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Luminescent heterohexanuclear complexes with platinum alkynyl and silver diphosphine as components

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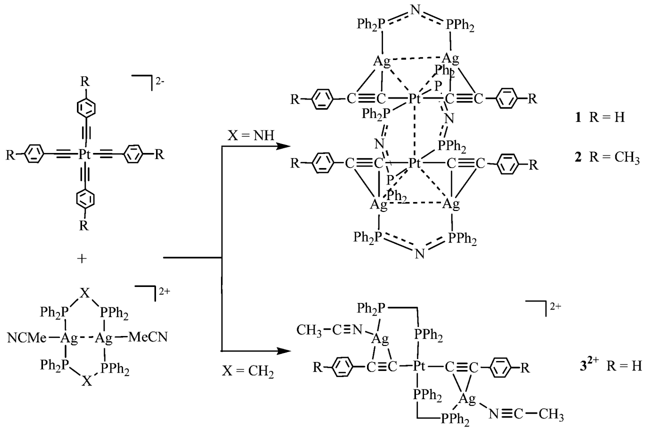
Reactions between the building blocks $[Ag_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2]^{2+}$ and $[Pt(C{\equiv}CC_6H_4R\text{-}p)_4]^{2-}$ (R = H, CH_3) afforded strongly luminescent acetylide-linked neutral heterohexanuclear complexes $Pt_2Ag_4(\mu\text{-}Ph_2PNPPh_2)_4(C{\equiv}CC_6H_4R\text{-}p)_4$ (R = H, 1; CH_3, 2) for X = NH, but a heterotrinuclear complex cation $[PtAg_2(\mu\text{-}PPh_2CH_2PPh_2)_2(C{\equiv}CC_6H_5)_2(CH_3CN)_2]^{2+}$ (3^{2+}) for X = CH_2.

The chemistry of metal alkynyl complexes has been the subject of intense study in recent years because of the potential applications of these complexes as luminescent, non-linear optical, electrical conductive and liquid-crystalline materials.[1] Relative to homometallic alkynyl complexes,[2] the chemistry concerning heterometallic alkynyl complexes has received less attention.[3] Furthermore, most of them were attained by direct reactions of alkynyl with simple metal ions or metal components; in few cases were they derived from self-assembly between a metal alkynyl and another metal component.[4]

We are interested in developing luminescent molecular materials utilizing metal alkynyl and metal diphosphine as building blocks, where the former block affords a potential bridging alkynyl and the latter possesses easily substituted coordination sites. Thus, self-assembly between $[Pt(C{\equiv}CC_6H_4R\text{-}p)_4]^{2-}$ (R = H, CH_3) and $[Ag_2(\mu\text{-}PPh_2XPPh_2)_2(MeCN)_2]^{2+}$ results in neutral heterohexanuclear complexes $Pt_2Ag_4(\mu\text{-}Ph_2PNPPh_2)_4(C{\equiv}CC_6H_4R\text{-}p)_4$ (R = H, **1**; CH_3, **2**) for X = NH but a heterotrinuclear complex $[PtAg_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(C{\equiv}CC_6H_5)_2(CH_3CN)_2]^{2+}$ ($\mathbf{3}^{2+}$) for X = CH_2 (Scheme 1).

Complexes **1**, **2** and **3** $(SbF_6)_2$ were prepared by the reactions of $[NBu_4]_2[Pt(C{\equiv}CC_6H_4R\text{-}p)_4]$[5] with $[Ag_2(PPh_2XPPh_2)_2(MeCN)_2](SbF_6)_2$[6] (X = NH, **1** and **2**; CH_2, **3** $(SbF_6)_2$) in equimolar ratios and characterized by elemental analyses, IR, ^{31}P NMR, and UV–Vis spectroscopy† and X-ray crystallography.‡ A 20–30 cm^{-1} red shift of the ν(C≡C) vibration in complexes **1–3** $(SbF_6)_2$ (2055, 2058 and 2058 cm^{-1}, respectively) relative to that in the precursor compound $[NBu_4]_2[Pt(C{\equiv}CC_6H_4R\text{-}p)_4]$ (R = H, 2083 cm^{-1}; CH_3, 2077 cm^{-1}) is the consequence of π-bridging of the alkynyl. The ^{31}P NMR spectra show one triplet and one doublet due to remarkable Pt–P (J_{Pt-P} = 1000–1300 Hz) and Ag–P (J_{Ag-P} = 400–550 Hz) couplings, respectively, for both the Pt_2Ag_4 and $PtAg_2$ complexes because there are two sets of inequivalent P donors (bonded to Pt and Ag, respectively) in each complex.



