol, yield 82%) obtained after evaporating the solution to 10 mL was filtered off and dried under vacuum. Found: C, 75.8; H, 5.0; N, 14.4. Calc. for $C_{24}H_{18}N_4O$: C, 76.2; H, 4.8; N, 14.8%. IR (cm^{-1}): 3450, 3046 (ν_{C-H}), 1623, 1581, 1494, 1467, 1344 ($\nu_{C=C}$, $\nu_{C=N}$, ν_{C-N}), 1240 (ν_{Ph-O}), 858, 832, 775, 742, 715 (δ_{C-H}). ^1H NMR [$(CD_3)_2SO$]: δ 7.12 (4 H, d, Ph), 7.44 (4 H, d, Ph), 7.53 (2 H, t, py), 7.96 (2 H, t, py), 8.16 (2 H, d, py), 8.64 (2 H, s, CH=N) and 8.72 (2 H, t, py).

$[Ag_2L_2][BF_4]_2$ 1. The ligand L (0.19 g, 0.50 mmol) and $AgBF_4$ (0.10 g, 0.51 mmol) were mixed in methanol (25 mL), and after stirring for two hours the yellow solid (0.26 g, 0.23 mmol, yield 91%) obtained was filtered off and dried under vacuum. Found: C, 49.8; H, 3.3; N, 9.5. Calc. for $C_{24}H_{18}AgBF_4N_4O$: C, 50.3; H, 3.2; N, 9.8%. IR (cm^{-1}): 3466, 3059 (ν_{C-H}), 1627, 1591, 1493, 1438, 1290 ($\nu_{C=C}$, $\nu_{C=N}$, ν_{C-N}), 1240 (ν_{Ph-O}), 1060 (ν_{B-F}), 873, 859, 842, 777, 740 (δ_{C-H}). ^1H NMR [$(CD_3)_2SO$]: δ 7.03 (4 H, d, Ph), 7.50 (4 H, d, Ph), 7.81 (2 H, t, py), 8.11 (2 H, d, py), 8.25 (2 H, t, py), 8.81 (2 H, d, py) and 9.06 (2 H, s, CH=N). Crystals suitable for X-ray diffraction determination were obtained by slowly evaporating an acetonitrile solution in air.

$[Co_2L_3][BF_4]_4$ 2. The ligand L (0.34 g, 0.90 mmol) and $CoCl_2\cdot6H_2O$ (0.14 g, 0.59 mmol) were mixed in 25 mL methanol. The solution was refluxed for 1 h, then cooled to room temperature and $NaBF_4$ (0.2 g, 1.8 mmol) added. After stirring for 1 h the yellow solid (0.41 g, 0.26 mmol, yield 87%) formed was isolated and dried under vacuum. Found: C, 54.4; H, 3.4; N, 10.4. Calc. for $C_{72}H_{54}B_4Co_2F_{16}N_{12}O_3$: C, 54.0; H, 3.4; N, 10.5%. IR (cm^{-1}): 3445, 3071 (ν_{C-H}), 1631, 1596, 1494, 1443, 1308 ($\nu_{C=C}$, $\nu_{C=N}$, ν_{C-N}), 1242 (ν_{Ph-O}), 1058 (ν_{B-F}), 866, 842, 773, 763 (δ_{C-H}). Crystals suitable for X-ray diffraction determination were obtained by slowly diffusing diethyl ether into an acetonitrile–methanol (2 : 1) solution.

$[Ni_2L_3][BF_4]_4$ 3. The ligand L (0.34 g, 0.90 mmol) and $NiCl_2\cdot6H_2O$ (0.14 g, 0.59 mmol) were mixed in 25 mL methanol. The red solution was refluxed for 1 h and cooled to room temperature, then $NaBF_4$ (2 g, 1.8 mmol) was added. After refluxing for 1 h the yellow precipitate (0.29 g, 0.17 mmol, yield 59%) obtained was isolated and dried under vacuum. Found: C, 51.7; H, 3.8; N, 9.9. Calc. for $C_{72}H_{54}B_4F_{16}N_{12}Ni_2O_3\cdot4H_2O$: C, 51.7; H, 3.7; N, 10.1%. IR (cm^{-1}): 3427, 3074 (ν_{C-H}), 1629, 1595, 1492, 1446, 1308 ($\nu_{C=C}$, $\nu_{C=N}$, ν_{C-N}), 1242 (ν_{Ph-O}), 1060 (ν_{B-F}), 865, 838, 776, 746 (δ_{C-H}). Crystals suitable for X-ray diffraction determination were obtained by slowly diffusing diethyl ether into an acetonitrile–methanol (2 : 1) solution.

