PAPER

Cobalt(II), iron(II), zinc(II) and palladium(II) complexes of di-topic 4′-{4-[bis(2-pyridyl)aminomethyl]phenyl}-2,2′:6′,2′′-terpyridine. Synthetic and X-ray structural studies†

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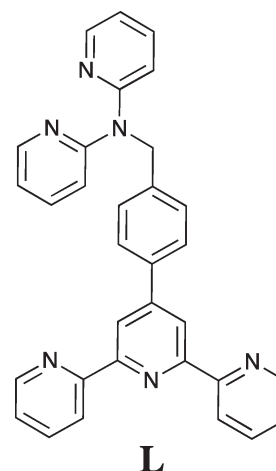
The di-topic terpy/dpa hybrid ligand, 4′-{4-[bis(2-pyridyl)aminomethyl]phenyl}-2,2′:6′,2′′-terpyridine (L), incorporating both 2,2′:6′,2′′-terpyridine (terpy) and 2,2′-dipyridylamino domains has been synthesised. The metal complexes [CoLCl$_2$], [ZnLCl$_2$], [ZnL(CH$_3$CO$_2$)$_2$], [Fe(L)$_2$(PF$_6$)$_2$] and [Fe(L)(HL)](PF$_6$)$_{0.5}$(ClO$_4$)$_{2.5}$ have been isolated. X-ray structures of all five structures show that the respective metal ions preferentially bind to the terpy site of L, with the dpa site in the first four complexes remaining empty. In the fifth complex, which was isolated following the attempted reaction of silver perchlorate with [Fe(L)$_2$(PF$_6$)$_2$], one dpa site is protonated. The crystal packing of all these species is dominated by extensive π-interactions. The 5-coordinate zinc(II) and cobalt(II) complexes are isostructural and exhibit a 3D network of interactions involving π-stacking as well as CH⋯Cl and CH⋯N hydrogen bonding. Similar interactions occur in the packing of [ZnL(CH$_3$CO$_2$)$_2$] and [Fe(L)(HL)](PF$_6$)$_{0.5}$(ClO$_4$)$_{2.5}$ giving rise to 3D arrays. Reaction of palladium(II) with L yields a product of stoichiometry Pd$_2$LCl$_4$ for which the evidence suggests that palladium binds at both the terpy and dpa domains. Based on this result, addition of [Pd(CH$_3$CN)$_2$Cl$_2$] to [Fe(L)$_2$](PF$_6$) in aceto-nitrile yielded a heterometallic complex in which the "free" dpa sites of [Fe(L)$_2$](PF$_6$) are now occupied by palladium ions to form a heterometallic product of type [FePd$_2$(L)$_2$Cl$_4$](PF$_6$)$_2$·1.5CH$_3$CN.

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Introduction

Di-, tri- and poly-pyridyl based ligands systems have been widely used as components in metallo-supramolecular chemistry, reflecting the coordination versatility of this heterocyclic amine ligand class.[1,2] For example, the metal ion chemistry of 2,2′:6′,2′′-terpyridine (terpy) and its derivatives has received a great deal of attention over many decades[3-6] as has 2,2′-dipyridylamine (dpa) and its extended (secondary amine-substituted) derivatives.[7,8] Thus, in the latter case a range of bridging groups have been employed to connect from two to four dpa units *via* their respective secondary amine sites for use in metal coordination/metallo-supramolecular studies and a variety of such systems have now been investigated in some detail.[7,8] As an example, in previous studies we have investigated the interaction of copper(II),[9] palladium(II)[9] and silver(I)[10,11] with such linked dpa ligands,

with our focus being on the supramolecular aspects of the resulting solid state structures. As an extension of these studies we now report the synthesis of the new linked "hybrid" ligand 4′-{4-[di-(2-pyridyl)aminomethyl]phenyl}-2,2′:6′,2′′-terpyridine (L) incorporating both dpa and 2,2′:6′,2′′-terpyridine domains together with an investigation of its interaction with selected metal ions.

L

Experimental

NMR spectra were recorded on a Bruker Avance DPX200 or DPX300 spectrometer. Electrospray mass spectra (ESI-MS) were obtained on a Finnigan LCQ-8 spectrometer. FTIR spectra were determined on a Bio-Rad FTS-40 spectrometer. All commercially available reagents were used as received.

Crystal structure determinations

Data were collected on either a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα generated from a rotating anode (0.71073 Å) with ω and ψ scans to approximately 56° 2θ or a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-Kα generated from a sealed tube (0.71073 Å) with ω scans to approximately 56° 2θ. Data integration and reduction were undertaken with SAINT and XPREP[12] and subsequent computations were carried out using the WinGX-32 graphical user interface.[13] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[14] Gaussian absorption corrections were applied using XPREP.[12] Structures were solved by direct methods using SIR97[15] then refined and extended with SHELXL-97.[16] Unless otherwise stated, ordered non-hydrogen atoms were refined anisotropically while partial occupancy non-hydrogen atoms were refined isotropically. Hydrogen atoms attached to carbon atoms were included in idealised positions and a riding model was used for their refinement. Hydrogen atoms bound to solvent water molecules that could not be located in the difference Fourier map were not included in the model. CCDC 988029–988033.

