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New U-shaped Components for Metallosupramolecular Assemblies: Synthesis and Coordination Chemistry of 2,6-bis(4-(3-pyridyloxy)phenoxy)pyrazine

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The new ligand 2,6-bis(4-(3-pyridyloxy)phenoxy)pyrazine (L) has been prepared and characterised. Reaction with a palladium (II) precursor yields a discrete complex of formula $[\text{Pd}(\text{L})_2](\text{ClO}_4)_2$, in which the ligand coordinates in a U-shaped fashion through the pyridine groups only, resulting in the complex containing two 22-membered chelate rings ($a = 15.288(9)$, $b = 10.118(4)$, $c = 22.720(12)$, $\beta = 95.450(12)$, $P2_1/n$, $Z = 2$, $\rho_{\text{calcd}} = 1.413 \text{ g cm}^{-3}$, 507 parameters, $R = 0.0433$). Reaction with silver nitrate yields a metallocyclic complex of formula $[\text{Ag}_2(\text{L})_2(\text{NO}_3)](\text{NO}_3)$, in which each silver is bound to one pyridine group of two different ligands, each of which is again in a U-shaped configuration ($a = 12.215(9)$, $b = 12.759(9)$, $c = 19.461(14)$, $\alpha = 90.949(10)$, $\beta = 103.214(10)$, $\gamma = 110.327(11)$, $P - 1$, $Z = 2$, $\rho_{\text{calcd}} = 1.591 \text{ g cm}^{-3}$, 755 parameters, $R = 0.0287$).

Keywords: Pyrazine; Self-assembly; Metallocyclic complex; U-shaped configuration

INTRODUCTION

The use of metal ions to control the formation of supramolecular assemblies has been an area of increasing attention over recent years [1–6]. At the heart of this rapidly expanding new field of metallosupramolecular chemistry is the desire to rationally prepare discrete molecular species and polynuclear arrays with novel structural motifs and potentially useful functional properties. The unique ability of appropriately selected metal ions to mediate the self-assembly of multiple components has been reflected in many beautiful molecular

assemblies appearing recently in the literature [7–10]. We, along with many other groups, have been involved in trying to understand the underlying rules that govern the self-assembly of such assemblies [11–14].

The potential functional properties of such systems are varied. There has been much discussion of the roles that metallosupramolecular assemblies might play in the construction of molecular machines and devices [15] and, with such applications in mind, much attention has been given to the ways in which the well-known energy- and electron-transfer properties of certain transition metal complexes might be incorporated into such assemblies [16–18]. A second functional aspect that has received considerable attention is that of molecular recognition [19]. A number of host-guest systems have been reported in which metallosupramolecular assemblies act as hosts for cations [20,21], anions [22–25] and for small neutral molecules [26]. In some cases, selective binding of guests has been observed, making these systems potentially useful as sensors [27].

We have recently reported a new type of metallosupramolecular host for monoatomic and polyatomic anionic guests [28] (Fig. 1). The quadruple helicate (**1**) is formed from two palladium(II) ions and four 1,4-bis(3-pyridyloxy)benzene ligands and possesses a central cavity within which lies one of the four counterions. ^1H NMR studies have shown that this helicate complex is able to encapsulate various anions but displays a selectivity for perchlorate ions, based on size complementarity

*Corresponding author.

