Letter

Structural characterization of an ordered crystalline modification of $[In(SePh)_3]_\infty$

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A triclinic modification of $[In(SePh)_3]_\infty$ has been structurally characterized by X-ray diffraction, demonstrating that it is chemically distinct from a previously reported monoclinic form. Thus, triclinic $[In(SePh)_3]_\infty$ is crystallographically ordered and contains five-coordinate trigonal bipyramidal indium centers with asymmetrically bridging [SePh] ligands, whereas the monoclinic form is disordered and contains six-coordinate octahedral indium centers with symmetrically bridging [SePh] ligands.

Until recently, the chemistry of selenolate and tellurolate derivatives had received relatively little attention by comparison with alkoxide and thiolate complexes, but is now an area of much interest.[1] For example, with respect to the heavier Group 13 elements, research in chalcogenolate complexes has been prompted by their potential use as single-source precursors to "13–16" materials.[2,3] The structural chemistry of Group 13/16 compounds, however, is still in its infancy,[4] and in this paper we report a structure for $[In(SePh)_3]_\infty$ that differs significantly from that previously reported.[5]

As a result of the inherent electrophilic nature of the indium center in a three-coordinate $[InX_3]$ molecule, such species typically exist as some form of oligomer. For example, the phenylselenolate complexes $[Np_2In(\mu\text{-}SePh)]_2$[6] and $[Mes_2In(\mu\text{-}SePh)]_2$[3] are dimers with symmetrically bridging [SePh] ligands. Monomeric three-coordinate selenolate complexes can normally only be attained by incorporation of very bulky substituents on either indium, for example $Mes^*In(SePh)_2$ ($Mes^* = 2,4,6\text{-}Bu^t_3C_6H_2$),[7] or selenium, such as $In(SeMes^*)_3$[8,9] and $In[SeE(SiMe_3)_3]_3$ ($E = C$, Si).[10] It is, therefore, not surprising that the parent arylselenolate, $[In(SePh)_3]_\infty$,[11] possesses a polymeric structure (Fig. 1),[5] in which each indium atom relieves its electron deficiency by octahedral coordination of six bridging [SePh] groups. The phenyl groups of this monoclinic form of $[In(SePh)_3]_\infty$, however, were observed to be severely disordered over two positions. In view of this disorder, we considered it appropriate to attempt to obtain the structure of an ordered material.

Significantly, we succeeded in obtaining triclinic crystals of $[In(SePh)_3]_\infty$ that were devoid of disorder and the structure, as determined by X-ray diffraction, is illustrated in Fig. 2–4. Selected bond lengths and angles are listed in Table 1. More important than simply representing an ordered structure, the molecular structure of the triclinic form of $[In(SePh)_3]_\infty$ is of interest because it is substantially different from that previously reported[5] in a number of respects, as summarized in

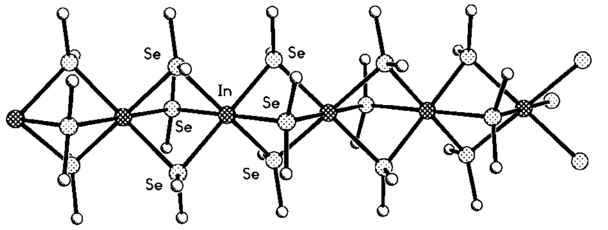

Fig. 1 A portion of the polymeric structure of monoclinic $[In(SePh)_3]_\infty$ (data taken from ref. 5). For clarity, only the *ipso* carbon atoms of the grossly disordered phenyl groups are shown.

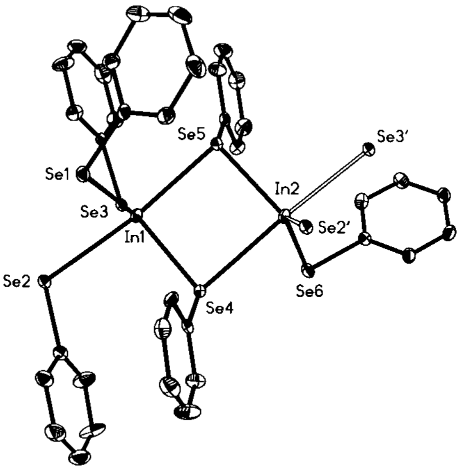

Fig. 2 ORTEP drawing illustrating the asymmetric unit of triclinic $[In(SePh)_3]_\infty$.

