Luminescent Alkynyl Platinum−Cadmium Complexes: Structural Characterization of an Unusual Decanuclear Cluster [Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$]

Juan Forniés,*,† Julio Gómez,‡ Elena Lalinde,*,‡ and M. Teresa Moreno‡

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain, and
Departamento de Química-Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de La Rioja,
26006, Logroño, Spain

The reaction of (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] with Cd(ClO$_4$)$_2$·6H$_2$O in a 1:1 molar ratio yields a white solid [PtCd-(C≡CPh)$_4$]$_n$ **1** (75% yield) together with yellow crystals of a very unusual decanuclear platinum−cadmium cluster [Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$] **2** in low yield. Slow diffusion of acetonic solutions of the starting materials under aerobic conditions only produces crystals of **2** which have been shown by an X-ray analysis to be composed of a big hexanuclear cation [Cd$_6$(μ_3-OH)$_4$]$^{8+}$ and four [Pt(C≡CPh)$_4$]$^{2-}$ anions, held together by Pt···Cd and π···Cd acetylide interactions. On the other hand, treatment of the insoluble product **1** with 1 equiv of NBu$_4$X yields tetranuclear mixed-metal soluble complexes (NBu$_4$)$_2$[{Pt(μ-C≡CPh)$_4$}$_2$(CdX)$_2$] (X = Cl **A**, Br **3**, CN **4**), which contain two platinate fragments connected by two CdX units through Pt···Cd and mainly Cd···C$_\alpha$ interactions. All complexes are strongly emissive in the solid state at room temperature.

Introduction

Several heteropolymetallic systems involving platinum(II) and cadmium(II) have been described and characterized;[1] however, crystallographic characterization has been limited to a few cases,[2−4] and in these, the metal centers are usually connected by a bridging ligand.[2] As far as we know, only three examples containing Pt(II)−Cd(II) interactions have been recently reported: the complexes [{Pt(phpy)$_2$}{Cd(cyclen)}](ClO$_4$)$_2$ and [{Pt(CH$_3$)$_2$(bipy)}{Cd(cyclen)}](ClO$_4$)$_2$ [Hphpy = 2-phenylpyridine; bipy = 2,2′-bipyridine; cyclen = 1,4,7,10-tetraazacyclododecane] with a short and totally unsupported Pt(II) → M dative bond [2.6389(8) and 2.6101(8) Å],[3] and the tetranuclear cluster (NBu$_4$)$_2$[{Pt(μ-C≡CPh)$_4$}$_2$(CdCl)$_2$] **A** reported by us,[4]

which displays four Pt···Cd bonding interactions [2.960(1) Å] and a rather unusual μ-$\kappa C^\alpha C^\alpha$ bonding mode for the alkynyl bridging ligands (its structure is shown in Scheme 1). Complex **A** was obtained (30% yield) as a yellow solid together with a trinuclear white adduct (NBu$_4$)$_2$[{Pt(μ-κC^α:η^2-C≡CPh)$_4$}-(CdCl$_2$)$_2$] **B** (45%) by mixing (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] and CdCl$_2$·2.5H$_2$O (1:2 molar ratio) in acetone, and both are the first examples of heteropolynuclear organocadmium complexes involving alkynyl ligands. As an extension of these studies we now report the behavior of (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] toward Cd-(ClO$_4$)$_2$·6H$_2$O. This reaction has led to two different derivatives: (i) a solid with the formula [PtCd(C≡CPh)$_4$]$_n$ (**1**) which is used to generate the complex (NBu$_4$)$_2$[{Pt(μ-C≡CPh)$_4$}$_2$-(CdX)$_2$] (X = Cl **A**) and related derivatives (X = Br **3**, CN **4**) and (ii) the very unusual decanuclear cluster [Pt$_4$Cd$_6$(C≡CPh)$_4$-(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$] **2**. The crystal structure of **2**, which can be described in terms of Pt···Cd and π-acetylide−Cd interactions between the octahedral cation [Cd$_6$(μ_3-OH)$_4$]$^{8+}$ and four [Pt(C≡CPh)$_4$]$^{2-}$ fragments, and luminescence properties of all complexes are included.

