

Nucleophilicity of selenide in $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$. Molecular assembly of a novel $\{\text{In}_2\text{Pt}_4\text{Se}_6\}$ core.

Jeremy S. L. Yeo^a, Jagadese J. Vittal^a, William Henderson^b and T. S. Andy Hor^{*a}

^a *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543. (E-mail: chmandyh@nus.edu.sg)*

^b *Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand. (E-mail: w.henderson@waikato.ac.nz)*

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Indium chalcogenides, especially the ternary systems, exhibit optical, magnetic and electronic properties that are technologically significant.ⁱ A good example is found in CuInSe_2 (CIS) which attracts interest in photovoltaic applications such as solar cellsⁱⁱ because of its favourable band gap and relatively high absorption coefficient. Although this is a potentially rich area, very little work has been done due to the general poor understanding of the molecular/solid state interface chemistry of indium chalcogenides and, critically, the lack of suitable building blocks for these materials. Materials such as MBX_2 ($\text{M} = \text{Na}, \text{K}, \text{Cs}, \text{Rb}$; $\text{B} = \text{Al}, \text{Ga}, \text{In}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$) are usually prepared by high-temperature melt or solid-state reactions.ⁱⁱⁱ In line with the recent surge in the use of organometallic complexes as precursors to semiconductors,^{iv} our long-standing interest in mixed-metal chalcogenides,^v and the documented conducting properties of Pt-based materials,^{vi} we report herein a facile synthesis of the first Pt/In selenide complex, taking advantage the coordinating behavior of $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ at the Se sites. In this paper, and our earlier spectroscopic reports,^{vii} we demonstrate a synthetic strategy that gives access to a large variety of mixed metal selenides

under ambient conditions. This brings us an important step forward in the development of ternary semiconducting selenides of a large mix of metal or metalloid combinations.

$\text{In}(\text{ClO}_4)_3$ reacts with $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ in MeOH at r.t. to give $\{[\text{Pt}_2(\mu_3\text{-Se}_2)_2(\text{PPh}_3)_4]_2\text{In}_2(\mu\text{-Se})_2\} \{\text{ClO}_4\}_2$, **1** (47%)[†] instead of the expected 1:2 addition product *viz.* $[\text{In}\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4\}_2][\text{ClO}_4]_3$. Single-crystal X-ray analysis revealed a planar $\{\text{In}_2\text{Se}_2\}$ core sandwiched by two hinged $\{\text{Pt}_2\text{Se}_2\}$ moieties. (Fig. 1) It can also be viewed as two trigonal bipyramidal $\{\text{InPt}_2\text{Se}_2\}$ fragments connected at the In(III) ends by two $\mu_2\text{-Se}$ with a center of inversion at the center of the architecture. This hexametallic structure resembles that of the semiconducting anion $[\text{Ga}_6\text{Se}_{14}]^{10-}$ (Fig. 2)^{viii} by having a double-tetrahedra $\{\text{M}_2\text{Se}_6\}$ edge-linked with another $\{\text{M}_2\text{Se}_6\}$ or double-planar $\{\text{Pt}_2\text{Se}_2\text{P}_4\}$. The source of the two $\mu_2\text{-Se}$ atoms is tentatively traced to the liberation of HSe^- from the slow decomposition of $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ in the presence of a strong Lewis acid such as $\text{In}(\text{ClO}_4)_3$. Similar decompositions in the sulfide systems under the influence of HX or RX are known although the sulfide analogue of **1** has insofar eluded detection or isolation. Like the sulfide analogue,^{ix} $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ also decomposes in CH_2Cl_2 .^x In a separate experiment, addition of dilute HCl to a suspension of $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ in MeOH resulted in an instantaneous formation of a bright yellow solution, which readily turned orange. The product is presently unidentified but tentative assignment of the intermediate suggests it to be $[\text{Pt}_2(\mu\text{-Se})(\mu\text{-SeH})(\text{PPh}_3)_4]\text{Cl}$, which is analogous to a recently isolated sulfur analog.^{xi}

