Unusual luminescent octanuclear stellate platinacycle self-assembled by Pt–Ag bonds†

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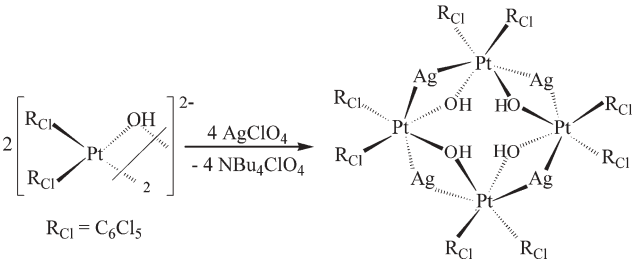
Received (in Cambridge, UK) 30th April 2007, Accepted 3rd July 2007
First published as an Advance Article on the web 23rd July 2007
DOI: 10.1039/b706439j

An unprecedented macrocyclic luminescent octanuclear cluster *cyclo*-[{Pt(C_6Cl_5)$_2$(μ-OH)(μ-Ag)}$_4$] (*Pt–Ag*) 2 was self-assembled by the formation of Pt(II)–Ag(I) bonds; the optical properties of this complex were also investigated.

Nanoscopic, macrocyclic platinum-containing assemblies are receiving increasing attention due to their intriguing topologies and their potential as functional materials.[1–4] The commonly used strategies for obtaining these systems involve self-assembly and templating processes based on strong metal-linking ligand–metal bonds or, in some instances, weaker forces such as hydrogen bonding.[1–4] The majority of the work has been focused on systems based on relatively strong Pt–X (X = N, P, C) bonds, but several examples containing less stable soft–hard Pt(II)–O bonds are also known.[5,6] In this area, luminescent platinum macrocycles are scarce and are limited to systems containing organic dye molecules as connectors or corners.[4,7,8]

Attractive interactions between closed or open shell metal centres (d^8, d^{10} or s^2) have been employed increasingly as a powerful tool for the generation of polymetallic systems, which display interesting photophysical and electronic properties.[9–12] Although the presence of metallophilic bonding interactions is a fairly common feature in extended chain supramolecular Pt(II)(d^8)[13–15] and mixed Pt(II)(d^8)–d^{10}(Ag(I), Au(I)),[16–18] s^2(Tl(I))[19,20] systems, the use of these non-covalent Pt–M bonds to build up macrocycles and cages has hardly been explored. We report here an unprecedented luminescent cyclic cluster, *cyclo*-[{Pt(C_6Cl_5)$_2$(μ-OH)(μ-Ag)}$_4$] (*Pt–Ag*) **2**, composed of two interlaced eight-membered rings of S_4 symmetry, [–Pt–Ag–]$_4$ and [–Pt–(OH)–]$_4$, which share their four Pt atoms.



Scheme 1

Macrocyclic cluster **2** was prepared as a bright yellow microcrystalline solid by reaction of the binuclear bis(μ-hydroxo) compound $(NBu_4)_2$[{Pt(C_6Cl_5)$_2$}$_2$(μ-OH)$_2$][21] **1** with 2 equiv. of $AgClO_4$ in a mixture of CH_2Cl_2–C_6H_6 (4 : 1) (Scheme 1). Cluster **2** was characterized by IR, elemental analysis and X-ray diffraction,‡ which was also used to confirm the binuclear nature of the precursor‡ (ORTEP view and selected bond lengths and angles in Fig. S1 in ESI†). The formation of **2** (Fig. 1) starting from

