SHORT COMMUNICATION

A Luminescent Heteronuclear Cluster Featuring an Unusual Cu₆ Boat-Shaped Core Assembled by Two Dialkynyl-Cycloplatinated Units

Álvaro Díez,[a] Ana García,[a] Elena Lalinde,*[a] and M. Teresa Moreno*[a]

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The synthesis and the structure of a luminescent octanuclear 2-pyridylethynyl cluster [Pt₂Cu₆(bzq)₂(C≡C–C₅H₄N-2)₆I₂] (1) is reported. An X-ray diffraction study of 1 reveals an unusual Pt₂Cu₆ species formed by a central dicationic hexanuclear copper(I) core [Cu₆(C≡C–C₅H₄N-2)₂I₂]²⁺ assembled by two monoanionic benzoquinolinate dialkynylplatinate(II)

[Pt(bzq)(C≡C–C₅H₄N-2)₂]⁻ fragments. Solid-state and solution photoluminescence properties at 298 K and at 77 K are discussed in the context of the structure.

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Introduction

Alkynyl-metal complexes have attracted considerable attention, specially due to the recent advances in the study of their attractive photophysical properties and extensive applications in molecular electronics.[1–15] Compared with polynuclear homometallic alkynyl complexes, the design of heterometallic complexes and/or multicomponent arrays has received less attention.[1,7,8,10,12,14–21] In this area, considerable interest has been paid to Pt^{II}–M^I (M = Cu, Ag, Au) heterometallic alkynyl complexes due to their rich structural topology[22–40] and interesting spectroscopic and optical properties.[1,14,17,41–52] In these systems, luminescence behavior is strongly influenced by the modification of the electron density of the C≡CR units through the variation of the R substituents, η²-M alkynyl bonding and also by metallophilic interactions (Pt···Pt, Pt···M, M···M).[1,14,17,22–52]

Pt^{II}–M^I heteropolynuclear alkynyl complexes have been prepared by direct reaction of Pt^{II} (d⁸) metal alkynyl complexes with M^I (d¹⁰) metal components[1,14,22,23,27–44,46–48] or by reaction of Pt^{II} metal units with polymeric M^I metal acetylides [M(C≡CR)]$_n$.[28,29,52] Mixed dimethylpyrazolate-alkynyl hexanuclear clusters Pt₂M₄ (M = Cu, Ag, Au) were prepared through double deprotonation of the coordinated pyrazoles in [cis-Pt(C≡CPh)₂(Hdmpz)₂] by the corresponding metal ions.[17]

Following our interest in heteropolynuclear benzoquinolinate platinum(II)-metal complexes,[53–55] we report here the synthesis and the photoluminescence of a Pt₂Cu₆ cluster [Pt₂Cu₆(bzq)₂(C≡C–C₅H₄N-2)₆I₂] (1), generated by treat-

ment of [Pt(bzq)(μ-Cl)]₂ with 2-ethynylpyridine (HC≡C–C₅H₄N-2) and CuI in presence of NEt₃. The molecular structure reveals the presence of a central dicationic hexanuclear copper(I) core [Cu₆(C≡C–C₅H₄N-2)₂I₂]²⁺ assembled by two external monoanionic benzoquinolinate dialkynylplatinate(II) [Pt(bzq)(C≡C–C₅H₄N-2)₂]⁻ fragments.

Results and Discussion

Cluster 1 [Pt₂Cu₆(bzq)₂(C≡C–C₅H₄N-2)₆I₂] was generated as a yellow microcrystalline solid by reaction of the binuclear benzoquinolinate bis(μ-chloro) compound [Pt(bzq)(μ-Cl)]₂ in CHCl₃ with 2-ethynylpyridine in presence of excess of NEt₃ and variable amounts of CuI (at least ratio Pt/CuI > 1:0.3). The best yield was obtained using the stoichiometric ratio (Pt/HC≡C–C₅H₄N-2/CuI 1:3:3). The new complex was fully characterized by elemental analysis, IR, ¹H NMR and X-ray diffraction. Suitable crystals for X-ray diffraction became available by slow diffusion of vapours of diisopropyl ether into a saturated dichloromethane solution at –30 °C of the product 1. Figures 1, 2, and 3 show different views of the molecule and Table 1 summarizes selected bond lengths and angles. Complex 1 is a very unusual octanuclear Pt₂Cu₆ species, which is formed by an hexanuclear dicationic central copper cluster [Cu₆(C≡C–C₅H₄N-2)₂I₂]²⁺ (Figure 3) enveloped by two monoanionic benzoquinolinate dialkynylplatinate(II) [Pt(bzq)(C≡C–C₅H₄N-2)₂]⁻ fragments (Figures 1 and 2).

