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Introduction

The versatility of N-heterocyclic ligands, especially derivatives and analogues of 2,2'-bipyridine¹ and of 2,2';2",6'-terpyridine,² is reflected in their utility in self-assembly processes leading to the formation of a wide variety of relatively stable, well-defined complexes like grids,^{3,4} squares,⁵ double, triple (and higher) and circular helicates,^{6,7} racks,^{8–10} cages^{11–14} and coordination polymers.^{15,16} The formation of such supramolecular architectures depends on many factors, such as the nature, flexibility

Self-assembly of transition metal ion complexes of a hybrid pyrazine-terpyridine ligand†

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A new hybrid pyrazine-terpyridine ligand L ($C_{34}H_{22}N_8$) and its complexes with different transition metal ions, M (M = Mn(\mathfrak{u}) 1, Zn(\mathfrak{u}) 2, Fe(\mathfrak{u}) 3, Co(\mathfrak{u}) 4, Cu(\mathfrak{u}) 5 and Cd(\mathfrak{u}) 6), have been synthesised. In the presence of a nitrate counter-anion, both Cu(n) and Cd(n) give complexes in which the ratio M : L is 2 : 1, whereas with perchlorate, trifluoromethanesulfonate or tetrafluoroborate, the other metal ions provide solids in which this ratio is 1:1. From mass spectral measurements and a single crystal, X-ray structure determination for the Fe(u) complex 3, however, all the latter species are concluded to be 2:2 complexes. Both the Fe(u) complex 3 and the Co(u) complex 4, generated from tetrafluoroborate reactant salts, have the composition $[M_2L_2F_2(H_2O)](BF_4)_2$, the presence of fluoride ligands being presumed to reflect the abstraction of fluoride ions from tetrafluoroborate by the metal ions under the preparative conditions. The crystal structure of complex 3 shows the Fe(n) centres to be inequivalent, one being high-spin and heptacoordinate with a FeN₄ F_2O coordination sphere, the other low-spin and octahedral with a FeN₆ sphere. The two ligand molecules differ markedly, one being heptadentate, the other clearly "hypodentate", with only three N-donor atoms of a terpyridine-like arm coordinated, although their conformations are similar, showing significant differences from that of C_2 symmetry found for the free ligand by a crystal structure determination. Mass spectra are consistent with the Cu(II) and Cd(II) complexes having the composition $[M_2L(H_2O)_n(NO_3)_{4-n}](NO_3)_{4-n}$ and the weak antiferromagnetic coupling observed for the Cu(1) complex is consistent with a preliminary crystal structure determination which indicates that the two Cu(u) centres are not bridged by a pyrazine unit.

and geometry of the binding subunits, the presence of specific molecules and anions, and the nature of the medium.¹⁷ The abundant complexes of transition metal ions with hetero-cyclic-N-donor ligands are used in many fields of science, for example, in medicine,^{18–20} nanotechnology,^{21,22} optoelectronics^{23,24} and catalysis.^{25,26}

The physical properties of pyrazine derivatives, such as dipole moment, π -stacking interactions and base strength, are usually quite different from those of other electron-deficient aza-aromatics.^{27,28} Metal ion complexes of pyrazine-based ligands have found applications as light-harvesting antennae,^{29,30} liquid crystals³¹ and molecular wires,^{32,33} and bridging pyrazine units have often proved to be efficient mediators of intermetallic coupling.^{34,35} Magnetic interactions between pyrazine-bridged paramagnetic centers take place mainly via the pyrazine ring³⁶ and while this is usually associated with antiferromagnetic exchange,^{37–39} some examples of copper(II) complexes which show ferromagnetic coupling are also known.⁴⁰ Exchange interactions mediated by the π -system of bridging pyrazine⁴¹ may differ depending on the relative orientations of the orbitals containing unpaired electrons on the two metal centres, so that a truly orthogonal arrangement

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 $[\]dagger$ Electronic supplementary information (ESI) available: A preliminary structure determination of the Cu(II) complex 5. CCDC 856604 (L) and 757398 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31982a



gives rise to ferromagnetic coupling, whereas antiferromagnetic coupling is expected when this is not so. $^{\rm 42}$

Following on from our successful synthesis of certain quaterpyridine transition metal complexes,^{43–45} we became interested in the ligand L 2,3-bis(6-(6-(pyridin-2-yl)pyridin-2-yl)pyridin-2-yl)pyrazine (Scheme 1) containing two N₄-donor subunits as an essentially double-quaterpyridine. The purpose of this work was to establish some of the coordination modes possible for L which might bind metal ions in various ways (Fig. 2). We have investigated physicochemical properties and characterised complexes with different transition metal ions. This characterisation involved the crystal structure determinations of the ligand and its Fe(π) complex, as well as both luminescence and magnetic susceptibility measurements on various other transition metal ion complexes.

