Solvent-induced lone pair activity tuning and vapoluminescence in a Pt$_2$Pb cluster$^{†}$

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We report a novel cluster, [$\text{Pt}$(C$_6$F$_5$)(bzq)]$_2$Pb(Spy)$_2$, that displays reversible vapoluminescence to specific organic vapours; this behaviour can be related to the stereochemical activity of the lone pair around the Pb$^{II}$ in the ground state and to the distinct distortion of the coordination environment (1 and 1-solvent) upon photoexcitation.

Controlling the photoluminescence of transition-metal complexes by external stimuli is currently attracting widespread interest due to the possibility of obtaining photofunctional materials. In this context, the development of vapochromic or vapoluminescent materials, which show solid-state reversible colour changes in response to volatile organic compounds (VOCs), has received increased attention in recent years.$^{1,2}$ In this field, most of the reported materials are based on Pt$^{III}$,$^{3,4}$ and Au$^{I}$,$^{5,6}$ compounds, though some interesting heterometallic systems [mainly Au-M (M = Ti,$^7$ Ag,$^8$ Cu$^{II}$,$^9$)] have also appeared.

The spectral changes (absorption and emission) generally originate from a variety of mechanisms. For many systems they arise due to subtle modifications in the intermolecular interactions (metallophilic, π-π stacking, hydrogen bonding or C-H···π secondary contacts), associated with the sorption/desorption process. In other substances, particularly 3d metal complexes,$^{1,9}$ and more rarely from Re$^{III}$,$^{10}$ and Pt$^{III}$,$^{11}$ or Au$^{I}$ complexes,$^{5,6}$ the volatile molecule becomes coordinated/dissociated in the first coordination sphere of the metal ion, promoting a change in the geometry of a chromophore or rarely, generating isomerisation. Other less common materials only show a slight colour change in the ground state, but they change the luminescence drastically, mainly as result of exciplex formation between the host-framework and the solvent absorbed guest.$^{12}$ Though remarkable efforts have been devoted to understanding the origin of the vapochromic/vapoluminescent responses, on many occasions it is not a simple task. Therefore, further design of vapochromic materials with the aim of probing the relationship between solid state structures and the photophysical response still remains a considerable challenge.

We are interested in constructing luminescent materials based on different attractive interactions between Pt$^{II}$ fragments and the borderline closed-shell Pb$^{II}$ ion.$^{13,14}$ We envisioned that the well known flexibility of Pb$^{II}$ would impart fascinating luminescence properties through different degrees of activity of the lone pair 6s.$^{15}$ We recently found that [{Pt(C$_{6}$F$_{5}$)(bzq)}$_{2}$Pb(OH$_{2}$)$_{2}$]$_{2}^{-}$ showed reversible interaction with acetone with concomitant change in colour and emission. The lack of suitable crystals for an X-ray study and also the low stability of this complex prevented us to establish the nature of this behaviour.$^{13}$ We report here the syntheses and remarkable structural and luminescence properties of a very stable Pt$_2$Pb cluster, which shows a dynamic and flexible core able to respond to solvent vapours through structural changes around the Pb$^{II}$ ion.