The formation of this cluster is relevant for several reasons: i) The incorporation of CuCl as a tweezer type [cis-PtL₂(μ-κCᵅ:η²-C≡CR)₂CuCl] adduct has been previously found, in a serendipity way, aiming to prepare mononuclear [cis-PtL₂(C≡CR)₂] complexes,[56–58] following the Sonogashira protocol (ML$_n$X/HC≡CR/base/CuI). However, as far as we know, this is the first occasion in which a copper

[a] Departamento de Química-Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de La Rioja,
26006 Logroño, Spain
Fax: +34-941-299621
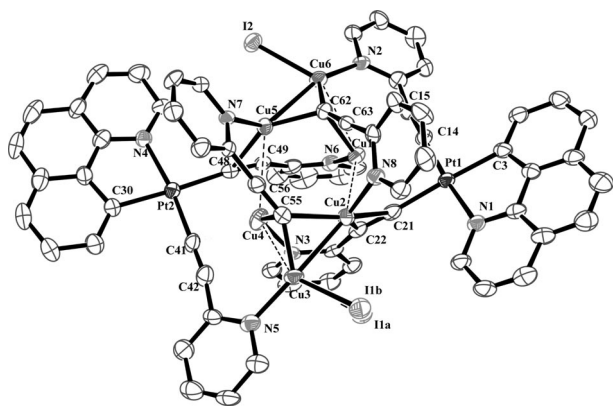E-mail: elena.lalinde@unirioja.es

Figure 1. ORTEP plot of the molecular structure of complex [Pt₂Cu₆(bzq)₂(C≡C–C₅H₄N-2)₆I₂] **1**·2CH₂Cl₂·0.5C₆H₁₄ with selected atom labelling. All hydrogen atoms are omitted for clarity.
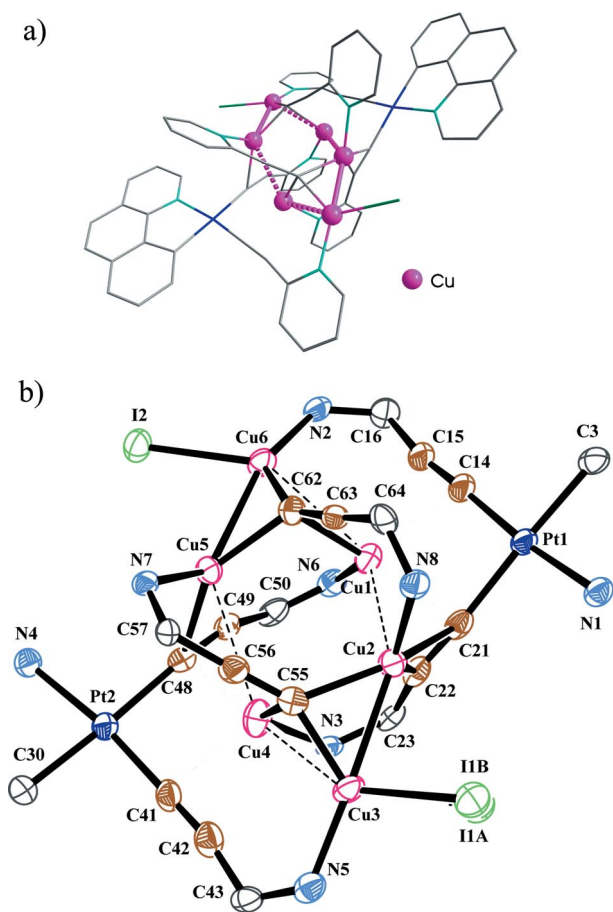

Figure 2. Schematic drawings showing a) the cluster copper core and b) the cluster assembly and the three different coordination modes of the HC≡C–C₅H₄N-2 ligands.
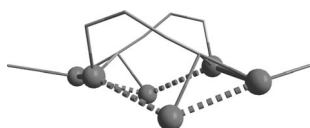
Figure 3. Schematic drawing showing the central copper core atoms.