Results and discussion

Synthesis and characterisation of ligand L

The ligand L was obtained using a multistep Stille-type coupling reaction 46 as outlined in Scheme 1.

6-Bromo-2,2'-bipyridine **A** was prepared from 2-trimethylstannylpyridine and 2,6-dibromopyridine by an adaptation of a literature method.⁴⁷ Compound **B** was obtained in a catalytic reaction of **A** with hexamethylditin and was treated with 2,6dibromopyridine under Pd(0) catalysis to obtain terpyridine **C**.



Fig. 1 Perspective view of the ligand L. Ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radius.



Fig. 2 Planar arrangements (conformations) of the ligand ${\sf L}$ for which metal ion chelation would be possible.

Compound **D** was prepared in the same way as compound **B** and then used in a Stille-type coupling reaction with 2,3dichloropyrazine under Pd(0) catalysis to obtain the ligand **L**. All steps of this procedure resulted in good yields, so that the ligand **L** can be considered a readily accessible potentially octadentate species. The overall yield for the synthesis of the ligand **L** starting from **A** is 47%.

Confirmation of the expected structure of L was provided by a single crystal, X-ray structure determination (Fig. 1), suitable crystals being obtained by vapour diffusion of diethyl ether into a nitromethane solution. As would be expected for a polypyridyl ligand of this type,² the conformation adopted by the terpyridine arms in the crystal is one where all N–C–C–N units have a *transoid* form and each set of three linked rings is essentially planar. It is not possible, however, to attain a conformation where the ligand overall is planar and the pyrazine**Dalton Transactions**

N atoms can also be included in true *transoid* arrangements. (This would involve complete overlap of the central pyridine units.) The observed structure is nonetheless consistent with an approach to this situation achieved by a twisting of approximately 35° of the terpyridine unit mean planes with respect to the pyrazine ring plane, giving the molecule essentially C_2 symmetry in the solid state. The molecule is thus chiral and the conical entities fit together, one within the next, to form columns of homochiral species running parallel to the *b* axis. These columns lie adjacent in an undulating fashion to form homochiral sheets parallel to the *ab* plane, with the absolute configuration alternating from one sheet to the next, so that the lattice is overall racemic (Fig. S1[†]). The structure of the ligand **L** is only the fourth crystal structure of a seven-ring compound not containing metal ions.^{48–50}

Clearly, the ligand L is not preorganised, at least in the solid state, for metal ion chelation, though of course it is well known that appropriate rearrangements of polypyridyl ligands are usually facile.² Two (idealised) planar conformations are shown in Fig. 2, one (A) being compatible with the binding of two metal ions in equivalent sites, the other (B) being compatible with the binding of up to four metal ions, and probably oligomer/polymer formation. Conformation A is similar to that of a large number of ditopic ligands known to form grid complexes^{3,4} but here grid formation would involve eight-coordination of the metal ion and thus be a possibility more likely to be observed with, say, the lanthanides, rather than the presently investigated transition metal ions.

Given that a non-planar conformation is observed for L in the solid state, other possibilities for its coordination modes arise, perhaps the most obvious being one where the pyrazine ring serves as no more than a link between two terpyridine-like binding sites. In that the conformations shown in Fig. 2 both involve clashes between aromatic CH groups, there is in fact a good reason to anticipate that even the bound ligand would not adopt a planar conformation. Because terpyridine is an excellent ligand for transition metal ions, giving rise to numerous complexes of practical interest,² our initial investigations of the coordination behaviour of L were therefore centred on its complexation by these species.

Synthesis and characterisation of complexes of L

Reactions with various transition metal salts were carried out in acetonitrile–dichloromethane (1:1) at room temperature for 48 h. In all cases, formation of complexes with the metal in its original oxidation state was efficient and the products were readily isolated as stable solids. However, while in all instances the reaction mixtures contained the metal salt and L in a molar ratio of 2:1, elemental analyses of the isolated solids showed that this ratio was retained only in the case of reactions with the hydrated nitrates of Cu(π) and Cd(π). With Mn (π), Fe(π), Co(π) and Zn(π) in the presence of weakly coordinating anions (ClO₄⁻, CF₃SO₃⁻ or BF₄⁻), the products proved all to be species with M:L 1:1, although on the basis of their mass spectra and a single crystal structure determination for the Fe(π) complex, it is concluded that all are, in fact, M₂L₂



