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 [CoLCl₂], [ZnLCl₂], [ZnL(CH₃CO₂)₂], [FeL₂(PF₆)₂] and [FeL(HL)][PF₆]₀.₅(ClO₄)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 [FeL₂(PF₆)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(CH₃CO₂)₂] and [FeL(HL)][PF₆]₀.₅(ClO₄)₂.₅ giving rise to 3D arrays. Reaction of palladium(II) with L yields a product of stoichiometry Pd₂LCl₄ for which the evidence suggests that palladium binds at both the terpy and dpa domains. Based on this result, addition of [Pd(CH₃CN)₂Cl₂] to [FeL₂](PF₆) in acetonitrile yielded a heterometallic complex in which the “free” dpa sites of [FeL₂](PF₆) are now occupied by palladium ions to form a heterometallic product of type [FePd₂(L)₂Cl₄](PF₆)₂·1.₅CH₃CN.

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 decades3–6 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.

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† CCDC 988029–988033. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00414k
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 XPREP12 and subsequent computations were carried out using the WinGX-32 graphical user interface.13 Multi-scan 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 SIR9715 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.

[CoLCl3]0.25DCM+0.5H2O. The solvent molecules are disordered over a two-fold special position. Formula C13.125H33.565Cl2.5CoN6O6.5, M 652.64, triclinic, space group P1 (No. 2), a 8.2650(10), b 11.1740(10), c 16.3972(2), α 91.485(5), β 91.292(5), γ 94.105(5), V 1590.59(3) Å3, Dc 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, μ(MoKα) 0.7073 Å, μ(MoKα) 0.825 mm−1, T[SADABS]min,max 0.753, 0.884, 26max 72.80, hkl range –13 13, –18 18, –27 27, N 70587, Nind 14630 (Rmerge 0.0342), Ndif 11328 (I > 2σ(I)), Nvar 391, residuals $ R_\text{P}$(F2) 0.0377, wR(F2) 0.1063, GoF (all) 1.055, Δρ/min, max −0.484, 0.969 e Å−3.

[CoL][NH4]0.25DCM+0.5H2O. 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 C0.504H39.560Cl2.5CoN6O6.5Zn2, M 1331.37, triclinic, space group P1 (No. 2), a 8.4229(5), b 11.1372(6), c 17.7581(11), α 79.710(3), β 79.382(4), γ 84.189(3), V 1604.02(16) Å3, Dc 1.378 g cm−3, Z 1, crystal size 0.477 by 0.061 by 0.043 mm, colourless, habit needle, temperature 150(2) Kelvin, μ(MoKα) 0.7073 Å, μ(MoKα) 0.970 mm−1, T[SADABS]min,max 0.539, 0.950, 26max 57.08, hkl range –11 11, –14 14, –23 23, N 39311, Nind 7979

Rmerge 0.0630, Nash 4912 (I > 2σ(I)), Nvar 378, residuals $ R_\text{P}$(F2) 0.0583, wR(F2) 0.1841, GoF (all) 1.020, Δρ/min, max −0.687, 1.154 e Å−3.

[CoL][CH2(NH2)2]3. Formula C12.95H36N6O2Zn, M 676.03, triclinic, space group P1 (No. 2), a 13.7825(9), b 14.6655(10), c 18.2258(11) Å, α 70.210(2), β 79.599(3), γ 64.388(3), V 3166.7(4) Å3, Dc 1.418 g cm−3, Z 4, crystal size 0.300 by 0.250 by 0.075 mm, colourless, habit plate, temperature 150(2) Kelvin, μ(MoKα) 0.71073 Å, μ(MoKα) 0.826 mm−1, T[SADABS]min,max 0.846, 0.940, 26max 60.14, hkl range −19 19, −20 20, −19 25, N 84652, Nind 18409 (Rmerge 0.0495), Nobs 13160 (I > 2σ(I)), Nvar 851, residuals $ R_\text{P}$(F2) 0.0437, wR(F2) 0.1179, GoF (all) 1.030, Δρ/min, max −0.377, 0.731 e Å−3.

[Fe(L)2(PF6)4]2.5H2O. 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 C16.95H36.5Cl2.5FeN2O2.5P2, M 1375.97, monoclinic, space group P21/c (No. 14), a 13.964(2), b 14.768(2), c 31.254(4) Å, β 102.320(9)°, V 6296.8(15) Å3, Dc 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, μ(MoKα) 0.71073 Å, μ(MoKα) 0.382 mm−1, T[SADABS]min,max 0.705, 0.963, 26max 41.60, hkl range –13 13, –14 14, –31 31, N 27263, Nind 6373 (Rmerge 0.0874), Nobs 4043 (I > 2σ(I)), Nvar 856, residuals $ R_\text{P}$(F2) 0.0571, wR(F2) 0.1599, GoF (all) 1.035, Δρ/min, max −0.254, 0.571 e Å−3.