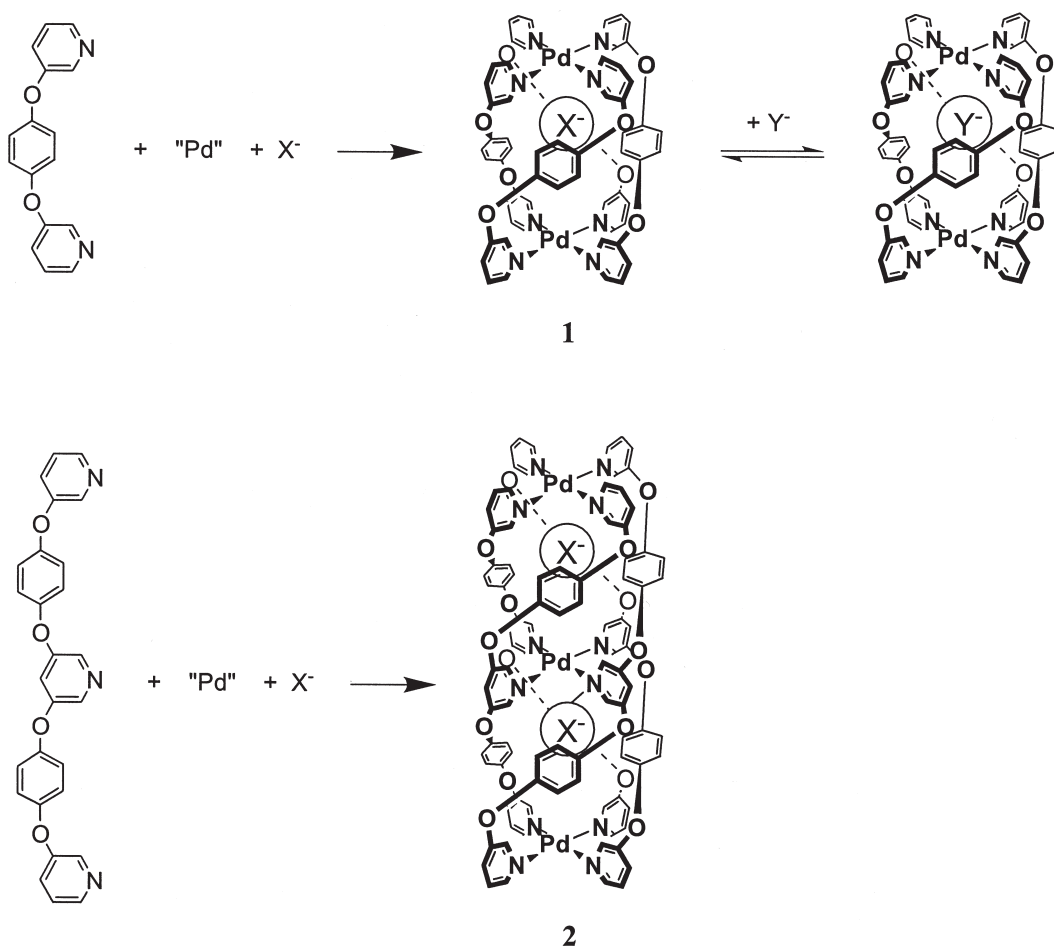


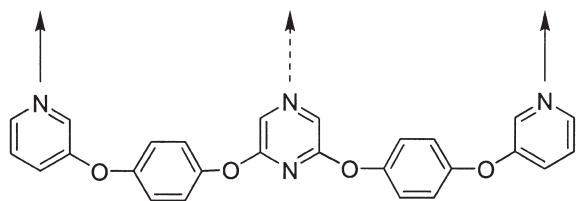
FIGURE 1 Self-assembly of quadruple helicates.

between the anion and the internal cavity of the helicate, employing a novel induced-fit mechanism [29]. We have been interested in extending this work to the preparation of the ditopic tripalladium(II) helicate (2), which might be expected to bind two anions simultaneously and in a cooperative manner. Such a species might be expected to show an amplification of anion selectivity [30].

We present here our first approach to this objective in the preparation of the new ligand 2,6-bis(4-(3-pyridyloxy)phenoxy)pyrazine (L), where the central donor unit is a 2,6-disubstituted pyrazine group, rather than the synthetically more challenging

3,5-disubstituted pyridine group depicted in 2. In order to form the desired quadruple helicate, L is required to bind in a W-shaped conformation to three metals, with coordination by both the pyridine and pyrazine donors (Scheme 1). While pyrazine is well known to be a poorer donor than pyridine, we thought that the presence of the additional pyridine donors might enhance the donor ability of the pyrazine in this instance. However, if the pyrazine were not to coordinate then L might be expected to act as an "extended-reach" [31,32] U-shaped ligand [33,34].

