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FULL PAPER

New U- and Y-shaped components for metallosupramolecular assemblies: synthesis and coordination chemistry of 2,6-bis(3-pyridyloxy)pyrazine

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The new ligand 2,6-bis(3-pyridyloxy)pyrazine (**1**) has been prepared and characterized. The ligand has inherent flexibility due to the two ether linkages and its ability to act as either a U-shaped, Y-shaped or W-shaped component in the preparation of metallosupramolecular assemblies has been assessed by reactions of **1** with late transition metal ions. Reaction with $Cu(NO_3)_2$ gives a discrete dimetallacyclic complex, with the ligand acting as a U-shaped component by binding through only the pyridine donors, and contains a rare $Cu_2(\mu\text{-}ONO_2)_2$ unit. Reaction with CuI also gives a discrete dimetallacyclic complex, with the ligand again acting as a U-shaped component, and the complex containing a central $Cu_2(\mu\text{-}I)_2$ unit. Reaction with $[Cu(CH_3CN)_4]BF_4$ gives the first example of a chiral 2-dimensional [6:3] metallopolymeric net species, with the ligand acting as a Y-shaped component by binding through both the pyridine and pyrazine donors. Reaction with $AgNO_3$ gives a centrosymmetric 2-dimensional [6:3] metallopolymeric net species, with the ligand again acting as a Y-shaped component.

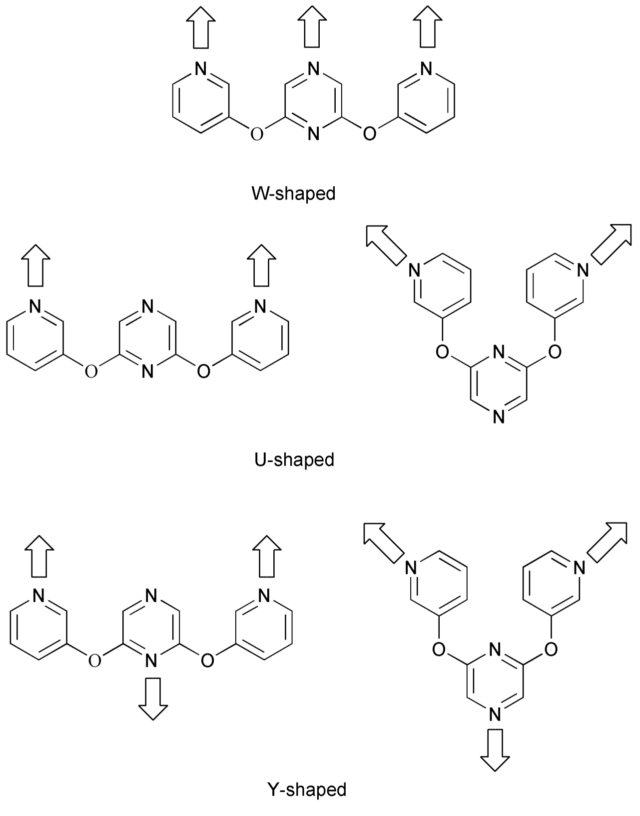
Introduction

The preparation of supramolecular assemblies with novel and potentially desirable structural and chemical properties continues to be an area of intense research.[1,2] In particular, methodologies whereby transition metal ions can be used as a "glue", holding together organic ligands in defined ways to produce metallosupramolecular assemblies, have been explored by many groups. By utilizing the well-understood geometrical preferences of certain metal ions, a rational approach to the preparation of metallosupramolecular assemblies with defined structures can be developed.

We have been involved in a program of preparing new metallosupramolecular species based on the assembly of flexible multi-heterocyclic ligands *via* transition metal centers.[3] In particular, we recently reported the chemistry of a new ligand, 2,6-bis(4-(3-pyridyloxy)phenoxy)pyrazine, which contains two different donor types (pyridine and pyrazine groups).[4] Palladium(II) and silver(I) complexes of this ligand showed a preference for coordination, in a U-shaped conformation, through the pyridine donors only.

We now report the preparation of the related ligand, 2,6-bis(3-pyridyloxy)pyrazine (**1**), which has been designed to act as a Y-shaped or W-shaped component, when both the pyridine and pyrazine groups coordinate, or as a U-shaped component when coordination is through the pyridine groups only (Scheme 1).

Reaction of **1** with silver(I), copper(I) and copper(II) salts shows that both pyridine and pyrazine donors can be utilized for bonding. Coordination by only the pyridine donors results in discrete bimetallic species, whereas coordination by both pyridine and pyrazine groups leads to 2-dimensional metallopolymeric species.



Scheme 1 Possible coordination modes for **1**.

Experimental

General

NMR spectra were recorded on a Varian 500 MHz NMR spectrometer. Melting points are uncorrected. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago. UV-visible spectra were recorded on a Perkin-Elmer Lambda-9 Uv/vis/nir spectrometer with a 60 mm MgO coated integrating sphere diffuse reflectance attachment.