[CoLCl$_2$]·0.25DCM·0.5H$_2$O. The solvent molecules are disordered over a two-fold special position. Formula C$_{32.25}$H$_{25.50}$Cl$_{2.5}$CoN$_6$O$_{0.5}$, M 652.64, triclinic, space group $P\bar{1}$ (#2), a 8.2650(10), b 11.1740(10), c 16.397(2) Å, α 91.485(5), β 91.295(5), γ 94.105(5)°, V 1509.5(3) Å^3, D_c 1.436 g cm^{-3}, Z 2, crystal size 0.300 by 0.250 by 0.150 mm, colour green, habit block, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.825 mm^{-1}, T(SADABS)$_{min,max}$ 0.753, 0.884, $2\theta_{max}$ 72.80, hkl range −13 13, −18 18, −27 27, N 70 587, N_{ind} 14 630 (R_{merge} 0.0342), N_{obs} 11 328 ($I > 2\sigma(I)$), N_{var} 391, residuals‡ $R_1(F)$ 0.0377, w$R_2(F^2)$ 0.1063, GoF (all) 1.055, $\Delta\rho_{min,max}$ −0.484, 0.969 e$^-$ Å^{-3}.

[ZnLCl$_2$]·0.7MeOH·0.3H$_2$O. The solvent molecules are disordered over a number of positions and required the use of bond length restraints to facilitate realistic modelling. One of the dpa pyridyl rings is disordered over two positions. Formula C$_{65.40}$H$_{56.80}$Cl$_4$N$_{12}$O$_3$Zn$_2$, M 1331.37, triclinic, space group $P\bar{1}$ (#2), a 8.4229(5), b 11.1372(6), c 17.7581(11) Å, α 79.110(3), β 79.382(4), γ 84.189(3)°, V 1604.02(16) Å^3, D_c 1.378 g cm^{-3}, Z 1, crystal size 0.477 by 0.061 by 0.043 mm, colour colourless, habit needle, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.970 mm^{-1}, T(SADABS)$_{min,max}$ 0.539, 0.950, $2\theta_{max}$ 57.08, hkl range −11 11, −14 14, −23 23, N 39 311, N_{ind} 7979

(R_{merge} 0.0630), N_{obs} 4912 ($I > 2\sigma(I)$), N_{var} 378, residuals§ $R_1(F)$ 0.0583, w$R_2(F^2)$ 0.1841, GoF (all) 1.020, $\Delta\rho_{min,max}$ −0.687, 1.154 e$^-$ Å^{-3}.

[ZnL(CH$_3$CO$_2$)$_2$]. Formula C$_{36}$H$_{30}$N$_6$O$_4$Zn, M 676.03, triclinic, space group $P\bar{1}$ (#2), a 13.7825(9), b 14.8655(10), c 18.2258(11) Å, α 70.210(2), β 79.959(3), γ 64.388(3)°, V 3166.7(4) Å^3, D_c 1.418 g cm^{-3}, Z 4, crystal size 0.300 by 0.250 by 0.075 mm, colour colourless, habit plate, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.826 mm^{-1}, T(SADABS)$_{min,max}$ 0.846, 0.940, $2\theta_{max}$ 60.14, hkl range −19 19, −20 20, −19 25, N 84 652, N_{ind} 18 409 (R_{merge} 0.0495), N_{obs} 13 160 ($I > 2\sigma(I)$), N_{var} 851, residuals¶ $R_1(F)$ 0.0437, w$R_2(F^2)$ 0.1179, GoF (all) 1.030, $\Delta\rho_{min,max}$ −0.377, 0.731 e$^-$ Å^{-3}.

[Fe(L)$_2$(PF$_6$)$_2$]·2.5H$_2$O. The crystals employed in this study displayed poor diffraction properties and despite careful handling at low temperatures prior to quenching in the cryostream and long exposure times from a high-intensity laboratory source few reflections were observed at better than 1.0 Å resolution and a lower than ideal data/parameter ratio resulted. Despite this and the presence of disordered water solvent, the data is more than sufficient to unambiguously establish the connectivity of the structure.