Scheme 1

The formation of neutral heterohexanuclear clusters for X = NH, in contrast to a heterotrinuclear coordination cation for X = CH_2, should be related to the easy deprotonation character of PPh_2NHPPh_2. Both heterohexanuclear and heterotrinuclear complexes are not derived from direct incorporation of the metal component $[Pt(C{\equiv}CC_6H_4R\text{-}p)_4]^{2-}$ (R = H, CH_3) with $[Ag_2(\mu\text{-}PPh_2XPPh_2)_2(MeCN)_2]^{2+}$ and self-assembly between the two components results in the occurrence of component rupture and recombination because of the strong affinity of P donors for Pt^{II} atoms. In fact, **1** and **2** are better regarded as the combination of one anionic component $[Pt_2(\mu\text{-}Ph_2PNPPh_2)_2(C{\equiv}CC_6H_4R\text{-}p)_4]^{2-}$ (R = H, **1**; CH_3, **2**) with two cationic fragments $[Ag_2(\mu\text{-}Ph_2PNPPh_2)]^{+}$.

As shown in Fig. 1, the neutral heterohexanuclear molecule adopts a face-to-face arrangement, in which each Pt^{II} atom is

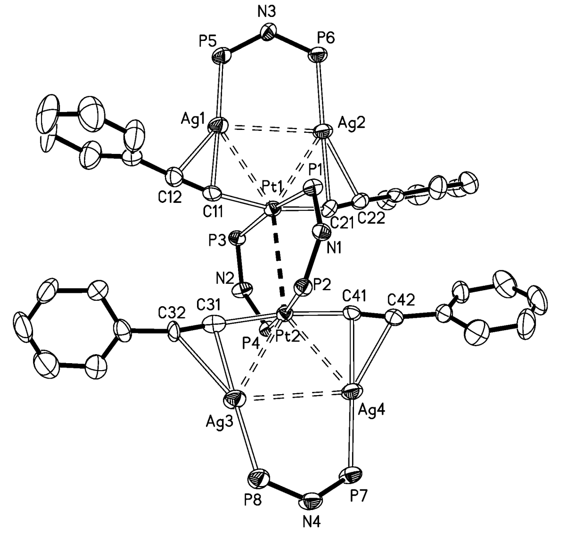


Fig. 1 ORTEP drawing of 1 (30% thermal ellipsoids) with atom labeling scheme. Selected bond distances (Å) and angles (°): Pt1–Pt2 3.1534(8), Pt1–Ag1 2.8994(15), Pt1–Ag2 2.9381(15), Pt2–Ag3 2.9347(15), Pt2–Ag4 2.9245(14), Ag1–Ag2 3.179(2), Ag3–Ag4 3.426(2), Pt1–P1 2.365(4), Pt1–P3 2.355(4), Pt1–C11, 1.996(19), Pt1–C21 1.980(17), Ag1–P5 2.380(5), Ag1–C11 2.313(15), Ag1–C12 2.527(18), P1–N1 1.596(13), P2–N1 1.587(13), C11–C12 1.23(2), C11–Pt1–C21 166.7(6), P1–Pt1–P3 172.27(14), C11–Pt1–P3 93.5(5), C21–Pt1–P3 88.1(5), C11–Pt1–P1 87.9(5), C21–Pt1–P1 92.3(5) , Ag1–Pt1–Ag2 65.98(4), Ag3–Pt2–Ag4 71.58(4), C11–Ag1–P5 173.5(5), C11–Ag1–C12 28.9(6), P5–Ag1–C12 146.5(4).

