Phosphinocarboxylic acids as building blocks in organometallic crystal engineering. Self-organisation of one-dimensional photoluminescent cyclometallated platinum(II) polymeric structures

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Diphenylphosphinopropanoic acid (Ppa) is utilised for the self-organisation of a luminescent organoplatinum polymeric material, the crystal structure of which features intermolecular hydrogen bonding and π-stacking interactions.

Tertiary phosphines are versatile ligands in coordination and organometallic chemistry, but functional groups which are capable of complementary hydrogen bonding, such as carboxylic acids,[1] are rarely incorporated.[2] Molecular self-assembly employing hydrogen bonding has generated considerable interest in the domain of supramolecular chemistry and molecular recognition.[3] From an organometallic perspective,[4,5] the resultant materials have potential applications in non-linear optics, conductivity and ferromagnetism. The use of π–π stacking interactions in crystal engineering has also been prominent.[6] Their importance is further emphasised by their manifestation, in tandem with hydrogen bonding, in the structures of biological molecules such as DNA and proteins. Our earlier work on cyclometallated-(6-phenyl-2,2′-bipyridine) platinum(II) complexes revealed favourable π–π interactions in solid and solution states.[7] Herein, we describe the employment of diphenylphosphinopropanoic acid[8] (Ppa) as a building block in the supramolecular assembly of an organometallic polymer directed by π-stacking and hydrogen-bonding interactions.

Treatment of Pt(L)Cl [HL = 4-(*p*-tolyl)-6-phenyl-2,2′-bipyridine][7] with Ppa in $CH_3CN–H_2O$ (1 : 1 v/v) at room temperature in the presence of excess NH_4PF_6 yielded $[Pt(L)(Ppa)]PF_6$ **1** as an orange crystalline solid in 75% yield.† Absorption bands at 1709 and 3448 cm^{-1} in the IR spectrum are assigned to ν(CO) and ν(OH) respectively of the Ppa ligand, while ^{195}Pt satellites (J_{PtP} 3943 Hz) are observed in the ^{31}P NMR spectrum.

The structure of **1** has been determined by X-ray crystallography (Fig. 1).‡ The tridentate cyclometallated ligand L and the phosphine are arranged in a distorted square-planar geometry about the platinum atom. The platinum–nitrogen bond length *trans* to the phenyl group [Pt(1)–N(1) 2.128(8) Å] is noticeably longer than that *trans* to the phosphine ligand [Pt(1)–N(2) 2.018(8) Å]; this is consistent with the greater *trans* influence exerted by the phenyl substituent. The crystal packing in **1** [Fig. 1(b)] reveals hydrogen bonding between two carboxylic acids in adjacent molecules, with clear directionality and short intermolecular contacts [2.65(1) Å] between successive oxygen atoms (O–H···O=C). π-Stacking between the aromatic planes of L (mean 3.68 Å) is more distant than that in $[Pt(6\text{-phenyl-}2,2'\text{-bipyridine})(PPh_3)]ClO_4$ (mean 3.35 Å), although an identical 'head–tail' orientation of the overlapping ligands is evident in both structures.[7] Infinite one-dimensional polymeric zig-zag chains linked by alternating hydrogen-bonding and π–π