cluster framework "[Cu₆(C≡C–C₅H₄N-2)₂I₂]²⁺" is formed using this synthetic via. ii) In the tweezer-type adducts, the Cu^I is η²-coordinated to both triple bonds and complete its coordination with a *chloride* ion originating from the platinum starting material whereas in the hexanuclear copper core in **1**, CuI is retained. iii) As can be observed in Figures 2 and 3, the hexanuclear core can be viewed as a dimer of an unusual trimetallic motif "Cu₃(C≡C–C₅H₄N-2)I". It is worth noting that in this unit, the CuI is associated to an alkynyl ligand in a μ₃-C$_α$ fashion and forms a short copper–copper bond (ca. 2.5 Å), suggesting that similar entities could be involved as intermediates in the "in situ" generation of CuC≡CR (HC≡CR/base/CuI system) or in catalyzed reactions (cross-coupling or azide-alkyne cycloadditions) involving alkynes and CuI.[59–63]

The central hexanuclear copper core forms a distorted six-membered boat or an open book shape supported by two μ₄-$\kappa^3 C^\alpha$:κN ethynyl ligands (C≡C–C₅H₄N-2) oriented in a *syn* fashion and Cu···Cu bonding interactions (Figures 2 and 3). Within the framework, two distances [Cu(2)–Cu(3) 2.5185(11), Cu(5)–Cu(6) 2.5338(10) Å] are shorter than the sum of metallic radii (2.56 Å) of two Cu atoms,[64] revealing the occurrence of metal–metal interactions, and four distances [Cu(1)–Cu(6) 2.8189(11), Cu(3)–Cu(4) 2.8629(11), Cu(1)–Cu(2) 3.0327(11), Cu(4)–Cu(5) 2.9998(12) Å] are close to the sum of the van der Waals radii for two Cu^I atoms (2.8 Å),[65] pointing to the presence of weak Cu^I···Cu^I interactions.

As can be seen in Figure 2 (b), the remaining four alkynyl ligands are σ bonded to both Pt(bzq) units, generating the dialkynylplatinate(II) units, which neutralize and complete the coordination environment of four copper ions. As a result, three types of copper environments and three different coordination modes for the alkynyl entities are found. Two of the four alkynyl fragments associated to the Pt units, the C(14)–C(15)–C(16)–N(2) and C(41)–C(42)–C(43)–N(5) entities, are acting as μ-κC^α:κN bridging ligands, being σ (C$^\alpha$) bonded to Pt and covalently bonded through the pyridin nitrogen atom to one of the copper centers [Cu(6), Cu(3); N–Cu 2.017(5), 2.000(6) Å, respectively]. The other two alkynyl groups associated to the platinum fragments [C(21)–C(22)–C(23)–N(3), C(48)–C(49)–C(50)–N(6)] exhibit a more unusual μ₃-κC^α:η^2:κN bonding mode. They are σ bonded to Pt [2.038(7), 2.050(6) Å], significantly η²-bonded to a second copper center [Cu(2) and Cu(5), respectively] [Cu–C$_\alpha$ 2.147(6), 2.141(6) Å; Cu–C$_\beta$ 2.028(6), 2.036(6) Å] and additionally by the pyridin nitrogen atom to the last type of copper atom [Cu(4) and Cu(1)] [N(3)–Cu(4) 2.048(5) and N(6)–Cu(1) 2.071(6) Å]. Finally, as commented above, the two alkynyl groups [C(55)–C(56)–C(57)–N(7) and C(62)–C(63)–C(64)–N(8)] associated with the two tricopper-alkynyl/iodide units, exhibit a rare μ₄-$\kappa^3 C^\alpha$:κN bridging mode. This type of ligand is coordinated to each one of the three different copper centers, through the C$_\alpha$ atom [C(55)–Cu(2,3,4) 1.936(6)–2.074(6) Å and C(62)–Cu(1,5,6) 1.928(6)–2.134(6) Å] and to a fourth copper center through the pyridine nitrogen center [N(7)–Cu(5) 2.006(5), N(8)–Cu(2) 2.015(6) Å] (Figure 3).

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Table 1. Selected bond lengths [Å] and angles [°] of $\mathbf{1}\cdot2CH_2Cl_2\cdot0.5C_6H_{14}$.

Cu–Cu bond lengths					
Cu(1)–Cu(6)	2.8189(11)	Cu(2)–Cu(3)	2.5185(11)	Cu(4)–Cu(5)	2.9998(12)
Cu(1)–Cu(2)	3.0327(11)	Cu(3)–Cu(4)	2.8629(11)	Cu(5)–Cu(6)	2.5338(10)

Pt···Cu separations					
Pt(1)–Cu(1)	3.1596(9)	Pt(2)–Cu(4)	3.0598(9)		

Pt(bzq)					
Pt(1)–N(1)	2.074(5)	Pt(1)–C(3)	2.042(7)	Pt(2)–N(4)	2.083(5)
Pt(2)–C(30)	2.021(6)				