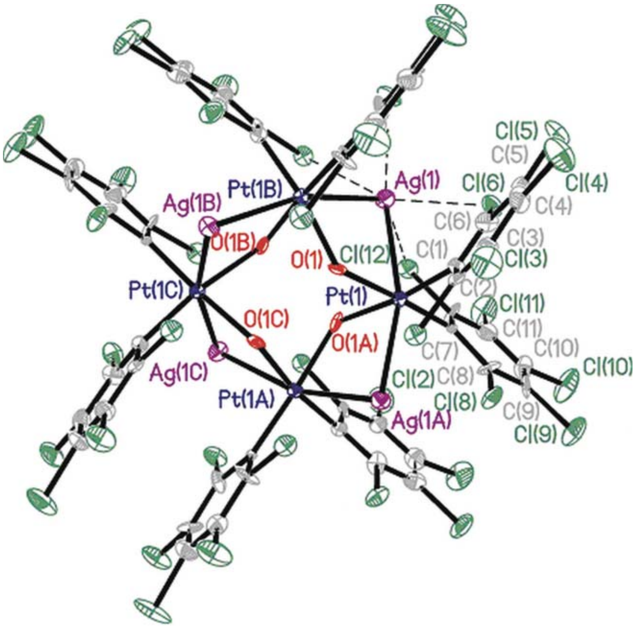


Fig. 1 ORTEP view of complex **2** showing the Ag···Cl interactions (involving only one Ag centre for clarity). Equivalent positions are indicated by "A" (y, $1 - x$, $2 - z$), "B" ($1 - y$, x, $2 - z$) and "C" ($1 - x$, $1 - y$, z) appended to the atom labels. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–C(1) 2.008(17), Pt(1)–C(7) 1.994(14), Pt(1)–O(1A) 2.072(11), Pt(1)–O(1) 2.085(12), Pt(1)–Ag(1A) 2.7811(15), Pt(1)–Ag(1) 2.8004(15), Ag(1)–Cl(6) 2.721(5), Ag(1)–Cl(2B) 2.739(5), Ag(1)–Cl(8B) 2.770(5), Ag(1)–Cl(12) 2.804(6), Ag(1A)–Cl(2) 2.740(5); O(1A)–Pt(1)–O(1) 84.3(6), O(1A)–Pt(1)–Ag(1A) 81.9(3), O(1)–Pt(1)–Ag(1A) 85.6(3), O(1A)–Pt(1)–Ag(1) 86.2(3), O(1)–Pt(1)–Ag(1) 81.2(3), Ag(1A)–Pt(1)–Ag(1) 163.08(5), Pt(1B)–Ag(1)–Pt(1) 78.87(4), Pt(1B)–O(1)–Pt(1) 117.0(5).

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† Electronic supplementary information (ESI) available: Experimental conditions and Fig. S1–S3. See DOI: 10.1039/b706439j

$(NBu_4)_2[\{Pt(C_6Cl_5)_2\}_2(\mu\text{-}OH)_2]$ **1** and Ag(I) involves the unusual cyclic condensation of two units of the binuclear bis(μ-hydroxo) structure into a $[Pt_4]^{4-}$ macrocycle $\{Pt(C_6Cl_5)_2(\mu\text{-}OH)\}_4{}^{4-}$ driven by the simultaneous formation of Pt–Ag bonds. This novel structure comprises four coplanar Pt(II) centres with four μ-OH bridging ligands, located alternately above and below the Pt_4 plane in order to accommodate the strain associated with the angle at the bridging OH groups. The Pt–O bond distances [2.072(11), 2.085(12) Å] are comparable to those found in the precursor **1** [2.122(4), 2.123(4) Å] but, as expected, the Pt–O–Pt angle increases from 98.67(16)° in dimer **1** to 117.0(5)° in complex **2**. Each platinum centre is also σ bonded to two C_6Cl_5 groups and completes a distorted octahedral coordination environment with the unbridged bonds to two Ag centres [Ag–Pt–Ag 163.08(5)°]. The four Ag(I) centres neutralize the central $[Pt_4]^{4-}$ cycle through eight short Pt–Ag bonds [2.7811(15), 2.8004(15) Å]. The Ag centres are arranged, as are the oxygen atoms, in an alternating up/down fashion with a very acute Pt–Ag–Pt angle [78.87(4)°], completing the cyclic octanuclear core of S_4 symmetry. The edge and diagonal Pt···Pt distances are 3.5454(9) and 5.0138(11) Å, respectively, and the Ag···Ag separations are 5.521(2) and 5.9319(19) Å. The silver atoms also establish short contacts with four *o*-Cl atoms of as many C_6Cl_5 rings [2.721(5)–2.804(6) Å], exhibiting a rare overall trigonal-prismatic environment (Fig. S2, ESI†). We[22–24] and others[16–18] have previously reported a wide variety of polynuclear platinum-silver complexes, and some alkynyl based metallocycles (M = Pt, Pd) have been shown to bind up to two Ag^+ cations in a "tweezer" fashion,[25,26] but the formation of a macrocycle based on this type of Pt–Ag bond does not have a precedent in the literature. It is interesting to note that the cluster crystallizes with four molecules of benzene and two of water. The octanuclear molecules are stacked in an eclipsed fashion with two molecules of benzene between successive clusters. The distance between the two benzene molecules is 3.659 Å. In addition, the relative parallel disposition of the pentachlorophenyl ligands of adjacent platinum atoms within the cluster and between neighbouring clusters results in the formation of square channels parallel to the crystallographic *c*-axis (see Fig. 2), which accommodate the remaining C_6H_6 and H_2O molecules.