[Fe(L)(HL)][PF6]2.5H2O. The solvent molecules are disordered. Formula C20.504H36.5Cl2.5FeN2O2.5P2, M 1429.19, monoclinic, space group P21/c (No. 14), a 9.1075(10), b 33.618(4), c 11.0207(12) Å, β 107.945(2)°, V 3210.2(6) Å3, Dc 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, μ(MoKα) 0.71073 Å, μ(MoKα) 0.435 mm−1, T[SADABS]min,max 0.6752, 0.7457, 26max 56.56, hkl range –12 12, –43 43, N 31618, Nind 14651 (Rmerge 0.0547), Nobs 9266 (I > 2σ(I)), Nvar 859, residuals $ R_\text{P}$(F2) 0.0823, wR(F2) 0.2357, GoF (all) 1.004, Δρ/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 1H NMR (200 MHz, CDC13, 300 K): δ 4.57 (s, CH3-2H), 7.36 (m, aromatic).
terpyridine (L). Di-[2-pyridyl]amine (0.213 g, 1.24 mmol) was dissolved in DMF (10 mL) and potassium hydroxide (0.348 g, 6.2 mmol) were stirred in DMF (3 mL). This solution was heated and stirred, resulting in a dark purple solution formed immediately and this was heated and stirred for 30 min. Ether vapour was diffused into an acetonitrile (5 mL). The solution was warmed 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).


[Fe(L)(HL)](PF6)0.5(ClO4)2.5H2O. AgClO4·H2O (2.23 mg, 0.01 mmol) in methanol (1 mL) was added to [Fe(L)(HL)](PF6)2·5H2O (12.5 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 small number of crystals suitable for diffraction studies. No further analysis was performed or accurate yield determined.

[PdCl2]Cl. PdCl2 (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, 25 mg (80%). MS (ESI) m/z = 1210 (L2CoCl2)6, 586 (LCoCl)4. Found: C, 39.76; H, 3.18; N, 10.75. C20H16Cl2Co2N6H2O 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.

Metal complex synthesis

[CoCl2]. CoCl2·6H2O (20 mg, 0.88 mmol) in warm acetonitrile (5 mL) was added to L (20 mg, 0.04 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 (L2CoCl2)6, 586 (LCoCl)4. Found: C, 49.76; H, 3.18; N, 10.75. C20H16Cl2Co2N6H2O 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.

[ZnLCl]. ZnCl2 (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 the reaction). The cobalt(II) centre is five-atomed 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 was washed with dichloromethane (2 × 20 mL). The combined dichloromethane layers were dried (Na2SO4) 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 C20H16ZnCl2N6: C, 78.01; H, 4.91; N, 17.06%.

1H NMR (300 MHz, CDCl3, 300 K) δ 5.00 (2H, s, CH2), 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). 13C NMR (CDCl3, 75 MHz, CDCl3, 300 K) δ 51.1, 114.6, 117.3, 118.8, 121.3, 123.7, 127.3, 127.7, 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)−.

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 in dimethylformamide in the presence of KOH.

The reaction of L with cobalt(II) chloride in acetonitrile/dichloromethane resulted in dark green crystals of [CoCl2]·0.25DCM·0.5H2O 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 CoCl2 was employed for the reaction). The cobalt(II) centre is five-
coordinate, adopting a distorted trigonal bipyramidal geometry (Addison τ parameter = 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].

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 ab 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.

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

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 ab 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.
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 “tolylyterpy” 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 dpapyridylH⋯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 “tolylyterpy” 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′-phenylterpy22 and 4′-pyridylterpy.23

The strong coordination of palladium(II) to both dpa9,24,25 and terpy26 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 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.

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.
Based on the success of this study in forming a heterometallic complex we investigated the possibility of using $[\text{Fe}(\text{L})_2](\text{PF}_6)_2$ as a metallo-ligand for the formation a heterometallic coordination polymer in conjunction with silver(I). Our choice of silver was based on our previous success in coordinating with the dpa site remaining uncoordinated and the crystal packing dominated by extensive $\pi$-interactions. Contrasting with the above, reaction of palladium(ii) 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 $[\text{Pd}((\text{CH}_3\text{CN})_2\text{Cl}_2]$ to $[\text{Fe}(\text{L})_2](\text{PF}_6)_2$ in acetonitrile yielded a heterometallic Fe/Pd (1:2) complex in which the evidence indicates that both non-metal bound dpa sites of $[\text{Fe}(\text{L})_2](\text{PF}_6)_2$ are now occupied by palladium ions to form a species of type $[\text{Fe}(\text{L})_2(\text{Cl})_2](\text{PF}_6)_2$.5CH$_3$CN. An initial attempt to form a related Fe(ii)/Ag(i) species led instead to a silver-free $[\text{Fe}(\text{II})\text{H}]^{2+}$ 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**

We thank the Australian Research Council for support.

**Notes and references**

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