Experimental Section

General Considerations. All reactions were carried out using distilled solvents purified by known procedures. IR spectra were recorded on a Perkin-Elmer FT-IR 1000 spectrometer from Nujol mulls between polyethylene sheets unless otherwise indicated. NMR spectra were recorded on a Bruker ARX 300 spectrometer, and chemical shifts are reported in ppm relative to external standards (SiMe$_4$). Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer; the mass spectra (FAB+) on a VG Autospec spectrometer. Conductivities of acetone solutions in ca. 5 × 10^{-4} mol L^{-1} solutions were measured with a Crison GLP 31 conductimeter. Luminescence and excitation spectra were registered in a Perkin-Elmer LS 50B luminescence spectrometer with a red sensitive photomultiplier type R928. The starting complex (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] was prepared as described elsewhere,[5] and Cd(ClO$_4$)$_2$·6H$_2$O was purchased from commercial suppliers.
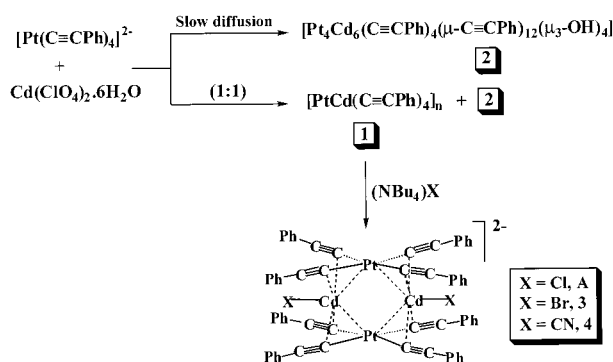
* Corresponding authors. E-mail: forniesj@posta.unizar.es; elena.lalinde@dq.unirioja.es.
† Universidad de Zaragoza-CSIC.
‡ Universidad de La Rioja, UA-CSIC.

 (1) Examples without X-ray: (a) Bochkarev, M. N.; Razuvaev, G. A.; Maiorova, L. P.; Makarenko, N. P.; Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *J. Organomet. Chem.* **1977**, *131*, 399. (b) Adeyemo, A.; Shamim, A.; Turner A.; Akinade, K. *Inorg. Chim. Acta* **1983**, *78*, 191. (c) Bonati F.; Clark, H. C. *Can. J. Chem.* **1979**, *57*, 483. (d) Minghetti, G.; Bonati, F.; Banditelli, G. *Inorg. Chem.* **1976**, *15*, 2649. (e) Bandini, A. L.; Banditelli, G.; Minghetti, G.; Bonati, F. *Can. J. Chem.* **1979**, *57*, 3237. (f) Banditelli, G.; Bandini, A. L.; Minghetti, G.; Bonati, F. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 539. (g) Al-Jibori, S. A.; Kalay, Z. M.; Al-Allaf, T. A. K. *Transition Met. Chem.* **1994**, *19*, 293. (h) Pettinari, C. *Main Group Met. Chem.* **1995**, *18*, 183. (i) Holloway, C. E.; Melnik, M. *Main Group Met. Chem.* **1995**, *18*, 421.
 (2) (a) Pettinari, C.; Marchetti, F.; Cingolani, A.; Troyanov, S. I.; Drozdov, A. *J. Chem. Soc., Dalton Trans.* **1998**, 3335. (b) Capdevila, M.; Carrasco, Y.; Clegg, W.; Coxall, R. A.; González-Duarte, P.; Lledós, A.; Ramírez, J. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3103. (c) Li, Z.; Loh, Z.-H.; Audi Fong, S.-W.; Yan, Y.-K.; Henderson, W.; Mok, K. F.; Andy Hor, T. S. *J. Chem. Soc., Dalton Trans.* **2000**, 1027.
 (3) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **1999**, *121*, 7405.
 (4) Charmant, J. P. H.; Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T.; Orpen, A. G.; Rueda. A. *Chem. Commun.* **1999**, 2045.

Scheme 1

Table 1. Crystallographic Data for 2

chem formula	$C_{128}H_{84}Cd_6O_4Pt_4$	fw	3140.71
a	16.105(2) Å	space group	$P\bar{4}2_1c$
b	16.105(2) Å	temp	293(2) K
c	20.250(4) Å	wavelength	0.71073 Å
vol	5252.2(15) Å^3	ρ(calcd)	1.986 (g cm^{-3})
Z	2	μ(Mo Kα)	6.547 mm^{-1}
$R(F)$ for [$F_o^2 >$ $2\sigma(F_o^2)$]^a	0.0696	R_w $(F_o^2)^b$	0.1867

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$.

Crystal Structure Determination for 2. All calculations were carried out using the program SHELXL-97.[6] The structure was solved by the Patterson method and refined on F^2. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon for the aromatic hydrogens and 1.5 times the U_{iso} value of their attached oxygen. Carbon atoms C(11)−C(16) and C(19)−C(24) were constrained to a regular hexagon; 72 restraints were applied for these atoms. Some crystallographic details are shown in Table 1.