The two edge-linked $\{\text{Pt}_2\text{Se}_2\}$ butterflies (dihedral angle 129.3°) are almost perpendicular (89.1°) to the central planar $\{\text{In}_2\text{Se}_2\}$ unit, thus giving a C_{2h} symmetry to the molecule. The $\{\text{M}_2\text{Se}_2\}$ ring is expected to be planar for substituted $\mu_2\text{-Se}$ (e.g. $\text{Pt}_2\text{Se}_2(\text{PPh}_3)_4$,^{xii} $[\text{Ga}_6\text{Se}_{14}]^{10-}$,^{viii} In_4Se_3 ^{xiii} and TlSe ^{xiv}) and folded when it is alkylated or metallated (e.g. $[(\text{Me}_3\text{CCH}_2)_2\text{InSePh}]_2$ ^{xv}). The entire structure is supported by strong In-Se (aver. 2.5963 \AA)

[c.f. In_2Se_3 (2.69 Å),ⁱⁱⁱ NaInSe_2 (2.76 Å)ⁱⁱⁱ and $[(\text{Me}_3\text{CCH}_2)_2\text{InSePh}]_2$ (2.74 Å)^{xv}] and Pt-Se bonds with no formal interactions among the metals.

There are four MeOH solvates, two of which are non-coordinating and two within electrostatic distances, directly above and below the $\{\text{In}_2\text{Se}_2\}$ plane. Thermogravimetric analysis (TGA) is consistent with the solvate disposition, with two discrete steps of weight loss below 100°C. The weight loss registered (3.2 %) agrees with the calculated value of 3.3 %. We are currently studying the thermal product(s) with the intention of relating them to the ternary products of $\text{Pt}_x\text{In}_y\text{Se}_z$. Other mixed-metal combinations are being investigated.

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Notes and References

† *Synthesis* of $\{[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4]_2\text{In}_2(\mu\text{-Se})_2\}\{\text{ClO}_4\}_2 \cdot 4\text{MeOH}$ (**1**): $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ (12.8 mg, 0.0310 mmol) was added to a suspension of $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ (49.2 mg, 0.0308 mmol) in MeOH (20 mL). The resultant brown solution (after 5 min) was stirred for 2 h and filtered. The brown filtrate was concentrated under reduced pressure and Et_2O was added to induce precipitation. The solid was collected by filtration, washed with Et_2O (100 mL), and dried under vacuum to give brown powder of **1** (0.0282 g, 47%). X-ray quality crystals were obtained from a MeOH solution of **1**. Found: C, 45.2; H, 3.4; P, 6.1. Calc. for $\text{C}_{148}\text{H}_{136}\text{Cl}_2\text{O}_{12}\text{Se}_6\text{P}_8\text{In}_2\text{Pt}_4$: C, 45.5; H, 3.5; P, 6.3%. $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (CD_3OD): δ_p 20.5 ppm [t, $^1J(\text{P-Pt}) = 3174$ Hz].

‡ *Crystallographic data:* crystal dimensions: 0.34 × 0.3 × 0.24 mm³, C₁₄₈H₁₃₆Cl₂O₁₂Se₆P₈In₂Pt₄ **1·4MeOH**: $M = 3908.99$, monoclinic, space group P2(1)/c, $a = 14.5465(7)$, $b = 27.2617(13)$, $c = 18.3583(9)$ Å, $\alpha = 90$, $\beta = 106.963(1)$, $\gamma = 90^\circ$, $V = 6963.5(6)$ Å³, $Z = 2$, $\mu(\text{Mo-K}) = 6.087 \text{ mm}^{-1}$. 37534 reflections measured, 12222 unique ($R_{\text{int}} = 0.0381$), final $R1$ and $wR2$ values 0.0319 and 0.0786 for 12222 independent reflections [$I \geq 2\sigma(I)$] and 822 parameters. The data collection was performed on a Bruker AXS SMART diffractometer, equipped with a CCD area-detector using Mo-K α radiation ($\lambda = 0.71073$ Å). The software SMART^{xvi} was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT^{xvi} for integration of intensity of reflections and scaling, SADABS^{xvii} for empirical absorption correction, and SHELXTL^{xviii} for space group and structure determination, refinements, graphics, and structure reporting. Hydrogen atoms were not located. The structures were refined by full-matrix least squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms, unless otherwise indicated [$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ (where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$]. Supplementary material including non hydrogen and hydrogen atomic coordinates, thermal parameters for the non hydrogen atoms, and complete tables of bond distances and angles has been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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