In our preliminary studies of the chemistry of this ligand, which we present here, this latter binding mode has been found to be preferred, giving complexes with large chelate rings or discrete metallomacrocyclic structures.



L

SCHEME 1

EXPERIMENTAL

Methods and Materials

4-(3-Pyridyloxy)phenol [35] and 2,6-dichloropyrazine [46] were prepared by literature procedures. NMR spectra were recorded on a Varian 500 MHz

TABLE I Crystal data and refinement parameters

	[Pd(L) ₂](ClO ₄) ₂ ·6CH ₃ CN·2H ₂ O	[Ag ₂ (L) ₂ (NO ₃)](NO ₃)·CH ₃ CN·0.5C ₄ H ₁₀ O
Formula	C ₆₄ H ₅₈ N ₁₄ O ₁₈ PdCl ₂	C ₅₆ H ₄₄ N ₁₁ O _{14.5} Ag ₂
M	1488.54	1318.71
Crystal system	Monoclinic	Triclinic
<i>a</i> (Å)	15.288(9)	12.251(9)
<i>b</i> (Å)	10.118(4)	12.759(9)
<i>c</i> (Å)	22.720(12)	19.461(14)
(α) (°)	90	90.949(10)
(β) (°)	95.450(12)	103.214(10)
(γ) (°)	90	110.327(11)
<i>V</i> (Å ³)	3499(3)	2754(4)
ρ_{calcd} (g cm ⁻³)	1.413	1.591
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>Z</i>	2	2
<i>F</i> (000)	1528	1334
Dimensions (mm)	0.41 × 0.19 × 0.13	0.51 × 0.46 × 0.30
Temperature (K)	168(2)	168(2)
2 θ_{max} (°)	48	53
No. measured	35205	35946
No. unique	5434	11107
No. with <i>I</i> > 2 σ (<i>I</i>)	3783	8684
Weighting, <i>a/b</i>	0.0694/0.000	0.0411/0.6696
Parameters	507	755
<i>wR</i> (all data)	0.1199	0.0772
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.0433	0.0287

NMR spectrometer. ES–MS spectra were recorded using a Micromass LCT TOF mass spectrometer. Melting points are uncorrected. Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago.

Preparation of 2,6-bis(4-3-pyridyloxy)phenoxy)pyrazine (L)

4-(3-Pyridyloxy)phenol (100 mg, 0.53 mmol), 2,6-dichloropyrazine (40 mg, 0.26 mmol) and K₂CO₃ (80 mg, 0.58 mmol) were stirred in dimethylformamide (2 ml) at 110°C for 20 h. The pale brown suspension was then cooled, diluted with water (8 ml) and extracted with ethyl acetate (5 × 15 ml). The combined organic extracts were washed with dil. aq. NaOH (10 ml), water (2 × 10 ml) and brine (10 ml) and dried (Na₂SO₄). Removal of solvent gave a brown oil which was crystallised from ethyl acetate/pet. ether to give **L** as a pale brown crystalline solid. Yield 92 mg (76%). Mp 102–103°C. Analysis: C₂₆H₁₈N₄O₂ requires: C, 69.33; H, 4.03; N, 12.43. Found: C, 69.30; H, 4.10; N, 12.54. ¹H NMR (500 MHz, CDCl₃) δ 7.01 (d, *J* = 6.5 Hz, 4H, H₃'/H₅'), 7.10 (d, *J* = 6.5 Hz, 4H, H₂'/H₆'), 7.26 (m, 4H, H₄'', H₅''), 8.06 (s, 2H, H₃, H₅), 8.37 (m, 2H, H₆''), 8.40 (br s, 2H, H₂'').

