



## Note

# Cadmium bis(phenylselenolate) as a precursor for the synthesis of polymeric Cd( $\mu$ -Se)clusters: Crystal and molecular structures of $[\text{Cd}_4(\text{SePh})_7(\text{PPh}_3)\text{X}]_n$ (X = Cl, Br)

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## ABSTRACT

The reaction of  $\text{Cd}(\text{SePh})_2$  with  $\text{CdX}_2$  (X = Cl (**1**), Br (**2**)) in MeOH in the presence of  $\text{PPh}_3$  at 130 °C under solvothermal conditions affords the products  $[\text{Cd}_4(\text{SePh})_7(\text{PPh}_3)\text{X}]_n$ , a one-dimensional assembly of adamantanoid  $[\text{Cd}_4(\text{SePh})_6(\text{PPh}_3)\text{X}]$  clusters joined into a polymeric chain by  $\mu$ -SePh bridges. Compounds **1** and **2** represent examples of extended one-dimensional chains of closed ME (M = metal, E = S, Se, Te) systems, whose importance is based not only on their properties, but by their possible use as precursor materials for design and development of new methodologies via a “bottom up” strategy to obtain different clusters from single components.

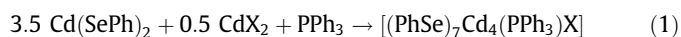
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## 1. Introduction

The search for the new metal–chalcogen containing building blocks is of current interest because of their manipulable particle size for meeting optoelectronic engineering properties for custom-design [1,2], as well as other materials and biological applications [3]. As part of our interest in organochalcogenide chemistry, we previously investigated the use of  $\text{Hg}(\text{EPh})_2$  (E = Se, Te) as a precursor for the preparation of nanoclusters using redistribution reactions [4–11]. The precursor  $\text{Cd}(\text{SePh})_2$  can be used in similar reactions to offer a facile route to yield Cd–Se clusters via a “bottom up” strategy. Mixed ligands tetranuclear clusters of the type  $[\text{M}_4(\text{EPh})_x(\text{E}'\text{Ph})_{10-x}]^{2-}$  (M = Cd, Zn; E = S; E' = Se; X = Cl, Br, I) and their  $^{113}\text{Cd}$  NMR spectroscopy has been reported [12]. The same group later reported the syntheses of  $[\text{M}_4(\text{EPh})_6\text{X}_4]^{2-}$ , through the oxidative reaction of the adamantanoid anions  $[\text{M}_4(\text{EPh})_{10}]^{2-}$  with  $\text{X}_2$  [13,14]. A series of different binary and ternary transition metal chalcogenide and chalcogenolate cluster molecules have been synthesized using organometallic compounds in which silyl groups are bonded to chalcogen atoms by the reaction of metal halides,  $\text{CdX}_2$  (X = Cl, Br, I) with phosphanes  $\text{PR}_3$ ,  $\text{Se}(\text{SiMe}_3)_2$  and  $\text{PhSeSiMe}_3$  in organic solvents [15–19]. We present herein the synthesis and the structural analysis of two new clusters,  $[\text{Cd}_4(\text{SePh})_7\text{XPPh}_3]_n$  where X = Cl (**1**), Br (**2**).

## 2. Results and discussion

The reaction of  $\text{Cd}(\text{SePh})_2$  with  $\text{CdX}_2$  (X = Cl, Br) in MeOH in the presence of  $\text{PPh}_3$  at 130 °C under solvothermal conditions affords the clusters **1** and **2** with a global reaction for the formation of monomer  $[\text{Cd}_4(\text{SePh})_7(\text{PPh}_3)\text{X}]$  (X = Cl (**1**), Br (**2**)).



The structures of **1** and **2** consist of adamantanoid  $[\text{Cd}_4(\text{SePh})_7(\text{PPh}_3)\text{X}]$  units (X = Cl, Br) (Figs. 1 and 2) in the polymeric 1-D assembly by Cd( $\mu$ -SePh)Cd interactions along the crystallographic axis *b* (Fig. 3). Crystal data and experimental conditions of the structures **1** and **2** are listed in Table 1 and selected interatomic distances and angles are in Table 2. In the monomeric unit  $[\text{Cd}_4(\text{SePh})_7(\text{PPh}_3)\text{X}]$ , the  $\text{Cd}^{2+}$  ions each present a distorted tetrahedral geometry and are linked through asymmetric  $[\mu\text{-(Ph)Se}]^-$  bridges: three to atoms Cd(1) and Cd(2) and four for atoms Cd(3) and Cd(4). The coordination spheres for Cd(1) and Cd(2) are completed by a halide ligand and a triphenylphosphine ligand, respectively. The Se7(a) and Se7(b) atoms are disordered over two positions for both compounds. The geometries of the two clusters are almost identical – the Cd–Se mean distances within the cluster, 2.640 Å in (**1**) and 2.641 Å in (**2**), and the Cd(2)–P distances, 2.602(3) Å for (**1**) and 2.614(3) Å for (**2**), are both equal within the error of the measurement.

