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A rapid screening, “combinatorial-type” survey of the metalloligand chemistry of $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2$ using electrospray mass spectrometry

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Electrospray mass spectrometry is a rapid and powerful technique for a combinatorial-like survey of the chemistry of the metalloligand $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2$, leading to the successful isolation and crystallographic characterisation of the novel protonated species $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})(\mu\text{-SH})$ together with a range of metallated derivatives.

The sulfido complex $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2$ **1** has attracted much interest in recent years, particularly for its ability to act as a metalloligand in the assembly of a diverse range of sulfido-bridged higher nuclearity aggregates.^{1,2} In this Communication, we describe how electrospray mass spectrometry (ESMS) can be used as a rapid, powerful combinatorial-type tool for surveying the metalloligand chemistry of **1** with a range of metal substrates. The utility of ESMS as a general technique for the characterisation of coordination and organometallic complexes is well-known,³ but as far as we are aware, there are no previous extensive studies which have used ESMS as the primary screening tool for surveying the reactivity of coordination complexes, the results of which are then used to target subsequent synthetic efforts. Advantages of this approach include the need for only minute amounts of material, rapid screening of potential substrates for further study, and the accepted general agreement between mass spectrometric data and solution speciation.³ In parallel studies, we are investigating the reactivity of the selenide analogue $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-Se})_2$.⁴

The positive-ion ES spectrum of **1** in methanol gives ions due to protonated **1**, $[\mathbf{1} + 2\text{H}]^{2+}$ (m/z 752) and $[\mathbf{1} + \text{H}]^+$ (m/z 1504), together with ions $[(\mathbf{1})_2 + \text{Ag} + \text{H}]^{2+}$ (m/z 1557) and $[(\mathbf{1})_2 + 2\text{Ag}]^{2+}$ (m/z 1611) formed by adventitious Ag^+ ions in the spectrometer.

Addition of a small quantity of formic acid increased the intensity of the m/z 752 ion. The novel mono-protonated complex $[\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})(\mu\text{-SH})]\text{PF}_6$ **2** was subsequently obtained by titration of **1** with HCl, followed by metathesis with NH_4PF_6 . This complex, which is related to the monomethyl complex $[\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})(\mu\text{-SMe})]^+$,⁵ has not been isolated previously. Complex **2** gives two distinct ^{31}P NMR signals [δ 20.2, $^1\text{J}(\text{PtP})$ 2705 and 23.0, $^1\text{J}(\text{PtP})$ 3582, $^2\text{J}(\text{PP})$ 15] together with a resonance for the SH proton at δ 3.48 in the ^1H NMR spectrum. Confirmation of its identity was obtained from an X-ray diffraction study, Fig. 1.[†] The dihedral angle of the four-membered Pt_2S_2 ring is 135° , which is similar to the methylated analogue $[\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})(\mu\text{-SMe})]^+$ (138°);⁵ There have only been two previous structural determinations on underivatized $\text{Pt}(\mu\text{-sulfide})_2\text{Pt}$ systems, with $[(\text{dppe})\text{Pt}(\mu\text{-S})_2\text{Pt}(\text{dppe})]$ being folded (140.2°)⁶ and $[(\text{dppy})_2\text{Pt}(\mu\text{-S})_2\text{Pt}(\text{dppy})_2]$ ($\text{dppy} = 2\text{-diphenylphosphinopyridine}$)⁷ being planar. Structural features of such $\{\text{M}_2\text{S}_2\}$ systems has attracted recent interest.^{1,8} The structure of **2** is the first containing the Pt–SH–Pt moiety, although $\mu\text{-SH}$ complexes of other metals such as palladium⁹ and nickel¹⁰ have been structurally characterised.