μ-PtκC^{α}:CuκN mode					
Pt(1)–C(14)	1.943(7)	Pt(2)–C(41)	1.947(7)	Cu(1)–C(14)	2.293(6)
Cu(1)–C(15)	2.425(7)	Cu(4)–C(41)	2.265(5)	Cu(4)–C(42)	2.521(7)
Cu(6)–N(2)	2.017(5)	Cu(3)–N(5)	2.000(6)	C(14)–C(15)	1.223(9)
C(41)–C(42)	1.223(9)				
Pt(1)–C(14)–C(15)	177.0(5)	Pt(2)–C(41)–C(42)	178.6(6)		
C(14)–C(15)–C(16)	169.9(7)	C(41)–C(42)–C(43)	170.7(7)		

μ_3-PtκC^{α}:Cuη^2:CuκN mode					
Pt(1)–C(21)	2.038(7)	Pt(2)–C(48)	2.050(6)	Cu(1)–C(21)	2.271(6)
Cu(1)–C(22)	2.412(6)	Cu(4)–C(48)	2.268(6)	Cu(4)–C(49)	2.634
Cu(2)–C(21)	2.147(6)	Cu(2)–C(22)	2.028(6)	Cu(5)–C(48)	2.141(6)
Cu(5)–C(49)	2.036(6)	Cu(4)–N(3)	2.048(5)	Cu(1)–N(6)	2.071(6)
C(21)–C(22)	1.277(10)	C(48)–C(49)	1.236(8)		
Pt(1)–C(21)–C(22)	170.7(5)	Pt(2)–C(48)–C(49)	168.8(5)		
C(21)–C(22)–C(23)	151.7(6)	C(48)–C(49)–C(50)	154.1(7)		

μ_4-Cu$_3\kappa C^{\alpha}$:CuκN mode					
Cu(2)–C(55)	2.052(6)	Cu(5)–C(62)	2.059(6)	Cu(5)–N(7)	2.006(5)
Cu(3)–C(55)	1.936(6)	Cu(6)–C(62)	1.928(6)	Cu(2)–N(8)	2.015(6)
Cu(4)–C(55)	2.074(6)	Cu(1)–C(62)	2.134(6)	C(55)–C(56)	1.248(8)
C(62)–C(63)	1.243(9)				
Cu(2)–C(55)–C(56)	131.5(5)	Cu(5)–C(62)–C(63)	131.3(5)		
Cu(3)–C(55)–C(56)	150.2(5)	Cu(6)–C(62)–C(63)	149.8(5)		
C(55)–C(56)–C(57)	173.3(7)	C(62)–C(63)–C(64)	175.1(6)		

Cu–I bond lengths					
Cu(3)–I(1A)	2.5107(14)	Cu(3)–I(1B)	2.599(5)	Cu(6)–I(2)	2.5540(9)

The Cu–C_{α}(alkyne) distances are unexceptional and range from 1.928(6) to 2.147(6) Å, the shortest distances being associated with the μ_4-$\kappa^3 C^{\alpha}$:κN ligands and the Cu–N distances [2.000(6)–2.071(6) Å] compare well with those observed in other related pyridin-alkyne-copper derivatives.[66–69] The dissimilarity in the alkynyl bonding modes is clearly reflected in the different values of distortion from linearity of these ligands. Whereas in the μ_4-$\kappa^3 C^{\alpha}$:κN alkynyl units associated to the Cu$_6$ core, the C_{α}–C_{β}–C_{γ} angles are close to linearity [173.3(7) and 175.1(6)°], in the μ_3-κC^{α}:η^2:κN ligands, the angles at C_{α} and C_{β} carbons [170.7(5), 168.8(5)/151.7(6), 154.1(7)°] are more bending than in the μ-κC^{α}:κN alkynyl units [177.0(5), 178.6(6)/ 169.9(7), 170.7(7)°]. As commented above (Figures 2 and 3), three different copper environments appear in the central hexanuclear framework: tetracoordinate Cu(2)/Cu(5) atoms with an N, C_{α}, $C_{\alpha}{\equiv}C_{\beta}$, Cu(3)/Cu(6) core; Cu(4)/Cu(1) centers bonded to a C_{α} and an N atom and weakly contacting with two copper centers and finally Cu(3)/Cu(6), which are bonded to Cu(2)/Cu(5), C_{α}, N and complete a tetracoordination with a terminal iodine ligand [I(1A)/I(1B) for Cu(3) (see Exp. Section, crystal structure determination)

and I(2) for Cu(6)]. Finally, we noted that the shortest Pt···Cu separations found [Pt(1)–Cu(1) 3.1596(9) Å and Pt(2)–Cu(4) 3.0598(9) Å] are close to the sum of the van der Waals radii (3.15 Å). This could be taken as evidence reflecting the fact that very weak Pt···Cu interactions are also present. Inspection of the packing of the crystal structure does not reveal the presence of intermolecular π-π interactions.