Formula C$_{64}$H$_{53}$F$_{12}$FeN$_{12}$O$_{2.50}$P$_2$, M 1375.97, monoclinic, space group $P2_1/n$ (#14), a 13.964(2), b 14.768(2), c 31.254(4) Å, β 102.320(9)°, V 6296.8(15) Å^3, D_c 1.451 g cm^{-3}, Z 4, crystal size 0.300 by 0.150 by 0.100 mm, colour purple, habit blade, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.382 mm^{-1}, T(SADABS)$_{min,max}$ 0.705, 0.963, $2\theta_{max}$ 41.60, hkl range −13 13, −14 14, −31 31, N 27 263, N_{ind} 6373 (R_{merge} 0.0874), N_{obs} 4043 ($I > 2\sigma(I)$), N_{var} 856, residuals‖ $R_1(F)$ 0.0571, w$R_2(F^2)$ 0.1599, GoF (all) 1.035, $\Delta\rho_{min,max}$ −0.254, 0.571 e$^-$ Å^{-3}.

[Fe(L)(HL)](PF$_6$)$_{0.5}$(ClO$_4$)$_{2.5}$·H$_2$O·1.5MeOH. The solvent molecules are disordered. Formula C$_{65.50}$H$_{57}$Cl$_{2.50}$F$_3$FeN$_{12}$O$_{12.50}$P$_{0.50}$, M 1429.19, monoclinic, space group $P2_1$ (#4), a 9.1075(10), b 33.618(4), c 11.0207(12) Å, β 107.945(2)°, V 3210.2(6) Å^3, D_c 1.479 g cm^{-3}, Z 2, crystal size 0.3 by 0.3 by 0.05 mm, colour purple, habit plate, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(MoKα) 0.435 mm^{-1}, T(SADABS)$_{min,max}$ 0.6752, 0.7457, $2\theta_{max}$ 56.56, hkl range −12 12, −43 43, −14 14, N 31 618, N_{ind} 14 651 (R_{merge} 0.0547), N_{obs} 9266 ($I > 2\sigma(I)$), N_{var} 859, residuals** $R_1(F)$ 0.0823, w$R_2(F^2)$ 0.2357, GoF (all) 1.004, $\Delta\rho_{min,max}$ −0.914, 1.005 e$^-$ Å^{-3}.

Ligand synthesis

4′-(4-Bromomethylphenyl)-2,2′:6′,2″-terpyridine. This precursor was prepared as described by Johansson *et al.*[17] ^{1}H NMR (200 MHz, CDCl$_3$, 300 K): δ 4.57 (s, CH$_2$, 2H), 7.36 (m, aromatic,

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§ $R_1 = \sum||F_o| − |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; w$R_2 = (\sum w(F_o{}^2 − F_c{}^2)^2/\sum(wF_c{}^2)^2)^{1/2}$ all reflections. w $= 1/[\sigma^2(F_o{}^2) + (0.1018P)^2 + 0.9483P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

¶ $R_1 = \sum||F_o| − |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; w$R_2 = (\sum w(F_o{}^2 − F_c{}^2)^2/\sum(wF_c{}^2)^2)^{1/2}$ all reflections. w $= 1/[\sigma^2(F_o{}^2) + (0.0523P)^2 + 1.5804P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

‖ $R_1 = \sum||F_o| − |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; w$R_2 = (\sum w(F_o{}^2 − F_c{}^2)^2/\sum(wF_c{}^2)^2)^{1/2}$ all reflections. w $= 1/[\sigma^2(F_o{}^2) + (0.08283P)^2 + 4.8947P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

** $R_1 = \sum||F_o| − |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; w$R_2 = (\sum w(F_o{}^2 − F_c{}^2)^2/\sum(wF_c{}^2)^2)^{1/2}$ all reflections. w $= 1/[\sigma^2(F_o{}^2) + (0.1437P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

‡ $R_1 = \sum||F_o| − |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; w$R_2 = (\sum w(F_o{}^2 − F_c{}^2)^2/\sum(wF_c{}^2)^2)^{1/2}$ all reflections. w $= 1/[\sigma^2(F_o{}^2) + (0.0501P)^2 + 0.5408P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

2H), 7.54 (m, aromatic, 2H), 7.87 (m, aromatic, 2H), 8.66–8.74 (m, aromatic, 6H) (corresponding to that reported previously).

4′-{4-[Di-(2-pyridyl)aminomethyl]phenyl}-2,2′:6′,2′′-terpyridine (L). Di-(2-pyridyl)amine (0.213 g, 1.24 mmol) and potassium hydroxide (0.348 g, 6.2 mmol) were stirred in DMF (20 mL) at 40 °C for 20 min. 4′-(4-Bromophenyl)-2,2′:6′,2′′-terpyridine (0.500 g, 1.24 mmol) was dissolved in DMF (10 mL) and added slowly while stirring was continued at 40 °C for a further 30 h. The solvent was removed under reduced pressure and the residue partitioned between dichloromethane (100 mL) and water (50 mL). The organic layer was washed twice with water (2 × 25 mL) and then the combined aqueous phases washed with dichloromethane (2 × 20 mL). The combined dichloromethane layers were dried (Na_2SO_4) and then taken to dryness on a rotary evaporator, resulting in a pale yellow solid. This was recrystallised from ethanol yielding 420 mg (70%) of a yellow crystalline solid; m.p. 181–183 °C. Found: C, 77.74; H, 4.99; N, 16.89. Calc. for $C_{32}H_{24}N_6$: C, 78.01; H, 4.91; N, 17.06%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ 5.58 (2H, s, CH_2), 6.87 (2H, m, Ar), 7.21 (2H, m, Ar), 7.33 (2H, m, Ar), 7.51 (4H, m, Ar), 7.83 (4H, m, Ar), 8.34 (2H, m, Ar) 8.68 (6H, m, Ar). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 51.1, 114.6, 117.3, 118.8, 121.3, 123.7, 127.3, 127.7, 136.8, 136.8, 137.3, 140.6, 148.3, 149.1, 150.2, 155.8, 156.3, 157.1. MS (ESI): m/z 493 (M + H)$^+$.