Fig. 3 (a) Perspective view of the cation **3**; (b) a view of the Fe(II) coordination spheres. Ellipsoids are drawn at the 20% level, hydrogen atoms are omitted for clarity. Relevant distances (Å): Fe1–N1A 2.016(7), Fe1–N8A 1.837(8), Fe1–N14A 2.046(6), Fe1–N26B 2.059(7), Fe1–N32B 1.828(9), Fe1–N38B 2.019(7), Fe2–N1B 2.226(8), Fe2–N8B 2.234(7), Fe2–N14B 2.262(7), Fe2–N20B 2.304(7), Fe2–O1W 2.033(8), Fe2–F1 1.861(4), Fe2–F2 1.869(4); and angles (°) N32B Fe1 N8A 169.8 (3), N1A Fe1 N14A 159.0(4), N38B Fe1 N26B 161.0(4), F1 Fe2 F2 174.7(2).

complexes. An additional complication does arise, however, in the case of the complexes prepared from tetrafluoroborate salts.

Thus, a single crystal structure determination (Fig. 3) on the complex derived from hydrated iron(II) tetrafluoroborate, the complex again being crystallised by vapour diffusion of diethyl ether into a nitromethane solution, showed the presence of two fluoride ions as ligands in the binuclear complex of composition [Fe₂L₂F₂(H₂O)](BF₄)₂·1.5H₂O. The fluoride ligands are presumed to arise from the abstraction of fluoride ions from tetrafluoroborate counterions in the presence of the Lewis-acidic metal ion.⁵¹ Such a process is well known and has been used in the preparation of coordination compounds containing a fluoride ion as a bridging ligand.⁵²⁻⁵⁴ The coordination environments of the two Fe(II) centres are completely different and can be seen as illustrating what might be considered the ambivalent character of the ligand L. One site, to which both fluoride ions and a water molecule are bound as well as four N-donors from one half of a ligand molecule, contains a high-spin, pentagonal bipyramidal Fe(II) centre, with fluoride ligands in the apical positions and water-O completing the equatorial pentagon, as might be expected from the known coordination chemistry of simple quaterpyridine ligands.43-45 The other site contains Fe(II) as a low-spin, pseudo-octahedral species, bound exclusively to pyridine-N



Fig. 4 Views (stick representations), from a similar perspective with respect to the pyrazine ring, of the conformation found for ligand **L** in the various environments described in the present work: (a) in the free ligand crystal; (b) in the heptadentate form found in complex **3**; (c) in the tridentate form found in complex **3**; (d) in the heptadentate form found in the Cu(1) complex **5** (see below).

donor atoms derived from two different ligands **L**. Thus, it is an analogue of $[Fe(terpy)_2]^{2+}$. While its binding to two metal ions means that all but one pyrazine-N of the eight N-donors of one ligand are coordinated, for the other ligand but three pyridine-N donors are bound, making it a genuinely hypodentate⁵⁵ species. The conformations of the two ligand molecules (Fig. 4) are nevertheless quite similar, with, in both cases, one terpyridine unit being rotated so as to be almost perpendicular to the remaining terpy–pyrazine unit.

As in the lattice of the free ligand, there are multiple contacts between the aromatic ring components of 3 indicative of the full range of interactions (CH…pi, CH…N, partial charge attractions) which fall under the descriptor of " π -stacking".⁵⁶ It may be that both inter- and intra-molecular interactions of this type (Fig. S2†) are important in the stabilisation, in the solid state, of the markedly hypodentate form of one ligand molecule in the binuclear cation of 3, since it is somewhat surprising that a 2:2 M:L complex with some ligand donors unbound should have crystallised from a medium in which the ratio was 2:1. It is also true, however, that once adapted to the binding of a metal ion, the conformation of the ligand is not markedly dependent upon other factors (Fig. 4).

