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Luminescence and aggregation studies of hexanuclear platinum–copper acetylide complexes. Crystal structure of the luminescent metal–metal bonded dimer [Pt$_2$Cu$_4$(C≡CPh)$_8$]$_2$

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Received 18th May 1999, Accepted 14th July 1999

The luminescent metal–metal bonded dimer of a known hexanuclear platinum–copper acetylide complex has been synthesized and characterized by X-ray crystallography; the complex is shown to exist in the dimeric form only in concentrated solution through a Pt–Pt bonding interaction.

The chemistry of alkynylmetal complexes has received growing attention because of the potential use of the complexes as non-linear optical, low dimensional, conducting, and liquid-crystalline materials.[1] The ability of alkynyl groups to coordinate to metal centres in terminal and various bridging modes has made them versatile ligands in the synthesis of polynuclear metal complexes.[2] Work by us[3] and others[4,5] has shown that homo- and hetero-metallic polynuclear platinum complexes could be prepared with μ-C≡CR bridging ligands; some of which have been shown to exhibit rich luminescence properties.[3,4a,b] In an attempt to further explore the rich luminescence behaviour of polynuclear platinum acetylide complexes, we were intrigued by the report by Forniés and co-workers on an interesting class of hexanuclear [Pt$_2$M$_4$(C≡CR)$_8$] complexes (M = Cu, Ag, Au).[5] In this communication, the synthesis, crystal structure, and luminescence behaviour of a novel polynuclear platinum–copper acetylide complex [Pt$_2$Cu$_4$(C≡CPh)$_8$]$_2$ **1**, which is a dimer of the hexanuclear complex [Pt$_2$Cu$_4$(C≡CPh)$_8$] (0.5**1**), are reported. The luminescence behaviour of the [Pt$_2$Ag$_4$(C≡CPh)$_8$]$_2$ **2** analogue and the related [Pt$_2$Cu$_4$(C≡CR)$_8$]$_2$ (R = C$_6$H$_4$OMe-*p* **3**) and [Pt$_2$Cu$_4$(C≡CR)$_8$] (R = Me$_3$Si **4**, ^{t}Bu **5**[5c]) derivatives are also reported. Preliminary results have previously been presented.[6] The present complexes feature an example of ligand-unsupported Pt(II)$\cdots$Pt(II) interaction, which plays a dominant role in the dimer formation process.[7]

Reaction of [NBu$_4$]$_2$[Pt(C≡CR)$_4$] (R = Ph, C$_6$H$_4$OMe-*p*) (0.1 mmol) with [Cu(MeCN)$_4$][PF$_6$] (0.2 mmol) in a 1:2 molar ratio in acetone (10 ml) under an inert atmosphere of nitrogen afforded both **1** and **3** as a deep red precipitate. Subsequent recrystallization by layering acetone onto a concentrated CH$_2$Cl$_2$ solution gave both **1** and **3** as air-stable garnet crystals. Similar reaction with R = Me$_3$Si gave **4** as yellow crystals. The preparation of compound **2** was similar to that for **1** except that [Ag(MeCN)$_4$][BF$_4$] was used in place of [Cu(MeCN)$_4$][PF$_6$], to give yellow crystals of [Pt$_2$Ag$_4$(C≡CPh)$_8$] as reported by Forniés and co-workers,[5a,c] and an additional red form of the same empirical formula.† It is likely that the red form is a dimer of [Pt$_2$Ag$_4$(C≡CPh)$_8$] with formula [Pt$_2$Ag$_4$(C≡CPh)$_8$]$_2$ **2**, similar to that of **1**. All the complexes show satisfactory elemental analyses, and have been characterized by IR and ^{1}H NMR spectroscopy. The shift in the ν(C≡C) absorption to a lower wavenumber (2028 cm^{-1}) in **1** than in [NBu$_4$]$_2$[Pt(C≡CPh)$_4$] (2077 cm^{-1}) is suggestive of a π-bonding mode of the alkynyl ligands.