Preparations

2,6-Bis(3-pyridyloxy)pyrazine (1). 3-Hydroxypyridine (922 mg, 9.7 mmol), 2,6-dichloropyrazine (700 mg, 4.6 mmol) and

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Cs_2CO_3 (3.258 g, 10 mmol) were stirred in dimethylformamide (10 mL) at 110 °C for 20 hours. The pale brown suspension was then cooled, diluted with water (80 mL) and extracted with ethyl acetate (5 × 30 mL). The combined organic extracts were washed with dilute aqueous NaOH (30 mL), water (2 × 30 mL) and brine (30 mL) and dried (Na_2SO_4). Removal of solvent gave **1** as an orange solid. Yield 1.20 g (97%). The product can be recrystallised from ethyl acetate/petroleum ether (bp 60–80) as pale orange needles. Mp 100–102 °C. Analysis: $C_{14}H_{10}N_4O_2$ requires: C, 63.16; H, 3.79; N, 21.04. Found: C, 63.44; H, 3.79; N, 21.33%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, J = 8.3, 4.4 Hz, 2H, H_5'), 7.39 (ddd, J = 8.3, 2.9, 1.4 Hz, 2H, H_4'), 8.20 (s, 2H, H_3, H_5), 8.40 (d, J = 2.9 Hz, 2H, H_2'), 8.43 (dd, J = 4.4, 1.4 Hz, 2H, H_6').

[Cu_2(1)$_2$(NO_3)$_4$]. $Cu(NO_3)_2\cdot 3H_2O$ (46 mg, 0.19 mmol) in methanol (2 mL) was added to **1** (50 mg, 0.19 mmol) in methanol (3 mL) to give a deep green solution. After 10 minutes reflux, the solution was cooled and a deep green solid formed. This was filtered off, washed with diethyl ether and dried. Yield 72 mg (84%). Mp 213–215 °C (decomp.). Analysis: $C_{28}H_{20}N_{12}O_{16}Cu_2\cdot MeOH$ requires: C, 37.16; H, 2.91; N, 17.33. Found: C, 37.19; H, 2.80; N, 17.14%. On standing in acetonitrile, the green solid transformed into blue plates suitable for X-ray analysis. The blue compound was prepared directly by carrying out the reaction in acetonitrile. Yield 86%. Mp 226–228 °C (decomp). Analysis: $C_{28}H_{20}N_{12}O_{16}Cu_2$ requires: C, 37.05; H, 2.22; N, 18.51. Found: C, 37.05; H, 2.66; N, 18.59%.

[Cu_2(1)$_2$$I_2$]. CuI (36 mg, 0.19 mmol) in acetonitrile (2 mL) was added to **1** (50 mg, 0.19 mmol) in hot acetonitrile (3 mL) to give a yellow solid. The suspension was refluxed for 10 minutes, then cooled and the solid filtered off, washed with ether and dried. Yield 71 mg (83%). Mp 216–218 °C. Analysis: $C_{28}H_{20}N_8O_4Cu_2I_2$ requires: C, 36.82; H, 2.21; N, 12.26. Found: C, 36.98; H, 2.08; N, 12.39%. Repeating the reaction by layering a solution of CuI in acetonitrile onto a solution of **1** in chloroform gave yellow-brown blocks suitable for X-ray analysis.

[Cu(1)(BF_4)]. [$Cu(CH_3CN)_4$]BF_4 (35 mg, 0.11 mmol) in acetonitrile (5 mL) was added to **1** (30 mg, 0.11 mmol) in acetonitrile (10 mL) and the solution heated under an argon atmosphere for 10 minutes to give a clear yellow solution. After cooling to room temperature, diethyl ether (*ca.* 12 mL) was added to give the product as a yellow microcrystalline solid, which was filtered off, washed with diethyl ether and dried. Yield 43 mg (91%). Mp 324–325 °C. Analysis: $C_{14}H_{10}N_4O_2CuBF_4\cdot CH_3CN\cdot H_2O$ requires: C, 40.40; H, 3.18; N, 14.71. Found: C, 40.24; H, 3.00; N, 14.69%. Recrystallisation by diffusing diethyl ether into an acetonitrile reaction solution gave crystals suitable for X-ray analysis.

[Ag(1)(NO_3)]. $AgNO_3$ (32 mg, 0.19 mmol) in hot methanol (2 mL) was added to **1** (50 mg, 0.19 mmol) in hot methanol (4 mL) to give an off-white suspension. On standing, the hot suspension deposited cream-coloured needles. The mixture was cooled and the solid filtered off, washed with methanol and diethyl ether and dried. Yield 76 mg (93%). Mp 229–231 °C. Analysis: $C_{14}H_{10}N_5O_5Ag$ requires: C, 38.56; H, 2.31; N, 16.05. Found: C, 38.54; H, 2.34; N, 16.21. Diffusion of diethyl ether into an acetonitrile solution of the complex gave crystals suitable for X-ray analysis.