Crystallography

Parameters for data collection and refinement of the three complexes are summarized in Table 1. Intensities were collected on a Siemens P4 four circle diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan mode. Data were corrected for Lorentz-polarization effects during data reduction using XSCANS[16] and a semi-empirical absorption correction from ψ scans was applied. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares methods and SHELXTL.[17] Anisotropic thermal parameters were refined for non-hydrogen atoms. For complex 1 the two BF_4^- anions and the lattice acetonitrile molecules were refined disordered. For 2 and 3 the four BF_4^- anions, the methanol and acetonitrile solvent molecules were found disordered in two occupied sites. To assist the refinement, several restraints were applied: (1) all B–F bonds restrained to be similar; (2) thermal parameters on adjacent atoms in disordered moieties were restrained to be similar.

CCDC reference number 186/1992.

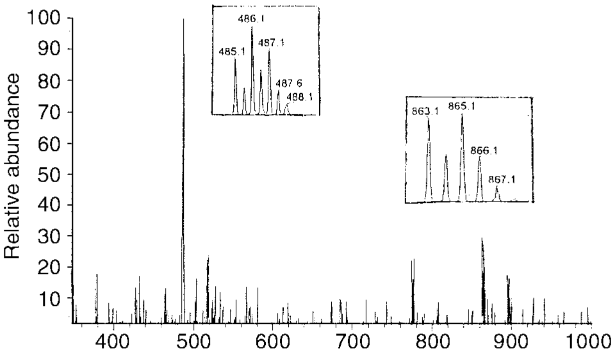

Fig. 1 Electrospray mass spectrum of the silver(I) complex in acetonitrile–methanol; the insets show the isotopic distributions for the main peak.

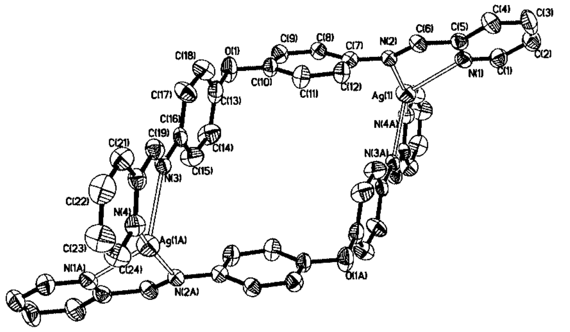

Fig. 2 An ORTEP[18] plot of one of the cage-like $[Ag_2L_2]^{2+}$ cations, showing 30% probability displacement ellipsoids of non-hydrogen atoms. Hydrogen atoms are omitted for clarity. Symmetry code A: $1 - x, 1 - y, -z$.

See http://www.rsc.org/suppdata/dt/b0/b0018201/ for crystallographic files in .cif format.

Results and discussion

The ligand is prepared by simply refluxing a methanol solution containing pyridine-2-carbaldehyde and bis(4-aminophenyl) ether. The ease of synthesis and high yield in a single-step reaction from commercial, inexpensive reagents make this an extremely attractive ligand system. Elemental analyses, IR and NMR spectra confirm the formation of the given ligand. It is said that the incorporated phenyl ether spacer sterically can prevent the two metal binding sites from co-ordinating to a single metal center. Also the central ether oxygen atom can introduce enhanced flexibility into the ligand backbone, as suggested by Hannon *et al.*,[14b] and this enhanced flexibility permits the ligand to support helical ligand arrays.

Structure of complex $1\cdot1.5CH_3CN$

Treatment of L with 1 equivalent of $AgBF_4$ in methanol under stirring resulted in precipitation of complex **1**. As shown in Fig. 1, ESI-MS (electrospray ionization mass spectroscopy) in acetonitrile–methanol solution reveals the presence of two main peaks. The base peak at *m*/*z* 486 corresponds to the most abundant ion $[Ag_2L_2]^{2+}$, and a peak at *m*/*z* 863 results from $[AgL_2]^+$. The presence of the $[AgL_2]^+$ species indicates that the $[Ag_2L_2]^{2+}$ cation may lose one silver(I) ion under the conditions of electrospraying. It can be seen from the ESI-MS spectrum that the dinuclear complex is the major species in solution.