Metal complex synthesis

[CoLCl₂]. $CoCl_2 \cdot 6H_2O$ (20 mg, 0.8 mmol) in warm acetonitrile (5 mL) was added to L (20 mg, 0.4 mmol) in dichloromethane (3 mL). This solution was heated and stirred, resulting in a dark green precipitate which was filtered off, washed with ether and dried in a vacuum. Yield, 24 mg (60%). MS (ESI) m/z = 1210 $(L_2Co_2Cl_3)^+$, 586 $(LCoCl)^+$. Found: C, 49.76; H, 3.18; N, 10.75. $C_{32}H_{24}Cl_4Co_2N_6 \cdot H_2O$ requires: C, 49.90; H, 3.40; N, 10.91%. Crystals for X-ray analysis were obtained upon slow evaporation of the mother liquor over one week.

[ZnLCl₂]. $ZnCl_2$ (27 mg, 2 mmol) in warm methanol (5 mL) was added to L (100 mg, 2 mmol) in warm dichloromethane (5 mL). The solution was left to evaporate resulting in a pale yellow crystalline product, a crystal of which was employed for an X-ray structure determination. Yield, 90 mg (71%). MS (ESI) m/z = 1221 $(L_2Zn_2Cl_3)^+$, 591 $(LZnCl)^+$. Found: C, 57.90; H, 3.76; N, 12.34. $C_{32}H_{24}Cl_2N_6Zn \cdot 2H_2O$ requires: C, 57.80; H, 4.24; N, 12.63%.

[ZnL(CH₃CO₂)₂]. $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (9 mg, 0.4 mmol) in warm acetonitrile (5 mL) was added to L (20 mg, 0.4 mmol) in warm dichloromethane (3 mL). The pale yellow solution was reduced in volume and left to evaporate resulting in small yellow crystals, which were filtered off and dried under vacuum. Yield, 10 mg (35%). MS (ESI) m/z = 615 $[LZn(OAc)]^+$. Found: C, 58.48; H, 4.72; N, 11.16. $C_{36}H_{30}N_6O_4Zn \cdot 3.5H_2O$ requires: C, 58.50; H, 5.04; N, 11.37%.

[Fe(L)₂](PF₆)₂. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.2 g, 0.5 mmol) in hot methanol/water (1 : 1) (15 mL) was added to L (0.5 g, 1 mmol) in dichloromethane/methanol (1 : 1; 20 mL). A dark purple solution formed immediately and this was heated and stirred until the volume was reduced to 20 mL.

Water (10 mL) was added to this solution followed by saturated aqueous NH_4PF_6. This resulted in precipitation of a purple product, which was filtered off, washed with ether and dried. Yield, 0.6 g (90%). MS (ESI) m/z = 1185 $[M - PF_6]^+$. ^{1}H NMR (acetonitrile-d_3, 300 MHz, 300 K), δ: 5.70 (s, 4H, CH_2), 6.99–7.09 (m, 8H), 7.17 (d, 4H), 7.31 (d, 4H), 7.70 (t, 4H), 7.81 (d, 4H), 7.90 (t, 4H) 8.22 (d, 4H), 8.37 (d, 4H), 8.60 (d, 4H), 9.15 (s, 4H). ^{13}C NMR (acetonitrile-d_3, 75 MHz, 300 K), δ: 50.4, 114.3, 121.2, 123.4, 126.9, 127.5, 128.2, 134.7, 137.3, 138.4, 142.9, 147.8, 150.0, 152.7, 156.7, 157.7, 159.9. IR (KBr disc, cm^{-1}) 1581 m, 1468 m, 1432 m, 1376 w, 851 s, 839 s, 783, m, 557 m. X-ray quality crystals of $[Fe(L)_2(PF_6)_2] \cdot 2.5H_2O$ were obtained by the slow diffusion of diethyl ether into an acetonitrile solution of the title complex.