Results and Discussion

The tetraalkynyl platinate compound (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] reacts with Cd(ClO$_4$)$_2$·6H$_2$O in acetone and in a 1:1 molar ratio to yield (75%) a white solid which analyzes as [PtCd(C≡CPh)$_4$]$_n$ (**1**). On exposure to air the filtrate slowly darkens, producing a small amount of yellow crystals of stoichiometry [Pt$_4$Cd$_6$-(C≡CPh)$_{16}$(OH)$_4$] **2** (18% yield) (Scheme 1). Attempts to obtain monocrystals of **1** by slow diffusion, at room temperature, of an acetone solution of Cd(ClO$_4$)$_2$·6H$_2$O into an acetone solution of (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] (1:1 molar ratio) only gives, under aerobic conditions, yellow crystals of complex **2**. As was expected, complex **2** was obtained in a better yield (79%) by using a more adequate molar ratio (1:1.5) of the starting materials. Its IR spectrum exhibits two ν(C≡C) absorptions at 2100 and 2056 cm^{-1} suggesting the presence of terminal and bridging alkynyl groups,[7] and a weak and broad band at 3672 cm^{-1} indicative of the presence of OH$^-$ groups. Unfortunately, complex **2** is not soluble in common organic solvents, preventing its characterization by NMR spectroscopy. However, its structure was definitively established by a single-crystal X-ray diffraction study (Figure 1). Selected bond distances and bond angles are shown in Table 2.

Complex **2** [Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$] is a very unusual decanuclear Pt$_4$Cd$_6$ species, which is formed by a cation [Cd$_6$(μ_3-OH)$_4$]$^{8+}$ and four [Pt(C≡CPh)$_4$]$^{2-}$ anions. As is shown in Figure 2a, the central framework of the six Cd atoms at the big cation, approximately forming an octahedron, is built by four μ_3-OH groups, which cap alternate faces of the octahedron with unexceptional Cd−O distances[8] in the range 2.221(12)−2.297(14) Å. The driving force which holds the four

Synthesis of [PtCd(C≡CPh)$_4$]$_n$ 1. To a solution of (NBu$_4$)$_2$[Pt-(C≡CPh)$_4$] (0.500 g, 0.461 mmol) in acetone (25 mL) was added under nitrogen Cd(ClO$_4$)$_2$·6H$_2$O (0.192 g, 0.461 mmol) at room temperature. Immediately a white solid started to precipitate, and after 30 min of stirring, the solid was filtered off and washed with acetone (0.246 g, 75% yield). On standing in air the filtrate slowly darkened, and after 2 days yellow crystals of **2** separated (0.044 g, 18% yield). Found for **1**: C, 53.6; H, 2.8. Calcd for C$_{32}$CdH$_{20}$Pt: C, 53.9; H, 2.8. IR (cm^{-1}): ν(C≡C) 2048 (s). Its high insolubility prevented NMR spectroscopic characterization.

Synthesis of [Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$] 2. A solution of (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] (0.067 g, 0.062 mmol) in 5 mL of acetone was successively layered with acetone (30 mL) and a solution of Cd-(ClO$_4$)$_2$·6H$_2$O (0.039 g, 0.092 mmol) in 5 mL of acetone and allowed to crystallize at room temperature for 1 week. Complex **2** was obtained as yellow crystals (79% yield), and one of them was adequate for an X-ray diffraction study. Found: C, 48.5; H, 2.8. Calcd for C$_{128}$Cd$_6$H$_{84}$O$_4$Pt$_4$: C, 48.9; H, 2.7. IR (cm^{-1}, in KBr): ν(C≡C) 2100 (w), 2056 (m); ν(O−H) 3672 (w). FAB(−) mass spectrum: m/z 1495 ([Pt$_2$(C≡CPh)$_8$Cd$_2$Cl$_2$]$^-$ 25%), 1424 ([Pt$_2$(C≡CPh)$_8$Cd$_2$]$^-$ 6%). Its low solubility prevented NMR spectroscopic characterization.

Synthesis of (NBu$_4$)$_2$[{Pt(μ-C≡CPh)$_4$}$_2$(CdX)$_2$] (X = Cl A, Br 3, CN 4). NBu$_4$Cl (0.044 g, 0.158 mmol) was added under nitrogen to a stirred white suspension of [PtCd(C≡CPh)$_4$]$_n$ **1** (0.113 g, 0.158 mmol) in acetone (20 mL) at room temperature, and the mixture was stirred for 90 min. The resulting yellow solution was filtered through Celite and evaporated to a small volume (2 mL). Upon addition of *n*-hexane (10 mL), complex **A** was obtained as a yellow solid (0.141 g, 90% yield).

Complexes **3** and **4** were obtained similarly by using the corresponding starting materials NBu$_4$Br (0.045 g, 0.140 mmol) and [PtCd-(C≡CPh)$_4$]$_n$ **1** (0.100 g, 0.140 mmol) (0.117 g, 81% yield); NBu$_4$CN (0.038 g, 0.140 mmol) and [PtCd(C≡CPh)$_4$]$_n$ **1** (0.100 g, 0.140 mmol) (0.096 g, 70% yield).