X-Ray crystallography

The crystal data, data collection and refinement parameters are listed in Table 1. All measurements were made with a Siemens CCD area detector using graphite monochromatised Mo-Kα (λ = 0.71073 Å) radiation. Intensities were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods using SHELXS,[5] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-96.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$.

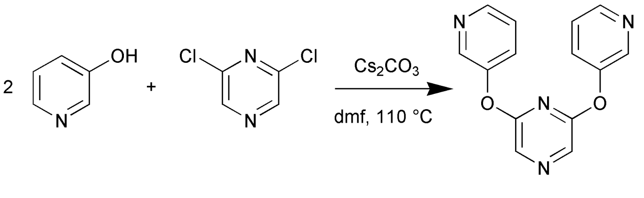
CCDC reference numbers 182092–182095.

See http://www.rsc.org/suppdata/dt/b2/b202593k/ for crystallographic data in CIF or other electronic format.

Results

Ligand and complex synthesis

The new ligand 2,6-bis(3-pyridyloxy)pyrazine (**1**) was prepared in high yield by a double nucleophilic substitution reaction of 3-hydroxypyridine and 2,6-dichloropyrazine (Scheme 2), which in turn was prepared from pyrazine *via* the di-*N*-oxide.[7] It was isolated as an orange crystalline solid and fully characterised by microanalysis and ^{1}H NMR spectroscopy.



1

Scheme 2

Reactions of **1** with Ag(I), Cu(I) and Cu(II) salts in acetonitrile or methanol solutions gave air-stable complexes in good to high yields. Reaction of **1** with 1 equivalent of $Cu(NO_3)_2$ in methanol solution gave a green solid, which elemental analysis showed to have a Cu : **1** ratio of 1 : 1 and suggested the presence of a methanol solvate molecule. The complex was only soluble in dmf and dmso, giving pale green solutions. UV-visible spectroscopy of a dmf solution showed a broad absorbance at 730 nm (ε = 42 mol^{-1} dm^3 cm^{-1}) and the solid-state reflectance spectrum shows a broad absorbance at 810 nm with shoulders at *ca.* 706 nm and *ca.* 1026 nm. While the complex appears to be insoluble in acetonitrile, on standing in acetonitrile the green solid transforms to a blue crystalline solid over a period of hours. This blue complex could be prepared independently by carrying out the reaction between $Cu(NO_3)_2$ and **1** in acetonitrile solution. Elemental analysis showed the blue crystals to retain a Cu : **1** ratio of 1 : 1 but now with no methanol solvate. The blue complex is again only soluble in dmf and dmso. In dmf solution, the UV-visible spectrum shows a broad absorbance at 780nm (ε = 36 mol^{-1} dm^3 cm^{-1}) and the solid-state reflectance spectrum shows two absorbances at 655 nm and 810 nm.

Reaction of **1** with CuI in acetonitrile solution gave an insoluble yellow product in high yield. Elemental analysis showed the complex to have a Cu : **1** ratio of 1 : 1. Reaction of [$Cu(CH_3CN)_4$]BF_4 with **1** in acetonitrile solution under an argon atmosphere gave a yellow solution, from which a yellow solid was obtained in high yield on addition of diethyl ether. Analysis showed the product to have a Cu : **1** ratio of 1 : 1. The solid was only soluble in dmf and dmso. However, the ^{1}H NMR spectrum of the product in dmso showed peaks due to free ligand only, suggesting that the ligand is displaced by the dmso.

Reaction of **1** with $AgNO_3$ in hot methanol solution gave off-white crystals in high yield. Elemental analysis showed the complex to have a Ag : **1** ratio of 1 : 1. ^{1}H NMR spectra of the complex in acetonitrile showed only peaks due to **1**, suggesting that the ligand is displaced by acetonitrile solvent in solution.

Table 1 Crystal data and refinement parameters

	$[Cu_2(\mathbf{1})_2(NO_3)_4]\cdot 2CH_3CN$	$[Cu_2(\mathbf{1})_2I_2]$	$[Cu(\mathbf{1})(CH_3CN)]BF_4\cdot CH_3CN\cdot 0.5H_2O$	$[Ag(\mathbf{1})(NO_3)]$
Formula	$C_{32}H_{26}N_{14}O_{16}Cu_2$	$C_{28}H_{20}N_8O_4Cu_2I_2$	$C_{18}H_{17}N_6O_{2.5}CuBF_4$	$C_{14}H_{10}N_5O_5Ag$
M	989.74	913.40	507.73	436.14
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
a/Å	8.148(6)	14.819(5)	8.211(7)	8.929(4)
b/Å	11.446(9)	15.055(5)	8.327(7)	18.100(9)
c/Å	11.866(9)	15.475(7)	9.356(6)	10.233(4)
α/°	108.12(2)	90.0	95.96(3)	90.0
β/°	96.74(2)	117.819(15)	107.60(2)	107.113(12)
γ/°	110.76(3)	90.0	116.67(2)	90.0
V/Å^3	950.6(13)	3053(2)	522.8(7)	1580.5(12)
ρ_{calcd}/g cm^{-1}	1.729	1.987	1.613	1.833
Space group	$P\bar{1}$	$C2/c$	$P1$	$P2_1/n$
Z	1	4	1	4
μ/mm^{-1}	1.214	3.464	1.111	1.313
F(000)	502	1760	257	864
T/K	168(2)	168(2)	168(2)	168(2)
No. measured	12475	19789	6286	19720
No. unique	3865	3116	3059	3202
No. with $I > 2\sigma(I)$	2567	2782	2492	2805
wR (all data)	0.1161	0.0484	0.1619	0.0575
$R1$ ($I > 2\sigma(I)$)	0.0465	0.0185	0.0638	0.0212