Fig. 1 shows a perspective drawing of **1** with the atomic numbering scheme.‡ The structure of **1** consists of two distorted octahedral arrays of Pt$_2$Cu$_4$ metal cores linked together by an unsupported Pt$\cdots$Pt interaction [Pt(2)$\cdots$Pt(3), 3.116(2) Å], with each octahedron consisting of two platinum metal centres in a mutually *trans* disposition and four copper atoms in an equatorial plane, bonded by the alkynyl ligands in a π-coordination mode. The Pt$\cdots$Cu bond distances of 2.931(2)–3.021(2) Å are suggestive of some very weak metal–metal bonding. However, the Cu$\cdots$Cu distances [3.084(3)–4.361(4) Å] are very long and no significant Cu–Cu bonding is thought to exist within the metal framework.[8] The two square-planar [Pt(C≡CPh)$_4$] fragments on the upper octahedron are found to be almost eclipsed, with a torsion angle Pt(1)–C(1)–Pt(2)–C(9) of 7.8° between adjacent fragments; the other two [Pt(C≡CPh)$_4$] fragments on the lower octahedron are found to be staggered, with a torsion angle Pt(3)–C(17)–Pt(4)–C(25) of 40.8°. The [Pt(C≡CPh)$_4$] fragments containing Pt(2) and Pt(3) have also been observed to be staggered, with a torsion angle of 44.6°.

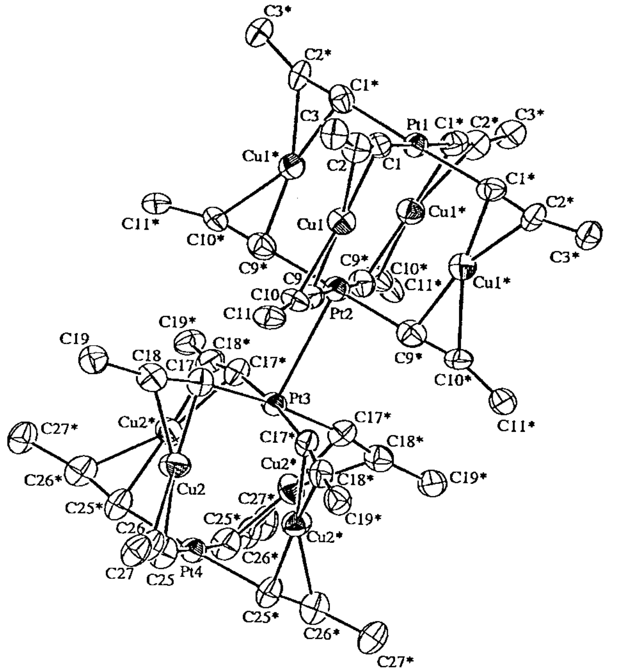

Fig. 1 Perspective drawing of complex **1** with atomic numbering scheme. All phenyl rings and hydrogen atoms with the exception of the *ipso* carbon atoms have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability levels. Selected bond lengths (Å) and angles (°): Pt(1)$\cdots$Pt(2) 3.858(2), Pt(3)$\cdots$Pt(4) 3.934(2), Pt(2)$\cdots$Pt(3) 3.116(2), Pt(1)$\cdots$Cu(1) 3.012(2), Pt(2)$\cdots$Cu(1) 3.021(2), Pt(3)$\cdots$Cu(2) 2.942(2), Pt(4)$\cdots$Cu(2) 2.931(2), Cu(1)–C(1) 1.97(1), Cu(1)–C(2) 2.13(2), Cu(1)–C(9) 2.00(1), Cu(1)–C(10) 2.16(1), Cu(2)–C(17) 2.04(1), Cu(2)–C(18) 2.14(2), Cu(2)–C(25) 2.03(2), Cu(2)–C(26) 2.13(2), C(1)–C(2) 1.18(2), C(9)–C(10) 1.22(2), C(17)–C(18) 1.22(2), C(25)–C(26) 1.17(2); C(1)–Pt(1)–C(1) 178.8(8), C(9)–Pt(2)–C(9) 178.0(8), C(17)–Pt(3)–C(17) 174.7(8), C(25)–Pt(4)–C(25) 176.6(9), C(1)–Pt(1)–C(1) 89.994(9), C(9)–Pt(2)–C(9) 89.98(2), C(17)–Pt(3)–C(17) 89.88(4), C(25)–Pt(4)–C(25) 89.95(3), C(1)–Pt(1)–Pt(2)–C(9) 7.84, C(1)–Pt(1)–Pt(3)–C(17) 36.81, C(1)–Pt(1)–Pt(4)–C(25) 4.02, C(9)–Pt(2)–Pt(3)–C(17) 44.64, C(9)–Pt(2)–Pt(4)–C(25) 3.81, C(17)–Pt(3)–Pt(4)–C(25) 40.83, Pt(1)–C(1)–Cu(1) 95.9(6), Pt(2)–C(9)–Cu(1) 97.5(6), Pt(3)–C(17)–Cu(2) 92.9(6), Pt(4)–C(25)–Cu(2) 92.0(6).