To establish the exact form of the complexes of $2:1 \text{ M}: \mathbf{L}$ stoichiometry, efforts were made to obtain crystals suitable for an X-ray structure determination. Only for the Cu(II) complex were adequate crystals obtained and unfortunately their diffraction data did not provide a satisfactory structure solution, although the low-quality result (ESI[†]) again showed the ligand to adopt a non-planar conformation (Fig. 4), one that could be

Table 1 Maximum absorption bands (λ_{max} [nm]) and molar absorption coefficients (ε [10⁴ M⁻¹ cm⁻¹]) of the studied compounds

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$\begin{array}{cccc} L & & & & & & & \\ [Mn_2L_2](ClO_4)_4 \ 1 & & & & & & \\ [Zn_2L_2](CF_3SO_3)_4 \ 2 & & & & & \\ [Zn_2L_2]_2F_2(H_2O)](BF_4)_2 \ 3 & & & & & \\ [Fe_2L_2F_2(H_2O)](BF_4)_2 \ 4 & & & & \\ [Co_2L_2F_2(H_2O)](BF_4)_2 \ 4 & & & & \\ [Cd_2L(NO_3)_4] \ 6 & & & & \\ \end{array}$	(4.0) (2.2); 308.0 (2.2); 334.5 (2.2) (3.0); 322.5 (3.2); 335.5 (2.7) (5.1); 329.0 (4.1); 555.0 (0.5) (3.2) (3.3); 304.5 (3.1); 336.5 (2.8)

considered simply a distortion of the planar conformation A (Fig. 2) with one pyrazine-N detached from one of the Cu(π) ions. The mass spectra of both complexes were dominated by peaks due to M₂L species and magnetic measurements on the Cu(π) complex (see below) showed very weak antiferromagnetic coupling consistent with the absence of a pyrazine bridge between the two centres.

Electronic absorption spectra and luminescence properties

Absorption and emission spectra of ligand L and its metal complexes were recorded at concentrations of 1×10^{-5} M in acetonitrile for the complexes and in dichloromethane for L at room temperature. Maximum absorption bands and molar absorption coefficients are listed in Table 1.

The electronic absorption spectra in the UV region showed bands typical for $\pi \to \pi^*$ ligand-based transitions.⁵⁷ In the case of the Fe(II) complex **3**, the broad absorption band in the visible region at 555 nm is assigned to an MLCT electronic transition.⁵⁸ As expected where the metal ion present is essentially incapable of oxidative quenching of the excited state, the Zn(II) and Cd(II) complexes **2** and **6** display broad luminescence bands with maxima at $\lambda_{em.} = 364$ nm ($\lambda_{ex.} = 320$ nm) and $\lambda_{em.} =$ 382 nm ($\lambda_{ex.} = 330$ nm) respectively, which are red shifted compared to the band in the emission spectrum of the ligand **L**, $\lambda_{em.} = 346$ nm ($\lambda_{ex.} = 288$ nm) (Fig. 5). In the other complexes, emission is completely quenched by the binding of the metal ion.

While emission occurs from both the $Zn(\pi)$ and $Cd(\pi)$ complexes, it is approximately 40 times more intense from the former than from the latter, consistent with stronger spinorbit coupling in the heavier metal ion providing a more efficient pathway for excited state deactivation. For the $Zn(\pi)$ complex, the quantum yield was determined, relative to anthracene as standard, as 0.07.

Magnetic properties

Susceptibility measurements on the di-iron complex **3** are shown in Fig. 6 and 7. At room temperature the effective magnetic moment is 5.17 BM, consistent with the presence of one high-spin (S = 2) and one (diamagnetic) low-spin (S = 0) Fe(II) centre. The effective magnetic moment decreased monotonically with decreasing temperature, falling to a value of 2.27 BM at 1.8 K. Fe–N bond distances observed in the crystal structure of **3** are completely consistent with the assignment of a high-spin state to the heptacoordinate FeN₄F₂O centre and a low



Fig. 5 The emission spectra of ligand L and complexes 2 and 6.



Fig. 6 Temperature dependences of experimental χ_m and μ_{eff} for complex **3**.



Fig. 7 Magnetization vs. magnetic field relation at 2 K. The solid line is the Brillouin function curve for non-coupled ions, the *g*-factor is taken as 2.00, S = 1/2.

spin state to the FeN₆ centre, the strong absorption band giving rise to the violet colour of the complex also being indicative of the presence of a low-spin FeN₆ moiety. Given the long Fe…Fe separation of 6.50 Å in the binuclear unit, it is unsurprising that negligible interactions are apparent between the two centres.

The presence of essentially only one unpaired electron at the lowest temperatures was confirmed by magnetization vs.



Fig. 8 Temperature dependences of experimental χ_m and μ_{eff} for complex 5, calculated per copper ion. The solid lines represent the calculated curves.

magnetic field measurements at 2 K (Fig. 7). The experimental curve lies only a little above the Brillouin function solid line,⁵⁹ for g = 2 and S = 1/2.