While microanalyses suggested 1 : 1 ligand : metal ratios for all complexes, their insolubility made further characterisation difficult. Therefore, X-ray crystallography was used to determine the detailed structural nature of the four complexes.

Structure of $[Cu_2(\mathbf{1})_2(NO_3)_4]$

Blue crystals suitable for X-ray analysis were obtained from a sample of the green solid being left to stand in acetonitrile solution. Fig. 1 shows a perspective view of the complex, which is found to be a $Cu_2\mathbf{1}_2$ dimetallacycle. The complex crystallizes in the space group $P\bar{1}$ with the asymmetric unit containing one **1** ligand, one copper atom, two coordinated nitrates and one disordered acetonitrile solvate molecule. A crystallographically imposed centre of inversion lies between the two copper atoms. Each ligand coordinates through the pyridine donors only, in *trans* fashion about each copper atom, and adopts a U-shaped conformation. The angles between the pyridine rings and the pyrazine ring are 78.6(4) and 97.8(4)°, while the angle between the two pyridine rings is 19.5(4)°. The copper atoms are also bridged by oxygen atoms from two bifurcating nitrate ions and each copper is further coordinated by a monodentate nitrate ion. The copper atoms adopt an approximately square pyramidal geometry with a τ value of 0.07.[8] The Cu–N distances are almost identical (1.998(3), 2.005(3) Å) and are typical, while the Cu–O distance to the terminal nitrate is also typical at 2.009(3) Å. The angle between the two Cu–N bond vectors is 9.8(4)°. The $Cu_2(\mu\text{-}ONO_2)_2$ unit is unsymmetrical, with the Cu–O distances being 2.369(4) Å (Cu1–O40) and 2.011(4) Å (Cu1–O40A). The Cu ··· Cu distance is 3.576(4) Å. This type of $Cu^{II}_2(\mu\text{-}ONO_2)_2$ unit, in which two nitrates bridge, each through one oxygen atom only, is rare, with only four other examples in the Cambridge Structural Database (CSD).[9] The data for these and the current example are listed in Table 2 and show that $[Cu_2(\mathbf{1})_2(NO_3)_4]$ is largely similar to the previous cases, with the bond distances being intermediate to these and the bond angles being only slightly different.

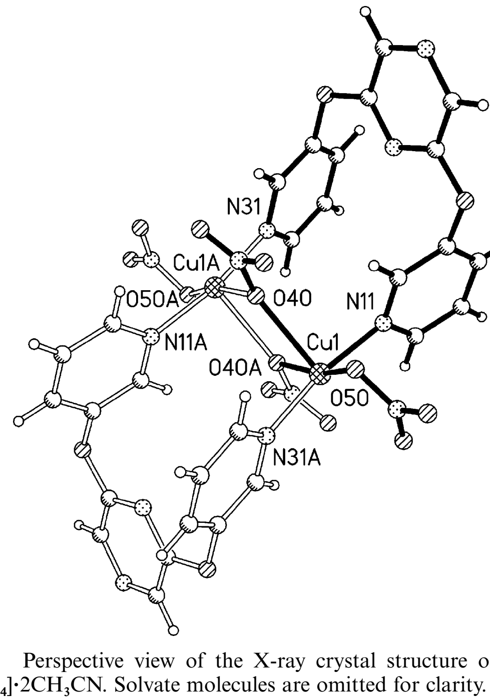


Fig. 1 Perspective view of the X-ray crystal structure of $[Cu_2(\mathbf{1})_2(NO_3)_4]\cdot 2CH_3CN$. Solvate molecules are omitted for clarity. Atom XA is related to atom X by the symmetry transformation ($-x$, $-y$, $-z$). Selected bond lengths (Å) and angles (°): Cu1–N11 2.005(3); Cu1–N31A 1.998(3); Cu1–O40 2.369(4); Cu1–O50 2.009(3); Cu1–O40A 2.011(4); N11–Cu1–N31A 170.19(11); N11–Cu1–O50 87.07(12); N11–Cu1–O40 92.61(11); N11–Cu1–O40A 93.46(12); O50–Cu1–O40 95.45(11); O50–Cu1–O40A 166.23(12); O40–Cu1–O40A 70.78(15); Cu1–O40–Cu1A 109.22(15).