Table 1 Photophysical data for the complex **1**–**5**

Complex	Absorption λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})[a]	Emission medium (T/K)	λ_{em}/nm (τ_0/μs)
$[Pt_2Cu_4(C\equiv CPh)_8]_2$ **1**	268 (194 800),	Solid (298)	700 (0.48 ± 0.05)
	364 (57 160),	Solid (77)	720
	418 (54 170)	EtOH–MeOH, 4:1 (77)	560, 725
$[Pt_2Ag_4(C\equiv CPh)_8]_2$ **2**	314 (70 000),	Solid (298)	659
	358 (73 300),	Solid (77)	688
	394 (77 830)		
$[Pt_2Ag_4(C\equiv CPh)_8]$ 0.5**2**		Solid (298)	545 (3.04 ± 0.30)
		Solid (77)	565
		EtOH–MeOH, 4:1 (77)	560
$[Pt_2Cu_4(C\equiv CC_6H_4OMe\text{-}p)_8]_2$ **3**	376 (59 040),	Solid (298)	740 (3.0 ± 0.3)
	436 (72 660)	Solid (77)	714
		EtOH–MeOH, 4:1 (77)	560, 740
$[Pt_2Cu_4(C\equiv CSiMe_3)_8]$ **4**	342 (20 640),	Solid (298)	595 (7.2 ± 0.7)
	404 (21 790)	Solid (77)	643
		EtOH–MeOH (77)	632
$[Pt_2Cu_4(C\equiv C^tBu)_8]$ **5**	340 (19 340),	Solid (298)	576 (6.0 ± 0.3)
	400 (18 110)	Solid (77)	615
		EtOH–MeOH, 4:1 (77)	610

[a] In CH_2Cl_2, [Pt] ≈ 10^{-5}.

Dissolution of complex **1** in dichloromethane gave a yellow solution, which upon increasing concentration turned red. The electronic absorption spectrum of a dilute solution of **1** in dichloromethane exhibits bands at 268 (ε = 194800 dm^3 mol^{-1} cm^{-1}), 364 (57160) and 418 (54170) nm. An absorption coefficient of the order of 10^4 indicates that the electronic transitions are both spin- and orbital-allowed. Close scrutiny of the electronic absorption spectra of **1** shows that in dilute solutions bands at *ca.* 364 and 418 nm dominate, while a new band grows in as a shoulder at *ca.* 530–540 nm as the complex concentration increases (Fig. 2). The shoulder at 530–540 nm is found not to obey Beer's Law and these observations are best interpreted in terms of an equilibrium occurring in solution. The bands at 364 and 418 nm which dominate the low-concentration spectra are logically assigned as being due to the monomeric $[Pt_2Cu_4(C\equiv CPh)_8]$ complex; the identity of which has been established by ^{195}Pt NMR studies which show only a singlet at δ −4110, characteristic of the monomeric species. It is likely that in dilute solutions, **1** exists as the dissociated monomeric $[Pt_2Cu_4(C\equiv CPh)_8]$ form (0.5**1**) while in concentrated solutions, dimerization of $[Pt_2Cu_4(C\equiv CPh)_8]$ to give **1** occurs, giving the following equilibrium:

$$\underset{0.5\mathbf{1}}{2[Pt_2Cu_4(C\equiv CPh)_8]} \overset{K}{\rightleftharpoons} \underset{\mathbf{1}}{[Pt_2Cu_4(C\equiv CPh)_8]}$$

with the dimerization equilibrium constant given by $K = [\mathbf{1}]/[0.5\mathbf{1}]^2$.