The structure of the dimeric $[Ag_2L_2]^{2+}$ box is shown in Fig. 2. An asymmetric unit consists of two halves of the molecular boxes. Both occupy an inversion center at (1/2, 1/2, 0) and (0, 1/2, −1/2). Each silver center is bound to two pyridylimine units to attain a distorted tetrahedral co-ordination geometry.

Table 1 Crystallographic data for complexes **1**–**3**

	1·1.5CH$_3$CN	**2**·0.5CH$_3$CN·0.5CH$_3$OH	**3**·0.5CH$_3$CN·0.5CH$_3$OH
Molecular formula	$C_{51}H_{40.5}Ag_2N_{9.5}O_2B_2F_8$	$C_{74.5}H_{59}B_4Co_2F_{16}N_{13.5}O_{3.5}$	$C_{74.5}H_{59}B_4F_{16}N_{13.5}Ni_2O_{3.5}$
M	1207.79	1657.45	1657.01
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*Cc*	*Cc*
a/Å	13.110(3)	22.780(4)	22.723(8)
b/Å	13.611(5)	18.835(3)	18.472(6)
c/Å	15.009(2)	20.144(6)	20.184(9)
α/°	105.68(1)		
β/°	92.66(2)	112.93(2)	112.71(4)
γ/°	98.31(3)		
V/Å^3	2541.2(11)	7770(3)	7815(5)
Z	2	4	4
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	0.851	0.522	0.576
No. reflections measured	9988	7817	7408
No. unique reflections	8736[*R*(int) = 0.056]	7319[*R*(int) = 0.046]	6592[*R*(int) = 0.092]
*R*1	0.070	0.077	0.075
*wR*2	020	0.22	0.18

Table 2 Selected bond lengths (Å) and angles (°)[a] of complex **1**·1.5CH$_3$CN

Ag(1)–N(1)	2.390(7)	Ag(2)–N(5)	2.413(7)
Ag(1)–N(2)	2.270(6)	Ag(2)–N(6)	2.282(6)
Ag(1)–N(3A)	2.450(6)	Ag(2)–N(7B)	2.421(7)
Ag(1)–N(4A)	2.242(7)	Ag(2)–N(8B)	2.240(7)
N(1)–Ag(1)–N(2)	72.4(2)	N(5)–Ag(2)–N(6)	72.0(2)
N(1)–Ag(1)–N(3A)	127.3(2)	N(5)–Ag(2)–N(7B)	131.6(2)
N(1)–Ag(1)–N(4A)	116.9(2)	N(5)–Ag(2)–N(8B)	118.2(3)
N(2)–Ag(1)–N(3A)	115.4(2)	N(6)–Ag(2)–N(7B)	116.4(2)
N(2)–Ag(1)–N(4A)	161.9(2)	N(6)–Ag(2)–N(8B)	158.1(2)
N(3A)–Ag(1)–N(4A)	72.5(2)	N(7B)–Ag(2)–N(8B)	72.8(3)

[a] Symmetry codes: A $-x + 1, -y + 1, -z$; B $-x, -y + 1, -z - 1$.

One ligand passes above the silver(I)–silver(I) axis, while the other passes beneath. The dihedral angle between two co-ordinated planes is *ca.* 68°. The Ag–N(pyridyl) distances (Table 2) are in the range 2.240(7)–2.413(7) Å and Ag–N(CH=N) distances in the range 2.270(6)–2.450(6) Å. There are three sets of bond angles N–Ag–N in the ranges 72.4(2)–72.8(3), 115.4(2)–118.2(3) and 127.3(2)–161.9(2)°, respectively.

As the molecular box occupies an inversion center, the opposite two phenyl rings are parallel to each other. The torsion angle between two neighboring phenyl rings of one ligand is *ca.* 87°. The dimensions of this distorted rhombic cavity are approximately 7 × 7 Å, measured from opposite phenyl rings. This cavity is larger than that of Pd-4,4′-ethylanepyridine {Pd(C$_5$H$_4$NCH$_2$CH$_2$C$_5$H$_4$N)(NH$_2$CH$_2$CH$_2$NH$_2$)]$_2$}[19] (4 × 6 Å) and of the five-co-ordinate Cu^{II}–4,4′-diaminodiphenylmethane ({Cu(NH$_2$C$_6$H$_4$CH$_2$C$_6$H$_4$NH$_2$)[CH$_2$(COOH)$_2$]Cl}$_2$$^{2+}$) (8 × 4 Å).[20] The increase in size of the cavity is due to the tetrahedral geometry of Ag^I with two bis-bidentate ligands. The intermetallic Ag···Ag and Ag···O separation is 12.3 and 7.1 Å, respectively, with the Ag···O···Ag angle *ca.* 120°.