Preparation of [Pd(L)₂](ClO₄)₂

Pd(py)₂I₂ (26 mg, 0.050 mmol) and AgOTf (26 mg, 0.1 mmol) were stirred in acetone (3 ml) for 30 min. The solution was then filtered through Celite and the solvent removed. The residue was redissolved in

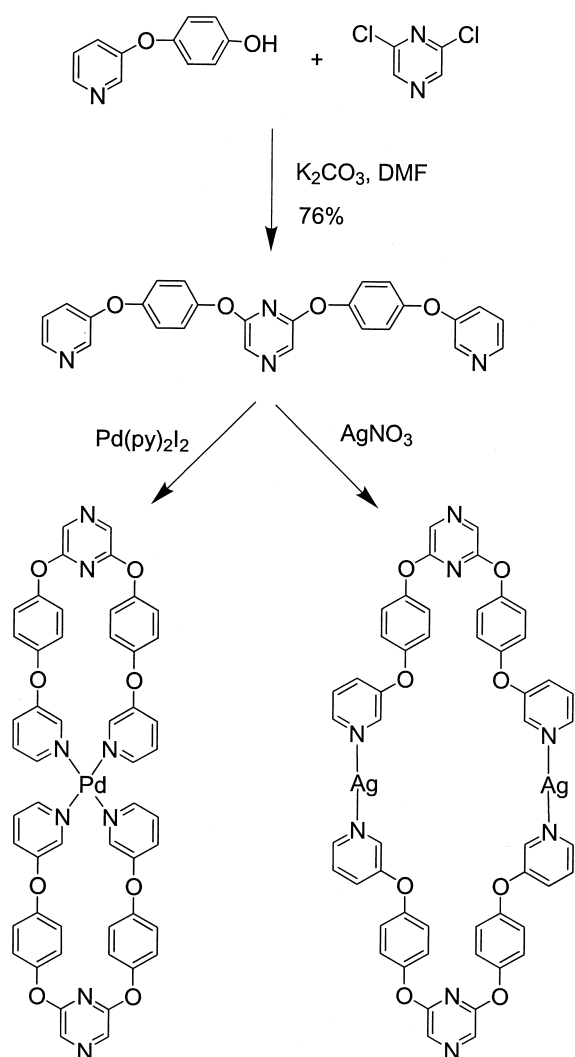
acetonitrile (2 ml) and added to a solution of **L** (30 mg, 0.067 mmol) and NaClO₄ (excess) to give a pale yellow solution. Diffusion of ether into this solution gave the product as a yellow-brown solid. Yield 28 mg (48%). Mp 210°C (decomp.). Analysis: C₅₂H₃₆N₈O₁₆PdCl₂·5H₂O requires: C, 48.18; H, 3.57; N, 8.64. Found: C, 48.06; H, 3.00; N, 8.75. ¹H NMR (500 MHz, CD₃CN) δ 7.26 (d, *J* = 9.0 Hz, 4H, H₃'/H₅'), 7.48 (d, *J* = 9 Hz, 4H, H₂'/H₆'), 7.68 (dd, *J* = 8.7, 5.4 Hz, 2H, H₅''), 7.84 (dd, *J* = 8.7, 2.0 Hz, 2H, H₄''), 8.25 (d, *J* = 2.0 Hz, 2H, H₂''), 8.37 (s, 2H, H₃, H₅), 8.78 (d, *J* = 5.4 Hz, 2H, H₆''). ES–MS (MeCN/HCO₂H) *m/z* 503 (100%) [Pd(L)₂]²⁺. Recrystallisation from acetonitrile in the presence of excess NaClO₄ gave pale yellow rods suitable for X-ray analysis.

Preparation of [Ag₂(L)₂](NO₃)₂

AgNO₃ (15.1 mg, 0.089 mmol) in acetonitrile (3 ml) was added to **L** (40 mg, 0.089 mmol) in hot acetonitrile (3 ml) to give a clear solution. Diethyl ether was added to the cooled solution to give the product as pale brown crystals. Yield 45 mg (82%). Mp 155–158°C. Analysis: C₅₂H₃₆N₁₀O₁₀Ag₂ requires: C, 50.34; H, 2.93. Found: C, 50.43; H, 3.04. Recrystallisation by diffusion of ether into an acetonitrile solution gave large colourless crystals suitable for X-ray analysis.

