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Nucleophilicity of the selenide ligands in $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$. Molecular assembly of a novel $\{In_2Pt_4Se_6\}$ core

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Abstract

Lewis basic $Pt_2(\mu\text{-}Se)_2(PPh_3)_4$ reacts with $In(ClO_4)_3$ to give a rare platinum–indium selenido aggregate, $\{[Pt_2(\mu_3\text{-}Se_2)_2(PPh_3)_4]_2In_2(\mu\text{-}Se)_2\}\{ClO_4\}_2$. Single-crystal X-ray diffraction analysis revealed a hexametallic framework supported by a planar $\{In_2Se_2\}$ square sandwiched by two $\{Pt_2Se_2\}$ hinged butterfly moieties. This structure resembles that of the semiconducting anion $[(Ga_6Se_{14})^{10-}]$ by having a common double-tetrahedra $\{M_2Se_6\}$ core. The planar $\{M_2Se_2\}$ ring also exists in other semiconductors like In_4Se_3 and TlSe. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Indium chalcogenides, especially the ternary systems, exhibit optical, magnetic and electronic properties that are technologically significant [1]. A good example is found in $CuInSe_2$ (CIS) which attracts interest in photovoltaic applications such as solar cells [2] because of its favorable 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. We herein report the synthesis and characterization of a rare {PtInSe} aggregate, taking advantage the coordinating behavior of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ at the Se sites. This paper and other spectroscopic reports [3] collectively, demonstrated a synthetic strategy that can potentially lead to a large variety of mixed metal selenides under ambient conditions.

2. Experimental

2.1. Synthesis of $\{[Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4]_2In_2(\mu\text{-}Se)_2\}\{ClO_4\}_2\cdot 4MeOH$ (1)

$In(ClO_4)_3\cdot 8H_2O$ (12.8 mg, 0.0310 mmol) was added to a suspension of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ [3a] (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. Anal. Calc. for $C_{148}H_{136}Cl_2In_2O_{12}P_8Pt_4Se_6$: C, 45.5; H, 3.5; P, 6.3%. $^{31}P\{^1H\}$-NMR (CD_3OD): δ_P 20.5 ppm [t, $^1J(P\text{–}Pt) = 3174$ Hz]. The ^{31}P-NMR spectrum was recorded at 121.39 MHz with 85% H_3PO_4 as external reference in a Bruker 300 MHz spectrometer.

3. X-ray diffraction analysis

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

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software SMART [4] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [4] for integration of intensity of reflections and scaling, SADABS [5] for empirical absorption correction, and SHELXTL [6] 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 $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$)].

3.1. Crystallographic data

Crystal dimensions: $0.34\times0.3\times0.24$ mm^3, $C_{144}H_{120}Cl_2In_2O_8P_8Pt_4Se_6\cdot4MeOH$ **1**: $M=3908.99$, monoclinic, space group $P2_1/c$, $a=14.5465(7)$, $b=27.2617(13)$, $c=18.3583(9)$ Å, $\alpha=90$, $\beta=106.963(1)$, $\gamma=90°$, $V=6963.5(6)$ Å^3, $Z=2$, $\mu(\text{Mo–K}_\alpha)=6.087$ mm^{-1}, 37 534 reflections measured, 12 222 unique ($R_{int}=0.0381$), final R_1 and wR_2 values 0.0319 and 0.0786 for 10 090 independent reflections [$I\geq2\sigma(I)$] and 822 parameters.

4. Results and discussion

$In(ClO_4)_3$ reacts with $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ in MeOH at room temperature to give $\{[Pt_2(\mu_3\text{-}Se_2)_2(PPh_3)_4]_2In_2(\mu\text{-}Se)_2\}\{ClO_4\}_2$, **1** (47%) instead of the expected 1:2 addition product viz. $[In\{Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4\}_2][ClO_4]_3$. Single-crystal X-ray analysis revealed a planar $\{In_2Se_2\}$ core sandwiched by two hinged $\{Pt_2Se_2\}$ moieties (Fig. 1). It can also be viewed as two trigonal bipyramidal $\{InPt_2Se_2\}$ fragments connected at the In(III) ends by two μ_2-Se with a center of inversion at the center of the architecture. This hexametallic structure resembles that of the semiconducting anion $[(Ga_6Se_{14})^{10-}]$ [7] **2** by having a double-tetrahedra $\{M_2Se_6\}$ edge-linked with another $\{M_2Se_6\}$ or double-planar $\{Pt_2Se_2P_4\}$.

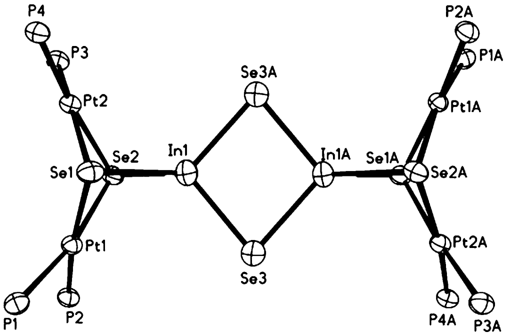
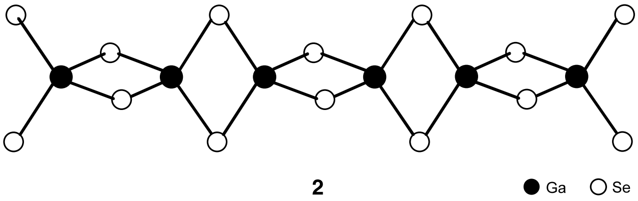