Susceptibility measurements on the dicopper complex 5 are shown in Fig. 8. The effective magnetic moment at room temperature is 1.8 BM and remains almost unaffected by changing temperature down to 25 K, after which there is a small decrease to 1.58 BM at 1.8 K. This slight temperature dependence indicates that any antiferromagnetic interactions between the Cu(II) centres must be weak and this conclusion is supported by an analysis of the susceptibility curve in terms of the Bleaney–Bowers equation (with modification to include allowance for extremely weak intermolecular interactions; see ESI†) providing a very low *J* value of $J = -0.87 \pm 0.02$ cm⁻¹.

Experimental

General consideration

6-Bromo-2,2'-bipyridine A was prepared according to literature methods.47 The metal salts were used without further purification as supplied from Aldrich. LC-MS analyses of the transition metal complexes were performed using a Varian LC MS/ MS TripleQuad 320 spectrometer equipped with an ESI ionisation interface. Acetonitrile was used as a mobile phase with a flow rate of 300 μ L min⁻¹ and nitrogen as a blanketing gas. ESI mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were measured using a Waters Micromass ZQ spectrometer. Microanalyses were performed using a Perkin-Elmer 2400 CHN microanalyser. IR spectra were obtained with a Perkin-Elmer 580 spectrophotometer and peak positions are reported in cm⁻¹. All electronic absorption spectra were recorded with a Shimadzu UVPC 2001 spectrophotometer, between 220 and 800 nm, in 10 \times 10 mm quartz cells using solutions 1 \times 10 $^{-5}$ M with respect to the metal ions. Excitation and emission spectra were measured at room temperature on a Hitachi 7000 spectrofluorimeter with excitation and emission slits of 2.5 nm. The quantum yield for the $Zn(\pi)$ complex 2 was measured using a relative method with anthracene as the standard.⁶⁰ As

calculated from the equation:⁶¹

$$\phi=\phi_{\mathrm{s}}rac{I_{\mathrm{x}}A_{\mathrm{s}}}{I_{\mathrm{s}}A_{\mathrm{x}}}rac{n_{\mathrm{x}}^{2}}{n_{\mathrm{s}}^{2}}$$

where ϕ is the quantum yield, subscript s stands for the reference and x for the sample. *A* is the absorbance at the excitation wavelength, *n* is the refractive index and *I* is the integrated emission intensity. This was 0.27 in ethanol solution.

Susceptibility measurements in the temperature range of 1.8–300 K were carried out on powdered samples of complexes, at a magnetic field of 0.5 T, using a Quantum Design SQUID magnetometer (type MPMS-XL5). Corrections for diamagnetism of the constituting atoms were calculated using Pascal's constants, ^{59,62} the value of 60×10^{-6} cm³ mol⁻¹ being used as the temperature-independent paramagnetism of copper(II) ion. The effective magnetic moments were calculated from the expression

$$\mu_{\rm eff} = 2.83 \sqrt{\chi_{\rm m}^{\rm corr} \times T}$$

The best exchange parameters were obtained by fitting with an agreement factor *R* defined as:

$$R = \sum_{i=0}^{n} \frac{(\chi_i^{\exp} T - \chi_i^{\operatorname{calc}} T)^2}{(\chi_i^{\exp} T)^2}$$

Standard deviations 63 were added to calculated exchange parameters.

SYNTHESIS OF 6-(TRIMETHYLSTANNYL)-2,2'-BIPYRIDINE B. 6-Bromo-2,2'-bipyridine A (1.433 g, 4.5 mmol), hexamethylditin (1.504 g, 4.6 mmol) and 5% of Pd(PPh₃)₄ (0.260 g, 0.2 mmol) were degassed for 10 minutes, dry DME (60 mL) was then added and the reaction mixture was heated at 80 °C for 15 h. The solvent was evaporated and the residue was pumped under vacuum overnight. The crude product **B** was then used immediately for the subsequent synthesis of compound C.