3. Found: C, 55.6; H, 5.7; N, 1.4. Calcd for Br$_2$C$_{96}$Cd$_2$H$_{112}$N$_2$Pt$_2$: C, 55.7; H, 5.5; N, 1.3. IR (cm^{-1}): ν(C≡C) 2093 (m). Λ_M (acetone): 226 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.52 (d, 16H, Ph), 6.94 (m, 24H, Ph), 3.50 (m, 16H, NCH$_2$−, Bu^n); 1.79 (m, 16H, −CH$_2$−, Bu^n); 1.44 (m, 16H, −CH$_2$−, Bu^n); 0.90 (t, 24H, −CH$_3$, Bu^n). FAB (−) mass spectrum: m/z 1826 ([Pt$_2$(C≡CPh)$_8$Cd$_2$Br$_2$(NBu$_4$)]$^-$ 27%), 1503 ([Pt$_2$(C≡CPh)$_8$Cd$_2$Br + 1]$^-$ 20%), 1503 ([Pt$_2$(C≡CPh)$_8$Cd$_2$Br + 1]$^-$ 20%), 791 ([Pt(C≡CPh)$_4$CdBr]$^-$ 60%), 591 ([Pt$_2$(C≡CPh)$_2$ − 1]$^-$ 100%), 477 ([Pt(C≡CPh)$_2$Br]$^-$ 58%).

4. Found: C, 59.7; H, 5.7; N, 2.6. Calcd for C$_{98}$Cd$_2$H$_{112}$N$_4$Pt$_2$: C, 60.0; H, 5.8; N, 2.9. IR (cm^{-1}): ν(C≡C) 2094 (s). Λ_M (acetone): 215 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.48 (d, 16H, Ph), 6.97 (m, 24H, Ph), 3.45 (m, 16H, NCH$_2$−, Bu^n); 1.76 (m, 16H, −CH$_2$−, Bu^n); 1.42 (m, 16H, −CH$_2$−, Bu^n); 0.92 (t, 24H, −CH$_3$, Bu^n). FAB (−) mass spectrum: m/z 1719 ([Pt$_2$(C≡CPh)$_8$Cd$_2$(CN)$_2$(NBu$_4$) + 1]$^-$, 3%), 1447 ([Pt$_2$(C≡CPh)$_8$Cd$_2$ − 3]$^-$ 3%), 619 ([Pt$_2$(C≡CPh)$_2$CN + 1]$^-$ 95%).

(5) Espinet, P.; Forniés, J.; Martínez, F.; Tomás, M.; Lalinde, E.; Moreno, M. T.; Ruiz, A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 791.

(6) Sheldrick, G. M. *SHELXL-97, program for crystal structure determination from diffraction data*; University of Göttingen: Göttingen, Germany, 1997.

(7) Polynuclear systems containing terminal and bridging alkynyl ligands are very rare: (a) Berenguer, J. R.; Eguizábal, E.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Martín, A. *Organometallics* **2000**, *19*, 490. (b) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *J. Chem. Soc., Dalton Trans.* **1994**, 135. (c) Vaid, T. P.; Veige, A. S.; Lobkovsky, E. B.; Glassey, W. V.; Wolczanski, P. T.; Liable-Sands, L.; Rheingold, A. L.; Cundari, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 10067. (d) Ara, I.; Berenguer, J. R.; Eguizábal, E.; Forniés, J.; Lalinde, E. *Organometallics* **2001**, *20*, 2686.

(8) (a) Prasad, P. A.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Chem. Commun.* **2000**, 1251. (b) Duhme, A. K.; Strasdeit, H. *Eur. J. Inorg. Chem.* **1998**, 657. (c) Weidenbruch, M.; Herrndorf, M.; Schäfer, A.; Phol, S.; Saak, W. *J. Organomet. Chem.* **1989**, *361*, 139.
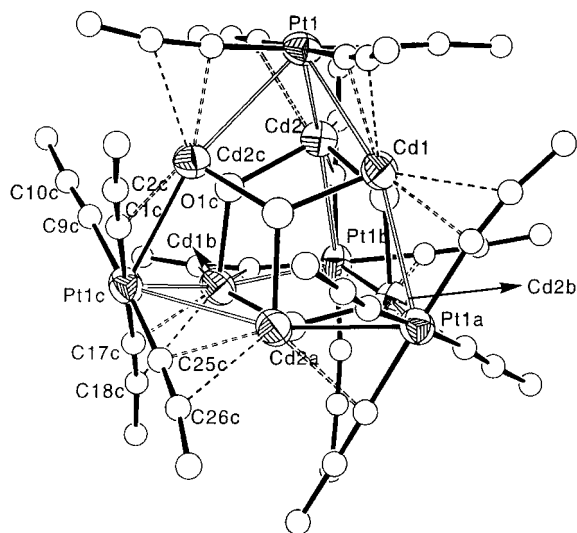
Figure 1. Structure of [Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$] **2** (phenyl groups have been omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Pt$_4$Cd$_6$(C≡CPh)$_4$(μ-C≡CPh)$_{12}$(μ_3-OH)$_4$] **2**