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bound to two *trans* alkynyl ligands in η^1 (σ) coordination and to two *trans* P donors from Ph_2PNPPh_2. The two platinums are bridged by two Ph_2PNPPh_2 to form an eight-membered ring $Pt(Ph_2PNPPh_2)_2Pt$. The Pt^{II} atoms exhibit approximate square-planar coordination geometry, in which the coordination planes of two platinum centres oriented parallel to each other are almost perpendicular to the plane built by the four P donors bonded to the Pt^{II} centres. It is noteworthy that Pt···Pt distances for **1** [3.1534(8) Å] and **2** [3.1114(9) Å] are much shorter than those observed in $Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(C\equiv CC_6H_4R\text{-}p)_4$ (3.25–3.44 Å),[7] indicative of the presence of stronger metal–metal interactions. The shortening of the Pt···Pt distance may be related to the linkage of the $[Ag_2(PPh_2PNPPh_2)]^+$ moiety by two alkynyls in the component $[Pt_2(\mu\text{-}Ph_2PNPPh_2)_2(C\equiv CC_6H_4R\text{-}p)_4]^{2-}$, which pulls the platinum atoms into close proximity as a result of the reduced donor strength of the alkynyls upon Ag^I π-coordination.[3,7] Each Ag^I atom is also bridged by one Ph_2PNPPh_2 ligand. The Ag–Ag and Ag–Pt distances are in the range 3.179(2)–3.330(2) and 2.8994(15)–2.9381(15) Å, respectively. Deprotonation of PPh_2NHPPh_2 in **1** and **2** is confirmed by the significantly shorter P–N distances (1.586–1.628 Å) compared with those (1.676–1.725 Å) in $[Ag_2(\mu\text{-}PPh_2NHPPh_2)_3](BF_4)_2$.[6]

In heterotrinuclear complex **3** $(SbF_6)_2$, each Pt atom is located in an approximately square-planar environment with P_2C_2 donors and the silver atom adopts a distorted triangle-planar geometry, bonded by phenylacetylide in a π-coordination (η^2-bonding) mode like that observed in **1** and **2**. The Pt···Ag distance (3.296(8) Å), however, is much longer than those found in **1** and **2**.

The absorption and emission data of complexes **1–3** $(SbF_6)_2$ are summarized in Table 1. Both **1** and **2** show two low-energy absorption bands (*ca.* 485 and 340–400 nm) in dichloromethane or acetonitrile. **3** $(SbF_6)_2$ also displays two absorption bands (*ca.* 370 and *ca.* 310 nm) in dichloromethane and acetonitrile.

Upon excitation at λ > 335 nm, complexes **1** and **2** exhibit strong luminescence in both the solid state and fluid solution at room temperature. Excitation of acetonitrile solutions of **1** and **2** in 298 K gave a low energy emission band at *ca.* 711 nm for **1** and 682 for **2** with a long-lived lifetime (τ_{em} = 8.7 µs for **1** and 12.1 µs for **2**). The emission lifetime in the microsecond time scale is suggestive of a triplet state origin. With reference to the literature work[3,7] on the related polynuclear Pt^{II}–Ag^I acetylide complexes together with the higher emission energy for **2** relative to **1**, the low energy emission is tentatively assigned as a metal cluster to acetylide $[Pt_2Ag_4 \rightarrow RC\equiv C^-]$ MMLCT triplet state origin in view of the short Pt–Pt and Pt–Ag contacts. The blue shift in the emission energies from **1** to **2** could be ascribed to the higher π* energy in **2** owing to the presence of an electron-donating methyl substituent in the acetylide $^-C\equiv CC_6H_4CH_3\text{-}p$. **3** $(SbF_6)_2$ displays an emission band at *ca.* 579 nm in the solid state with lifetime of 6.7 µs. In dichloromethane or acetonitrile, however, **3** $(SbF_6)_2$ shows different emission bands with variation in excitations. Excitation of **3** $(SbF_6)_2$ at 300–345 nm gives a broad emission band at *ca.* 420 nm, whereas an emission band at 530 nm is observed when it is excited at 420 nm. More detailed theoretical and spectroscopic studies are being pursued to assign origins of the dual emission bands.