The reactivity of complex **1** towards a range of halide-containing main group (e.g. Sn and Hg) and transition metal (e.g. Au) complexes can conveniently be monitored by ESMS, and allows the identification of novel sulfide-bridged aggregates. As an illustrative example, the reaction of **1** with the organogold(III) complexes $\text{AuCl}_2(\text{tolpy})$ **3a**¹¹ and $\text{AuCl}_2(\text{pap})$ **3b**¹² monitored by positive-ion ESMS show a single major peak in each case, due to the aggregate cations $[\text{Pt}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2\text{Au}(\text{tolpy})]^{2+}$ and $[\text{Pt}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2\text{Au}(\text{pap})]^{2+}$, as illustrated for the pap system in Fig. 2, with excellent agreement

between observed and calculated isotope patterns. On a synthetic scale, metathesis of the AuCl₂(tolpy) reaction solution with NH₄BF₄ gave yellow salts of [Pt₂(PPh₃)₄(μ₃-S)₂Au(tolpy)][BF₄]₂ **4**, Fig. 3.⁸ While there have been several studies on aggregates with {M₃S₂} cores containing Pt and Pd,^{1,13} this is the first time that the isoelectronic gold(III) centre has been incorporated, though gold(I) and silver(I) derivatives of the {Pt₂S₂} core have been known for some time.^{1,14} The isolation of silver(I) halide aggregates containing the isoelectronic {Au^{III}₂S₂} core has been reported.¹⁵ The successful formation of **4** is facilitated by the increased stability towards reduction (by sulfur-based ligands) of gold(III) complexes bearing *N,C*-cyclometallated ligands.¹⁶ The structure confirms the formulation of **4** as the first heterometallic aggregate of the {Pt₂S₂} core containing gold(III), and the presence of the methyl group allows for unambiguous assignment of N(1) and C(1) on the square-planar gold atom. The {Pt₂S₂} ring is, as expected, puckered (126.8°) with average Au–S bond distances 2.358(2) Å.

The successful isolation and characterisation of the novel species, initially identified by mass spectrometry experiments, clearly demonstrates the power of this methodology. It helps researchers identify possible products before they are synthesized on a macroscopic scale. This pre-synthesis scanning helps to cut down wastage and increases the chance of achieving successful syntheses. Extension to organo-tin(IV) halides leads to the successful isolation of a range of adducts of complex **1** with SnMeCl₂⁺, SnMe₂Cl⁺, and SnPhCl₂⁺ moieties (derived from SnMeCl₃, SnMe₂Cl₂ and SnPhCl₃, respectively), their formulation being confirmed by single crystal X-ray diffraction studies. Full details will be reported in due course. Although **1** is a good model for this methodology, it is neither unique nor exclusive. One can anticipate similar success in other systems.

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Captions for Figures

Fig. 1. Molecular structure of $[\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})(\mu\text{-SH})][\text{PF}_6]$ (**2**). The phenyl rings of the PPh_3 ligands have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pt(1)–S(1), 2.3289(8); Pt(1)–S(1A), 2.3536(8); Pt(1)–P(1), 2.2965(8); Pt(1)–P(2), 2.2712(8); Pt(1)–S(1)–Pt(1A), 91.01(3); Pt(1)–S(1A)–Pt(1A), 91.01(3); S(1)–Pt(1)–S(1A), 78.91(4); S(1)–Pt(1A)–S(1A), 78.91(4); P(1)–Pt(1)–P(2), 98.97(3); P(1)–Pt(1)–S(1A), 78.91(4); S(1)–Pt(1A)–S(1A), 78.91(4); P(1)–Pt(1)–P(2), 98.97(3); P(1)–Pt(1)–S(1), 167.60(3); P(2)–Pt(1)–S(1), 92.88(3); P(1)–Pt(1)–S(1A), 89.06(3); P(2)–Pt(1)–S(1A), 171.27(3).

Fig. 2. Positive ion ES spectrum of a 1:1 mixture of **1** and $\text{AuCl}_2(\text{pap})$ **3** in MeOH at a cone voltage of 20 V, demonstrating the facile and exclusive formation of $[\text{Pt}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2\text{Au}(\text{pap})]^{2+}$. The inset shows (a) observed and (b) calculated isotope patterns for the dication.