Pt(1)−C(1)	2.010(15)	Pt(1)−C(9)	1.99(2)
Pt(1)−C(17)	2.010(16)	Pt(1)−C(25)	2.025(19)
Pt(1)−Cd(1)	3.2234(8)	Pt(1)−Cd(2)	2.8570(14)
Pt(1)−Cd(2c)	3.2509(15)	Cd(1)−O(1)	2.221(12)
Cd(2)−O(1)	2.297(14)	Cd(2)−O(1c)	2.285(13)
Cd(1)−C(17)	2.364(15)	Cd(1)−C(18)	2.69(2)
Cd(2)−C(1)	2.489(18)	Cd(2)−C(25b)	2.342(19)
Cd(2)−C(26b)	2.624(19)	Cd(2)−C(9)	2.681(16)
C(1)−C(2)	1.22(3)	C(9)−C(10)	1.21(3)
C(17)−C(18)	1.24(3)	C(25)−C(26)	1.29(3)
C(1)−C(2)−C(3)	176(2)	C(9)−C(10)−C(11)	175(3)
C(17)−C(18)−C(19)	170(2)	C(25)−C(26)−C(27)	170.8(19)
Pt(1)−C(1)−Cd(2)	78.0(6)	Pt(1)−C(9)−Cd(2)	73.7(5)
Pt(1)−C(17)−Cd(1)	94.6(6)	Pt(1)−C(25)−Cd(2c)	96.0(7)
Cd(2)−Pt(1)−Cd(1)	76.70(4)	Cd(2)−Pt(1)−Cd(2c)	78.07(4)
Cd(1)−Pt(1)−Cd(2c)	73.34(3)	Pt(1a)−Cd(1)−Pt(1)	156.48(6)
Pt(1)−Cd(2)−Pt(1b)	161.16(5)	O(1a)−Cd(1)−O(1)	96.6(7)
O(1)−Cd(1)−Pt(1)	80.0(4)	O(1a)−Cd(1)−Pt(1)	84.4(4)
O(1c)−Cd(2)−O(1)	94.3(7)	O(1c)−Cd(2)−Pt(1)	86.9(3)
O(1)−Cd(2)−Pt(1)	87.3(3)	O(1c)−Cd(2)−Pt(1b)	82.8(3)
O(1)−Cd(2)−Pt(1b)	77.8(3)		

[Pt(C≡CPh)$_4$]$^{2-}$ anions together in approximately a tetrahedral array (see Figure 1) and connects to the whole cation is Pt···Cd and π···Cd acetylide interactions. The central core "Pt$_4$Cd$_6$(μ-OH)$_4$" can be alternatively described as a tetrahedral array of Pt atoms, edge-bridged by six cadmium atoms and face capped by μ_3-OH hydroxyl groups (see Figure 2b).

The platinum−cadmium and π−cadmium acetylide interactions constitute a rather complicated structural system which can be summarized as follows: each Cd atom, located in the equatorial position of the octahedron [Cd(2) and their symmetry-related equivalents Cd(2a−c)], is bonded to one Pt fragment through a Pt−Cd bond [Pt(1)−Cd(2) distance 2.8570(14) Å] and a Cd−C$_\alpha$ bond of one of the acetylide groups of this platinate fragment [Cd(2)−C(1) 2.489(18) Å]. In addition, this Cd [Cd(2, 2a−c)] displays an asymmetric π−Cd acetylide interaction with an acetylide group of another platinate moiety [Cd(2)−C(25b) 2.342(19) Å, Cd(2)−C(26b) 2.624(19) Å] and a weak Pt−Cd interaction [Pt(1b)−Cd(2) 3.2509(15) Å]. On the other hand, the other two Cd atoms which are located at the apex of the octahedron [Cd(1) and Cd(1b)] are asymmetrically bonded to two acetylide groups of two different [Pt(C≡CPh)$_4$]$^{2-}$ moieties [Pt(1) and Pt(1a)] [Cd(1)−C(17) or
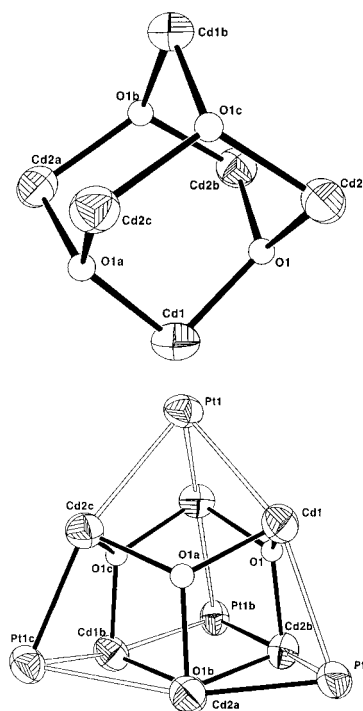