Table 1 Photophysical data for complexes **1**,**2**, and **3** $(SbF_6)_2$

	Medium (298K)	Absorption λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Emission λ_{max}/nm (τ_{em}/µs)
1	Solid		712 (7.2)
	CH_2Cl_2	487 (19140), 401 (10970)	705 (7.4)
	MeCN	485 (23930), 346 (50000)	711 (8.7)
2	Solid		704 (9.2)
	CH_2Cl_2	485 (10340), 401 (9386)	698 (11.4)
	MeCN	484 (17635) , 350 (64460)	682 (12.1)
3 $(SbF_6)_2$	Solid		579 (6.7)
	CH_2Cl_2	376 (18890), 312 (20800)	528, 420 (8.8)
	MeCN	365 (17740), 313 (19430)	533, 413 (9.3)

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Notes and references

† $[NBu_4]_2[Pt(C\equiv CC_6H_4R\text{-}p)_4]$ (R = H or CH_3) and $[Ag_2(\mu\text{-}Ph_2PXPPh_2)_2(MeCN)_2](SbF_6)_2$ (X = NH or CH_2) in CH_2Cl_2 solutions were mixed in an equimolar ratio and stirred at room temperature for one day to give red or yellow solutions. Layering hexane onto the concentrated solutions afforded in a few days red or yellow crystals. Yield: 39% for **1**·MeOH·5H_2O, 41% for **2**·4CH_2Cl_2, 40% for **3** $(SbF_6)_2$·6H_2O. Elemental analyses were satisfactory for the complexes. For **1**·MeOH·6H_2O, IR (Nujol) ν/cm^{-1}: 2055 (m, C≡C); ^{31}P NMR ($CDCl_3$, ppm): 53.3 (s), 21.9 (s). For **2**·4CH_2Cl_2, IR (Nujol) ν/cm^{-1}: 2058 (m, C≡C); ^{31}P NMR ($CDCl_3$, ppm): 53.0 (d, J_{Ag-P} = 458 Hz), 2.9 (t, J_{Pt-P} = 1032 Hz). For **3** $(SbF_6)_2$·6H_2O, IR (Nujol) ν/cm^{-1}: 2102, 2058 (m, C≡C); ^{31}P NMR ($CDCl_3$, ppm): 11.8 (t, J_{Pt-P} = 1250 Hz), 2.3 (d, J_{Ag-P} = 528 Hz).

‡ *Crystal data* for **1**·MeOH·5H_2O: $C_{129}H_{114}Ag_4N_4O_6P_8Pt_2$, M = 2885.66, monoclinic, space group $P2_1/n$, a = 18.5759(3), b = 22.4019(3), c = 29.9701(1) Å, β = 103.836(1)°, V = 12109.7(3) Å^3, Z = 4, μ(Mo–Kα) = 3.097 mm^{-1}, D_c = 1.583 g cm^{-3}. The structure, refined on F^2, converged for 15810 unique reflections (R_{int} = 0.0546) and 11380 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0681 and wR_2 = 0.1596 and a goodness-of-fit = 1.276. CCDC 210710.

Crystal data for **2**·4CH_2Cl_2: $C_{136}H_{115}Ag_4Cl_8N_4P_8Pt_2$, M = 3158.34, monoclinic, space group $P2_1/c$, a = 13.6487(4), b = 34.4909(8), c = 28.4079(9) Å, β = 96.295(1)°, V = 13292.6(7) Å^3, Z = 4, μ(Mo–Kα) = 2.981 mm^{-1}, D_c = 1.578 g cm^{-3}. The structure, refined on F^2, converged for 17401 unique reflections (R_{int} = 0.0621) and 12861 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0796 and wR_2 = 0.1821 and a goodness-of-fit = 1.251. CCDC 210711.

Crystal data for **3** $(SbF_6)_2$·6H_2O: $C_{35}H_{36}AgF_6NO_3P_2Pt_{0.5}Sb$, M = 1021.75, orthorhombic, space group $Pbca$, a = 18.1670(3), b = 20.5004(4), c = 22.0406(3) Å, V = 8208.6(2) Å^3, Z = 8, μ(Mo–Kα) = 2.968 mm^{-1}, D_c = 1.654 g cm^{-3}. The structure, refined on F^2, converged for 7021 unique reflections (R_{int} = 0.0414) and 4524 observed reflections with $I > 2\sigma(I)$ to give R_1 = 0.0502 and wR_2 = 0.1106 and a goodness-of-fit = 1.166. CCDC 210712.

See http://www.rsc.org/suppdata/cc/b3/b305284b/ for crystallographic data in .cif format for all three compounds.

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