Synthesis, Photophysics and Electrochemistry of Novel Luminescent Trinuclear Heterometallic Materials. Crystal Structure of [Pt^{II}(dppy)$_2$(PhC≡C)$_2${Cu^{I}(MeCN)$_2$}$_2$][PF$_6$]$_2$ (dppy = 2-diphenylphosphinopyridine)

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Treatment of [Pt(dppy)$_2$(PhC≡C)$_2$] (dppy = 2-diphenylphosphinopyridine) with 2 equivalents of [Cu(MeCN)$_4$]$^+$ or [Ag(MeCN)$_4$]$^+$ in dichloromethane afforded the trinuclear heterometallics, [Pt^{II}(dppy)$_2$(PhC≡C)$_2${Cu^{I}(MeCN)$_2$}$_2$]$^{2+}$ or [Pt^{II}(dppy)$_2$(PhC≡C)$_2${Ag^{I}(MeCN)}$_2$]$^{2+}$, in high yield; their photophysics and electrochemistry have been studied and the crystal structure of [Pt^{II}(dppy)$_2$(PhC≡C)$_2$-{Cu^{I}(MeCN)$_2$}$_2$] [PF$_6$]$_2$ determined.

There has been a growing interest in the study of heterometallic metal–metal bonded systems, which serve as models for the understanding of metal–metal bonding interactions. Although a number of homometallic d^8–d^8 and d^{10}–d^{10} complexes are known and their photophysics well studied,[1] corresponding studies on the heterometallic systems are rare.[2] In this communication, we report on the synthesis, photophysics and electrochemistry of a series of luminescent heterotrimetallic d^{10}–d^8–d^{10} complexes of platinum(II). The X-ray crystal structure of [Pt^{II}(dppy)$_2$(PhC≡C)$_2${Cu^{I}(MeCN)$_2$}$_2$][PF$_6$]$_2$ (dppy = 2-diphenylphosphinopyridine) is also reported.

Reaction of [Pt(dppy)$_2$(PhC≡C)$_2$] **1** with 2 equivalents of [M^{I}(MeCN)$_4$]$^+$ (M = Cu or Ag) in dichloromethane afforded [Pt^{II}(dppy)$_2$(PhC≡C)$_2${M^{I}(MeCN)$_x$}$_2$]$^{2+}$, isolated as either PF$_6^-$ or BF$_4^-$ salts [M^{I} = Cu^{I}, x = 1 or 2 (**2**); M^{I} = Ag^{I}, x = 1 (**3**)]. Recrystallization of [Pt^{II}(dppy)$_2$(PhC≡C)$_2${Cu^{I}-(MeCN)$_x$}$_2$][PF$_6$]$_2$ from MeCN–diethyl ether gave complexes with x = 2, while recrystallization from MeOH or CH$_2$Cl$_2$–diethyl ether gave complexes with x = 1. Attempts to prepare the analogous heterobimetallics by dropwise addition of a solution of [Cu(MeCN)$_4$]$^+$ to 1 equivalent of [Pt(dppy)$_2$-(PhC≡C)$_2$] **1** in dichloromethane did not give [Pt(dppy)$_2$(PhC≡C)$_2$Cu(MeCN)$_x$]$^+$ as the product. Instead, the heterotrimetallic PtCu$_2$ complex is obtained in lower yield. On the other hand, a similar reaction using [Ag(MeCN)$_4$]$^+$ and [Pt(dppy)$_2$(PhC≡C)$_2$] in 1 : 1 mole ratio did give the heterobimetallic complex [Pt(dppy)$_2$(PhC≡C)$_2$-Ag][BF$_4$] **4**. All the complexes show satisfactory elemental analyses and have been characterized by ^{1}H and ^{31}P NMR spectroscopy.†