Figure 2. Perspectives of (a) the central cation [Cd$_6$(μ_3-OH)$_4$]$^{8+}$ and (b) the central "Pt$_4$Cd$_6$(μ-OH)$_4$" framework in **2**.

Cd(1)−C(17a) 2.364(15) Å, Cd(1)−C(18) or Cd(1)−C(18a) 2.69(2) Å], and these acetylide interactions probably also cause weak Pt−Cd interactions [Pt(1)−Cd(1) or Pt(1a)−Cd(1) 3.2234(8) Å]. As far as the Pt−Cd interactions are concerned, it has to be said that in the whole cluster (see Figure 2b) there are four short Pt−Cd distances which are close to the sum of covalent radii (2.76 Å)[9] and eight longer Pt···Cd distances [3.2234(8) and 3.2509(15) Å] which are below the van der Waals limit (3.3 Å).[9] Obviously none of them, even the shortest, can be considered exclusively as a Pt−Cd dative bond,[3] but rather they can be considered as a part of the interaction of the fragment Pt−C≡CPh with the Cd center and in which the shortest Pt−Cd distance is associated with the longest Cd−C length and vice versa. Finally, it should be noted that according to the IR spectrum there are four alkynyl ligands, one from each platinum unit, which remain as terminal functions, as the interaction of Cd(2) with the C(9)≡C(10) fragment is negligible [Cd(2)···C(9) 2.681(16) Å].

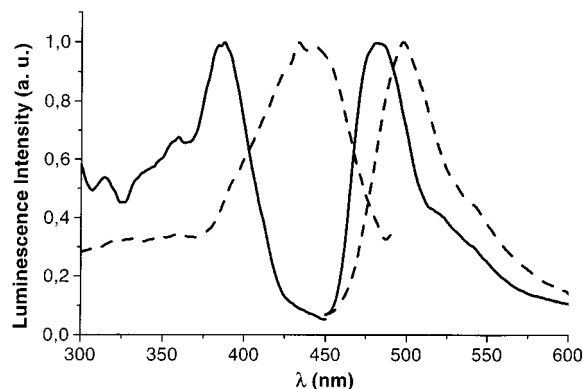All attempts to obtain crystals of [PtCd(C≡CPh)$_4$]$_n$ **1** failed, but the observation of a ν(C≡C) band at 2048 cm^{-1} indicates the presence of η^2-alkynyl−Cd interactions, and its extreme insolubility suggests its polymeric nature, probably based on alkynyl platinate fragments acting as bis(chelating) bridging ligands between cadmium centers. Similar examples of trinuclear cations M$_2$M′ [Pt$_2$Ag, Ti$_2$Ag, Pt$_2$Cu] formed by two orthogonal "L$_n$M(C≡CR)$_2$" fragments acting as bidentate diyne ligands toward Cu(I) or Ag(I) have been reported recently.[10] As is shown in Scheme 1, treatment of **1** with 1 equiv of (NBu$_4$)Cl in acetone produces the tetranuclear complex (NBu$_4$)$_2$[{Pt(μ-C≡CPh)$_4$}-(CdCl)$_2$] **A** in very high yield (90%), and the analogous

(9) Rodgers, G. E. *Química Inorgánica. Introducción a la Química de la Coordinación, del estado sólido y descriptiva;* McGraw-Hill: New York, 1995; p 198.

