

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

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Experimental

General Procedures and Materials. The starting materials (NBu₄)[{Pt(C₆Cl₅)₂}₂(μ-OH)₂] (**1**)^{§1} and AgClO₄^{§2} were prepared as described elsewhere. Elemental analyses were carried out with a Perkin-Elmer 2400-Series II microanalyser. IR spectra of KBr discs were recorded on a Spectrum One Perkin-Elmer spectrophotometer (4000–350 cm⁻¹). Conductivities were measured in acetone solution (*ca.* 5 × 10⁻⁴ molL⁻¹) using a Jenway 4510 conductimeter. UV-visible spectra in solution were obtained on a Hewlett Packard 8453 spectrometer. Diffuse reflectance UV-vis (DRUV) spectra of pressed powder were recorded on a Unicam UV-4 spectrophotometer with an integrating sphere accessory type Spectralon RSA-UC-40 Labsphere. Emission, excitation spectra and lifetimes were obtained on a Perkin-Elmer Luminescence Spectrometer LS 50B and on a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter. Quantum yield in solid state was measured upon excitation at 390 nm using a F-3018 Integrating Sphere mounted into a Fluorolog 3-11 Tau-3 spectrofluorimeter. Data were fitted using the Jobin-Yvon software package.

Caution: Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Preparation of crystals of $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}_6\text{Cl}_5)_2\}_2(\mu\text{-OH})_2]$ ^{§1} (1**).** Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of *n*-hexane into a solution of **1** in CH_2Cl_2 at 5 °C.

Synthesis of *cyclo*- $[\{\text{Pt}(\text{C}_6\text{Cl}_5)_2(\mu\text{-OH})(\mu\text{-Ag})\}_4]\cdot\text{C}_6\text{H}_6$ (*Pt-Ag*) (2**).** C_6H_6 . To a solution of $(\text{NBu}_4)_2[\{\text{Pt}(\text{C}_6\text{Cl}_5)_2\}_2(\mu\text{-OH})_2]$ (**1**) (0.10 g, 0.05 mmol) in CH_2Cl_2 (20 cm³) was added AgClO_4 (0.02 g, 0.10 mmol) and the amount of C_6H_6 required to dissolve it (*ca.* 5 cm³). Almost immediately a bright yellow solid formed and after 30 min of stirring under exclusion of day-light, it was filtered, washed with *n*-hexane and vacuum dried (**2**: 0.05 g, 0.01 mmol, 40% yield). Anal. Found: C, 19.7; H, 0.4. $\text{C}_{54}\text{H}_{10}\text{Ag}_4\text{Cl}_{40}\text{O}_4\text{Pt}_4$ requires: C, 23.9; H, 0.9%. IR (Nujol, cm⁻¹): ν_{max} 3565 (m), 3264 (m), 1492 (w), 1333 (vs), 1312 (s), 1299 (s), 1287 (vs), 1210 (m), 1030 (w), 1108 (w), 950 (w), 845 (w; C_6Cl_5 : X-sensitive vibr.),^{§3} 739 (w), 703 (w), 670 (s), 628 (s; Pt–C),^{§4} 530 (sh), 516 (w) and 360 (w). Λ_{M} (acetone): 135 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$.

Crystals of **2** suitable for X-ray diffraction analysis were obtained by room temperature slow diffusion of a three-layer system: i) a C_6H_6 solution of AgClO_4 overlaid on ii) a thin layer of pure $\text{CH}_2\text{ClCH}_2\text{Cl}$ overlaid on iii) a CH_2Cl_2 solution of **1**. The $\text{CH}_2\text{ClCH}_2\text{Cl}$ interlayer was introduced to avoid immediate reaction between the upper and lower solutions.

References

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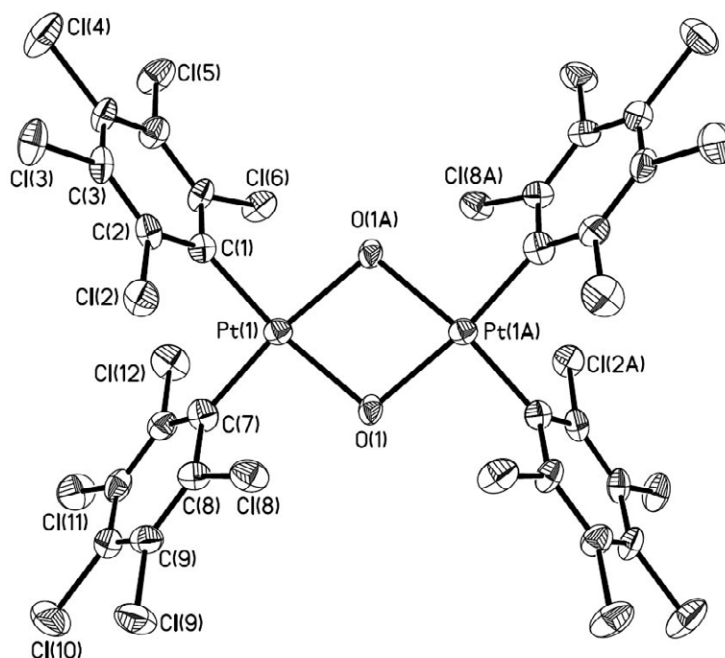