It is interesting that the two pyridine rings co-ordinated to one silver(I) atom stack with the two phenyl rings attached to one oxygen atom, forming a two-dimensional sheet (Fig. 3). For the stacked pairs III and IV′B($-x$, $1 - y$, $-1 - z$), IVA($1 - x$, $1 - y$, $-z$) and III′C(x, y, $1 + z$), the dihedral angle for each pair is *ca.* 6.0° (Table 3), the center-to-plane separation *ca.* 3.40 Å and the shortest interplanar atom–atom separation *ca.* 3.30 Å. These distances are similar to the standard distance for a strong π-stacking interaction between two aryl rings (3.35 Å for graphite[21] and 3.10 Å for 4,5-diazafluorene rings[22]). The dihedral angles between I and II′C, II and I′ are larger than 20°, indicating weak π-stacking interactions between them. There are also π-stacked interactions between pyridine rings themselves. The interplanar distances are in the range of 3.3–3.5 Å.

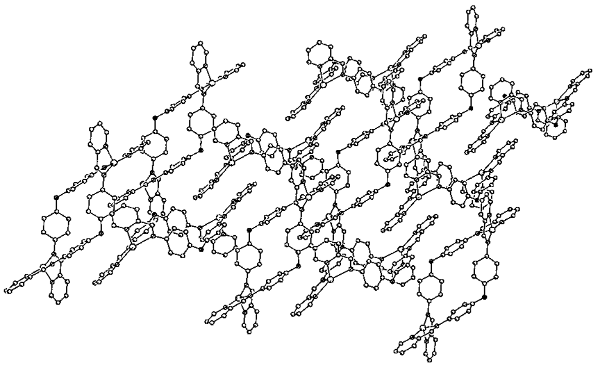

Fig. 3 Perspective view of the two dimensional sheets showing the π–π stacking interactions in complex **1**·1.5CH$_3$CN. Anions and solvent molecules are omitted for clarity.

For a [M$_2$L$_2$]$^{n+}$ cation of a bis-bidentate ligand the flexibility of the ligand makes possible both double-helix and non-helical box conformations. It is postulated that steric effects and non-covalent weak interactions such as π–π stacked interactions are the main factors affecting the assembly of helical or non-helical structure.[13] To examine this, the structures of [Co$_2$L$_3$]$^{4+}$ and [Ni$_2$L$_3$]$^{4+}$ cations were studied.

Structure of complex 2·0.5CH$_3$CN·0.5CH$_3$OH

Interaction of 3 equivalents of ligand and 2 equivalents of cobalt(II) salt in methanol led to the formation of a red solution. A yellow solid with high yield (>80%) was obtained on treatment with NaBF$_4$. ESI-MS of complex **2** ($m/z = 313.3$) reveals that [Co$_2$L$_3$]$^{4+}$ is the most stable fragment in solution. Modeling indicates that this formulation is consistent only with a triple helix.

The structure of complex **2** (Fig. 4) confirms the formation of a dinuclear triple helix. The complex contains two cobalt(II) ions and three ligands together with four BF$_4$$^-$ anions and disordered lattice methanol and acetonitrile molecules. Each cobalt center co-ordinates to three pyridylimine binding units with Co–N(pyridyl) distances in the range 2.098(8)–2.165(8) Å and Co–N(CH=N) distances in the range 2.117(6)–2.192(7) Å. There are three sets of bond angles N–Co–N in the ranges 76.3(3)–78.3(3), 88.5(3)–102.8(3) and 163.5(3)–176.7(3)°, respectively (Table 4). A pseudo-octahedral co-ordination array of nitrogen atoms provided by three pyridylimine (C$_5$H$_4$NCH=N) moieties is in *fac* configuration. The pyridyl nitrogen atom is situated *trans* to the imine (CH=N) nitrogen atom of another ligand. Co-ordination to the metal center

Table 3 Dihedral angles (°) for selected planes of complex **1**·1.5CH$_3$CN

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle		
			I	II	III
I	C(1), C(2), C(3), C(4), C(5), N(1)	0.010			
II	C(7), C(8), C(9), C(10), C(11), C(12)	0.006	47.7		
III	C(13), C(14), C(15), C(16), C(17), C(18)	0.006	63.6	89.1	
IV	C(20), C(21), C(22), C(23), C(24), N(5)	0.003	66.7	88.9	3.0

