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Synthesis, structural characterisation and luminescence studies of the first alkynyl stabilised platinum–cadmium complexes

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The simple 1:2 adduct $(NBu_4)_2[\{Pt(\mu\text{-}\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CPh)_4\}(CdCl_2)_2]$ 2 containing unusual η^2-alkyne Cd interactions, as well as the unexpected tetranuclear dimer $(NBu_4)_2[\{Pt(\mu\text{-}\kappa C^\alpha C^\alpha\text{-}C{\equiv}CPh)_4\}_2(CdCl)_2]$ 1 stabilised by alkynyl bridging ligands and platinum–cadmium bonding interactions, have been characterised by X-ray crystallography and their luminescence properties have been also investigated.

Although cadmium organometallics have long been used in organic synthesis,[1] there have been relatively few studies on the species themselves.[2] In particular, alkynyl cadmium complexes are limited to the polymeric derivatives $[Cd(C{\equiv}CR)_2]_n$, (R = H,[3a] Ph,[3a,b] C_6H_{13}[3b]) and to the recently reported mononuclear complex $[Cd(C{\equiv}CPh)_2(tmen)]$,[3c] which is the only example of a structurally characterised cadmium alkynyl complex. Heteropolynuclear organocadmium species with Cd(II) in different environments and with nuclearity ranges from two to seven (or even larger, *i.e.* 9 or 13), have been reported,[1,2] but, up to now, complexes of this type involving alkynyl ligands are unknown.

In the last few years we have shown that anionic homoleptic alkynylplatinate(II) species are suitable precursors for the synthesis of remarkable trinuclear species $[\{Pt(\mu\text{-}\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CR)_4(ML_n)_2]^{x-}$ displaying very unusual η^2-alkyne–M bonding interactions [ML_n = $Pd(\eta^3\text{–}C_3H_5)$,[4a] x = 0; HgX_2,[4b] $CoCl_2$,[4c] x = 2). By using a similar synthetic approach we have now been able to prepare the first examples of organometallic mixed-metal platinum–cadmium compounds.[5] Here, we report the syntheses, X-ray crystal structures and luminescence properties of a trinuclear complex $(NBu_4)_2[\{Pt(\mu\text{-}\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CPh)_4\}(CdCl_2)_2]$ **2**, stabilised by unusual η^2-alkynyl–Cd interactions, along with the unexpected tetranuclear cluster $(NBu_4)_2[\{Pt(\mu\text{-}\kappa C^\alpha C^\alpha\text{-}C{\equiv}CPh)_4\}(CdCl)]_2$ **1** containing four Pt(II)–Cd(II) interactions and with alkynyl bridging ligands displaying a rather unusual $\mu\text{-}\kappa C^\alpha C^\alpha$ bonding mode.

The complex $(NBu_4)_2[Pt(C{\equiv}CPh)_4]$[6] was treated in acetone at room temperature with $CdCl_2{\cdot}2.5H_2O$ (1:2 molar ratio) with the aim of preparing 1:2 adducts analogous to the trinuclear PtM_2 (M = Hg,[4b] Co[4c]) derivatives mentioned above. However, after 50 min of stirring a microcrystalline yellow solid (**1**, 30% yield) was obtained by partial evaporation of the solvent and cooling.† Complex **1** was identified by a single-crystal X-ray diffraction study as the unexpected tetranuclear compound $(NBu_4)_2[\{Pt(\mu\text{-}\kappa C^\alpha C^\alpha\text{-}C{\equiv}CPh)_4\}_2(CdCl)_2]$ (see below). In addition, evaporation of the filtrate to dryness and treatment with isopropyl alcohol gave the desired trinuclear adduct $(NBu_4)_2[\{Pt(\mu\text{-}\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CPh)_4\}(CdCl_2)_2]$ **2** as a white solid (45% yield). As might be expected, if the reaction is carried out under similar conditions, but with a 1:1 molar ratio, only the 1:1 Pt/Cd complex **1** is obtained, in high yield (82%).

X-Ray structure analyses of both compounds have been carried out (Fig. 1 and 2). As can be seen, while the anion in **2**‡

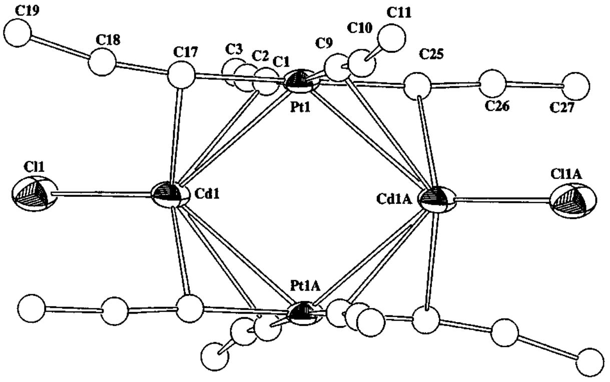

Fig. 1 Structure of the anion $[\{Pt(\mu\text{-}\kappa C^\alpha C^\alpha\text{-}C{\equiv}CPh)_4\}_2(CdCl)_2]^{2-}$ in complex **1**. Selected interatomic distances (Å) and angles (°): Pt–C(1) 2.013(5), Pt–C(9) 2.014(5), Pt–Cd 2.960(1), Cd–C(1) 2.463(4), Cd–C(9) 2.604(5), C(1)–C(2) 1.210(7), C(9)–C(10) 1.208(7); C(2)–C(1)–Pt(1) 178.7(5), C(10)–C(9)–Pt(1) 174.3(5), C(1)–C(2)–C(3) 172.6(5), C(9)–C(10)–C(11) 172.9(6).