X-ray Crystallography

The crystal data, data collection and refinement parameters are listed in Table I. All measurements were made with a Siemens CCD area detector using



SCHEME 2

graphite monochromatised Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. Intensities were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods using SHELXS [47] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-96 [48]. 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 $\sum w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$.

RESULTS AND DISCUSSION

The new ligand 2,6-bis(4-(3-pyridyloxy)phenoxy)pyrazine was prepared, as a pale brown crystalline solid, by the reaction of 4-(3-pyridyloxy)phenol (prepared [35] in two steps from 3-hydroxypyridine

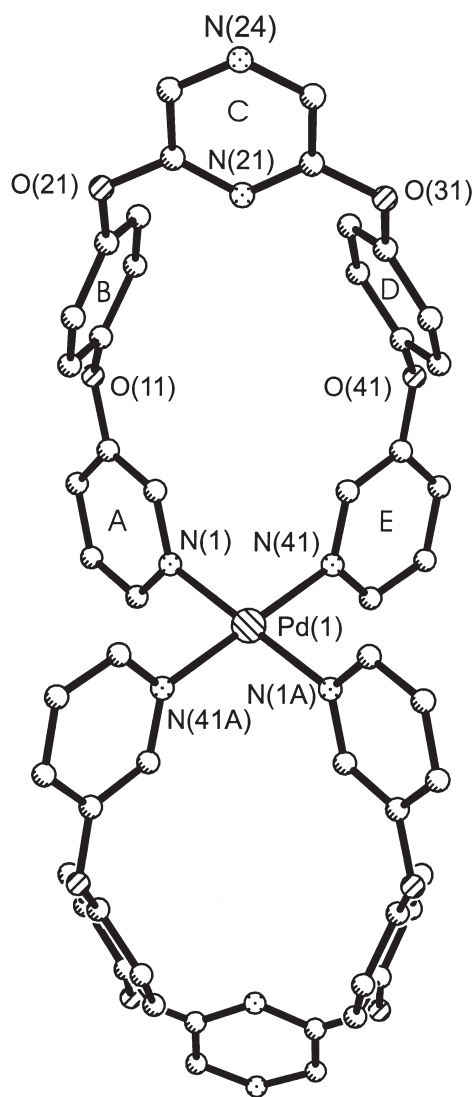


FIGURE 2 Perspective view of the X-ray crystal structure of [Pd(L)₂](ClO₄)₂·6CH₃CN·2H₂O. Hydrogen atoms, counterions and solvate molecules are not shown. Selected bond lengths (Å) and angles (°): Pd(1)–N(1): 2.053(3); Pd(1)–N(41): 2.062(3); N(1)–Pd(1)–N(41): 90.27(13).

and 4-bromoanisole) with 2,6-dichloropyrazine, in the presence of base in dimethylformamide solvent in good yield (Scheme 2). The ligand was characterised by elemental analysis and ¹H NMR spectroscopy.

Reaction Of L With Pd(II)

The ligand was initially reacted with Pd(py)₂I₂ in the presence of AgOTf, using the method employed to prepare the previously reported quadruple helicate [28]. The use of this palladium precursor appears to help the self-assembly process by allowing the slow, thermodynamic replacement of the pyridine ligands by the pyridyl subunits of the ligand L. A ¹H NMR examination of the reaction solution showed the presence of an equilibrium mixture of various