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angle		
			I′	II′	III′
I′	C(25), C(26), C(27), C(28), C(29), N(5)	0.01			
II′	C(31), C(32), C(33), C(34), C(35), C(36)	0.01	45.5		
III′	C(37), C(38), C(39), C(40), C(41), C(42)	0.01	67.4	85.9	
IV′	C(44), C(45), C(46), C(47), C(48), N(8)	0.01	63.4	79.8	6.2

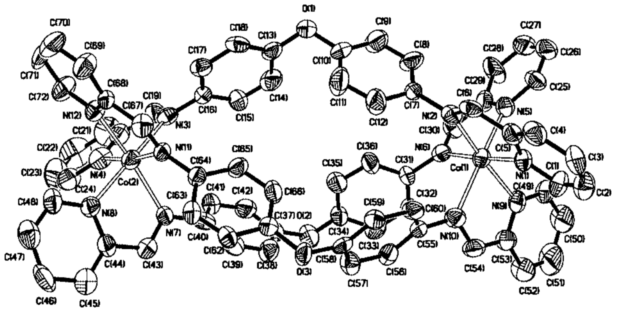

Fig. 4 An ORTEP plot of the triple-helical [Co$_2$L$_3$]$^{4+}$ cation, showing 30% probability displacement ellipsoids of non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

causes internuclear twisting among the pyridine and benzene rings, the dihedral angles between them being listed in Table 5. The building units, particularly the bridging groups (C$_6$H$_4$-OC$_6$H$_4$) are packed face-to-face and edge-to-face to each other. The distances between each stacked pair of phenyl rings (3.82 Å) are larger than the standard distance for a strong π–π stacking interaction between two aryl rings.[21,22] The perpendicular or T-shape arrangement of the phenyl rings is consistent with the preferred orientation in crystalline benzene. This same interaction has also been shown to be important to both protein structure and protein–ligand binding.[23]

Structure of complex 3·0.5CH$_3$CN·0.5CH$_3$OH

Reaction of L with nickel dichloride in refluxing methanol yielded a red solution from which a yellow solid was obtained on treatment with NaBF$_4$. ESI-MS shows one strong peak corresponding to [Ni$_2$L$_3$]$^{4+}$ (*m*/*z* = 313), consistent with formation of a triple-helical structure.

Crystal structure analysis reveals that the nickel(II) complex is similar to that of cobalt not only in molecular structure (Fig. 5) but also in crystal packing. Each nickel(II) center is bound to three pyridylimine units to attain a pseudo-octahedral co-ordination geometry. The Ni–N(pyridyl) distances in the range 2.096(9)–2.153(9) Å and Ni–N(CH=N) distances in the range 2.111(7)–2.189(8) Å. There are three sets of bond angles N–Ni–N in the ranges 76.5(3)–78.1(4), 88.1(3)–102.2(3) and 164.4(3)–175.6(3)°, respectively (Table 4). Co-ordination to the metal center forces internuclear twisting between the phenylene ring and pyridylimine unit and the logical consequence is the formation of a triple-helical array. The dihedral angles among the six phenyl rings are given in Table 5; the shortest inter ligand atom–atom contact is *ca.* 3.6 Å, indicating the presence of weak aromatic π–π stacked interactions and CH···π interactions operating between the bridging groups of the bis-bidentate Schiff base ligands.

Table 4 Selected bond distances (Å) and angles (°) of complexes **2**·0.5CH$_3$CN·0.5CH$_3$OH and **3**·0.5CH$_3$CN·0.5CH$_3$OH