When a suspension of [Pb(Spy)$_2$] in CH$_2$Cl$_2$ is treated with the solvate [Pt(bzq)(C$_6$F$_5$)(acetone)]$_{16}$ (1:2 molar ratio) it gradually dissolves, to afford a deep red solution from which a novel luminescent (orange-red) compound, formulated as [{Pt(C$_6$F$_5$)(bzq)}$_{2}$Pb(Spy)$_2$]$_{1}$ (I), is isolated as an orange solid in high yield (Experimental in ESI). Interestingly, a visual and reversible change in the luminescence of the solid from orange-red to yellow-orange was observed in contact with a drop of acetone. We found the formation of two pseudopolymorphs depending on the solvent. Crystallization at low temperature from CH$_2$Cl$_2$/n-hexane or acetone/n-hexane produces orange crystals of stoichiometry [{Pt(C$_6$F$_5$)(bzq)}$_{2}$Pb(Spy)$_2$]$_{1}$CH$_2$Cl$_2$ (1:1.5CH$_2$Cl$_2$) and [{Pt(C$_6$F$_5$)(bzq)}$_{2}$Pb(Spy)$_2$(acetone)]$_{1}$acetone (2:1-acetone), respectively. The X-ray structure of 1:1.5CH$_2$Cl$_2$ (Fig. 1, Tables S1 and S2, ESI) revealed the formation of a bent [Pt-Pb-Pt 140.753(9)º] Pt$_2$Pb cluster with a very short Pt-Pb bond [Pt(1)-Pb 2.7832(3) Å], supported by a bridging (μ-κN,S) pyridine-2-thiolate ligand (Spy), and a longer Pt-Pb [Pt(2)-Pb 3.1642(3) Å] bond, which is associated with the more unusual 6 e’ (μ-κN,S;2κS) Spy’ bridging ligand. The short Pt-Pb distance is only slightly longer than the sum of the covalent radii (2.75 Å), and both distances are in the range reported for the relatively scarce number of species containing Pt-Pb bonds.$^{17,18}$ The Pb-N [2.565(5), 2.683(5) Å] and Pb-S(2) [2.797(1) Å] distances are comparable to those reported for [Pb(Spy-CF$_3$)$_2$]$_{2}$.$^{18}$ The Pb-S(1) distance [3.545(2) Å] is far of bonding interaction. As has been previously noted,$^{15}$ the exact geometry around Pb$^{II}$ is not easy to define. In this system, the lead centre exhibits a primary “Pt$_4$N$_2$S$_2$” distorted square pyramidal five-coordination, with the N atoms [N(2)-Pb-N(4) 151.72(15)°] and the Pt atoms [Pt-Pb-Pt 140.753(9)°] defining the basal positions and the bridging S(2) centre the apex (Fig. S1, ESI). Short intra-(Spy ‘bzq) and intermolecular (bzq ‘bzq) π π contacts are also observed (Fig S3, ESI).

The structure of [{Pt(C$_6$F$_5$)(bzq)}$_{2}$Pb(Spy)$_2$(acetone)]$_{1}$acetone (2:1-acetone) (Fig. 1, Tables S1 and S3, ESI) shows that one of the two and a half molecules of acetone present in the lattice is directly ligated to the Pb$^{II}$ centre, causing a remarkable change in its coordination sphere. The Pb-O distance [2.775(5) Å] reported for Pt$_2$Pb cluster

![Image](image1.png)
acetone is the presence of a ν(C=O) band at 1696 cm⁻¹, lower than that of the free acetone (~1720 cm⁻¹). Curiously, the coordination of the acetone causes the rupture of the Pb-S bond (Fig. S4, ESI) and enforces a small conformational change in the five membered ring (PbNC5Spt), resulting in a final cis geometry of N atoms around PbII [N(2)-Pb-N(4) 84.20(13)°] and also in a more acute Pt-Pb-Pt angle [133.291(8)°] compared to that in 1. This rearrangement seems to be accompanied by a decrease in the lone pair activity in relation to 1 (also supported by TD-DFT).

Thus, in 2 the local Pt₄N₂O environment around the PbII ion is more holodirected, and displays less asymmetric and slightly shorter (within average) Pb-N [2.497(4), 2.568(4) Å] and Pb⁴⁺Pt [2.8401(3), 2.9790(3) Å] distances in relation to those found in 1. These changes seem to be responsible for the observed photoluminescent behaviour. In fact, despite the incorporation of a greater amount of acetone solvent (density: 2.046 g/cm³) and the solvate powder (Fig. S7 and Table 1 for details). The emission bands (620 1, 580 nm 2) do not change significantly at low temperature and display similar excitation spectra, suggesting that the remarkable blue-shift in the emission of 2 in relation to 1 could be related to the occurrence of a smaller Stokes shift in 2.