Structure of $[Cu_2(\mathbf{1})_2I_2]$

Layering an acetonitrile solution of CuI onto a chloroform solution of **1** gave crystals suitable for X-ray analysis. Fig. 2 shows a perspective view of the complex, which crystallizes in the space group $C2/c$, and is found to be a dimetallacyclic $Cu_2\mathbf{1}_2$ species. The asymmetric unit contains one **1** ligand, one copper atom and one iodide ion. A crystallographically imposed centre of inversion lies between the two copper atoms. Each ligand acts as a U-shaped component and coordinates through the pyridine donors only. The angle between the pyridine rings is 52.6(2)° and the angles between the pyrazine ring and the pyridine rings are 62.4(2)° and 104.2(2)°. Each copper atom has an approximately tetrahedral geometry, being coordinated by a pyridine from each ligand with almost identical Cu–N distances (2.0272(19), 2.0334(18) Å) and by two iodide ions which each bridge the two copper atoms. The angle between the two Cu–N bond vectors is 48.2(2)°. The Cu–I distances are 2.7540(10) Å (Cu1–I1) and 2.6853(9) Å (Cu1–I1A) and the Cu ··· Cu distance is 2.803(2) Å. The CSD contains twenty one other examples of discrete $[CuN_2(\mu\text{-}I)_2CuN_2]$ units. Analysis of the structural parameters of these shows $[Cu_2(\mathbf{1})_2I_2]$ to be typical.[14]

Structure of $[Cu(\mathbf{1})(CH_3CN)](BF_4)$

Vapour diffusion of diethyl ether into an acetonitrile solution gave crystals of $[Cu(\mathbf{1})(BF_4)]$ suitable for X-ray analysis. Fig. 3

Table 2 Structural data for $Cu^{II}_2(\mu\text{-}ONO_2)_2$ units

Complex	Cu–O/Å	Cu ··· Cu/Å	Cu–O–Cu/°	O–Cu–O/°	Ref.
$[Cu_2(py)_4](NO_3)_4$	2.042, 2.542	3.69	106.8	73.2	10
$[Cu_2(bprym)(NO_3)_4]_n$[a]	1.965, 2.300	3.418	106.3	73.7	11
$[Cu_2(alim)_4(NO_3)_4]$[b]	2.021, 2.461	3.685	110.2	69.8	12
$[Cu_2(bpethy)(NO_3)_4]$[c]	2.013, 2.531	3.766	111.44	68.66	13
$[Cu_2(\mathbf{1})_2(NO_3)_4]$	2.011, 2.369	3.576	109.22	70.78	This work

[a] bprym = 2,2′-bipyrimidine. [b] alim = 1-allylimidazole. [c] bpethy = 1,2-bis(4-pyridyl)ethyne.

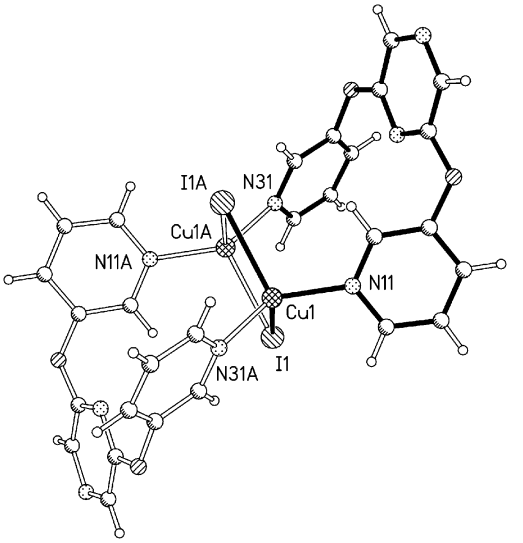


Fig. 2 Perspective view of the X-ray crystal structure of $[Cu_2(\mathbf{1})_2I_2]$. Atom XA is related to atom X by the symmetry transformation (−*x*, −*y*, −*z* + 1). Selected bond lengths (Å) and angles (°): Cu1–N11 2.0272(19); Cu1–N31A 2.0334(18); Cu1–I1 2.7540(10); Cu1–I1A 2.6853(9); N11–Cu1–N31A 131.84(7); N11–Cu1–I1 98.21(5); N11–Cu1–I1A 107.81(5); I1–Cu1–I1A 117.98(3); Cu1–I1–Cu1A 62.02(3).