Fig. 1 shows the perspective view of the cation of **2**, [Pt^{II}(dppy)$_2$(PhC≡C)$_2${Cu^{I}(MeCN)$_2$}$_2$]$^{2+}$.‡ The co-ordination geometry around each copper atom is a distorted tetrahedron while that for platinum is distorted square planar. The Cu $\cdots$ Pt $\cdots$ Cu moiety is held together by two bridging dppy and μ-η^2-PhC≡C$^-$ ligands. The two phosphorus atoms are co-ordinated to the central Pt atom and the two nitrogen atoms of the dppy ligands to the two separate Cu atoms. The copper–acetylide π interaction is essentially symmetrical with the Cu–C(22) and Cu–C(23) distances of 2.101(4) and 2.173(3) Å being quite similar. Similar Cu–C distances are found in [(PhC≡CCu)$_n$][4a] and [{PhC≡CCu(PMe$_3$)}$_4$].[4b] The C(22)–C(23) distance of 1.212(6) Å is indistinguishable from that found in unco-ordinated acetylenes (1.18–1.21 Å).[5] Slight deviation from linearity is observed in the arrangement of the acetylide moiety with a C(22)–C(23)–C(24) angle of 169.5(3)°. The Pt $\cdots$ Cu separation is 3.250(1) Å.

The electronic absorption spectra of complexes **2**–**4** show similar patterns, with a low-lying band at *ca.* 350 nm, similar to that observed for the monomer **1**. With reference to previous spectroscopic studies on the square-planar bis(tertiary phosphine)dialkynyl d^8 complexes[6] and the observed insensitivity of the band maxima to the nature of M^{I}, the band at *ca.* 350 nm is assigned to a metal-to-ligand charge-transfer (m.l.c.t.) [5d(Pt) $\longrightarrow$ π*(PhC≡C$^-$)] transition. However, since the 5d$_{xz}$ and 5d$_{xy}$ orbitals on Pt have the right symmetry to interact with the π(PhC≡C$^-$) orbitals, the transition is likely to have some intraligand (i.l.) character [π(PhC≡C$^-$) $\longrightarrow$ π*(PhC≡C$^-$)] mixed into it. [The PhC≡C–Pt–C≡CPh axis is taken to be the x- axis and P–Pt–P to be the y axis.]

Excitation of both solid and fluid solutions of **2**–**4** at λ > 370 nm resulted in long-lived low-energy photoluminescence. The photophysical data are collected in Table 1. The monomeric

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† Compound **2** was prepared by the reaction of a CH$_2$Cl$_2$ solution (10 cm^3) of **1** (0.1 mmol) with [Cu(MeCN)$_4$]PF$_6$ (0.2 mmol) in CH$_2$Cl$_2$ (10 cm^3) under an atmosphere of nitrogen. Reduction of volume followed by addition of diethyl ether gave the crude product which was recrystallized from MeCN–diethyl ether. Yield 80% (Found: C, 46.05; H, 2.85; N, 5.10. C$_{58}$H$_{50}$Cu$_2$F$_{12}$N$_6$P$_4$Pt requires C, 46.30; H, 3.35; N, 5.60%). ^{31}P NMR (MeCN): δ 20.95 ($J_{\mathrm{Pt-P}}$ 2644 Hz). The preparation of compound **3** was similar to that for **2** except that [Ag(MeCN)$_4$]BF$_4$ was used in place of [Cu(MeCN)$_4$]PF$_6$. Yield 40% (Found: C, 46.35; H, 2.65; N, 3.75. C$_{54}$H$_{44}$Ag$_2$B$_2$F$_8$N$_4$P$_2$Pt requires C, 46.50; H, 3.20; N, 4.00%). ^{31}P NMR (MeCN): δ 20.94 ($J_{\mathrm{Pt-P}}$ 2562 Hz). Compound **4** was prepared as for **3** except that the ratio of **1** to [Ag(MeCN)$_4$]BF$_4$ is 1 : 1. Yield 45% (Found: C, 53.25; H, 3.55; N, 2.55. C$_{50}$H$_{38}$AgBF$_4$N$_2$P$_2$Pt requires C, 53.70; H, 3.40; N, 2.50%). ^{31}P NMR (MeCN): δ 20.48 ($J_{\mathrm{Pt-P}}$ 2580 Hz).