[Fe(L)(HL)](PF₆)₀.₅(ClO₄)₂.₅·H₂O·1.5MeOH. $AgClO_4 \cdot H_2O$ (2.23 mg, 0.01 mmol) in methanol (1 mL) was added to $[Fe(L)_2](PF_6)_2 \cdot 2.5H_2O$ (12.5 mg, 0.01 mmol) in warm acetonitrile (5 ml). The solution was warmed and stirred for 30 min. Ether vapour was diffused into this solution resulting in the formation of small number of crystals suitable for diffraction studies. No further analysis was performed or accurate yield determined.

[Pd₂LCl₃]Cl. $PdCl_2$ (15 mg, 0.08 mmol) in 2 M HCl (2 mL) was slowly added to L (20 mg, 0.04 mmol) in dichloromethane/methanol (1 : 1; 10 mL). The resulting solution was heated and stirred for 30 min resulting in formation of a pale yellow precipitate. This product was filtered off and dried under vacuum. Yield, 30 mg (86%). MS (ESI) m/z = 811 $(M - Cl)^+$. Found: C, 39.39; H, 3.53; N, 8.99. $C_{32}H_{24}Cl_4N_6Pd_2 \cdot 7H_2O$ requires: C, 39.59; H, 3.94; N, 8.66%.

[FePd₂(L)₂Cl₄](PF₆)₂·1.5CH₃CN. $Pd(CH_3CN)_2Cl_2$ (4.9 mg, 0.02 mmol) in acetonitrile (3 mL) was added to $[Fe(L)_2](PF_6)_2 \cdot 2.5H_2O$ (25 mg, 0.02 mmol) in warm acetonitrile (5 ml). The solution was warmed and stirred for 30 min. Ether vapour was diffused into this solution resulting in the formation of a purple microcrystalline product over 2 days. Yield, 25 mg (80%). MS (ESI) m/z = 1541 $(M - PF_6)^+$. ^{1}H NMR (acetonitrile-d_3, 300 MHz, 300 K), δ: 5.63 (s, 4H, CH_2), 6.92–7.05 (m, 8H), 7.12 (d, 4H), 7.33 (d, 4H), 7.65 (t, 4H), 7.79 (d, 4H), 7.88 (t, 4H) 8.19 (d, 4H), 8.35 (d, 4H), 8.55 (d, 4H), 9.12 (s, 4H). Found: C, 46.95; H, 3.22; N, 10.50. $C_{64}H_{48}Cl_4 F_{12}FeN_{12}P_2Pd_2 \cdot 1.5CH_3CN$ requires: C, 47.05; H, 3.02; N, 10.82%.

Results and discussion

The difunctional ligand L containing terpy and dpa moieties was obtained in 70% yield by the direct reaction of dpa with previously reported 4′-(4-bromomethylphenyl)-2,2′:6′,2′′-terpyridine[17] in dimethylformamide in the presence of KOH.

The reaction of L with cobalt(II) chloride in acetonitrile/dichloromethane resulted in dark green crystals of $[CoLCl_2] \cdot 0.25DCM \cdot 0.5H_2O$ whose X-ray structure (Fig. 1) showed that the cobalt cation coordinates at the terpy site (in a second experiment a similar product showing the absence of coordination at the dpa site was also obtained even when a several-fold excess of $CoCl_2$ was employed for the reaction). The cobalt(II) centre is five-
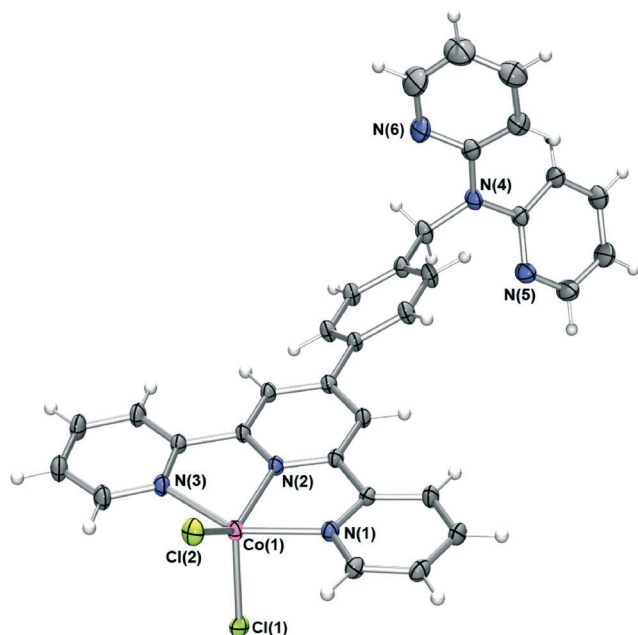
Fig. 1 X-ray structure of [CoLCl₂]·0.25DCM·0.5H₂O. Solvent molecules have been removed for clarity. Thermal ellipsoids are shown at the 50 percent probability level.

Fig. 2 Representation of the one-dimensional stack that propagates parallel to the crystallographic $\bar{a}b$ vector in [CoLCl₂]·0.25DCM·0.5H₂O. Double headed arrows indicate the presence of arene–arene interactions.