Fig. 3. Molecular structure of one of the cations of $[\text{Pt}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2\text{Au}(\text{tolpy})][\text{BF}_4]_2$ (**4**) with thermal ellipsoids at the 50% probability level. The phenyl rings of PPh_3 have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt(3)–S(3), 2.371(3); Pt(3)–S(4), 2.362(3); Pt(4)–S(3), 2.377(3); Pt(4)–S(4), 2.360(3); Au(2)–S(3), 2.357(4); Au(2)–S(4), 2.371(4); Pt(3)–P(5), 2.302(3); Pt(3)–P(6), 2.274(3); Pt(4)–P(7), 2.269(3); Pt(4)–P(8), 2.296(3); Au(2)–C(13), 1.94(3); Au(2)–N(2), 2.18(2); Pt(3)–S(3)–Pt(4), 87.66(11); Pt(3)–S(4)–Pt(4), 88.25(11); Pt(3)–S(3)–Au(2), 82.81(11); Pt(3)–S(4)–Au(2), 82.68(11); Pt(4)–S(3)–Au(2), 82.42(11); Pt(4)–S(4)–Au(2), 82.46(11); S(3)–

Pt(3)–S(4), 78.20(12); S(3)–Pt(4)–S(4), 78.12(12); P(5)–Pt(3)–P(6), 99.92(12); P(7)–Pt(4)–P(8), 98.92(12); P(5)–Pt(3)–S(3), 167.06(12); P(7)–Pt(4)–S(3), 170.87(12); P(5)–Pt(3)–S(4), 88.88(12); P(7)–Pt(4)–S(4), 93.07(12); S(3)–Au(2)–S(4), 78.31(11); C(13)–Au(2)–N(2), 81.0(9); C(13)–Au(2)–S(3), 107.8(6); C(13)–Au(2)–S(4), 173.7(6); N(2)–Au(2)–S(3), 171.2(6); N(2)–Au(2)–S(4), 93.0(6).

Footnotes

[¶] Crystal data for **2**·CH₂Cl₂: C₇₃H_{62.5}Cl₂F₆P₅Pt₂S₂, M = 1733.78, monoclinic, $a = 21.3742(6)$, $b = 18.7308(6)$, $c = 17.1833(5)$ Å, $\beta = 90.025(1)^\circ$, $V = 6879.4(4)$ Å³, $T = 223(2)$ K, space group $C2/c$, $Z = 4$, $\rho_{\text{calc}} = 1.674$ g·cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å, 17188 reflections measured, 6043 unique ($R_{\text{int}} = 0.0217$) which were used in all calculations. The data were collected on a Bruker AXS SMART diffractometer and solved by direct methods in conjunction with standard difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions. Refinement converged to $R_F = 0.0218$, $wR(F^2) = 0.0518$ (all data).

[§] Crystal data for **4**: C₁₆₈H₁₃₀Au₂B₂F₈N₂P₈Pt₄S₄, M = 3900.65, triclinic, $a = 18.0900(2)$, $b = 21.3643(2)$, $c = 23.0658(2)$ Å, $\alpha = 98.643(1)^\circ$, $\beta = 95.966(1)^\circ$, $\gamma = 93.923(1)^\circ$, $V = 8733.4(2)$ Å³, $T = 220(2)$ K, space group = $P\bar{1}$, $Z = 2$, $\rho_{\text{calc}} = 1.483$ g·cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å, 83105 reflections measured, 30322 unique ($R_{\text{int}} = 0.0562$) which were used in all calculations. There are two independent cations present, one of which exhibits little disorder. In the other cation, the tolyp ligand is disordered (occupancies 50:50). Isotropic thermal parameters of all the non-hydrogen atoms of the disordered ligands were refined. The two BF₄⁻ anions show high thermal activities; one BF₄⁻ was disordered (occupancies 70:30), and the anion with 70% occupancy was found to be further disordered along one B–F axis (40:30). Common isotropic thermal parameters

were refined for the atoms in the anions. Refinement converged normally with $R_F = 0.0735$, $wR(F^2) = 0.1208$ (all data).