SYNTHESIS OF 6-BROMO-2,2':6',2"-TERPYRIDINE C. TO a mixture of 6-(trimethylstannyl)-2,2'-bipyridine B (3.339 g, 10.0 mmol), 2,6dibromopyridine (2.475 g, 10.0 mmol), LiCl (1.002 g, 20.0 mmol) and Pd(PPh₃)₄ (0.600 g, 0.5 mmol), under an argon atmosphere, degassed toluene (100 mL) was added gradually by a syringe. The reaction mixture was stirred and heated at reflux for 24 h, then the toluene was evaporated off under reduced pressure. The residue was purified by column chromatography on alumina using dichloromethane-hexane (1:1) as an eluent to afford 2.103 g (64%) of compound C. ¹H NMR (300 MHz, CDCl₃): δ = 8.71 (d, J = 4.8 Hz, 1H), 8.60 (m, J = 6.8 Hz, 2H), 8.48 (d, J = 4.3 Hz, 1H), 8.46 (d, J = 4.3 Hz, 1H), 7.96 (t, J = 7.9 Hz, 1H), 7.86 (t, J = 7.9 Hz, 1H), 7.71 (t, J = 7.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 4.8 Hz, 1H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 153.7, 149.2, 139.1, 138.0, 136.9, 128.0, 123.9, 121.6, 121.4, 121.1, 119.8 ppm. ESI-MS: $m/z = 334 (100) [Na(C_{15}H_{10}N_3Br)]^+$. Anal. calc. for C₁₅H₁₀N₃Br (312.16): C, 57.71; H, 3.23; N, 13.46; found: C, 57.73; H, 3.26; N, 13.43%.

SYNTHESIS OF 6-(TRIMETHYLSTANNYL)-2,2':6',2"-TERPYRIDINE D. The compound C (1.433 g, 4.5 mmol), hexamethylditin (1.504 g, 4.6 mmol) and 5% of Pd(PPh₃)₄ (0.260 g, 0.2 mmol) were degassed for 10 minutes, then dry DME (60 mL) was added and the reaction mixture was heated at 80 °C for 15 h. The solvent was evaporated and the residue was pumped under vacuum overnight. The crude product **D** was then used immediately for the subsequent synthesis of ligand **L**.

SYNTHESIS OF 2,3-BIS(6-(6-(PYRIDIN-2-YL)PYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRIDIN-2-YLPYRID AZINE L. To a mixture of 6-(trimethylstannyl)-2,2':6',2"-terpyridine D (1.818 g, 4.5 mmol), 2,3-dichloropyrazine (0.274 g, 1.8 mmol), LiCl (0.402 g, 9.4 mmol) and Pd(PPh₃)₄ (0.266 g, 0.2 mmol), under an argon atmosphere, degassed toluene (100 mL) was added gradually by a syringe. The reaction mixture was stirred and heated at reflux for 24 h, then the toluene was evaporated off under reduced pressure. The residue was purified by column chromatography on alumina using dichloromethane-ethyl acetate (3:2) as an eluent to afford 0.730 g (73%) of ligand L. ¹H NMR (300 MHz, CDCl₃): δ = 8.74 (s, 2H), 8.62 (d, J = 4.8 Hz, 2H), 8.52 (d, J = 7.6 Hz, 2H), 8.51 (d, J = 8.0 Hz, 2H), 8.28 (d, J = 7.7 Hz, 2H), 8.08 (d, J = 7.7 Hz, 2H), 8.02 (t, J = 7.6 Hz, 2H), 7.80 (t, J = 7.6 Hz, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.52 (d, J = 7.9 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 156.52, 156.00, 155.08, 155.01, 154.78, 152.61, 148.97, 142.56, 137.47, 136.70, 123.61, 121.00, 120.84, 120.72, 120.31 ppm. ESI-MS: m/z = 565(100) $[Na(C_{34}H_{22}N_8)]^+$. Anal. calc. for $C_{34}H_{22}N_8$ (542.59): C, 75.26; H, 4.09; N, 20.65; found C, 75.22; H, 4.11; N, 20.63%.

 $[Mn_2L_2](ClO_4)_4$ (1): A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (23.8 mg, 66 µmol) and ligand L (17.8 mg, 33 µmol) in $CH_3CN-CH_2Cl_2$ 1:1 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The complex **1** was isolated as a yellow solid by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. LC-MS m/z (%) = 952 (15) $[Mn_2L-(ClO_4)_3]^+$, 738 (30) $[MnL(ClO_4)(CH_3CN)]^+$, 706 (30) $[Mn_2L_2(ClO_4)_2(H_2O)]^{2+}$, 633 (45) $[MnLCl]^{2+}$, 565 (80) $[NaL]^+$, 299 (10) $[MnL]^{2+}$. Anal. calc. for $[Mn_2(C_{34}H_{22}N_8)_2](ClO_4)_4$ (1592.86): C, 51.27; H, 2.78; N, 14.07; found: C, 51.25; H, 2.74; N, 14.08%.