The presence of different bonding modes in the alkynyl groups is reflected in its IR (Nujol) spectrum, which exhibits several $\nu_{C{\equiv}C}$ absorptions in the expected range [2077(s), 2044(s), 1973(m), 1939(m), 1890(s) cm^{-1}]. **1** is insoluble in the usual organic solvents, except in CH_2Cl_2 in which it is only slightly soluble. The proton spectrum (see Exp. Section for details) also confirms the presence of three different pyridyl groups and only one type of bzq ligand, the resonances due to H^6 and H^5 protons of the pyridyl groups being particularly significant. The considerable upfield shift of the H^6 signals, (9.03, 8.99, 8.94 ppm) with respect to those observed in (NBu$_4$)[Pt(bzq)(C≡C–C$_5$H$_4$N-2)$_2$] (δ = 8.39 ppm),[70] clearly support the hypothesis that the pyridyl groups are involved in the coordination.

The absorption spectrum in CH_2Cl_2 solution (5×10^{-5} M) displays intense high-energy bands (220–348 nm), which are probably due to ligand-centred (^{1}IL $\pi \rightarrow \pi^*$) transitions of the benzoquinolinate and $C \equiv C–C_5H_4N$-2 ligands, and a medium band at 374 nm ($\varepsilon = 3.9 \times 10^3$ M^{-1}cm^{-1}). According to previous assignments in alkynyl platinum complexes, this band is tentatively assigned to spin-allowed metal-to-ligand [Pt(d)$\rightarrow$bzq] charge transfer ^{1}MLCT, probably mixed with some ^{1}LL′CT. In (NBu$_4$)[Pt(bzq)(C$\equiv$C–C$_5$H$_4$N-2)$_2$] a similar band is observed at 393 nm.[70] The coordination of the C$\equiv$C–C$_5$H$_4$N-2 to copper centers, which decreases the donor capabilities of the acetylide groups towards the Pt center could explain the observed shift to higher energies (393–374 nm). The cluster also exhibits a weak low-energy band at 425 nm ($\varepsilon = 1.2 \times 10^3$ M^{-1}cm^{-1}), which obey Beers' Law in the concentration range studied (10^{-4}–10^{-5} M), being tentatively attributed to the [Pt$_2$Cu$_6$(C$\equiv$C–C$_5$H$_4$N-2)$_6$I$_2$] core. The unambiguous assignment of this band is not easy and probably can be attributed to mixed orbital parentage. With reference to previous spectroscopic works on polynuclear copper(I) complexes,[10,14,71–74] this low energy band may be associated with cluster-centered transitions (d/sp Cu) probably mixed with metal (or cluster) perturbed intraligand transition [Cu/π(C$\equiv$C–C$_5$H$_4$N-2)$\rightarrow$$\pi^*$(C$\equiv$C–C$_5H_4$N-2)]. However, due to the presence in the cluster of donor iodide ligands and also η^2-alkynyl-Cu bonding interactions, some contribution of halide and/or acetylide-to-copper charge transfer could not be excluded. The solid-state diffuse reflectance UV/Vis spectrum exhibits a very broad band with tail to 500 nm, which is absent in (NBu$_4$)[Pt(bzq)(C$\equiv$C–C$_5$H$_4$N-2)$_2$], being also associated to the [Pt$_2$Cu$_6$(C$\equiv$C–C$_5$H$_4$N-2)$_6$I$_2$] core.

Compound **1** is emissive in solid state and in CH_2Cl_2 solution at room temperature and at 77 K. As can be seen in Figure 4, excitation of solid at 460 nm produces an orange emission with λ_{max} at 638 nm, which is slightly red-shifted to 660 nm at 77 K. Time-resolved emission measurements reveal mono-exponential decay with lifetimes in the microsecond range (10.9 µs at 298 K, 18.9 µs at 77 K), indicative of a spin-forbidden triplet parentage.