Fig. 3 X-ray structure of [ZnLCl₂]·0.7MeOH·0.3H₂O. Solvent molecules and protons have been removed for clarity. Thermal ellipsoids are shown at the 50 percent probability level. The pyridyl group comprising N(4) exhibits minor positional disorder and was modelled over two sites. For clarity only one of these is shown.

coordinate, adopting a distorted trigonal bipyramidal geometry (Addison τ parameter[18] = 1.19) with the Ni(1) and N(3) pyridine nitrogens occupying the axial positions and the remaining pyridyl group and two chloride ions in the equatorial positions. The coordination bond lengths and angles of the cobalt(II) centre are similar to other cobalt(II) chloride terpyridyl complexes of type [Co(terpy)Cl₂].[19]

Adjacent complexes are involved in a complex web of intermolecular interactions forming an infinite three dimensional network; the close to planar "tolylterpy" sections of the molecule undergo a series of offset face-to-face arene–arene interactions indicated by ring centroid–ring centroid separations of 3.5–3.7 Å forming a one-dimensional stack that extends parallel to the crystallographic $\bar{a}b$ vector (Fig. 2). This arrangement is further stabilised by a series of hydrogen bonds between aromatic protons and coordinated chloride ions (CH···Cl distances of between 3.0 and 3.2 Å). More of these hydrogen bonds (CH···Cl distances of between 2.81 and 2.86 Å) and further arene–arene interactions bridge these one-dimensional chains resulting in two-dimensional sheets. Each of these sheets is further bridged by interactions involving the dpa part of the ligand. The N(5)-containing dpa pyridine acts as a hydrogen bond acceptor from an adjacent terpy pyridyl hydrogen donor (C(14)H···N(5) = 2.6 Å) and is also involved in edge-to-face π stacking, forming a three-dimensional network of interactions.

Interaction of zinc(II) chloride with **L** under similar conditions to those employed for the cobalt(II) complex (with methanol substituted for acetonitrile) resulted in formation of a pale yellow species of type [ZnLCl₂]. This 5-coordinate zinc(II) complex is isostructural (Fig. 3) with the cobalt(II) complex described above and forms the same three-dimensional
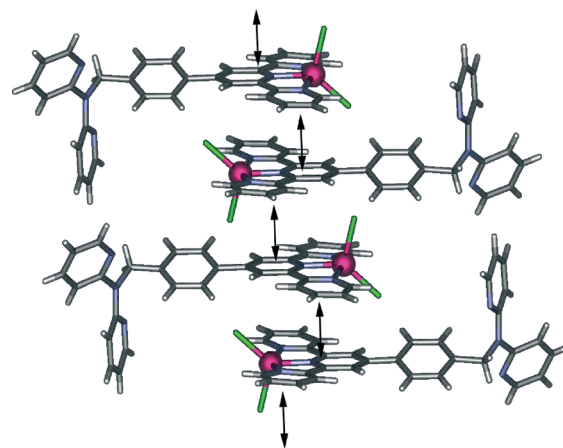
network of interactions consisting of arene-stacking and both CH···Cl and CH···N hydrogen bonding. Indeed, interactions of this type appear to dominate the crystal packing of each of [M(L′)Cl₂] (where **L′** is any ligand incorporating the "tolylterpy" motif); similar crystal packing arrangements to those found in the present study for both the zinc(II) and cobalt(II) complexes of **L** are present in each of the eight other [M(L′)Cl₂] structures in the literature.[20]

Reaction of zinc acetate in acetonitrile with **L** in dichloromethane resulted in yellow crystals whose X-ray structure is shown in Fig. 4. The zinc centre again has a distorted trigonal bipyramidal geometry with the metal bound to the terpy domain of **L**; the remaining two coordination sites are occupied by oxygens from monodentate acetate ions. Once again two pyridyl group occupy the axial positions, with the third and the anions in the equatorial plane, an arrangement that

has been observed in two other [Zn(terpyR)(OAc)₂] structures reported previously.[21] Unlike the two chloride-bound complexes above, [ZnL(CH₃CO₂)₂] crystallises with two chemically identical but crystallographically distinct molecules in the asymmetric unit.

The dpa site is again not coordinated to a metal ion. In a similar fashion to the two chloride complexes, the relatively planar "tolylterpy" sections of the ligands lie closely above and below each other forming infinite one-dimensional chains which are further stabilised by CH⋯O hydrogen bonds. These chains interact with adjacent stacks through further dpa$_{pyridyl}$H⋯O hydrogen bonds.