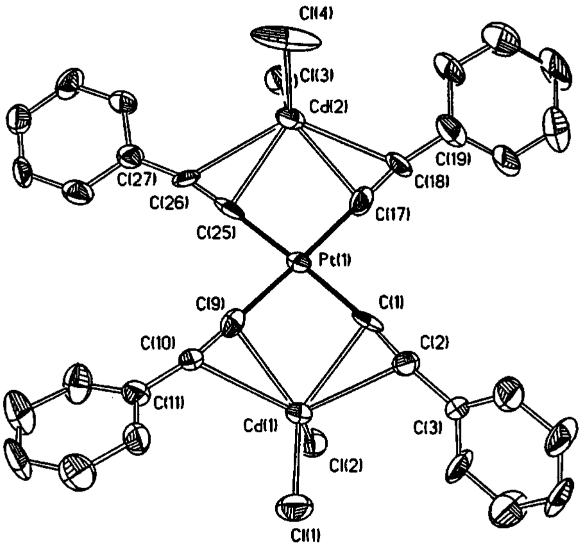

Fig. 2 Structure of the anion $[\{Pt(\mu\text{-}\kappa C^\alpha{:}\eta^2\text{-}C{\equiv}CPh)_4\}(CdCl_2)_2]^{2-}$ in complex **2** (phenyl groups have been omitted for clarity). Selected interatomic distances (Å) and angles (°): Pt(1)–C(1) 1.989(13), Pt(1)–C(9) 2.012(13), Pt(1)–C(17) 2.003(13), Pt(1)–C(25) 1.996(15), Cd(1)–C(1) 2.459(11), Cd(1)–C(9) 2.403(11), Cd(1)–C(2) 2.576(12), Cd(1)–C(10) 2.670(11), Cd(2)–C(17) 2.423(12), Cd(2)–C(25) 2.428(11), Cd(2)–C(18) 2.598(14), Cd(2)–C(26) 2.657(12); C(2)–C(1)–Pt(1) 173.1(10), C(10)–C(9)–Pt(1) 178.3(10), C(18)–C(17)–Pt(1) 176.8(12), C(26)–C(25)–Pt(1) 176.9(10), C(1)–C(2)–C(3) 173.4(13), C(9)–C(10)–C(11) 169.7(12), C(17)–C(18)–C(19) 168.5(14), C(25)–C(26)–C(27) 167.3(13).

is the expected 1 : 2 bis(η^2-alkyne) adduct, the centrosymmetric tetranuclear anion of **1**‡ is formed by two eclipsed 'Pt(C≡PCh)$_4$' units which are connected by two CdCl fragments. In **2**, the two chlorine atoms and the midpoints of the respective *cis* η^2-alkyne fragments form a pseudo-tetrahedral coordination environment about each cadmium, with the CdCl$_2$ fragments almost perpendicular to the coordination plane of the platinum atom (97.4 and 91.1°). On the other hand, in **1** the cadmium atoms are in a rather complicated environment formed by a chlorine atom, four C$_\alpha$ atoms of four alkynyl entities and two Pt–Cd bonds.

The Cd–Cl distances are very similar in the two complexes [2.435(2) **1**, 2.393(4)–2.427(3) Å **2**] and are comparable to other Cd–Cl distances.[2e] It is worth noting that although in both anions the alkynyl ligands remain σ-bonded to the platinum centre their interactions with the cadmium centres are very different in the two complexes. Thus, in **2**, each cadmium is η^2-bonded to two *cis* alkynyl functions, which have the common bonding mode μ-κC$^\alpha$: η^2(σ–π). The Cd atoms are displaced from the Pt(II) coordination plane [1.0878 Å Cd(1) and 0.4405 Å Cd(2)], generating non-planar PtC$_4$Cd cores. The Pt–Cd distances [Pt(1)–Cd(1) 3.2063(10) Å and Pt(1)–Cd(2) 3.3117(10) Å] are close to the sum of van der Waals radii (3.4 Å)[7] suggesting that only very weak interactions, if any, are present. In contrast, in the tetranuclear anion of **1**, the cadmium atoms are bonded only to the C$_\alpha$ carbon atoms of four alkynyl functions (two associated with each Pt atom), which display the less usual μ-κC$^\alpha$C$^\alpha$(σ-Pt, σ-Cd) bonding mode. The interactions of the C$_\beta$ atoms with Cd centres can be considered negligible. The very short Pt–Cd distance, close to the sum of the Pauling covalent radii,[8] and the Pt–C$_\alpha$–Cd bond angles, somewhat smaller than 90° [range 78.59(16)–82.15(16)°], support the possibility of direct bonding interactions between Pt(II) and Cd(II). The donor properties of a d^8 ML$_n$ complex, particularly enhanced in anionic platinate complexes, are now well documented.[9,10] Presumably, in this complex the four Pt···Cd bonding interactions are responsible for the structure and stability of this tetranuclear anionic cluster. However, the particular preference for the final rhombic planar Pt$_2$Cd$_2$ metal core [Cd–Pt–Cd 104.49(3)°; Pt–Cd–Pt 75.51(3)°] with the chlorine atoms also contained in the same plane is not clear at the moment. Probably, the driving force in the formation of **1** could be rationalised as an equilibrium between Pt···Cd, Cd···alkynyl and Cd···Cl bonding interactions.