The yellow cluster **2** is insoluble in benzene and chlorinated solvents but it is slightly soluble in acetone or tetrahydrofuran yielding nearly colourless solutions probably due to partial breaking of the Pt–Ag bonds as suggested by conductivity measurements (135 S cm^2 mol^{-1}, acetone solution). Along the same lines, the UV/VIS spectrum of **2** in the solid state exhibits a low energy absorption at 450 nm, which disappears in acetone solution ($\lambda_{abs}{}^{max}$ = 412 nm) (Fig. S3, ESI†). In contrast to previously reported extended Pt–Ag chains, which were found to be non-emissive,[17,27] complex **2** exhibits a bright long-lived green–yellow emission (λ_{em} = 521 nm, λ_{exc} = 340–460 nm; Φ_{solid} = 29%, λ_{exc} = 390 nm; τ = 5–6 μs at 298 K) which is slightly red-shifted (529 nm) at 77 K (Fig. 3). This emission is related to three excitation maxima at 340, 390 and 466 nm, respectively. The nature of the emission is suggested to be phosphorescence of the $^3(d\sigma^*p\sigma)$ excited state related to the Pt–Ag bonding interactions. Similar emissive states have been reported for bimetallic complexes $[PtAg(\mu\text{-}dppm)_2(C{\equiv}CPh)_2]PF_6$ ($\lambda_{max}{}^{298}$ = 495 nm)[28] and $[PtAg(\mu\text{-}dppm)_2(CN)_2]CF_3SO_3$ ($\lambda_{max}{}^{298}$ = 450 nm)[29] containing also Pt–Ag bonds. Interestingly, fluid colourless solutions of **2** in acetone or thf do not emit but they exhibit an intense blue luminescence upon freezing (470 nm, acetone; 468 nm, thf), which is only related with two excitation maxima at 358 and 412–415 nm, respectively. The remarkable blue-shift in relation to the emission in the solid state and the absence of the low energy feature in the excitation spectra (seen at 466 nm in the solid state) suggests that the cyclic geometry is not present in solution. It is also noteworthy that green–yellow crystals of **2**, become white and non-emissive almost immediately (1 min or less) upon exposure to acetone vapours. This white form reverts to the emissive green–yellow form upon exposure to air (≈2 min). Although the source of the observed vapochromism is not known, the associated change in the colour of the complex and the quenching of the luminescence could likely be due to the fact that the absorbed molecules bind in a reversible way to the Ag(I) centres. These interactions presumably modify the platinum–silver distances in the cyclic framework.