A plot of $[\mathbf{1}]/(A_{530nm})^{\frac{1}{2}}$ *vs.* $(A_{530nm})^{\frac{1}{2}}$ over the concentration range 1×10^{-3} M < [**1**] < 1×10^{-2} M, yields a straight line (Fig. 2 insert). Analysis of the absorption spectral data gives a K value of 85 ± 10 M^{-1} (T = 298 K) and a molar absorption coefficient ε(530 nm) = (52.9 ± 0.5) × 10^3. A similar K value has also been obtained when starting from $[Pt_2Cu_4(C\equiv CPh)_8]$ for the aggregation studies. A dimerization model appears to account for the aggregation at concentrations <10^{-2} M. However, upon increasing the concentration of **1** further, the plot of $[\mathbf{1}]/(A_{530nm})^{\frac{1}{2}}$ *vs.* $(A_{530nm})^{\frac{1}{2}}$ starts to deviate slightly from linearity at very high Pt(II) concentrations (≈10^{-2} M < [**1**] < 10^{-1} M), suggesting that higher oligomers may form which also absorb in a similar region. Similarly, dissolution of the red form $[Pt_2Ag_4(C\equiv CPh)_8]_2$ **2** in dichloromethane gave a yellow solution, which turned red with increasing concentration. On the other hand, dissolution of the yellow form $[Pt_2Ag_4(C\equiv CPh)_8]$ in dichloromethane gave a yellow solution which, upon increasing the concentration, turned red. This is supportive of the assignment that the yellow form corresponds to the monomeric $[Pt_2Ag_4(C\equiv CPh)_8]$ while the red form is the dimer $[Pt_2Ag_4(C\equiv CPh)_8]_2$. A similar aggregation phenomenon is also observed in $[Pt_2Cu_4(C\equiv CC_6H_4OMe\text{-}p)_8]$, but is absent in $[Pt_2Cu_4(C\equiv C^tBu)_8]$ and $[Pt_2Cu_4(C\equiv CSiMe_3)_8]$. It is likely that the $[Pt_2Cu_4(C\equiv C^tBu)_8]$ and $[Pt_2Cu_4(C\equiv CSiMe_3)_8]$ complexes, with the bulky ^{t}Bu and Me_3Si groups, do not favour a dimerization process. Similar dimerization or oligomerization processes have been reported for other square-planar d^8 metal complexes in solution,[9] in which the planarity of the molecule could lead to extensive stacking interactions.[7]

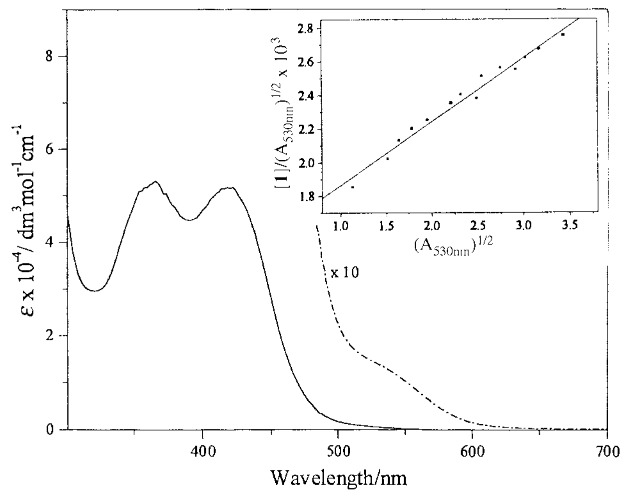

Fig. 2 UV-Vis absorption spectra of $[Pt_2Cu_4(C\equiv CPh)_8]_2$ **1** with concentrations 5.06 × 10^{-4} M (—) and 1.0 × 10^{-2} M (–•–) in CH_2Cl_2 at 298 K. The insert shows a plot of $[\mathbf{1}]/A_{530nm})^{\frac{1}{2}}$ *vs.* $(A_{530nm})^{\frac{1}{2}}$ over the concentration range 1 × 10^{-3} M < [**1**] < 1 × 10^{-2} M in dichloromethane solution.