 $[Zn_2L_2](CF_3SO_3)_4$ (2): A mixture of $Zn(CF_3SO_3)_2$ (21.0 mg, 58 µmol) and ligand L (15.7 mg, 29 µmol) in $CH_3CN-CH_2Cl_2$ 1:1 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The complex 2 was isolated as a white solid by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. LC-MS m/z (%) = 755 (30) $[Zn_2L_2(CF_3SO_3)_2]^{2+}$, 575 (20) $[ZnL_2]^{2+}$, 565 (50) $[NaL]^+$, 311 (30) $[Zn_2L_2(CH_3OH)]^{4+}$, 303 (10) $[ZnL]^{2+}$. Anal. calc. for $[Zn_2(C_{34}H_{22}N_8)_2](CF_3SO_3)_4$ (1812.24): C, 47.72; H, 2.45; N, 12.37; S, 7.08; found: C, 47.70; H, 2.44; N, 12.35; S, 7.06%.

 $[Fe_2L_2F_2(H_2O)](BF_4)_2 \cdot 1.5H_2O$ (3): A mixture of $Fe(BF_4)_2 \cdot 6H_2O$ (20.4 mg, 60 µmol) and ligand L (16.4 mg, 30 µmol) in CH₃CN-CH₂Cl₂ 1:1 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The complex 3 was isolated as a violet solid by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. LC-MS m/z (%) = 685 (10) $[FeL(BF_4)]^+$, 660 (10) $[Fe_2L_2(BF_4)F(H_2O)]^{2+}$, 652 (20) $[Fe_2L_2(BF_4)F]^{2+}$, 617 (15) $[Fe_2L_2F_2]^{2+}$, 565 (25) $[NaL]^+$, 380 (15) $[Fe_2L(BF_4)F]^{2+}$, 299 (10) $[FeL]^+$. Anal. calc. for $[Fe_2(C_{34}H_{22}N_8)_2F_2(H_2O)]$ -(BF₄)₂·1.5H₂O (1453.52): C, 56.19; H, 3.40; N, 15.42; found: C, 56.22; H, 3.42; N, 15.44%.

 $[Co_2(L)_2F_2(H_2O)](BF_4)_2$ (4): A mixture of $Co(BF_4)_2 \cdot 6H_2O$ (20.1 mg, 59 µmol) and ligand L (16.0 mg, 30 µmol) in CH₃CN-CH₂Cl₂ 1 : 1 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The complex 4 was isolated as a yellow solid by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. LC-MS m/z (%) = 672 (10) $[Co_2L_2(BF_4)F(H_2O)_2]^{2+}$, 663 (15) $[Co_2L_2(BF_4)F(H_2O)]^{2+}$, 687 (20) $[Co_2L_2(BF_4)_2]^{2+}$, 654 (10) $[Co_2L_2(BF_4)F]^{2+}$, 620 (15) $[Co_2L_2F_2]^{2+}$, 445 (30) $[Co_2L(BF_4)_2(H_2O)_3]^{2+}$, 415 (10) $[Co_2L(BF_4)_2]^{2+}$. Anal. calc. for $[Co_2(C_{34}H_{22}N_8)_2F_2(H_2O)](BF_4)_2$ (1414.66): C, 57.01; H, 3.24; N, 15.64; found: C, 57.06; H, 3.20; N, 15.62%.

 $[Cu_2L(NO_3)_2(H_2O)_2](NO_3)_2$ (5): A mixture of $Cu(NO_3)_2 \cdot 5H_2O$ (16.4 mg, 59 µmol) and ligand L (16.0 mg, 30 µmol) in $CH_3CN-CH_2Cl_2$ 1:1 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The complex 5 was isolated as a blue solid by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. ESI-MS m/z (%) = 565 (70) $[Na(L)]^+$, 405 (15) $[Cu_2(L)(NO_3)_2(H_2O)]^{2+}$, 396 (10) $[Cu_2(L)-(NO_3)_2]^{2+}$, 303 (20) $[Cu(L)]^{2+}$. Anal. calc. for $[Cu_2(C_{34}H_{22}N_8)-(H_2O)_2(NO_3)_2](NO_3)_2$ (953.73): C, 42.82; H, 2.75; N, 17.62; found: C, 42.80; H, 2.71; N, 17.64%.

 $[Cd_2L(NO_3)_4]$ (6): A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (18.8 mg, 61 µmol) and ligand L (16.6 mg, 31 µmol) in $CH_3CN-CH_2Cl_2$ 1:1 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The complex **6** was isolated as a yellow solid by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. ESI-MS m/z (%) = 955 (10) [CdL-(NO₃)₃]⁺, 565 (100) [NaL]⁺, 445 (20) [Cd_2L(NO₃)_2]²⁺, 276 (70) [Cd_2L(NO₃)]³⁺. Anal. calc. for [Cd₂(C₃₄H₂₂N₈)(NO₃)₄] (1015.43): C, 40.22; H, 2.18; N, 16.55.; found: C, 40.25; H, 2.16; N, 16.53%.