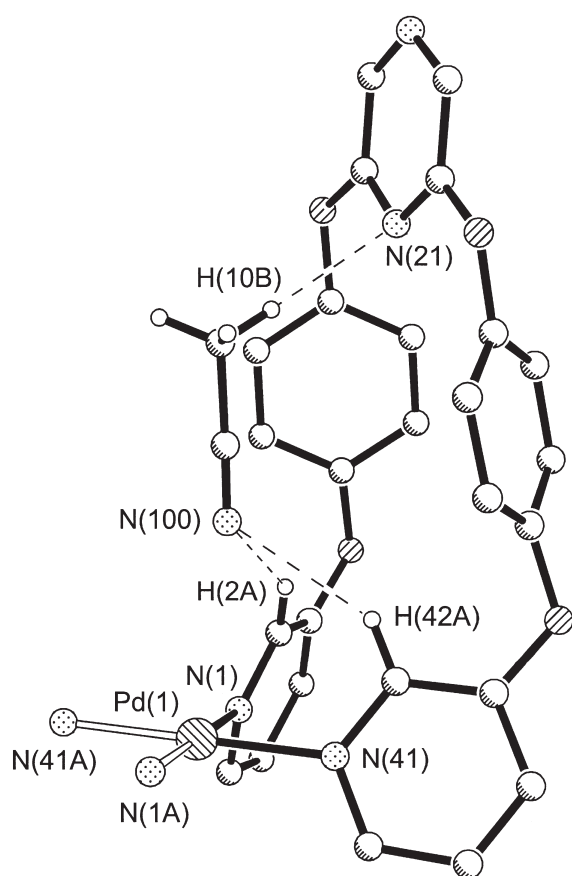


FIGURE 3 Diagram showing the interactions between the acetonitrile solvate molecule and the coordinated ligand L.

[PdL(py)] species. Addition of ether led to a single product, which was recrystallised from acetonitrile. The ^1H NMR spectrum of the product shows only one set of peaks for L, implying a high degree of symmetry in the complex and consistent with the formation of a quadruple helicate. However, the ES-MS spectrum of the complex showed the major peak to be due to $[\text{Pd}(\text{L})_2]^{2+}$ ($m/z = 503; 100\%$), suggesting that the complex might not have the desired $[\text{Pd}_3(\text{L})_4]^{6+}$ formulation. Further, a ^1H NMR titration study of the product treated with other anions showed no evidence for encapsulated-anion exchange, as was characteristic of the previous helicate complex [29].

Rod-shaped crystals, suitable for X-ray analysis, were obtained from a concentrated acetonitrile solution of this compound. Figure 2 shows a perspective view of the complex, which is found to have the formulation $[\text{Pd}(\text{L})_2](\text{ClO}_4)_2$, as suggested by the ES-MS data. The complex crystallises in the space group $P2_1/n$, with the asymmetric unit containing half a complex unit, one perchlorate anion, and one water and three acetonitrile solvate molecules. The perchlorate anion is disordered over two sites, with three of the oxygen being shared and the water is disordered over two sites.