Upon excitation of **1** at λ > 350 nm in 77 K EtOH–MeOH glass (4:1 v/v), dual luminescence behaviour is observed with emission maxima occurring at *ca.* 560 and 725 nm, while excitation of solid samples of **1** at 77 K and 298 K gave rise only to the long-lived intense red emissions centred at *ca.* 720 and 700 nm, respectively (Table 1). The emission lifetime in the microsecond range is suggestive of a triplet origin. It is likely that the low-energy emission which is absent in the mononuclear $[Pt(C\equiv CPh)_4]^{2-}$, is characteristic of the polynuclear mixed metal acetylide core. Solid samples of 0.5**2** are found to emit at 545 nm while those of the dimeric red form **2** emit at a lower energy with an emission maximum at 659 nm. In view of the solid-state emission characteristics of the yellow 0.5**2** and the red **2**, and the occurrence of an emission at a higher energy of 595 and 576 nm in solid samples of the monomeric **4** and **5**, respectively, it is likely that the low energy emission at *ca.* 700 nm in **1** is characteristic of the dimeric $[Pt_2Cu_4(C\equiv CPh)_8]_2$ cluster, while the band at 560 nm observed in the 77 K glass is attributed to the monomeric [$Pt_2Cu_4(C{\equiv}CPh)_8$] species which is in equilibrium with the dimeric species in solution. The lower emission energies of **4** and **5** than 0.5**1** are in line with the better σ-electron donating ability of the ^{t}BuC≡C and $Me_3SiC{\equiv}C$ groups than PhC≡C, and with reference to our previous studies on polynuclear metal acetylides,[10] are suggestive of an emissive origin of substantial acetylide-to-metal cluster core ligand-to-metal charge transfer [$RC{\equiv}C^- \rightarrow Pt_2Cu_4$] LMCT triplet character. Similarly, the 545 nm band in 0.5**2** is tentatively assigned as derived from a [$RC{\equiv}C^- \rightarrow Pt_2Ag_4$] LMCT triplet state. On going from the monomeric 0.5**1** and 0.5**2** to the respective dimeric **1** and **2**, a red shift in the emission energies occurs from 560 nm in 0.5**1** to 700 nm in **1** and from 545 nm in 0.5**2** to 659 nm in **2**. This could be ascribed to the increase in delocalization over the dimeric metal cluster core by interaction of two Pt_2M_4 units upon formation of an unsupported Pt–Pt bond in the dimer, which lowers the LUMO energy, resulting in a narrower HOMO–LUMO gap, *i.e.* the dimer emission is thought to originate from the triplet states derived from an acetylide-to-metal–metal bonded cluster core ligand-to-metal–metal bond charge transfer [$RC{\equiv}C^- \rightarrow M_4Pt{-}PtM_4$] LMMCT character. The observation of a lower emission energy for **3** than **1** is also in line with the greater electron richness of the methoxy substituted phenylacetylide ligand.

Acknowledgements

V. W.-W. Y. acknowledges financial support from the Research Grants Council and The University of Hong Kong. K.-L. Y. acknowledges the receipt of a postgraduate studentship administered by The University of Hong Kong.

Notes and references

† Compound **1**. Yield, 51%. Calc. for $C_{128}H_{80}Cu_8Pt_4$: C, 52.89; H, 2.75. Found: C, 52.78; H, 2.64%. IR (Nujol) ν/cm^{-1}: 2028 (m, C≡C). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, Me_4Si): δ 7.00–7.20 (m, Ph). ^{195}Pt NMR (107 MHz, 298 K, CD_2Cl_2, H_2PtCl_4): δ −4110 (s). Compound **2**. Yield, 25%. Calc. for $C_{128}H_{80}Ag_8Pt_4$: C, 47.12; H, 2.45. Found: C, 47.28; H, 2.56%. IR (Nujol) ν/cm^{-1}: 2047 (m, C≡C). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, Me_4Si): δ 7.2–7.4 (m, Ph). Compound **3**. Yield, 30%. Calc. for $C_{144}H_{112}O_{16}Cu_8Pt_4 \cdot 0.5CH_2Cl_2$: C, 50.61; H, 3.30. Found: C, 50.61; H, 3.27%. IR (Nujol) ν/cm^{-1}: 2025 (m, C≡C). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, Me_4Si): δ 1.6 (s, 24H, OMe), 6.70 (d, 16H, C_6H_4, $J = 8.8$ Hz), 7.25 (d, 16H, C_6H_4, $J = 8.8$ Hz). Compound **4**. Yield, 45%. Calc. for $C_{40}H_{72}Si_8Cu_4Pt_2$: C, 33.80; H, 5.07. Found: C, 33.55; H, 5.03%. IR (Nujol) ν/cm^{-1}: 1952 (m, C≡C). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, Me_4Si): δ 0.28 (s, Me_3Si). Compound **5** was prepared according to a literature procedure.[5c]

‡ Crystal data. [$C_{128}H_{80}Cu_8Pt_4$], $M_r = 2906.77$, tetragonal, centrosymmetrical, space group $P4/n$ (no. 85), $a = 15.937(2)$, $c = 21.982(5)$ Å, $V = 5583(1)$ Å^3, $Z = 2$, $D_c = 1.729$ g cm^{-3}, μ(Mo-Kα) = 65.06 cm^{-1}, $F(000) = 2784$, 319 parameters, $T = 301$ K, 4533 unique reflections, 2375 observed [$I > 3\sigma(I)$], $R = 0.036$, $R_w = 0.052$. CCDC reference number 186/1570. See http://www.rsc.org/suppdata/dt/1999/2913/ for crystallographic files in .cif format.

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Communication 9/03986D