‡ *Crystal data*. C$_{58}$H$_{50}$Cu$_2$F$_{12}$N$_6$P$_4$Pt, M = 1505.12, triclinic, space group $P\bar{1}$, crystal dimensions 0.11 × 0.25 × 0.25 mm, a = 10.201(1), b = 11.449(2), c = 13.937(2) Å, α = 103.31(1), β = 104.43(1), γ = 90.60(1)°, U = 1530.0(8) Å^3, Z = 1, D_c = 1.633 g cm^{-3}, μ(Mo-Kα) = 31.75 cm^{-1}, $F(000)$ = 744, no. of parameters = 376, R = 0.032 and R' = 0.041 for 5821 observed data with $I > 3\sigma(I)$ $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.55F_o^2)^2]$. Diffraction data were collected on an Enraf-Nonius diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The structure was solved by the heavy-atom method and refined by full-matrix least squares. All calculations were performed on a MicroVax II computer using the Enraf-Nonius SDP package.[3] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Photophysical data for complexes **1**–**4**

Complex	Absorption λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission Medium (T/K)	λ_{em}/nm (τ_0/μs)
1	266 (34 770), 350 (18 055)	Solid (298)	452, 502 (0.07 ± 0.01)
	430 (20)^a	Solid (77)	452, 499
		CH_2Cl_2 (298)	431, 450, 494 (0.044 ± 0.004)^b
		$CHCl_3$ (77)	443, 487
2	265 (sh) (46 895), 330 (sh) (12 865)^a	Solid (298)	576 (6.3 ± 0.6)
	262 (sh) (33 670), 348 (14 390)^c	Solid (77)	608
		CH_2Cl_2 (298)	522 (0.42 ± 0.04)^d
		MeCN (298)	527 (1.5 ± 0.1)^d
		Pr^{n}CN (77)	540
3	255 (sh) (48 960), 355 (11 420)^a	Solid (298)	501 (5.7 ± 0.3)
	255 (sh) (43 805), 352 (12 505)^c	Solid (77)	488, 545 (sh)
		CH_2Cl_2 (298)	588 (1.1 ± 0.1)^e
		MeCN (298)	440, 566
		EtOH–MeOH, 4:1 (77)	460 (sh), 510
4	260 (sh) (49 080), 372 (11 955)	Solid (298)	555 (1.0 ± 0.1)
	455 (3205)^a	Solid (77)	500, 603 (sh)
	260 (sh) (42 420), 350 (15 965)^c	CH_2Cl_2 (298)	527, 640 (1.2 ± 0.1)^f
		MeCN (298)	571, 609 (1.8 ± 0.2)^f
		Pr^{n}CN (77)	528
		EtOH–MeOH, 4:1 (77)	558

[a] In CH_2Cl_2. [b] [Complex] ≈ 1 mmol dm^{-3}. [c] In MeCN. [d] [Complex] ≈ 0.1 mmol dm^{-3}. [e] [Complex] ≈ 0.05 mmol dm^{-3}. [f] [Complex] ≈ 0.2 mmol dm^{-3}.

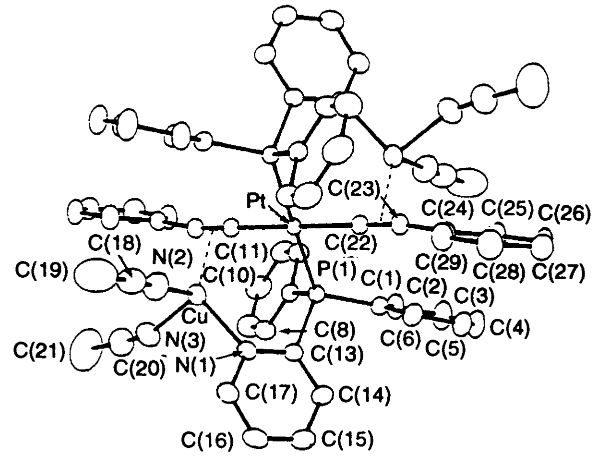

Fig. 1 Perspective drawing of the cation of **2**, $[Pt^{II}(dppy)_2(PhC{\equiv}C)_2\{Cu^I(MeCN)_2\}_2]^{2+}$, showing the atomic numbering scheme. Selected bond distances (Å) and angles (°): Pt–P(1) 2.3198(9), Pt–C(22) 2.002(4), Cu–N(1) 2.062(4), Cu–N(2) 2.093(5), Cu–N(3) 2.059(5), Cu–C(22) 2.101(4), Cu–C(23) 2.173(3), Cu–X 2.049(5), C(22)–C(23) 1.212(6), Pt···Cu 3.250(1), P(1)–Pt–C(22) 86.6(1), N(1)–Cu–N(2) 103.4(2), N(1)–Cu–N(3) 100.3(2), N(2)–Cu–N(3) 100.3(2), Pt–C(22)– C(23) 177.7(3), C(22)–C(23)–C(24) 169.5(3),Cu–C(22)–C(23) 76.9(2), Cu–C(23)–C(22) 70.3(2), N(1)–Cu–X 125.1(1), N(2)–Cu–X 111.4(1), N(3)–Cu–X 113.1(1), Cu–X–C(22) 86.4(3), Cu–X–C(23) 93.6(3) [X is the mid-point of C(22)–C(23)]