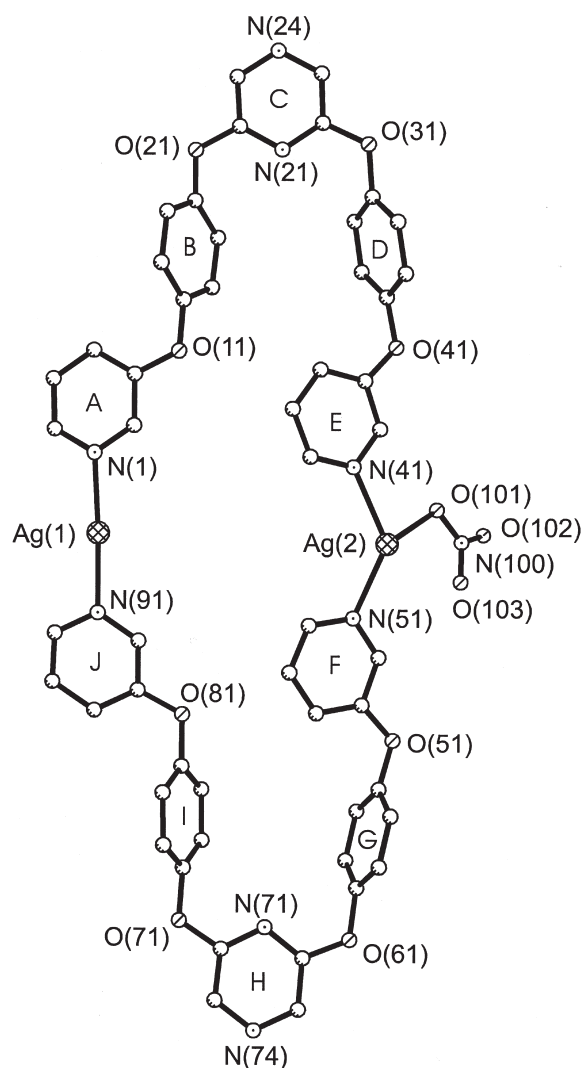


FIGURE 4 Perspective view of the X-ray crystal structure of $[\text{Ag}_2(\text{L})_2(\text{NO}_3)](\text{NO}_3) \cdot \text{CH}_3\text{CN} \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$. Hydrogen atoms, counterions and solvate molecules are not shown. Selected bond lengths (Å) and angles ($^\circ$): $\text{Ag}(1)-\text{N}(1)$: 2.166(2); $\text{Ag}(1)-\text{N}(91)$: 2.179(2); $\text{Ag}(2)-\text{N}(41)$: 2.302(2); $\text{Ag}(2)-\text{N}(51)$: 2.214(2); $\text{Ag}(2)-\text{O}(101)$: 2.407(2); $\text{N}(100)-\text{O}(101)$: 1.241(3); $\text{N}(100)-\text{O}(102)$: 1.225(3); $\text{N}(100)-\text{O}(103)$: 1.221(3); $\text{N}(1)-\text{Ag}(1)-\text{N}(91)$: 172.46(7); $\text{N}(41)-\text{Ag}(2)-\text{N}(51)$: 130.95(8); $\text{N}(41)-\text{Ag}(2)-\text{O}(101)$: 88.91(8); $\text{N}(51)-\text{Ag}(2)-\text{O}(101)$: 128.81(7).

The palladium atom is square planar and is coordinated by the two pyridine rings of each ligand in a *cis* fashion ($\text{N}(1)-\text{Pd}(1)-\text{N}(41)=90.27(13)^\circ$). The pyrazine group of the ligand is not coordinated and as a result the ligand adopts a U-shaped conformation. This coordination mode requires the formation of a 22-membered chelate ring. While not unprecedented, chelate rings of this size are certainly unusual, especially in complexes of this type [36–38]. Moreover, ligands that give these large chelate rings generally coordinate in a *trans* fashion to the metal ion [39]. The dimensions of the cavity generated by this chelate ring are defined by the $\text{Pd}(1)-\text{N}(21)$ distance (8.013(6) Å) and the intercentroid distance of the two phenyl rings of L

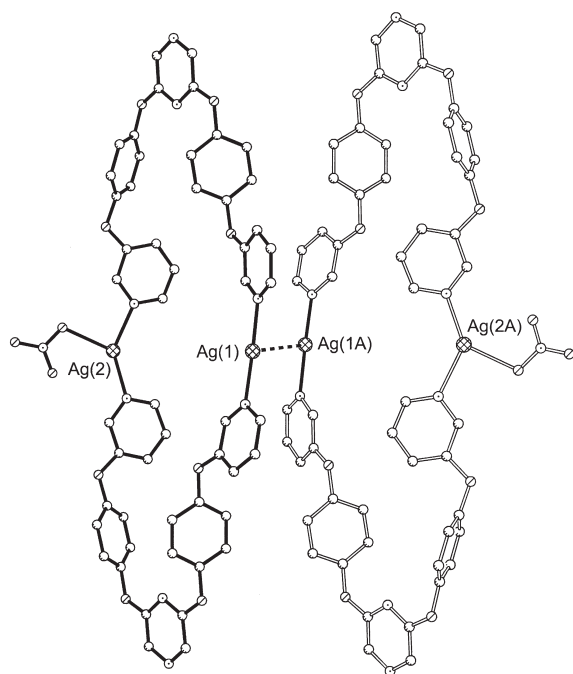


FIGURE 5 Diagram showing the self-association between adjacent metallocyclic units.

(5.009(6) Å). The angles between the rings of the ligand are 69.5(4) (C–B), 55.2(4) (C–D), 131.1(5) (C–A) and 125.0(5)° (C–E) and the angle between the pyrazine ring and the PdN₄ coordination plane is 90.5(5)°.