In diluted (5×10^{-5} M) fluid CH_2Cl_2 solution at 298 K (Figure 5, top), **1** exhibits two broad emissions features with maxima at ca. 560 and 635 nm, suggesting the presence of multiple emissions, a fact that has precedents in coinage metal clusters.[14,17,71–74] The excitation spectra resemble the solution absorption spectra, indicating that the emissive states are also characteristic of the cluster core. When frozen to 77 K (Figure 5, down), the two emission bands are well resolved with maxima that are slightly blue shifted in relation to fluid solution (540 and ca. 615 nm). In addition, a distinctive high-energy band merges at 485 nm. The two low-energy maxima are related with similar excitation profiles and have comparable decays (70 µs, 540 nm; 59 µs, 615 nm, λ_{exc} 390 nm), suggesting the existence of close excited states. It is worth noting that the phosphorescence lifetimes at 77 K (solid state and glasses) are longer than at room temperature, indicating that they are mainly determined by non-radiative decay rates, which usually decreases
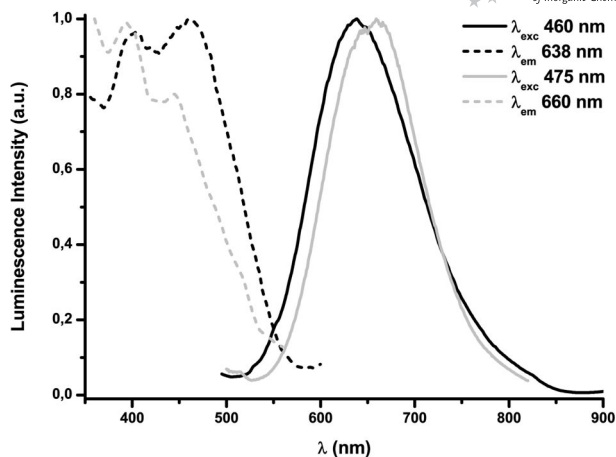

Figure 4. Normalized excitation and emission spectra of **1** in solid state at 298 K (black) and at 77 K (red).

with lowering temperature. The photophysical behaviour observed in solution with several excited states is not unexpected due to the complex architecture of the cluster. For comparative purposes, we have examined the solid state emission spectra of a freshly prepared sample of the polymeric species [CuC$\equiv$C–C$_5$H$_4$N-2]$_n$ and have found them to be quite different. In fact, [CuC$\equiv$C–C$_5$H$_4$N-2]$_n$ exhibits a rather weak high-energy structured emission (303, 350 max, 405 nm, λ_{exc} 255 nm) at 298 K, which is practically unaltered at 77 K. This result suggests that presumably in the cluster **1**, both the dialkynylcyclometallated units [Pt(bzq)(C$\equiv$C–C$_5$H$_4$N-2)$_2$]$^-$ and the central hexanuclear [Cu$_6$(C$\equiv$C–C$_5$H$_4$N-2)$_2$I$_2$]$^{2+}$ core are related with the dual (or multiple emission) found in solution and glass state. However, in solid state, deactivation seems to occur mainly through the lower emissive excited state.

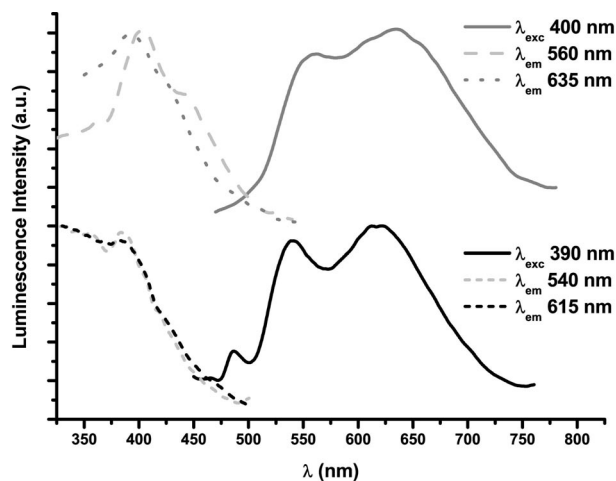Figure 5. Normalized excitation and emission spectra of **1** in CH_2Cl_2 (5×10^{-5} M) at 298 K (top) and at 77 K (down).