Reaction of ferrous ammonium sulfate with L followed by addition of ammonium hexafluorophosphate led to isolation of a purple product of type [Fe(L)₂(PF₆)₂]. The nature of this compound was investigated by mass spectrometry, NMR and IR spectroscopy as well as by an X-ray structure determination (Fig. 5). The ESI mass spectrum of this product showed a parent peak corresponding to [Fe(L)₂(PF₆)]⁺ and the X-ray structure determination showed that the iron(II) is six coordinate with the two terpy units of two molecules of L coordinated in the commonly observed bis-terpy octahedral motif. The dpa units are, once again, not coordinated. The crystal packing of the complex is dominated by arene–arene interactions and aromatic CH⋯F hydrogen bonds resulting in a three-dimensional array, with the uncoordinated dpa groups participating in a series of edge-to-face and offset face-to-face arene–arene stacking. The "tolylterpy" parts of the molecule interact with each other in a 'terpy embrace' motif similar to that observed previously in the iron(II) and ruthenium(II) complexes of 4′-phenylterpy[22] and 4′-pyridylterpy.[23]

The strong coordination of palladium(II) to both dpa[9,24,25] and terpy[26] has been well documented and this provided a motivation for investigating the interaction of this metal ion with L. Reaction of L in dichloromethane/methanol (1:1) with palladium(II) chloride in 2 M hydrochloric acid resulted in a pale yellow precipitate. Elemental analysis of the isolated
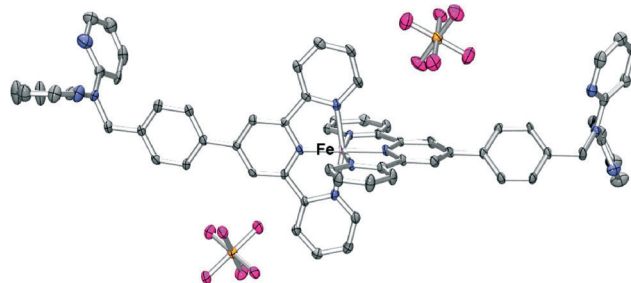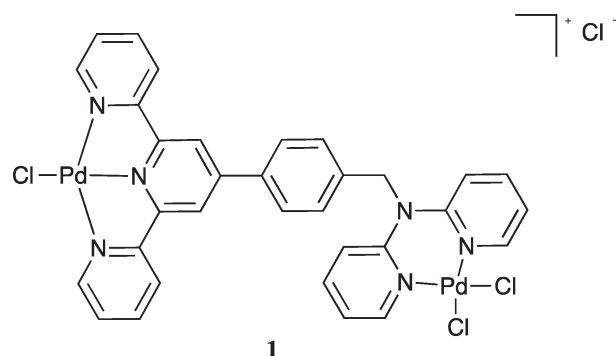

Fig. 5 X-ray structure of [Fe(L)₂(PF₆)₂]·2.5H₂O. Solvent water molecules and protons have been removed for clarity. Thermal ellipsoids are shown at the 30 percent probability level.

solid gave a Pd:L ratio of 2:1. The mass spectrum also revealed a parent peak corresponding to two palladium and one L in solution, in accord with formation of a homodinuclear species of type **1**. Unfortunately crystals of **1** suitable for an X-ray diffraction study were not obtained.

1

In view of the above result bis(acetonitrile)dichloropalladium(II) in acetonitrile was added to [Fe(L)₂](PF₆)₂ in acetonitrile and the warm solution stirred for 30 minutes. The solution remained dark purple. Ether vapour was then diffused into the reaction mixture to yield a dark purple precipitate. The ¹H NMR spectrum of this product exhibited a noticeable shift of the (single) methylene proton signal relative to the starting complex (in keeping with the occurrence of palladium coordination at both dpa sites). The mass spectrum revealed a parent peak corresponding to [FePd₂L₂Cl₄PF₆]⁺; such a stoichiometry corresponds to a structure of type **2**. Further, the isotopic distribution of this ion (Fig. 6) is in agreement with a trinuclear structure and the elemental analysis of the isolated product also corresponded to the proposed stoichiometry. Unfortunately, crystals suitable for an X-ray structure determination were again not obtained; however, on the basis of the above evidence the product was assigned the trinuclear structure **2**.
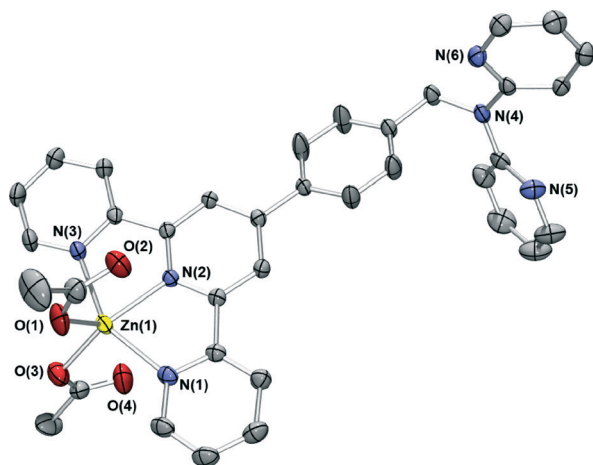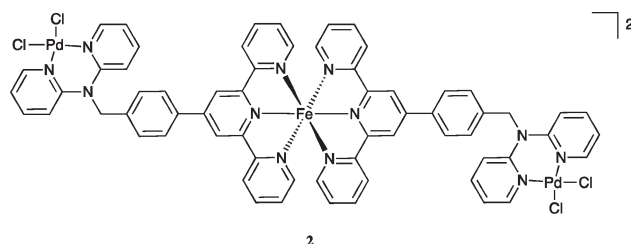