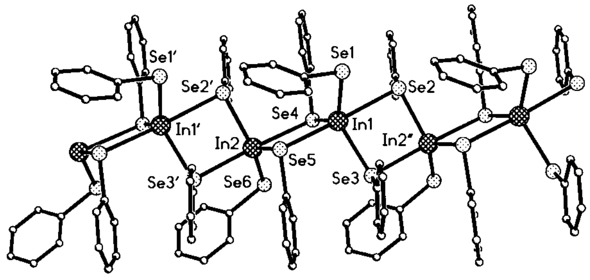

Fig. 3 A portion of the polymeric structure of triclinic $[In(SePh)_3]_\infty$.

Table 1 Selected bond lengths (Å) and angles (°) for triclinic $[In(SePh)_3]_\infty$

In1–Se1	2.556(1)	In2–Se2′	2.596(1)
In1–Se2	2.966(1)	In2–Se3′	2.856(1)
In1–Se3	2.610(1)	In2–Se4	2.986(1)
In1–Se4	2.604(1)	In2–Se5	2.624(1)
In1–Se5	2.835(1)	In2–Se6	2.549(1)
In1–Se2–In2′	90.61(3)	In1–Se4–In2	88.88(3)
In1–Se3–In2′	92.80(3)	In1–Se5–In2′	91.82(3)

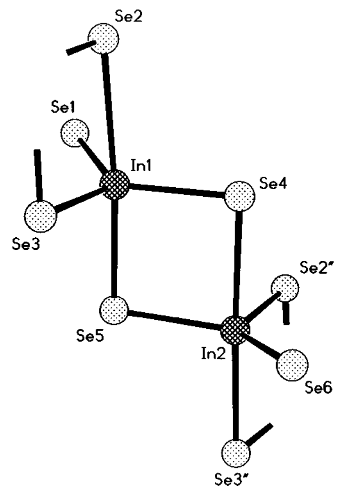

Fig. 4 The trigonal bipyramidal coordination geometry in [In(SePh)$_3$]$_\infty$ (carbon and hydrogen atoms are omitted for clarity).

Table 2. Firstly, instead of being six-coordinate, the indium centers of the triclinic structure are five-coordinate. Thus, each indium center is coordinated to one terminal and four bridging [SePh] ligands in a trigonal bipyramidal geometry that is most clearly seen in Fig. 4. A second distinction between the two structures is that the [SePh] ligands of the triclinic structure do not bridge the indium centers symmetrically, but are asymmetrically disposed. Specifically, whereas the In–Se bond lengths in the monoclinic structure fall in the narrow range 2.77–2.79 Å,[5] those of the bridging ligands in the triclinic form span the substantial range of 2.56–2.99 Å (Table 1). The asymmetry of the bridging In–Se interactions is a consequence of each bridging [SePh] ligand occupying an axial position to one indium but an equatorial position to the other. Of the two types of bridging interactions, the equatorial In–Se bonds are considerably shorter than the axial ones (Table 3), as is often observed for trigonal bipyramidal complexes of the main group elements.[12] It is interesting to note that the axial In–Se bond lengths also fall into two classes, with In1–Se2 and In2–Se4 (2.98 Å average) being longer than In1–Se5 and In2–Se3′ (2.85 Å average). Another distinction between the [SePh] coordination modes in the triclinic and monoclinic structures of In(SePh)$_3$ is that one of the equatorial ligands attached to each indium in the triclinic form remains terminal; as would be expected, this ligand has the shortest In–Se bond length (2.55 Å average). It is worthwhile to point out that, in view of these differences in bonding, the monoclinic and triclinic forms of [In(SePh]$_3$]$_\infty$ are not polymorphs of each other since they are chemically distinct.[13]

Table 2 Comparison of triclinic and monoclinic forms of [In(SePh)$_3$]$_\infty$

	Triclinic	Monoclinic[a]
Ordered/disordered	Ordered	Disordered
In coordination	Five-coordinate (*TBPY*)	Six-coordinate (O_h)
[SePh] bridging interaction	Asymmetric	Symmetric
Range of *d*(In–SePh)	2.56–2.99 Å	2.77–2.79 Å
In···In separation	3.94 Å	3.63 Å
Calcd density	2.09 g cm^{-3}	2.29 g cm^{-3}

[a] Ref. 5.