An interesting feature of the structure is the presence of an acetonitrile solvent molecule which lies above the cavity formed by the ligand and forms three C–H···N hydrogen bonds to the complex (Fig. 3). The strongest interaction is between H(10B) of the methyl group of the acetonitrile and N(21) of the pyrazine ring. The N···H distance is 2.440(6) Å and the C–H···N angle is almost linear at 175.1(5)°. Two weaker interactions exist between N(100) of the acetonitrile and the H(2A) and H(42A) protons on the pyridine rings. These have distances and angles of 2.449(5) Å, 129.3(5)° and 2.501(5) Å, 123.5(5)°, respectively. A recent analysis of the Cambridge Structural Database has found that C–H···N hydrogen bonds are more common than was perhaps previously thought, with almost 1000 examples with a C–H···N distance of ≤2.45 Å and a C–H···N angle of between 120.0 and 180.0° [40]. This, and related [41], analyses confirm that the C(102)–H(10B)···N(21) interaction in this instance is indeed strong.

Reaction Of L With Ag(I)

Reaction of AgNO₃ with L in a 1:1 ration leads to the formation of a pale brown crystalline solid, which analyses as [AgL(NO₃)]. Both ES–MS and ¹H NMR spectra showed peaks due only to L, suggesting that

in solution the equilibrium between reactants and products lies largely in favour of the reactants. Recrystallisation by diffusion of diethyl ether into an acetonitrile solution gave large colourless crystals suitable for X-ray analysis. Figure 4 shows a perspective view of the complex, which crystallises in the space group *P*-1, with the asymmetric unit containing a 48-membered [Ag₂L₂(NO₃)] metallocyclic complex, an uncoordinated NO₃⁻ anion along with an acetonitrile and half a diethyl ether solvate molecule.

One Ag is two coordinate, being coordinated to one pyridine group of each ligand in an approximately linear fashion (N(1)–Ag(1)–N(91) 172.5(7)°). The other Ag is three-coordinate, being bound to the other two pyridine groups of the two ligands and one oxygen of a nitrate and is approximately trigonal planar. Thus, the ligands again adopt a U-shaped conformation with the pyrazine groups uncoordinated. The dimensions of the metallocycle are defined by the Ag···Ag distance (7.821(4) Å) and the N(21)···N(71) distance (21.009(4) Å). The angles between the planes of the rings are 120.5(5) (C–B), 114.4(5) (C–D), 17.7(5) (C–A), 29.4(5) (C–E), 71.7(5) (H–G), 115.3(5) (H–I), 23.4(5) (H–F) and 20.4(5)° (H–J).

Examination of the molecular packing reveals additional interactions between adjacent metallocycles, related by a centre of inversion (Fig. 5). Adjacent two-coordinate Ag atoms weakly interact (Ag···Ag 3.2797(18) Å), in a manner that has recently been identified for similar supramolecular silver complexes [42–44]. The pyridine rings coordinated to these Ag atoms form weak π-stacking interactions between metallocycles, with a closest C–C distance of 3.509(4) Å.

CONCLUSIONS

We have prepared a new ligand, 2,6-bis(4-(3-pyridyloxy)phenoxy)pyrazine, which is found to coordinate in an “extended-reach” U-shaped configuration to both palladium(II) ions (in a chelating fashion) and to silver(I) ions (in a bridging fashion). In both cases, only the pyridine donors coordinate. Given the considerable flexibility inherent in the ligand structure and the various coordination modes available to it, it is somewhat surprising that it adopts such similar conformations in the two complexes. We are currently exploring ways in which the ligand might be induced to adopt other coordination modes, in particular, the W-shaped conformation required to produce a trimetallic quadruple helicate. We are also exploring ways in which the uncoordinated pyrazine donors in the palladium(II) and silver(I) complexes can be used to link up the complexes into extended

metallo-supramolecular arrays. Such a strategy for the generation of polymetallic arrays has recently been reported [45].

Acknowledgements

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