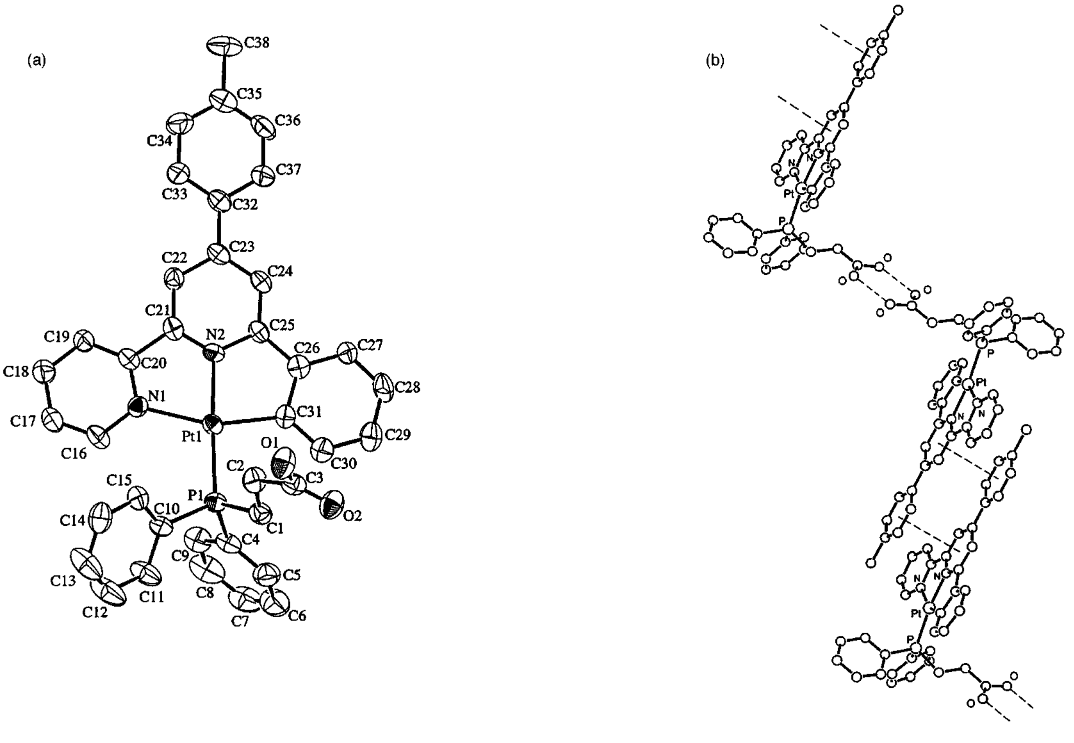

Fig. 1 (a) Perspective view of cation in **1** [40% thermal ellipsoids, all hydrogens are omitted including H(1) attached to O(1)]. Selected bond distances (Å) and angles (°): Pt(1)–P(1) 2.249(3), Pt(1)–N(1) 2.128(8), Pt(1)–N(2) 2.018(8), Pt(1)–C(31) 2.03(1), O(1)–C(3) 1.31(1), O(2)–C(3) 1.21(1), N(1)–Pt(1)–N(2) 76.7(3), N(1)–Pt(1)–C(31) 158.0(4), N(2)–Pt(1)–C(31) 82.1(4), P(1)–Pt(1)–N(2) 172.7(2), O(1)–C(3)–O(2) 124(1). (b) Crystal packing in **1**, showing infinite polymeric zig-zag chains linked by alternating hydrogen-bonding and π–π interactions (anion and all hydrogens are omitted for clarity).

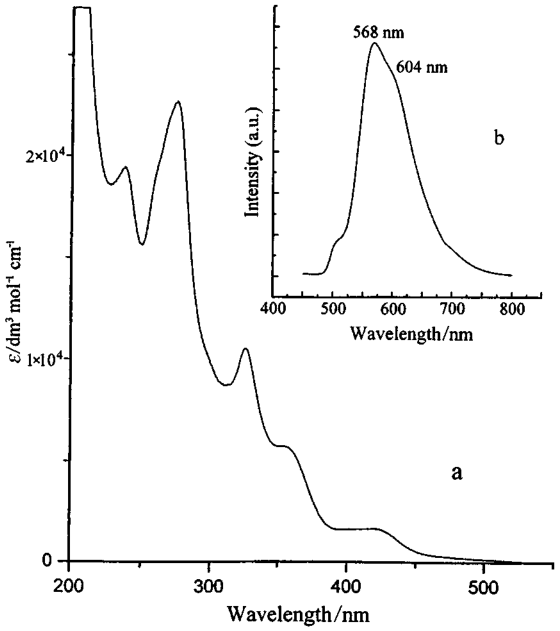

Fig. 2 UV–VIS absorption (a, in CH_3CN) and solid-state emission (b, E_{ex} 350 nm) spectra of **1** at room temperature.