complex **1** also exhibits photoluminescence both in the solid state and in fluid solutions; however, for this complex the excited states are short-lived and vibronic structures are observable in the emission spectrum with a vibrational progression of *ca.* 2114 cm^{-1}, comparable to the ν(C≡C) stretching frequency of 2140 cm^{-1} in the ground-state molecule. This is assigned to the ^{3}m.l.c.t./i.l. [5d(Pt) $\longrightarrow$ π^*(PhC≡C$^-$)]/[π(PhC≡C$^-$) $\longrightarrow$ π^*(PhC≡C$^-$)] transition. For complexes **2**–**4**, the emission occurs at longer wavelength (> 540 nm) although in some cases, a higher energy band at *ca.* 440–500 nm is also observable. We believe that the emission displays multiple luminescence. When the complexes are excited at $\lambda \leqslant 350$ nm, the high energy band is dominant. However, upon excitation at longer wavelengths ($\lambda > 400$ nm), the low energy band becomes predominant, with the high energy one of much lower intensity or in many cases absent. The high energy emission is likely to be ^{3}m.l.c.t./i.l. in origin, similar to that of the monomer **1**. The low energy emission is likely to be perturbed by the presence of the M^I centre. A comparison of the solid-state emission spectra of **2** and $[Cu_2(dppy)_2(MeCN)_2][PF_6]_2$ shows that the low energy band at *ca.* 576 nm at 298 K (608 nm at 77 K) is only present in **2** {$\lambda_{em} \approx 467$ nm for $[Cu_2(dppy)_2(MeCN)_2][PF_6]_2$}. This suggests that this transition is unlikely to be a $^3[\pi\pi^*$(dppy)/m.l.c.t.(Cu $\longrightarrow$ dppy)] transition of the Cu(dppy) chromophore as found in other phosphine complexes of copper(I)[7] but is unique to the Pt···Cu system. However, in dichloromethane **2** displays an emission band at *ca.* 522 nm, comparable to that observed in $[Cu_2(dppy)_2(MeCN)_2][PF_6]_2$ ($\lambda_{em} \approx 533$ nm). It is likely that in solution the non-rigidity of the complex renders the Pt···Cu perturbation insignificant and only emissions characteristic of the separate entities are observable. However, in the solid-state, **3** displays an emission band at *ca.* 501 nm, similar to that observed for $[Ag_2(dppy)_2(MeCN)_2][BF_4]_2$. The low energy emission band has been obscured by the intense $^3[\pi\pi^*$(dppy)/m.l.c.t.(Ag $\longrightarrow$ dppy)] transition in the solid state at 298 K, which reveals its presence on lowering the temperature to 77 K as a shoulder at *ca.* 545 nm and in CH_2Cl_2 as a discrete band at *ca.* 588 nm. The observation of the 588 nm band in CH_2Cl_2 suggests that the Pt···Ag interaction is strong enough to exist in solution.

Cyclic voltammetric studies on complexes **1** and **3** in MeCN (0.1 mol dm^{-3} NBu_4PF_6) showed only couples characteristic of dppy oxidation. No reduction processes were observed for **1** or dppy up to -2.0 V *vs.* the ferrocenium–ferrocene couple, while irreversible reduction couples were observed at -0.48 and -0.92 V for **3**, corresponding to Ag^I–Ag^0 reductions. Complex **2** displays quasi-reversible oxidation couples at *ca.* $+0.40$ and $+0.68$ V *vs.* the ferrocenium–ferrocene couple in addition to the ligand-centred oxidations, and an irreversible reduction process at *ca.* -1.06 V. The oxidation processes are tentatively assigned to Cu^I $\longrightarrow$ Cu^{II} oxidations and the reduction is also likely to be metal centred in nature.

It is envisaged that the presence of easily displaced acetonitrile ligands in these novel complexes would provide a synthetic strategy for the generation of a wide variety of novel polymetallic supramolecular species.

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