Single crystal structure determination

For the ligand, diffraction data were collected at -100 °C by the φ -scan method on an Enraf-Nonius KappaCCD diffractometer with graphite-monochromated MoK_{α} radiation ($\lambda =$ 0.7107 Å) and for the complex 3 at room temperature, by the same method on a SuperNova diffractometer with mirrormonochromated CuK_{α} radiation ($\lambda = 1.54178$ Å). The data were corrected for Lorentz-polarization and absorption effects.⁶⁴ Accurate unit-cell parameters were determined by a leastsquares fit of 5974 (L) and 2700 (3) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SHELXS-97⁶⁵ and SIR92⁶⁶ and refined with the full-matrix least-squares procedure on F^2 by SHELXL97.⁶⁵ Scattering factors incorporated into SHELXL97 were used. All nonhydrogen atoms were refined anisotropically, while hydrogen

Table 2 Crystal data and structural refinement parameters for ligand L and Fe (ii) complex ${\bf 3}$

Compound	L	3
Formula	C34H22N8	C ₆₈ H ₄₉ B ₂ F ₁₀ Fe ₂ N ₁₆ O _{2.5}
Formula weight	542.60	1453.52
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c
a (Å)	9.4930(2)	27.264(4)
b (Å)	20.5040(5)	24.8297(19)
<i>c</i> (Å)	14.2010(4)	21.8128(16)
β(°)	104.980(1)	112.636(12)
$V(Å^3)$	2670.21(11)	13 629 (2)
Z	4	8
$d_{\rm x} ({\rm g}{\rm cm}^{-3})$	1.35	1.41
F(000)	1128	5872
$\mu (mm^{-1})$	0.084	4.15
Θ range (°)	1.79-29.10	2.85-63.15
hkl range	$-12 \le h \le 12$	$-31 \le h \le 31$
	$-21 \le k \le 28$	$-27 \le k \le 28$
	$-19 \le l \le 19$	$-24 \le l \le 24$
Reflections		
Collected	12 365	68 141
Unique (R_{int})	7126 (0.047)	10678(0.143)
With $I > 2\sigma(I)$	4097	3811
No. of parameters	379	906
Weighting scheme		
A	0.0592	0.12
В	0	0
$R(F)\left[I > 2\sigma(I)\right]$	0.063	0.094
$wR(F^2)$ $[I > 2\sigma(I)]$	0.120	0.222
R(F) [all data]	0.131	0.219
$wR(F^2)$ [all data]	0.141	0.265
Goodness of fit	1.011	1.00
max/min $\Delta \rho$ (e Å ⁻³)	0.19 / -0.22	0.56/-0.30

atoms were placed in the calculated positions, and refined by a 'riding model' with the isotropic displacement parameters set at 1.2 (1.5 for methyl groups) times the U_{eq} value for an appropriate non-hydrogen atom. Relevant crystal data are listed in Table 2, together with refinement details.

In 3 the residual electron density was interpreted as the partially disordered water molecules, weakly bound to the rest of the structure. The positions of hydrogen atoms for these water molecules have not been found. In this structure there still are large areas devoid of any electron density (of *ca.* 987 Å³, located around 0,1/2,0) and this can be related to the relatively poor quality of the crystals of **3**. Throughout the refinement process, weak constraints were applied to the geometry of one of the anions as well as to the anisotropic thermal parameters of certain atoms (ISOR).

Conclusions

The linking of two terpyridine units through a pyrazine bridge produces an octa-aza donor ligand capable of acting as either a quaterpyridine-terpyridine or a simple terpyridine binding unit towards transition metal ions. Thus, despite its relatively limited rotational flexibility, it is a versatile species exhibiting variable denticity, this possibly being dependent on the counteranions associated with the transition metal cation. There is some parallel in its behaviour with that of a simple quaterpyridine which displays tridentate coordination in forming a mixed-ligand species in the presence of 2,2'-bipyridine.⁹ It would appear that repulsive interactions which would arise in a planar conformation of L are important in limiting its coordinative behaviour to that of a nonplanar chelate. That binuclear species, of either M₂L or M₂L₂ stoichiometry, are obtained with quite different juxtapositioning of the two metal ion centres indicates that the complexes may be useful for examination of bimetallic catalysis, especially where different roles may be assigned to the two centres.

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