Several possible assignments of the transitions have been suggested for emissive polynuclear copper complexes, but their photophysical behaviour is still not well understood.[75] In some cases, the nature of the emissive state depends on the intra and/or intermolecular Cu···Cu separa-

tions. In particular, if the Cu–Cu distance is short enough, the Cu 4s/p orbitals become the LUMO because of stabilization by Cu···Cu bonding interactions. Due to all of the aforementioned it is difficult to assign the luminescence of cluster **1**. Notwithstanding, taking into account previous spectroscopic works on polynuclear copper clusters,[10,14,71–74] the low energy emission observed in solid state (638 nm, 298 K; 660 nm, 77 K) and in glass at 77 K (615 nm) is suggested to derive from a excited state involving the short Cu···Cu interaction.[76] The emission is proposed to have a substantial ligand-to-metal charge transfer ^{3}LMCT [2-pyridylethynyl→Cu$_n$] character probably mixed with a Cu^I-centered d/sp character. It is possible that the additional high energy emission seen in glass state (540 nm) and in fluid solution (560 nm) originates from intraligand $^3\pi$-π^* excited states of the 2-pyridylethynyl ligands associated to the platinum fragments perturbed by coordination [η or κN] to the copper. Finally, in comparison to the structured ^{3}MLCT/^{3}LLCT emission seen in [Pt(bzq)(C≡C–C$_5$H$_4$N-2)$_2$]$^-$ (495, 530, 569 nm),[70] the less intense high-energy asymmetrical feature observed in glass state at 485 nm (Figure 5) is attributable to a similar ^{3}MLCT transition.

Research into other alkynyl ligands of particular interest in relation to structural and optical properties is under way.

Experimental Section

General Remarks: All reactions were carried out under argon atmosphere and solvents were dried by standard procedures and distilled before use. Proton NMR spectra were recorded on a Bruker AVANCE 400 spectrometer with chemical shifts externally referenced to SiMe$_4$. Infrared spectra were recorded with a Nicolet Nexus FT-IR spectrometer as Nujol mulls between polyethylene sheets and C, H and N analyses were carried out with a Carlo–Erba EA1110 CHNS-O microanalyzer. Mass spectra were obtained on a HP-5989B mass spectrometer (ES technique). UV/Vis spectra were recorded on a Hewlet Packard 8453 spectrometer. Diffuse reflectance UV/Vis (DRUV) spectra of pressed powder were recorded on a Shimazdu UV-3600 spectrophotometer with a Harrick Praying Mantis accessory. Excitation and emission spectra were obtained on a Jobin–Yvon Horiba Fluorolog 3–11 Tau-3 spectrofluorimeter, with lifetimes measured operating in the phosphorimeter mode. The precursor [Pt(bzq)(μ-Cl)]$_2$ was prepared according to literature method.[77] HC≡C–C$_5$H$_4$N-2 was used as received.

Synthesis of [Pt$_2$Cu$_6$(bzq)$_2$(C≡C–C$_5$H$_4$N-2)$_6$I$_2$] (1): A yellow suspension of [Pt(bzq)(μ-Cl)]$_2$ (0.15 g, 0.18 mmol) was treated in CHCl$_3$ (20 mL) with HC≡C–C$_5$H$_4$N-2 (112 μL, 1.10 mmol), CuI (0.21 g, 1.10 mmol) and NEt$_3$ (1 mL). Immediately the suspension changes to dark yellow. The mixture was stirred for 5 h and the resulting dark yellow solid was filtered and washed with CHCl$_3$ (5 mL). Yield: 0.30 g (82%). MS (ES+): m/z (%) = 1345 [Pt$_2$Cu$_3$(bzq)$_2$(C≡C–C$_5$H$_4$N-2)$_4$] (83), 1180 [Pt$_2$Cu$_2$(bzq)$_2$(C≡C–C$_5$H$_4$N-2)$_3$] (68); (ES–): m/z (%) = 996 [M/2 – 1H] (100); 819 [M/2 – bzq] (20); 600 [Pt(bzq)(C≡C–C$_5$H$_4$N-2)I – 1H] (71). IR: ν(C≡C) 2077 (s), 2044 (s), 1973 (m), 1939 (m), 1890 (s) cm^{-1}. C$_{68}$H$_{40}$Cu$_6$I$_2$N$_8$Pt$_2$ (1994.38): calcd. C 40.95, H 2.02, N 5.62; found C 40.72, H 1.51, N 5.17. Due to its limited solubility, only the ^{1}H NMR spectrum in CD$_2$Cl$_2$ could be recorded and the assignment of the signals was made on the basis of previous assignments in related complexes