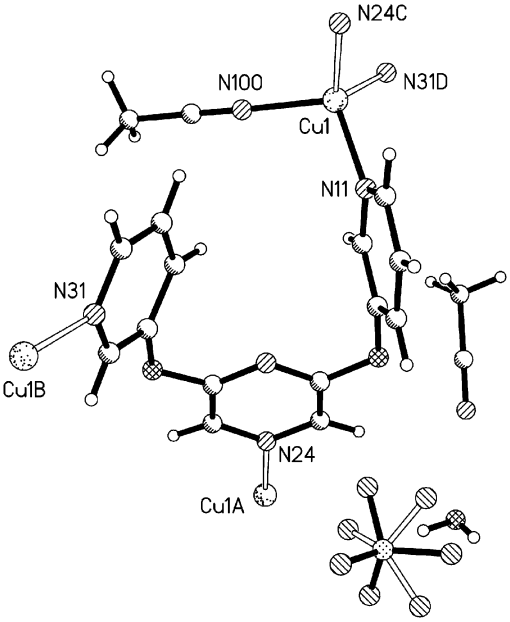


Fig. 3 Perspective view of the X-ray crystal structure of $[Cu(\mathbf{1})(CH_3CN)](BF_4)\cdot CH_3CN\cdot 0.5H_2O$. Atom XA to XD are related to atom X by the symmetry transformations (*x*, *y*, *z* + 1), (*x* − 1, *y* − 1, *z*), (*x*, *y*, *z* − 1) and (*x* + 1, *y* + 1, *z*), respectively. Selected bond lengths (Å) and angles (°): Cu1–N11 2.018(7); Cu1–N100 1.954(8); Cu1–N24C 2.020(7); Cu1–N31D 1.998(7); N11–Cu1–N100 107.8(3); N11–Cu1–N24C 108.2(3); N11–Cu1–N31D 114.9(3); N24C–Cu1–N31D 109.4(3); N24C–Cu1–N100 106.5(3); N31D–Cu1–N100 109.6(3).

shows a perspective view of the complex, which crystallizes in the space group *P*1. The asymmetric unit contains one copper atom, one ligand, one acetonitrile, which is coordinated to the copper, one acetonitrile solvate molecule and half a water solvate molecule. The copper atom adopts an almost regular tetrahedral geometry, being coordinated by two pyridine donors and the less sterically hindered N_4 nitrogen of one pyrazine donor, each from different ligands, as well as the acetonitrile. The Cu–N distances are all typical, being in the range 1.954(8)–2.020(7) Å. The angle between the pyridine rings is 44.5(7)° and the angles between the pyridine rings and the pyrazine ring are 78.7(7)° and 122.3(7)°. In this case the ligand acts as a Y-shaped component, with the pyridine donors arranged in a divergent manner. The angle between the pyridine N–Cu bond vectors is 114.9(7)°.

Fig. 4 shows a perspective view of the extended structure of the complex. Each copper atom acts as a three-connected node by connecting the pyridine rings of two **1** ligands and the pyrazine ring of a third **1** ligand. Similarly, each **1** ligand also acts as a three-connected node, with the two pyridine donors and the pyrazine donor of each **1** ligand coordinating to different copper atoms. The extended structure is therefore a 2-dimensional [6:3] net.[15] The acetonitrile ligands, which complete the coordination sphere of each copper atom, all lie on the same side of the 2-D sheet.

The structure is interesting for two reasons. Firstly, while a number of [6:3] net coordination polymers have now been reported, examples where the metal atom has a tetrahedral coordination geometry are rare.[16] Normally, a T-shaped metal node is used;[17] less frequently, planar trigonal and trigonal bipyramidal coordination geometries have been employed.[18] In these cases, the ligands used have generally had rigid, planar structures. The combination of a tetrahedral metal centre with such planar ligands tend to form diamondoid networks rather than a 2-D sheet polymer. In the present case however, the inherent flexibility in the ligand structure means that the non-planar metal geometry can be compensated for by the ligand and so a planar structure can result.

A second feature of the extended structure is that the overall structure is chiral, with all the acetonitrile ligands being on the same side of the 2-D sheet. To our knowledge, this represents the first example of a chiral [6:3] coordination polymer. Since the complex is in the space group *P*1, all the sheets within the crystal have the same chirality. Adjacent sheets are inter-digitated, with the coordinated acetonitrile ligands of one sheet lying in a space generated by the pyridine rings of the next sheet. The closest contact between adjacent sheets is 2.810(7) Å (between a hydrogen of the methyl group of the coordinated acetonitrile and N_1 of a pyrazine ring). The BF_4^- counterions and acetonitrile and water solvate molecules occupy positions between the sheets and within the cavities. All make a number of hydrogen bonding interactions with hydrogen atoms on the ligands (the shortest is a F ··· H interaction at 2.255(7) Å).