(10) (a) Ara, I.; Berenguer, J. R.; Lalinde, E.; Moreno, M. T. *J. Organomet. Chem.* **1996**, *510*, 63. (b) Hayashi, Y.; Osawa, M.; Kobayashi, K.; Sato, T.; Sato, M.; Wakatsuki, Y. *J. Organomet. Chem.* **1998**, *569*, 169. (c) Yamazaki, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3051.
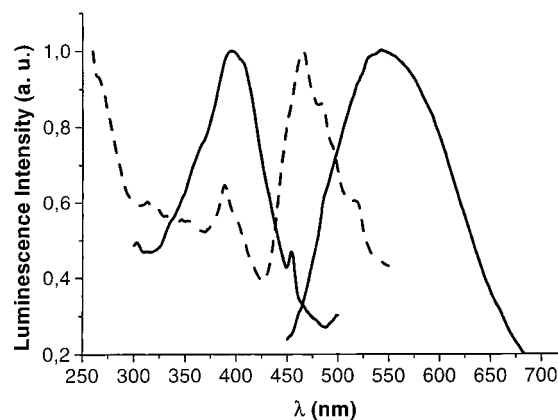
Table 3. Emission and Excitation Spectral Data for Complexes A and **1**−**4**

compound		λ_{max}^{em}/nm	λ_{max}^{exc}/nm
(NBu$_4$)$_2$[{Pt(μ-$\kappa C^{\alpha}C^{\alpha}$−C≡CPh)$_4$}$_2$(CdCl)$_2$] **A**	KBr, 298 K	495	433
	CHCl$_3$, 298 K	495	442
	CHCl$_3$, 77 K	482, 527 (sh)	386, 312, 296
[PtCd(C≡CPh)$_4$] **1**	KBr, 298 K	543	395
[Pt$_4$Cd$_6$(C≡CPh)$_{16}$(μ_3-OH)$_4$] **2**	KBr, 298 K	466, 484, 494, 517	389
(NBu$_4$)$_2$[{Pt(μ-$\kappa C^{\alpha}C^{\alpha}$−C≡CPh)$_4$}$_2$(CdBr)$_2$] **3**	KBr, 298 K	497	438
	CHCl$_3$, 298 K	494	415
	CHCl$_3$, 77 K	481, 520 (sh)	387, 359, 314, 295
(NBu$_4$)$_2$[{Pt(μ-$\kappa C^{\alpha}C^{\alpha}$−C≡CPh)$_4$}$_2$(CdCN)$_2$] **4**	KBr, 298 K	498	442
	CHCl$_3$, 298 K	494	452
	CHCl$_3$, 77 K	485, 527 (sh)	393, 341, 290

Figure 3. Emission and excitation spectra of complex **3** in the solid state at 298 K (− − −) and in frozen solution (N$_2$ liq) in CHCl$_3$(—).

Figure 4. Excitation and emission spectra of complexes **1** (—) and **2** (− − −) in the solid state at 298 K.

tetranuclear derivatives (NBu$_4$)$_2$[{Pt(μ-C≡CPh)$_4$}(CdX)$_2$] (X = Br **3**, CN **4**) are also easily obtained by treatment of **1** with (NBu$_4$)X salts (X = Br$^-$, CN$^-$). However, attempts to prepare the μ-hydroxy-cluster derivative **2** by reacting **1** with Cd(OH)$_2$ in acetone have failed, probably due to the extremely low solubility of both reactants in this solvent. Conductivity measurements of **3** and **4** indicate that they behave as 2:1 electrolytes, and FAB(−) mass spectrometry showed peaks at m/z 1826 (**3**) or 1719 (**4**) due to [{Pt(C≡CPh)$_4$CdX}$_2$ + (NBu$_4$)]$^+$. In addition, their IR spectra exhibit, as in the chloride complex **A**, the ν(C≡C) absorption (2093 cm^{-1} **3**, 2094 cm^{-1} **4**) slightly shifted to higher frequencies when compared to the anionic species [Pt(C≡CPh)$_4$]$^{2-}$ (2075 cm^{-1}),^{5} thus suggesting a similar formulation (see Scheme 1), with the cadmium atoms bonded only to the C$_\alpha$ carbon atoms of the alkynyl functions.

The luminescence properties of all complexes have been examined, and the results are summarized in Table 3. Complexes **A**, **3**, and **4** are strongly emissive in the solid state at room temperature and in frozen (N$_2$ liquid) CHCl$_3$ solutions, while in fluid solutions at room temperature the emission is extremely weak. Interestingly, all the emission and excitation spectra for the three complexes are nearly identical. In the solid state the emission maximum at room temperature is around 495 (**A**) to 498 (**4**) nm with a low-energy tail and the excitation spectra show maxima in the range of 433 (**A**) to 442 (**4**) nm. To illustrate this, Figure 3 displays both the emission and excitation spectra of **3** (X = Br) in the solid state (discontinuous line) and also in frozen CHCl$_3$ solution (bold line). As can be observed, the emission maximum observed at 497 nm in the solid state is blue shifted to 481 nm in a frozen solution, and the low-energy tail appears as a shoulder near 520 nm. The maximum value of the excitation spectrum notably shifts to higher energies (λ_{max}^{exc} 387 nm at 77 K, CHCl$_3$, vs 438 nm in the solid state or 415 nm at room temperature in CHCl$_3$). The similarity in the emission of the three complexes (**A**, **3**, **4**) is further support of a similar