The different bonding mode of the alkynyl ligand in both complexes is particularly reflected in the ν(C≡C) absorption, which in **1** is shifted to slightly higher frequency (2095 cm^{-1}) than in the starting material [(NBu$_4$)$_2$[Pt(C≡CPh)$_4$][6] 2075 cm^{-1}] and in **2** is shifted to a lower frequency (2066 cm^{-1}).

The presence of metal–metal interactions in **1** is also suggested by preliminary studies of the optical properties of both complexes, which are strongly emissive in frozen solutions (CHCl$_3$) and in the solid state at room temperature. Complex **2** displays a structured emission (maxima at *ca.* 432 and 471 nm; $\lambda^{\text{exc}}_{\text{max}}$ = 335 nm, Stokes shift 6703 cm^{-1}) with a vibrational spacing of 2095 cm^{-1} characteristic of ν(C≡C), which is somewhat similar to that of the precursor (NBu$_4$)$_2$[Pt(C≡CPh)$_4$] (vibronic structural band at *ca.* 447 nm). Thus, the presence of two CdCl$_2$ units η$_2$ attached to the acetylenic entities does not induce a significant change in this emission, which on the basis of previous spectroscopic work with alkynyl compounds is attributed to a $\pi^*/p_z \longrightarrow d_{z^2}$ transition (MLCT).[11] In contrast, complex **1** exhibits an asymmetric emission (with a low energy tail) centred at $\lambda^{\text{exc}}_{\text{max}}$ *ca.* 495 nm (20202 cm^{-1}, hwhm of 1873 cm^{-1}). The absence of vibronic progression in the emission profile and the observed red-shift of both the emission and excitation maxima ($\lambda^{\text{exc}}_{\text{max}}$ 433 nm) suggest a significant contribution of the Pt–Cd interactions to the orbitals (probably HOMO) involved in the optical transition. On the basis of previous results,[12] we tentatively attribute this emission to the transition π*(C≡CPh) ⟶ CC (Pt$_2$Cd$_2$) (cluster centred to ligand charge transfer), mixed with a metal–metal (Pt–Cd) based charge transfer. Further investigation of the reactivity of other alkynyl platinum complexes towards different cadmium substrates and studies (including molecular orbital calculations) of their properties are currently in progress.

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Notes and references

† Experimental details and spectroscopic data (including emission and excitation spectra of **1** and **2**) available as supplementary material upon request to the authors.

‡ *Crystallographic data*: **1**·2CH$_2$Cl$_2$, C$_{49}$H$_{58}$CdCl$_3$NPt, M = 1074.80, monoclinic, space group $C2/m$, a = 20.490(5), b = 16.330(7), c = 16.311(4) Å, β = 120.013(16)°, V = 4726(3) Å^3, Z = 4, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 3.609 mm^{-1}, 5560 independent reflections measured at 173 K, 4560 data with $I > 2\sigma(I)$, 364 parameters. Final R indices: R_1 = 0.0383, wR_2 = 0.1074 (0.0485 and 0.1116 for all data). One of the phenyl rings was found to be disordered with common *ipso*-C(11) and *para*-C(14) positions. The disorder was modelled with fixed 50% site occupancy for the disordered *meta* and *para* carbons.

2·0.6H$_2$O: empirical formula, C$_{64}$H$_{92}$Cd$_2$Cl$_4$N$_2$Pt·0.6H$_2$O, M = 1461.60, monoclinic, space group $I2/a$, a = 40.625(6), b = 20.3820(10), c = 25.482(4) Å, β = 106.540(10)°, V = 20227(5) Å^3, Z = 12, λ (Mo-Kα) = 0.71073 Å, μ (Mo-Kα) = 2.981 mm^{-1}, 17819 independent reflections measured at 150 K, 10355 data with $I > 2\sigma(I)$, 1024 parameters. Final R indices R_1 = 0.0745, wR_2 = 0.1882. The crystallographic assymetric unit contains 1.5 molecules of compound **2**, the core of the two molecules are essentially identical. The discussion of the structure refers to the molecule on a general position. The geometric parameters for the molecule residing on a centre of symmetry can be found in the supplementary material. CCDC 182/1408. See http://www.rsc.org/suppdata/cc/1999/2045/ for crystallographic files in .cif format.

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