Interestingly, complex 1 can be converted to 2 through sorption of acetone vapour (Fig. 1). When powder 1 is exposed to Me₂CO vapour, the solid-state luminescence colour changes from orange-red (620 nm) to yellow-orange (580 nm) in a few minutes (~10 min), indicating the transformation has occurred. On standing, the acetone was completely lost in ~12 h, recovering 1. The desolvation, when passing a stream of air onto the sample 1·x(acetone) to 1. Conclusively, powder X-ray diffraction (PXRD) diagrams were recorded for the acetone was completely lost in 12h, recovering 1. Subsequent treatment of the crushed powder 1 with a drop of acetone leads again to the initial yellow-orange emissive phase (2·x(acetone)). The characteristic emission of 1 and 2 can be recovered several times by sequential and repetitive path (grinding and treatment with acetone). The loss of acetone molecules, determined by TGA (Fig S10, ESI), fits to a molar ratio acetone/1 of ca. 2:1 [2·x(acetone), x~1]. Conclusively, powder X-ray diffraction (PXRD) diagrams were recorded for solid samples of 1 and 1 exposed to saturated acetone vapour (2·x(acetone)) at 298 K. The diffraction peaks correspond approximately to those calculated from the diffraction data of the single crystal X-ray analysis of 1·1.5CH₂Cl₂ and 2·1.5acetone, respectively (Fig S11, ESI).

Vapour response of 1 to other donor solvents such as MeCN, MeOH and THF is also relatively fast [MeCN (~10 min) > MeOH (20 min) > THF (30 min)], provoking a distinct shift to the yellow region in the photoemission (Fig. S12 and S13, Table 1). However, no-donor solvents such as toluene, hexane or even diethyl-ether do not trigger a response. The solvated products, 1·x(solvent), possibly similar to 2·x(acetone), were obtained as pure phases by addition of a drop of the respective solvent to 1. The desolvation process for 1·THF (Fig. S8b), examined by emission spectroscopy, followed a similar pattern to 2·x(acetone).

It is assumed that these donor solvents L are able to approach to the PbII, causing a change in the local environment from a distorted holodirected “Pb₂N₂S” to a more symmetrical “Pb₂N₂L”.

As listed in Table 1, in the solvates the phosphorescence yields are smaller and the calculated non-radiative constants, knr, are larger than those of 1. The presence of a more rigid 6c Spy bridging ligand in 1 could explain the lower observed knr value.

<table>
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Table 1 Luminescence Properties of $\{[\text{Pt(C}_6\text{F}_5)(\text{bzq})]_2\text{Pb(Spy)}_2\}$
the associated Pt(bzq) fragment (μ-Spy 48% Ptbqz 50% 1 vs μ-Spy 35% Ptbqz 64% 2). The calculated phosphorescence (560 nm 1, 531 nm 2) reproduces the observed trend and can be ascribed to an admixture of intraligand (bzq, more important in 2) and ligand (Spy)-to-metal (Pt-Pb) charge transfer transitions. The different Stokes shift (4593 cm⁻¹ 1 vs 3231 cm⁻¹ 2) reflects the smaller geometrical change in the excited state of the more symmetrical solvate 2 and is consistent with the observed blue shift in the emission.

In summary, complex 1 represents an unusual example of vapoluminescent lead-based material. X-ray and DFT studies suggest that the change in the emission colour of 1 upon uptake VOCs can be primarily attributed to a different distortion of the geometry around the lead center upon photoexcitation. Further studies of similar clusters are currently in progress to understand the role of the Pt fragments and the thiolates ligands in this mechanism assumption.

Acknowledgment. This work was supported by the Spanish MICINN (CTQ2008-066669-C02-01,02/BQU and a grant for S. R.). The authors also thank CESGA for computer support.

Notes and references