As the individual components of the complex are achiral, the reaction between **1** and $[Cu(CH_3CN)_4]BF_4$ is an example of the generation of a chiral metallosupramolecular structure from achiral components by self-assembly. While a number of examples have been reported where chiral supramolecular species have been prepared by using chiral ligands[2] or octahedral metal centres (which are inherently chiral), examples of chiral species formed from achiral components are much less common.[19] Such systems represent the initial stages in a

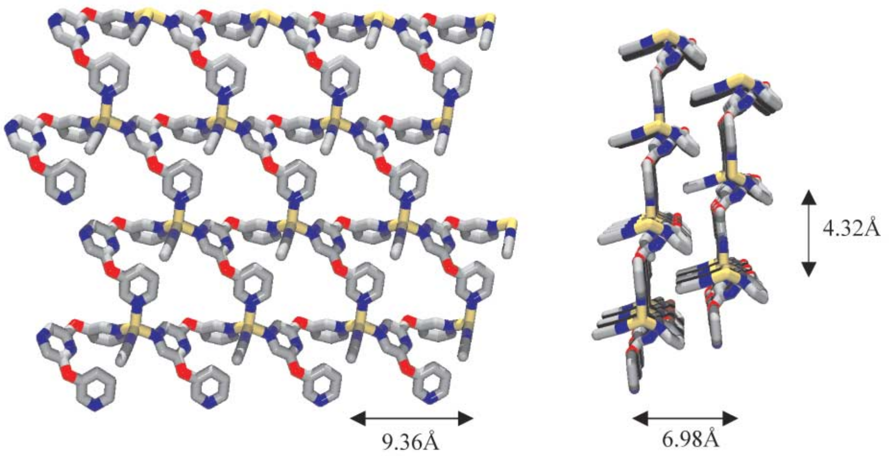


Fig. 4 Perspective view of the molecular packing of [Cu(**1**)(CH_3CN)](BF_4)·CH_3CN·0.5H_2O and selected intersheet and intrasheet distances. Hydrogen atoms, counterions and solvate molecules are not shown.

new level of development in metallosupramolecular self-assembly and have many potentially useful properties, *e.g.* enantioselective recognition and separation.[20]

Structure of [Ag(1)(NO$_3$)]

Diffusion of diethyl ether into an acetonitrile solution of [Ag(**1**)(NO_3)] gave crystals suitable for X-ray analysis. Fig. 5 shows a perspective view of the complex, which crystallises in the space group $P2_1/n$. The asymmetric unit contains one **1** ligand, one silver atom and one nitrate. The silver atom has an approximately tetrahedral geometry, being coordinated by two pyridine nitrogens and one pyrazine nitrogen, each from different ligands, and one oxygen of the nitrate counterion. The Ag–N distances are 2.2437(17) and 2.3026(17) Å for the bonds to the pyridine donors, while the Ag–N distance to the pyrazine nitrogen is longer, at 2.4806(16) Å, reflecting the poorer donor ability of pyrazine compared to pyridine. The Ag–O distance is 2.3521(17) Å. The angle between the two pyridine rings is 18.6(2)° and the pyridine nitrogens are arranged divergently, giving an angle between the pyridine N–Ag bond vectors of 161.4(2)°. The angles between the pyrazine ring and the pyridine rings are 63.4(2)° and 82.0(2)°.

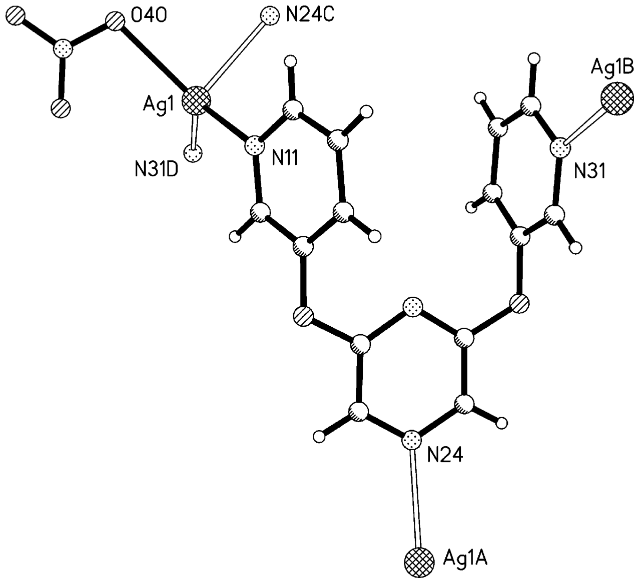


Fig. 5 Perspective view of the X-ray crystal structure of [Ag(**1**)(NO_3)]. Atom XA to XD are related to atom X by the symmetry transformations ($x + 1/2, -y + 1/2, z - 1/2$), ($x + 1/2, -y + 1/2, z + 1/2$), ($x - 1/2, -y + 1/2, z + 1/2$) and ($x - 1/2, -y + 1/2, z - 1/2$), respectively. Selected bond lengths (Å) and angles (°): Ag1–N11 2.2437(17); Ag1–O40 2.3521(17); Ag1–N24C 2.4806(16); Ag1–N31D 2.3026(17); N11–Ag1–O40 129.67(6); N11–Ag1–N24C 99.19(6); N11–Ag1–N31D 117.86(6); O40–Ag1–N24C 87.07(6); O40–Ag1–N31D 110.12(6); N24C–Ag1–N31D 99.06(6).