2·0.5CH$_3$CN·0.5CH$_3$OH		**3**·0.5CH$_3$CN·0.5CH$_3$OH	
Co(1)–N(1)	2.098(8)	Ni(1)–N(1)	2.096(9)
Co(1)–N(2)	2.117(6)	Ni(1)–N(2)	2.111(7)
Co(1)–N(5)	2.162(7)	Ni(1)–N(5)	2.137(8)
Co(1)–N(6)	2.137(8)	Ni(1)–N(6)	2.173(8)
Co(1)–N(9)	2.132(7)	Ni(1)–N(9)	2.136(8)
Co(1)–N(10)	2.167(7)	Ni(1)–N(10)	2.135(8)
Co(2)–N(3)	2.192(7)	Ni(2)–N(3)	2.189(8)
Co(2)–N(4)	2.165(8)	Ni(2)–N(4)	2.153(9)
Co(2)–N(7)	2.168(6)	Ni(2)–N(7)	2.184(9)
Co(2)–N(8)	2.118(8)	Ni(2)–N(8)	2.127(8)
Co(2)–N(11)	2.160(7)	Ni(2)–N(11)	2.161(8)
Co(2)–N(12)	2.127(7)	Ni(2)–N(12)	2.151(9)
N(1)–Co(1)–N(2)	78.3(3)	N(1)–Ni(1)–N(2)	77.7(3)
N(1)–Co(1)–N(5)	102.2(3)	N(1)–Ni(1)–N(5)	94.0(3)
N(1)–Co(1)–N(6)	176.7(3)	N(1)–Ni(1)–N(6)	89.6(3)
N(1)–Co(1)–N(9)	92.5(3)	N(1)–Ni(1)–N(9)	101.9(3)
N(1)–Co(1)–N(10)	89.6(3)	N(1)–Ni(1)–N(10)	175.6(3)
N(2)–Co(1)–N(5)	88.5(3)	N(2)–Ni(1)–N(5)	171.6(4)
N(2)–Co(1)–N(6)	98.6(3)	N(2)–Ni(1)–N(6)	102.2(3)
N(2)–Co(1)–N(9)	170.9(3)	N(2)–Ni(1)–N(9)	88.1(3)
N(2)–Co(1)–N(10)	102.8(3)	N(2)–Ni(1)–N(10)	98.1(3)
N(5)–Co(1)–N(6)	76.4(3)	N(5)–Ni(1)–N(6)	76.5(3)
N(5)–Co(1)–N(9)	94.1(3)	N(5)–Ni(1)–N(9)	94.7(3)
N(5)–Co(1)–N(10)	165.2(3)	N(5)–Ni(1)–N(10)	90.3(3)
N(6)–Co(1)–N(9)	90.5(3)	N(6)–Ni(1)–N(9)	166.1(4)
N(6)–Co(1)–N(10)	92.3(3)	N(6)–Ni(1)–N(10)	92.3(3)
N(9)–Co(1)–N(10)	76.3(3)	N(9)–Ni(1)–N(10)	76.8(3)
N(3)–Co(2)–N(4)	78.2(3)	N(3)–Ni(2)–N(4)	78.1(4)
N(3)–Co(2)–N(7)	101.2(2)	N(3)–Ni(2)–N(7)	97.6(3)
N(3)–Co(2)–N(8)	171.7(3)	N(3)–Ni(2)–N(8)	90.3(3)
N(3)–Co(2)–N(11)	97.7(3)	N(3)–Ni(2)–N(11)	101.8(3)
N(3)–Co(2)–N(12)	91.7(3)	N(3)–Ni(2)–N(12)	172.3(3)
N(4)–Co(2)–N(7)	96.4(3)	N(4)–Ni(2)–N(7)	172.0(3)
N(4)–Co(2)–N(8)	93.9(3)	N(4)–Ni(2)–N(8)	95.3(3)
N(4)–Co(2)–N(11)	172.3(3)	N(4)–Ni(2)–N(11)	96.8(3)
N(4)–Co(2)–N(12)	96.3(3)	N(4)–Ni(2)–N(12)	94.5(4)
N(7)–Co(2)–N(8)	77.1(2)	N(7)–Ni(2)–N(8)	78.0(3)
N(7)–Co(2)–N(11)	90.8(3)	N(7)–Ni(2)–N(11)	90.7(3)
N(7)–Co(2)–N(12)	163.5(3)	N(7)–Ni(2)–N(12)	90.0(3)
N(8)–Co(2)–N(11)	90.4(3)	N(8)–Ni(2)–N(11)	164.4(3)
N(8)–Co(2)–N(12)	91.5(3)	N(8)–Ni(2)–N(12)	92.1(3)
N(11)–Co(2)–N(12)	77.2(2)	N(11)–Ni(2)–N(12)	77.1(3)

From the assembly of the non-helical molecular box [Ag$_2$L$_2$]$^{2+}$ and molecular triple helices [Co$_2$L$_3$]$^{4+}$ and [Ni$_2$L$_3$]$^{4+}$ it is suggested that steric effects do not appear to play a major role in determining the assembled product, while the π–π interactions are considered to be important in stabilizing these complexes. Understanding the factors that control the assembly of both helical and non-helical structures is essential as the field of metallosupramolecular chemistry expands into the develop-