formulation of **3** and **4** as tetranuclear dianionic Pt$_2$Cd$_2$ species with Pt(II)−Cd(II) bonding interactions comparable to those seen for **A** (Pt···Cd 2.960(1) Å)^4 and clearly indicates that the influence of the ligands bound to Cd(II) on the central chromophore is negligible. It should be noted that the intensity of the observed emission is greatly increased in relation to that seen in the precursor (NBu$_4$)$_2$[Pt(C≡CPh)$_4$].^{11} This mononuclear complex exhibited a clear vibronic structural band (λ_{max}^{em} 447 nm, vibrational spacing 2045−2080 cm^{-1}) assignable, on the basis of previous studies on alkynyl platinum complexes^{12} and some recent theoretical studies,^{12a,13} to a π*(C≡C)/p$_z$(Pt) → π*d(Pt)/π(C≡C) LMCT transition.^{14a} The change in the emission profile and the clear red-shift displacement observed as a result of the coordination of the CdX units suggest a significant contribution of the Pt−Cd interactions (and probably also alkynyl C$_\alpha$−Cd) to the orbitals involved in the optical transition. However, the assignment of the emissive state in this type of complex is somewhat uncertain.^{15} In these sandwich

(11) Chartmant, J. P. H.; Forniés, J.; Gómez, J.; Lalinde, E.; Merino, R. R. I.; Moreno, M. T.; Orpen, A. G. *Organometallics* **1999**, *18*, 3353.

(12) (a) Yip, H.-K.; Lin, H.-H.; Wang, Y.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2939. For some reviews see: (b) Yam, V. W. W.; Lo, K. K.-W.; Wong, K. M.-C. *J. Organomet. Chem.* **1999**, *578*, 3. (c) Chan, C. W.; Cheng, L. K.; Che, C. M. *Coord. Chem. Rev.* **1994**, 132 and references given therein.

(13) (a) Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732. (b) Long, N. J.; Martin, A. J.; Vilar, R.; White, A. J. P.; Williams, D. J. Younus, M. *Organometallics* **1999**, *18*, 4261. (c) Ara, I.; Berenguer, J. R.; Eguizábal, E.; Forniés, J.; Gómez, J.; Lalinde, E.; Sáez-Rocher, J. M. *Organometallics* **2000**, *19*, 4385. (d) Ara, I.; Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2000**, *19*, 3137.

(14) (a) EHMO calculations on [Pt(C≡CPh)$_4$]$^{2-}$: HOMO π*Pt(d,60%)− π(C≡CPh); LUMO πPt(p$_z$,10%)−π*(C≡CPh). (b) EHMO calculations on [Pt(C≡CPh)$_4$CdCl]$_2^{2-}$ (**A**): HOMO π*Pt(d,36%)− π(C≡CPh); LUMO πPt(p$_z$,10%)−π*(C≡CPh)Cd(sp,4%). (c) Using the program CACAO, version 4.0: Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 3399.

[Pt](μ-C≡CR)[M] heteropolynuclear platinum alkynyl systems not only πPt(d)−π(C≡CR) and πPt(p$_z$)−π*(C≡CR) interactions but also πM/C≡C, Pt···M, and even Pt···Pt bonding[11,16] could be involved in the ground and/or excited state.[14b]

For complexes **1** and **2** their low solubility has precluded the study in fluid solutions. Their emission spectra in the solid state at room temperature are shown in Figure 4, and the data are shown in Table 3. Complex **2** displays a structured emission (maxima at 466, 484, 494, and 517 nm, λ_{max}^{exc} = 389 nm) with a vibrational spacing of 2071 cm^{-1}, characteristic of ν(C≡C), and, in contrast, complex **1** exhibits an asymmetric red-shifted emission (with a low-energy tail) centered at λ_{max}^{em} 543 nm (hwhm of 4610 cm^{-1}; λ_{max}^{exc} 395 nm, Stokes shift 6900 cm^{-1}).

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(15) We had previously suggested[4] that the emission can be attributed as an alkynyl to cluster transition π*(C≡CPh) → CCPt$_2$Cd$_2$ (cluster centered to ligand charge transfer) probably mixed with a metal−metal (Pt−Cd) based charge transfer.

In order to carry out a more detailed and definitive assignment of the emitting states of these systems, additional work, including the preparation of systematically modified derivatives, is necessary. Synthesis, optical properties, and theoretical studies of other platinum−cadmium complexes are in progress.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Yam, V. W. W.; Yu, K. L.; Wong, K. M. Ch.; Cheung, K. K. *Organometallics* **2001**, *20*, 721.