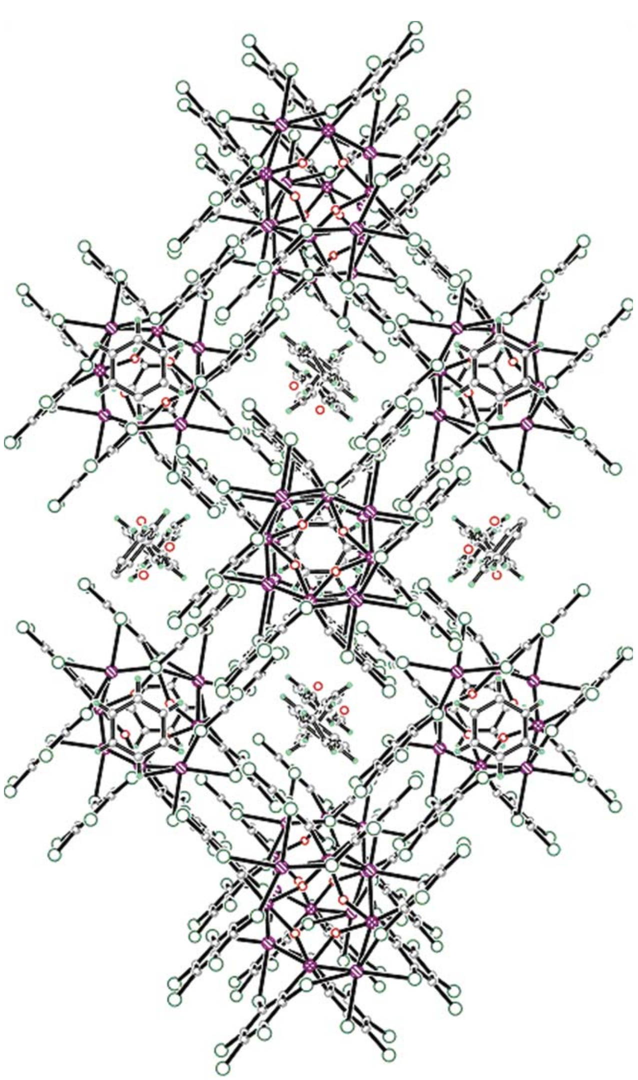

Fig. 2 Unit-cell packing diagram for the crystal structure of *cyclo*-$[\{Pt(C_6Cl_5)_2(\mu\text{-}OH)(\mu\text{-}Ag)\}_4]\cdot 4C_6H_6\cdot 2H_2O$ **2** showing the solvent molecules in the lattice.

In summary, the unprecedented macrocyclic, luminescent octanuclear cluster **2** is generated by an unusual isomerization of a $\{[Pt](\mu\text{-}OH)_2[Pt]\}^{2-}$ core to a $\{[Pt]_4(\mu\text{-}OH)_4\}^{4-}$ tetraanion, driven

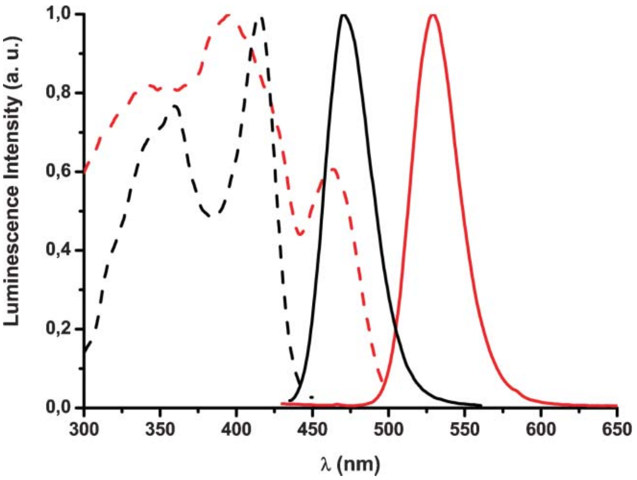

Fig. 3 Normalized excitation and emission spectra of **2** in the solid state at 77 K (red, —) and in acetone 10^{-4} M at 77 K (black, —) with the wavelength used: (red, ---) λ_{em} 529; (red, —) λ_{exc} 390; (black, ---) λ_{em} 470; (black, —) λ_{exc} 415.

by the simultaneous formation of Pt(II)–Ag(I) bonds. A remarkable blue-shift is observed in its emission on going from the solid state to glassy solution (acetone, thf) a feature attributed to destruction of the cyclic geometry in solution. The cluster exhibits also an interesting and reversible vapochromic response to acetone vapours. In our experience, this type of cluster is not formed either with similar pentafluorophenyl derivatives or with other binuclear pentachlorophenyl complexes when reacted with silver salts.[30,31] Research into other related systems, with particular interest in their optical properties is under way.

This work was supported by the Spanish MEC and FEDER (Projects CTQ08606-C02-01-02, and CTQ2005-03141).

Notes and references

‡ *Crystal data* for **2**: formula $C_{72}H_{32}Ag_4Cl_{40}O_6Pt_4$, 150 K, yellow crystals, tetragonal space group $I\bar{4}$, $a = b = 17.179(3)$, $c = 16.451(7)$ Å; $V = 4855(2)$ Å^3; $Z = 2$; $R_1 = 0.0465$; $wR_2 = 0.1037$; GOF = 1.032. There are two independent benzene sites, disordered about twofold axes. These were treated as rigid hexagons, in each case with three atoms in the asymmetric unit and three pseudo-atoms (zero occupancy) used to complete the hexagonal template. CCDC 645528.

Crystal data for **1**: formula $C_{56}H_{74}Cl_{20}N_2O_2Pt_2$, 100 K, white crystals, triclinic, space group $P\bar{1}$, $a = 12.846(3)$, $b = 16.273(3)$, $c = 18.070(4)$ Å, $\alpha = 77.19(3)$, $\beta = 73.55(3)$, $\gamma = 82.65(3)°$, $V = 3524.1(12)$ Å^3; $Z = 2$; $R_1 = 0.0436$; $wR_2 = 0.0943$; GOF = 1.033. Compound **1** crystallizes with two independent half-dianions per asymmetric unit, both lying about independent inversion centres. There are also two independent Bu_4N^+ cations on general positions, one of which suffers nearly whole-body disorder, with 14 of the 17 atoms split into two disorder components. CCDC 645527.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706439j

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