Fig. S1 Molecular structure of the anion $[\{\text{Pt}(\text{C}_6\text{Cl}_5)_2\}_2(\mu\text{-OH})_2]^{2-}$ in **1**. Only one of the two independent anions is shown. The additional "A" letter in the atom labels indicates atoms at equivalent position $(-x, 1-y, 1-z)$. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)-C(1) 1.985(6), Pt(1)-C(7) 1.985(6), Pt(1)-O(1) 2.122(4), Pt(1)-O(1A) 2.123(4), Pt(1)-Pt(1A) 3.2201(14); C(1)-Pt(1)-C(7) 96.9(2); C(7)-Pt(1)-O(1) 90.9(2); C(1)-Pt(1)-O(1A) 90.83(19); O(1)-Pt(1)-O(1A) 81.33(16); Pt(1)-O(1)-Pt(1A) 98.67(16).

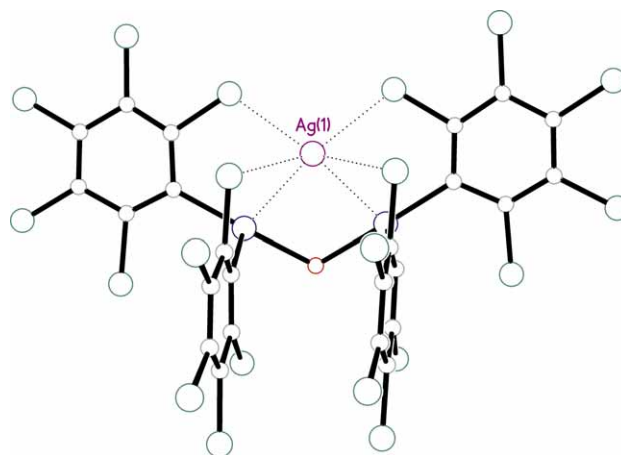
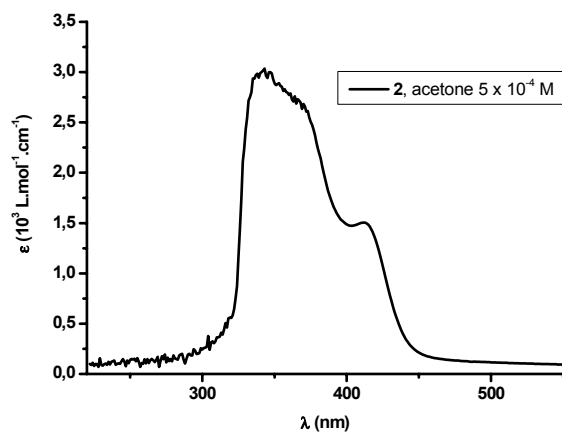
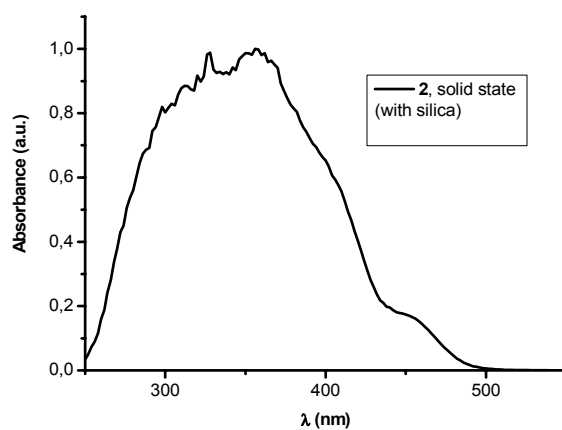


Fig. S2 Prismatic trigonal environment for Ag atoms in complex **2** showing the Ag \cdots Cl interactions.



(a)



(b)

Fig. S3 (a) Absorption spectrum of **2** in acetone solution 5×10^{-4} M; (b) Diffuse Reflectance UV-vis (DRUV) spectrum of **2** in the solid state (with silica).