(see labelling Scheme in ref.[70]) and the results of a two dimensional ^{1}H-^{1}H COSY experiment. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ = 10.21 [d, J(H,H) = 5.2, $^3J_{Pt,H}$ = 33.5 Hz, H^2, bzq], 9.03 (d, $J_{H,H}$ = 4.0 Hz, H^6, C$_5$H$_4$N-2), 8.99 (d, $J_{H,H}$ = 4.7 Hz, H^6, C$_5$H$_4$N-2), 8.94 (d, $J_{H,H}$ = 4.2 Hz, H^6, C$_5$H$_4$N-2), 8.42 (d, $J_{H,H}$ = 8.3 Hz, H^4, bzq), 8.28 (d, $J_{H,H}$ = 5.3, $^3J_{Pt,H}$ = 42.0 Hz, H^9, bzq), 7.90 (d, $J_{H,H}$ = 7.7 Hz, H^5, bzq), 7.81 (m, H^3, H^6, H^7, bzq), 7.63 (s br, H^8, bzq), 7.32 (m, H^3, H^4, H^5, C$_5$H$_4$N-2), 7.05 (m, H^5, C$_5$H$_4$N-2), 6.79 (m, H^5, C$_5$H$_4$N-2) ppm.

X-Ray Crystal Structure Determination: Crystallographic details are given in Table 2. Two molecules of CH$_2$Cl$_2$ and a half of *n*-hexane were found in the asymmetric unit. The *n*-hexane molecule was modeled adequately. The data collections were performed on a NONIUS κCCD area-detector diffractometer at 173(1) K using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. Images were processed using the DENZO and SCALEPACK suite of programs,[78] the structure was solved by Patterson using the SHELXS-97 program[79] and the absorption correction was performed using MULTISCAN.[80] The structure was refined by full-matrix least-squares of F^2 with SHELXL-97.[79] All hydrogen atoms were constrained to idealized geometries and were assigned isotropic displacement parameters equal to 1.2 times the U_{iso} value of their attached carbon for aromatic and CH$_2$ hydrogens and 1.5 times for the methyl group. Disordered iodine atoms were found, with occupancies of 80% for I1A and 20% for I1B. In order to establish the identities of the N and metalated C atoms of the bzq ligand, the structure was refined in nine different ways (with the identities of the C and N of each ligand in one position, with the element types reversed, and with 50/50 hybrid scattering factor at each of the affected atomics sites). Examination of the ΔMSDA values for bonds involving these atoms[81,82] revealed the correct assignment, which is the one that appears in the Figure. Finally, ten peaks bigger than 1 e Å^{-3} have been observed near to the solvent, the metals or iodine atoms, with no chemical meaning.

Table 2. Crystallographic data for compound [Pt$_2$Cu$_6$(bzq)$_2$(C≡C–C$_5$H$_4$N-2)$_6$I$_2$]·2CH$_2$Cl$_2$·0.5(C$_6$H$_{14}$) (**1**·2CH$_2$Cl$_2$·0.5C$_6$H$_{14}$).

Empirical formula	C$_{73}$H$_{51}$Cl$_4$Cu$_6$I$_2$N$_8$Pt$_2$
M_w	2207.24
T /K	173(1)
λ(Mo-K_α) /Å	0.71073
Crystal system, space group	triclinic, $\bar{P}1$
Crystal dimensions [mm]	0.12 × 0.10 × 0.05
a /Å, a /°	10.89950(10), 97.64
b /Å, β /°	17.6513(2), 95.95
c /Å, γ /°	17.9795(3), 91.3580(10)
V /Å^3, Z	3407.47(8); 2
$\rho_{calcd.}$ /Mg/m^3	2.151
Absorption coefficient /mm^{-1}	7.036
$F(000)$	2098
θ range for data collection /°	1.16 to 26.92°
Index ranges	–13 ≤ h ≤ 12, –22 ≤ k ≤ 22, –22 ≤ l ≤ 22
Reflections collected	46648
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14339/2/839
Goodness-of-fit on $F^{2[a]}$	1.023
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0446, $wR2$ = 0.0985
R indices (all data)[a]	$R1$ = 0.0701, $wR2$ = 0.1085
Largest diff. peak & hole /e Å^{-3}	2.073 and –1.776

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$; goof $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

CCDC-730695 contains additional crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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[75] Previous assignments in polynuclear copper systems include ligand to metal CT (^{3}LMCT), halide to metal CT (^{3}XMCT), metal to ligand CT (^{3}MLCT), halide to ligand CT (^{3}XLCT), ligand centered π-π* states, metal centered Cu^I d$\rightarrow$s transitions and cluster centered (^{3}CC) excited states. For polynuclear complexes a common feature is the mixing of states, so the single assignments may be only approximations.

[76] In solid state, the excitation spectra have a significant contribution around 500 nm, which almost disappear in solution and in glass (77 K). As one referee point, this fact could be suggestive of that the Cu···Cu interactions in the Cu$_6$ cluster are loosened to some extent in solution.

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