Fig. 1. Molecular structure of $\{[Pt_2(\mu_3\text{-}Se_2)_2(PPh_3)_4]_2In_2(\mu\text{-}Se)_2\}\{ClO_4\}_2\cdot4MeOH$ (**1**). The methanol solvates, ClO_4^- counterions and phenyl ligands are omitted for clarity. Selected bond lengths (Å) and angles (°): In(1)–Se(1) 2.6522(7), In(1)–Se(2) 2.6169(7), In(1)–Se(3) 2.5565(8), In(1)–Se(3A) 2.5780(8), In(1A)–Se(3) 2.5780(8), Pt(1)–Se(1) 2.5003(5), Pt(1)–Se(2) 2.4755(6), Pt(2)–Se(1) 2.4684(5), Pt(2)–Se(2) 2.4918(5), In(1)–Se(3)–In(1A) 82.00(2), Se(3)–In(1)–Se(3A) 98.00(2), Se(1)–In(1)–Se(2) 75.810(19), Se(1)–In(1)–Se(3) 120.95(3), Se(1)–In(1)–Se(3A) 123.92(3), Se(2)–In(1)–Se(3) 119.39(3), Se(2)–In(1)–Se(3A) 120.29(3), Pt(1)–Se(1)–Pt(2) 87.703(18), Pt(1)–Se(2)–Pt(2) 87.737(18), Se(1)–Pt(1)–Se(2) 81.171(18), Se(1)–Pt(2)–Se(2) 81.482(18).



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The source of the two μ_2-Se atoms is tentatively traced to the liberation of HSe^- from the slow decomposition of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ in the presence of a strong electrophile such as $In(ClO_4)_3$. Similar decompositions in the sulfide systems under the influence of HX or RX are known although the sulfide analog of **1** has so far eluded detection or isolation. Like the sulfide analog [8], $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ also decomposes in CH_2Cl_2 [9]. In a separate experiment, addition of dilute HCl to a suspension of $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ in MeOH resulted in an instantaneous formation of a bright yellow solution, which readily turned orange. The resultant product was identified as $[Pt_2(\mu\text{-}SeH)_2(PPh_3)_4]Cl_2$ [3b].

The two edge-linked $\{Pt_2Se_2\}$ butterflies (dihedral angle 129.3°) are almost perpendicular (89.1°) to the central planar $\{In_2Se_2\}$ unit, thus giving a C_{2h} symmetry to the molecule. The $\{M_2Se_2\}$ ring is expected to be planar for substituted μ_2-Se (e.g. $Pt_2Se_2(PPh_3)_4$ [10], $[Ga_6Se_{14}]^{10-}$ [7], In_4Se_3 [11] and TlSe [12]) and folded when it is alkylated or metallated (e.g. $[(Me_3CCH_2)_2In\text{-}SePh]_2$ [13]). The entire structure is supported by strong In–Se (average 2.5963 Å) (cf. In_2Se_3 (2.69 Å) [14], $NaInSe_2$ (2.76 Å) [14] and $[(Me_3CCH_2)_2InSePh]_2$ (2.74 Å) [13]) 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 $\{In_2Se_2\}$ 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 decomposition product(s) with the intention of relating them to the ternary products of $Pt_xIn_ySe_z$. Other mixed-metal combinations are being investigated.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151821 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) A.C. Jones, P. O'Brien, CVD of Compounds Semiconductors. Precursor Synthesis, Development and Applications, VCH, New York, 1997, p. 307;
(b) M.I. Mitkova, in: M.F. Thorpe, M.I. Mitkova (Eds.), Amorphous Insulators and Semiconductors, Kluwer Academic Publishers, Netherlands, 1997, p. 73.
[2] J.S. Park, Z. Dong, S. Kim, J.H. Perepezko, J. Appl. Phys. 87 (2000) 3683 (and references therein).
[3] (a) J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2001) 315;
(b) J.S.L. Yeo, J.J. Vittal, W. Henderson, T.S.A. Hor, J. Chem. Soc. Dalton Trans. (2002) 328.
[4] SMART and SAINT Software Reference Manuals, Version 4.0, Siemens Energy and Automation, Inc., Analytical Instrumentation, Madison, WI, 1996.
[5] G.M. Sheldrick, SADABS, a Software for Empirical Absorption Correction, University of Göttingen, 1993.
[6] G.M. Sheldrick, SHELXTL, Version 5.03, Siemens Energy and Automation, Inc., Analytical Instrumentation, Madison, WI, 1996.
[7] H.-J. Deiseroth, F.-S. Han, Angew. Chem. Int. Ed. Engl. 20 (1981) 962.
[8] (a) R.R. Gukathasan, R.H. Morris, A. Walker, Can. J. Chem. 61 (1983) 2490;
(b) C.E. Briant, C.J. Gardner, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, J. Chem. Soc. Dalton Trans. (1984) 2645.
[9] P.K. Khanna, C.P. Morley, M.B. Hursthouse, K.M.A. Malik, O.W. Howarth, Heteroat. Chem. 6 (1995) 519.
[10] A. Bencini, M.D. Vaira, R. Morassi, P. Stoppioni, Polyhedron 15 (1996) 2079.
[11] (a) J.H.C. Hogg, H.H. Sutherland, Chem. Commun. (1971) 1568;
(b) J.H.C. Hogg, H.H. Sutherland, Acta Crystallogr. Sect. B 29 (1973) 1590.
[12] M.J. Taylor, P.J. Brothers, in: A.J. Downs (Ed.), Chemistry of Aluminium, Gallium, Indium and Thallium (and reference 5), Chapman & Hall, United Kingdom, 1993, p. 213.
[13] O.T. Beachley, Jr., J.C. Lee, Jr., H.J. Gysling, S.-H.L. Chao, M.R. Churchill, C.H. Lake, Organometallics 11 (1992) 3144.
[14] J. Weis, H. Schäfer, G. Schön, Z. Naturforsch. Teil. B 31 (1976) 1336.