Table 3 Summary of the average trigonal bipyramidal coordination environment about each indium in triclinic [In(SePh)$_3$]$_\infty$

	d(In–Se)/Å
In–SePh (eq, term)	2.56
In–SePh (eq, bridge)	2.61
In–SePh (axial, short)	2.85
In–SePh (axial, long)	2.98

Finally, the average In···In separation of 3.94 Å[14] in triclinic [In(SePh)$_3$]$_\infty$ is significantly greater than that in its monoclinic counterpart (3.63 Å).[5] Correspondingly, the calculated density of the monoclinic form (2.29 g cm^{-3})[5] is greater than that for the triclinic form (2.09 g cm^{-3}). The shorter separation in the latter complex is presumably due to each [In···In] unit being bridged by three [SePh] ligands, which therefore requires a closer approach of the indium centers. In this regard, the complex [MeIn(SePh)(μ-SePh)]$_\infty$,[15] with only a single bridging [SePh] ligand, has an even greater In···In separation (4.19 Å) than that in doubly bridged triclinic [In(SePh)$_3$]$_\infty$.

It is also worth noting that the In···In separation in triclinic [In(SePh)$_3$]$_\infty$ is greater than the values for other complexes that possess similar [In(μ-SePh)$_2$In] cores (Table 4). This difference is most probably a result of the fact that the indium centers in triclinic [In(SePh)$_3$]$_\infty$ are five-coordinate, whereas those in the other complexes, for example [R$_2$In(μ-SePh)]$_2$, are four-coordinate. Thus, the greater In···In separation in triclinic [In(SePh)$_3$]$_\infty$ is merely a consequence of the substantially longer In–SePh bond to the axial site.[18]

In conclusion, [In(SePh)$_3$]$_\infty$ has been shown to exist in a triclinic form that differs from the previously reported monoclinic structure in a number of important respects. Specifically, triclinic [In(SePh)$_3$]$_\infty$ is crystallographically ordered and contains five-coordinate trigonal bipyramidal indium centers with asymmetrically bridging [SePh] ligands, whereas the monoclinic form is disordered and contains six-coordinate octahedral indium centers with symmetrically bridging [SePh] ligands. As such, the monoclinic and triclinic forms are chemically distinct.

Experimental

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques.[19] [In(SePh)$_3$] was prepared according to the literature method[11] and crystals suitable for X-ray diffraction were obtained by evaporation of a toluene solution at room temperature.

Table 4 Summary of In–Se and In···In distances in [X$_a$In(SePh)$_b$] complexes

	d(In–SePh)/Å Terminal	*d*(In–SePh)/Å Bridging	*d*(In···In)/Å	Reference
[In(SePh)$_3$]$_\infty$ (triclinic)	2.56	2.61_{eq}, 2.92_{ax}	3.94_{av}	This work
[In(SePh)$_3$]$_\infty$ (monoclinic)	—	2.78	3.63	5
[Mes$_2$In(μ-SePh)]$_2$	—	2.73	3.86	15
[Np$_2$In(μ-SePh)]$_2$	—	2.74	3.75	6
[MeIn(SePh)(μ-SePh)]$_\infty$	2.54	2.68	4.19	15
[NpIn]$_2$(μ-PBu^t)(μ-SePh)	—	2.76	3.95	16
[Ph$_4$P][In(SePh)$_4$]	2.58	—	—	17
[Ph$_4$P][In(SePh)$_3$(SeH)]	2.55	—	—	17

Table 5 Crystal, intensity collection and refinement data for $[\mathrm{In(SePh)_3}]_\infty$

Formula	$C_{18}H_{15}InSe_3$
Formula weight	583
Lattice	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	7.3207(1)
b/Å	11.0326(2)
c/Å	23.3628(4)
α/°	81.490(1)
β/°	86.265(1)
γ/°	84.381(1)
U/Å^3	1854.73(5)
Z	4
Temperature/K	222
μ(Mo-Kα)/mm^{-1}	7.155
No. meas. refl.	7960
No. independ. refl.	7960
R_1	0.0533
wR_2	0.1048

Crystallographic data for $In(SePh)_3$ were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector, as summarized in Table 5. The structure was solved using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures using SHELXTL.[20] Hydrogen atoms attached to carbon were included in calculated positions.

CCDC reference number 440/136. See http://www.rsc.org/suppdata/nj/1999/957/ for crystallographic files in .cif format.

Acknowledgements

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