Fig. 4 X-ray structure of [ZnL(CH₃CO₂)₂]. Only one of the two chemically identical but crystallographically unique complexes in the asymmetric unit are shown for clarity. Thermal ellipsoids are at the 50 percent probability level.
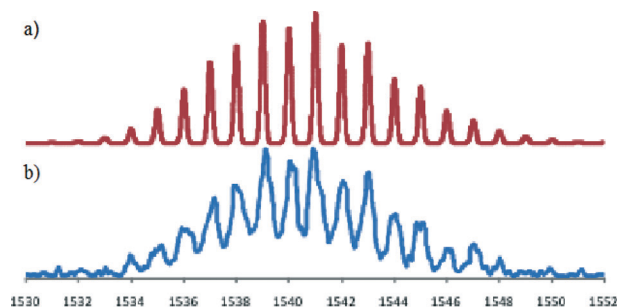

2

Fig. 6 (a) Predicted mass spectral distribution for $[FePd_2L_2Cl_4PF_6]^+$. (b) Observed isotopic distribution for this ion in the ESI mass spectrum of $[(L)_2FePd_2(L)_2Cl_4](PF_6)_2$.
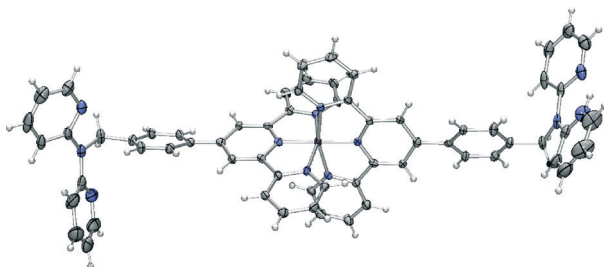

Fig. 7 X-ray structure of $[Fe(L)(HL)](PF_6)_{0.5}(ClO_4)_{2.5}\cdot H_2O\cdot 1.5MeOH$. Solvent molecules and anions have been removed for clarity. Thermal ellipsoids are shown at the 50 percent probability level.

Based on the success of this study in forming a heterometallic complex we investigated the possibility of using $[Fe(L)_2](PF_6)_2$ as a metallo-ligand for the formation a heterometallic coordination polymer in conjunction with silver(ı). Our choice of silver was based on our previous success in coordinating silver(ı) with dpa ligands[11] and the well established propensity for silver(ı) to form coordination complexes with nitrogen donor ligands when other metal ions have not been successful.[27] Accordingly, an acetonitrile solution of $[Fe(L)_2](PF_6)_2$ was mixed with one equivalent of $AgClO_4\cdot H_2O$ in methanol to yield a small number of purple crystals suitable for diffraction studies, following diffusion of ether vapour into the resulting purple solution. X-ray analysis revealed a mixed-anion complex of composition $[Fe(L)(HL)](PF_6)_{0.5}(ClO_4)_{2.5}\cdot H_2O\cdot 1.5MeOH$ (Fig. 7).

In this complex, the iron(ıı) centre adopts the expected octahedral geometry, bound to one terpyridine domains from each ligand, one dpa moiety is protonated and both of these remain uncoordinated. The crystal packing is again dominated by π-interactions. In this case the bis-terpyridine groups form a classical one-dimensional terpyridine embrace motif[28] with the network again extended to three dimensions by further π-stacking involving the dpa groups.

Conclusions

A new di-functional hybrid terpy/dpa ligand **L** along with five crystal structures of its metal derivatives are reported. In each complex the metal ion preferentially binds to the terpyridine moiety, with the dpa site remaining uncoordinated and the

crystal packing dominated by extensive π-interactions. Contrasting with the above, reaction of palladium(ıı) with **L** gives a complex for which the evidence indicates that this metal ion binds at both the terpy and dpa domains. Based on this result, addition of $[Pd(CH_3CN)_2Cl_2]$ to $[Fe(L)_2](PF_6)$ in acetonitrile yielded a heterometallic Fe/Pd (1:2) complex in which the evidence indicates that both non-metal bound dpa sites of $[Fe(L)_2](PF_6)$ are now occupied by palladium ions to form a species of type $[FePd_2(L)_2Cl_4](PF_6)_2\cdot 1.5CH_3CN$. An initial attempt to form a related Fe(ıı)/Ag(ı) species led instead to a silver-free $[FeL_2H]^{3+}$ species in which protonation of one of the two unoccupied dpa sites of dpa has occurred. Further studies involving **L** directed towards the synthesis of other heteronuclear species are planned for the future.

Acknowledgements

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