Table 5 Selected dihedral angles (°) for complexes $\mathbf{2}\cdot0.5CH_3CN\cdot0.5CH_3OH$ and $\mathbf{3}\cdot0.5CH_3CN\cdot0.5CH_3OH$

Plane	Atoms defining plane	Mean deviation/Å	Dihedral angles				
			I	II	III	IV	V
$\mathbf{2}\cdot0.5CH_3CN\cdot0.5CH_3OH$							
I	C(7), C(8), C(9), C(10), C(11), C(12)	0.01					
II	C(13), C(14), C(15), C(16), C(17), C(18)	0.01	88.5				
III	C(31), C(32), C(33), C(34), C(35), C(36)	0.01	73.4	25.4			
IV	C(37), C(38), C(39), C(40), C(41), C(42)	0.01	25.8	74.6	85.9		
V	C(55), C(56), C(57), C(58), C(59), C(60)	0.01	84.3	7.8	33.1	73.3	
VI	C(61), C(62), C(63), C(64), C(65), C(66)	0.01	3.4	88.6	71.2	26.2	87.4
$\mathbf{3}\cdot0.5CH_3CN\cdot0.5CH_3OH$							
I	C(7), C(8), C(9), C(10), C(11), C(12)	0.02					
II	C(13), C(14), C(15), C(16), C(17), C(18)	0.02	88.9				
III	C(31), C(32), C(33), C(34), C(35), C(36)	0.02	84.4	8.6			
IV	C(37), C(38), C(39), C(40), C(41), C(42)	0.02	3.1	88.7	87.0		
V	C(55), C(56), C(57), C(58), C(59), C(60)	0.02	73.4	25.0	33.4	71.8	
VI	C(61), C(62), C(63), C(64), C(65), C(66)	0.01	25.0	75.7	74.3	24.8	86.8

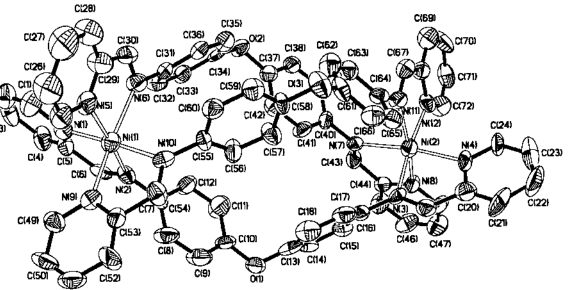

Fig. 5 An ORTEP plot of the triple-helical $[Ni_2L_3]^{4+}$ cation, showing 30% probability displacement ellipsoids of non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

ment of new supramolecular structure and devices.[24] Constable and co-workers[25] and Williams and co-workers[26] have studied the co-ordination chemistry of both helical and non-helical oligopyridine, bis(benzimidazole) compounds respectively. This paper describes two helical and one non-helical metal complex, reinforcing the importance of ligand design in controlling the outcome of assembly properties. The syntheses of related ligands designed to favor exclusive formation of either helical or non-helical structures is underway.