The extended structure of the complex is shown in Fig. 6 and is found to be similar to that observed for [Cu(**1**)(CH_3CN)](BF_4). Each silver atom acts as a three-connected node, connecting three different **1** ligands and each **1** ligand connects three silver atoms. The extended structure is therefore again a [6:3] net, based on tetrahedral metal centres. The **1** ligands lie in two different orientations, related by the 2_1 screw axis, with the angle between the pyrazine N–Ag bond vectors being 41.8(2)°.

While the gross topology of the 2-D structure is the same as that of [Cu(**1**)(CH_3CN)](BF_4), there are significant differences in this case. The angle between the pyridine N–Ag bond vectors is larger in this case (129.1(2)° *cf.* 114.9(7)°), and this, combined with the two different ligand orientations, means that a planar sheet structure cannot be achieved. The sheets instead are folded, with a repeat distance of 8.53 Å (Fig. 6) and the nitrate ligands lie on alternating sides of the sheets, pointing approximately perpendicular to the plane of the sheets. Adjacent sheets are arranged such that the nitrates of one sheet lie within cavities of the adjacent sheet, with one of the non-coordinated oxygens of the nitrate forming a weak hydrogen bond with a pyridine ring hydrogen (2.532(18) Å).

Discussion

Reaction of **1** with silver(I), copper(I) and copper(II) salts gives complexes in which **1** adopts a variety of conformations, due to the inherent flexibility engendered by the ether linkages in the backbone. As shown in Scheme 1, the ligand can potentially adopt Y-, W- and U-shaped conformations, depending on the angles between the pyridine rings, the angles between the pyridine rings and the pyrazine ring and the degree to which the pyrazine and pyridine donors are utilised for coordination. The conformations adopted by **1** in the four complexes are shown in Fig. 7.

In none of these cases was the W-shaped conformer observed. In the two instances where **1** adopted the U-shaped conformation, discrete dimetallacyclic structures resulted, with the two pyridine N–Ag bond vectors being convergent and approximately parallel. By contrast, in the two cases where **1** adopts the Y-shaped conformation, with both pyridine and pyrazine donors involved in coordination, the pyridine rings are approximately parallel in one case and almost orthogonal in the other. Further, in these two cases, the pyridine N–M bond vectors are divergent. It is clear that by incorporating flexibility into the design of the ligand, a variety of resulting structures can be formed. The specific conformation of the ligand in a particular complex, and therefore the structure of the complex

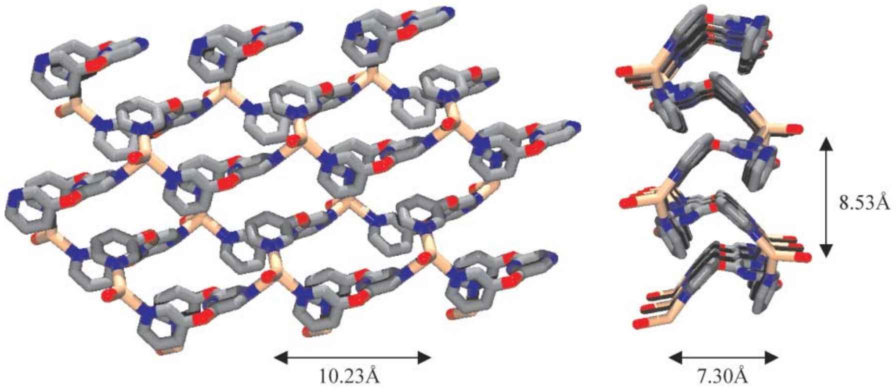


Fig. 6 Perspective view of the molecular packing of [Ag(**1**)(NO_3)] and selected intrasheet distances. Hydrogen atoms and the nitrogen and non-coordinated oxygen atoms of the nitrates are not shown.

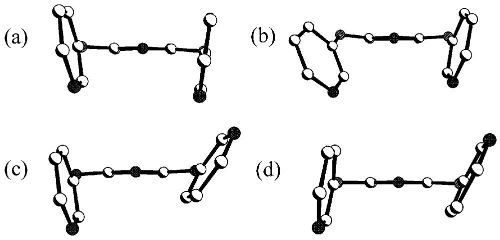


Fig. 7 Conformations of **1** in the four complexes. (a) [Cu_2(**1**)$_2$(NO_3)$_4$] (b) [Cu_2(**1**)$_2$$I_2$]; (c) [Cu(**1**)($CH_3CN$)]($BF_4$); (d) [Ag(**1**)($NO_3$)].

itself, appears to be determined by more subtle factors, such as the interaction the counterion or solvent molecules make with the metal ion and molecular packing interactions.

These results have shown that both pyridine and pyrazine donors in **1** can be utilised in coordination. We are currently extending these studies to try to determine the factors that determine the involvement of the pyrazine donor. Such an understanding may enable us to prepare complexes with **1** adopting the as yet unobserved W-shaped conformer and to connect discrete metallacyclic units together to generate heterometallic metallopolymeric species.[21]

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