interactions are therefore created. This combination of supramolecular synthons is rarely encountered in coordination compounds.[9]

The absorption spectrum of **1** [Fig. 2(a)] contains a broad low-energy absorption at 430 nm (ε_{max} 1560 $dm^3 mol^{-1} cm^{-1}$) which is tentatively assigned, like analogous cyclometallated platinum(II) derivatives,[10] to a metal-to-ligand charge transfer (MLCT) transition, namely (5d)Pt$\rightarrow\pi^*$(L). Complex **1** exhibits luminescence in solution and in the solid state. Emission at 542 nm in CH_3CN solution at room temperature is similarly ascribed to ^{3}MLCT. The solid-state emission is red-shifted to 568 nm with a shoulder at 604 nm [Fig. 2(b)] and is at a higher energy than the metal–metal-to-ligand charge transfer (MMLCT) emission (630 nm) of $[Pt_2(6\text{-phenyl-}2,2'\text{-bipyridine})_2(\mu\text{-dppm})]^{2+}$ which exhibits close intramolecular Pt–Pt contacts [3.270(1) Å].[7] The emission is therefore proposed to originate from ^{3}MLCT accompanied by partial excimeric character. Similar shifts in emission energy have recently been found for transmetallated gold(III) complexes.[11] A blue shift to 528 nm with well-resolved vibronic structure is observed in the frozen state, where the vibrational spacing of 1240 cm^{-1} is comparable to the skeletal stretching of the free ligand L.

Finally, it is pertinent to note that ligation of diphenylphosphinopropanoic acid does not necessitate the formation of complexes with complementary hydrogen bonding in the solid state. The molecular structure of the silver(I) dimer $[(PPh_3)(Ppa)Ag]_2(\mu\text{-}Cl)_2$ **2**, synthesised from the reaction of $[AgCl(PPh_3)]_4$ with Ppa, is comprised of bulky peripheral phenyl groups and no hydrogen bonding is apparent.[12] This situation is expected for complexes with congested geometry where possible hydrogen-bonding motifs are segregated and such interactions are precluded. Our future work will exploit phosphinocarboxylic acids as versatile building blocks in transition metal-based crystal engineering.

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Notes and references

† Satisfactory elemental analysis has been obtained. Selected data for **1**: ^{1}H NMR (CD_3CN): 2.44 (s, 3, Ph*Me*), 2.87–3.22 (m, 4, PC_2H_4), 6.64–8.33 (m, 24, aryl H); ^{31}P NMR (CD_3CN): 18.75 (J_{PtP} 3943 Hz); IR (KBr, cm^{-1}): 1709 ν(CO), 3448 ν(OH).

‡ Crystal data for **1**: $\{[C_{38}H_{32}N_2O_2PtP]PF_6\}$, M = 919.71, triclinic, $P\bar{1}$ (No. 2), a = 9.715(2), b = 20.479(8), c = 9.245(2) Å, α = 101.76(3), β = 95.01(2), γ = 88.46(3)°, V = 1794(1) Å^3, Z = 2, D_c = 1.703 g cm^{-3}, μ(Mo-Kα) = 40.53 cm^{-1}, F(000) = 904, T = 301 K. A yellow crystal of dimensions 0.15 × 0.10 × 0.25 mm was used. A total of 4688 independent reflections were measured on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) using ω–2θ scans. The structure was solved by Patterson methods and all 51 non-H atoms were refined anisotropically. The H(1) atom bonded to O(1) was located in the difference Fourier map. Convergence for 463 variable parameters by least-squares refinement on F with $w = 4F_o^2/[\sigma^2(I) + (0.024F_o^2)^2]$ for 3954 absorption-corrected (min, max transmission 0.596, 1.000) reflections with $I > 3\sigma(I)$ was reached at R = 0.044 and wR = 0.058. CCDC 182/1015.

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