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References

1 J.-M. Lehn, *Supramolecular Chemistry: Concept and Perspectives*, VCH, Weinheim, 1995; *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J.-M. Lehn, Pergamon, Oxford, 1996, vol. 9, pp. 165–211, 213 and 282.
2 M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; R. W. Saalfrank and I. Bernt, *Curr. Opinion Solid State Mater.*, 1998, **3**, 407; L. R. MacGillivray and J. L. Atwood, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1018.
3 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; D. Philp and J. F. Stoddart, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1155; E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67; J. Xu, T. N. Parac and K. N. Raymond, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2878.
4 R. Ziessel, A. Harriman, J. Suffert, M.-T. Youinou, A. D. Cian and J. Fischer, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2509; G. Baum, E. C. Constable, D. Fenske and T. Kulke, *Chem. Commun.*, 1997, 2043; N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63; P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis and S. B. Wild, *Chem. Commun.*, 1998, 1153; M. J. Hannon, S. Bunce, A. J. Clarke and N. W. Alcock, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1277.
5 J.-C. Chambron, C. O. Dietrich-Buchecker and J. P. Sauvage, *Top. Curr. Chem.*, 1993, **165**, 132; J.-C. Chambron, C. O. Dietrich-Buchecker, V. Heitz, J.-F. Nierengarten, J.-P. Sauvage, C. Pascard and J. Guilhem, *Pure Appl. Chem.*, 1995, **67**, 233 and references therein.
6 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117; K. N. Power, T. L. Hennigar and M. J. Zaworotko, *Chem. Commun.*, 1998, 595; S. R. Batten, B. F. Hoskins and R. Robson, *New J. Chem.*, 1998, **22**, 173; A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1999, **5**, 1803.
7 C. Dietrich-Buchecker and J. P. Sauvage, *Chem. Commun.*, 1999, 615; J. Rebek, Jr., *Acc. Chem. Res.*, 1999, **32**, 278.
8 P. Baxter, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 69; D. W. Johnson, J. Xu. R. W. Saalfrank and K. N. Raymond, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2882.
9 H. Rauter, E. C. Hillgeris, A. Erxleben and B. Lippert, *J. Am. Chem. Soc.*, 1994, **116**, 616; M. Fujita and K. Ogura, *Bull. Chem. Soc. Jpn.*, 1995, **69**, 1471; B. Olenyuk, A. Fechtenkotter and P. J. Stang, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1707; M. J. Hannon, C. L. Painting and W. Errington, *Chem. Commun.*, 1997, 307; *Chem. Commun.*, 1997, 1805.
10 P. J. Bonitatebus, Jr., S. K. Mandal and W. H. Armstrong, *Chem. Commun.*, 1998, 939; B. J. McNelis, L. C. Nathan and C. J. Clark, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1831.
11 N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature* (*London*), 1999, **398**, 794; P. N. W. Baxter, J.-M. Lehn and K. Rissanen, *Chem. Commun.*, 1997, 1323; P. N. W. Baxter, G. S. Hanan and J.-M. Lehn, *Chem. Commun.*, 1996, 2019.
12 C. Y. Duan, Z. H. Liu, X. Z. You, F. Xue and T. C. W. Mak, *Chem. Commun.*, 1997, 381; C. He, C. Y. Duan, C. J. Fang, Y. J. Liu and Q. J. Meng, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1207; Z. H. Liu, C. Y. Duan, S. H. Yang and X. Z. You, *Chem. Lett.*, 1999, 1734.
13 A. Bilyk, M. M. Harding, P. Turner and T. W. Hambley, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2783; C. O. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, N. Armaroli, V. Balzani and L. D. Cola, *J. Am. Chem. Soc.*, 1993, **115**, 11237.
14 (*a*) N. Yoshida and K. Ichikawa, *Chem. Commun.*, 1997, 1091; (*b*) M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin and W. Errington, *Chem. Commun.*, 1997, 1807.
15 M. J. Hannon, C. L. Painting and N. W. Alcock, *Chem. Commun.*, 1999, 2023.
16 XSCANS, Version 2.1, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.
17 SHELXTL, Version 5.0, Siemens Industrial Automation, Inc., Analytical Instrumentation, Madison, WI, 1995.
18 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
19 M. Fujita, S. Nagao, M. Iida, K. Ogata and K. Ogura, *J. Am. Chem. Soc.*, 1993, **115**, 1574.
20 Y. Zhang, M. Nishiura, J. Li, D. Wei and T. Imamoto, *Inorg. Chem.*, 1999, **38**, 825.

21 D. F. Shriver, P. Arkins and C. H. Langford, *Inorg. Chem.*, 2nd edn., W. H. Freeman and Company, New York, 1997.
22 Z. H. Liu, C. Y. Duan, J. Hu and X. Z. You, *Inorg. Chem.*, 1999, **38**, 1719.
23 S. K. Burley and C. A. Pestko, *Adv. Protein Chem.*, 1998, **39**, 125.
24 E. C. Constable, *Chem. Ind.* (*London*), 1994, 56 and references therein; *Nature* (*London*), 1990, **346**, 314; *Nature* (*London*), 1993, **362**, 412 and references therein.
25 E. C. Constable and M. D. Ward, *J. Am. Chem. Soc.*, 1990, **112**, 1256; E. C. Constable, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 1450; E. C. Constable, S. M. Elder, J. Healy and M. D. Ward, *J. Am. Chem. Soc.*, 1990, **112**, 4590; E. C. Constable, M. J. Hannon and D. A. Tocher, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1883.
26 A. F. Williams, C. Piguet and G. Bernardinelli, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **11**, 1490; C. Piguet, G. Bernardinelli and A. F. Williams, *Inorg. Chem.*, 1989, **28**, 2920; S. Rüttimann, C. Piguet, G. Bernardinelli, B. Bocquet and A. F. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 4230; C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani and A. F. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 7440.