Thermogravimetric analysis (TGA) of compounds **1** and **2** in a dynamic nitrogen flow shows that the thermal decomposition in the range 25–700 °C occurs in three successive steps. Both

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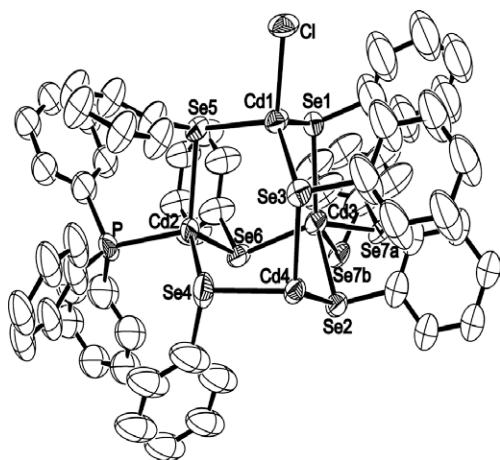


Fig. 1. Molecular structure of **1** with key atoms labeled (all H-atoms have been omitted for clarity). Thermal ellipsoids are at the 50% probability level.

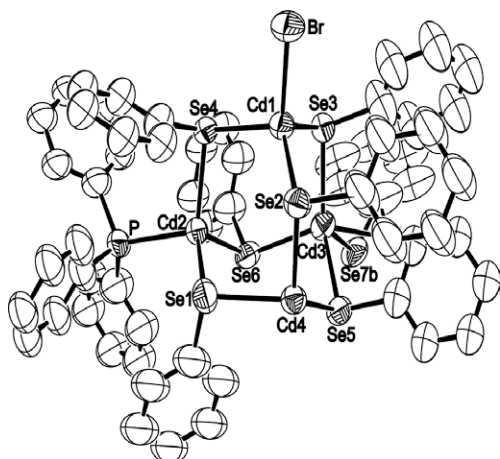


Fig. 2. Molecular structure of **2** with key atoms labeled (all H-atoms have been omitted for clarity). Thermal ellipsoids are at the 50% probability level.

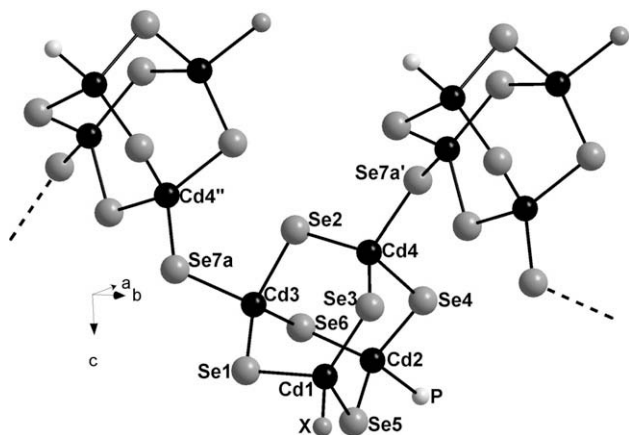


Fig. 3. Assembly of  $[\text{Cd}_4(\text{SePh})_7\text{XPPH}_3]$  ( $\text{X} = \text{Cl}, \text{Br}$ ), a polymeric one-dimensional assembly of  $(\mu\text{-Se})\text{Cd}$  clusters. Phenyl groups and Se7b were omitted. Symmetry transformations used to generate equivalent atoms: (')  $0.5-x, 0.5+y, 0.5-z$ ; (")  $0.5-x, 0.5+y, 0.5-z$ .

Table 1

Crystal data and structure refinement for **1** and **2**.

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{60}\text{H}_{50}\text{Cd}_4\text{Cl}_1\text{P}_1\text{Se}_7$	$\text{C}_{60}\text{H}_{50}\text{Cd}_4\text{Br}_1\text{P}_1\text{Se}_7$
Formula weight	1839.74	1884.20
<i>T</i> (K)	293(2)	296(2)
Radiation (Å)	Mo K $\alpha$ , 0.71073	Mo K $\alpha$ , 0.71073
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>
Unit cell dimensions		
<i>a</i> (Å)	28.7134(9)	29.1149(4)
<i>b</i> (Å)	13.6276(3)	13.6536(2)
<i>c</i> (Å)	32.8962(7)	33.0127(5)
$\beta$ (°)	95.756(3)	96.544(2)
<i>V</i> (Å <sup>3</sup> )	12807.2(6)	13037.8(3)
<i>Z</i> , Calculated density (g cm <sup>-3</sup> )	8, 1.908	8, 1.920
Absorption coefficient (mm <sup>-1</sup> )	5.391	5.867
<i>F</i> (0 0 0)	6976	7120
Crystal size (mm)	0.26 × 0.17 × 0.05	0.17 × 0.16 × 0.06
$\theta$ Range (°)	2.11–26.0	1.73–25.85
Index ranges	$-35 \leq h \leq 34$ , $-15 \leq k \leq 16$ , $-40 \leq l \leq 40$	$-35 \leq h \leq 35$ , $-15 \leq k \leq 16$ , $-40 \leq l \leq 40$
Reflections collected	42 981	95 618
Reflections unique	12 587 [ <i>R</i> <sub>int</sub> = 0.0995]	12 606 [ <i>R</i> <sub>int</sub> = 0.0997]
Completeness to $\theta_{\text{max}}$	99.8%	99.9%
Absorption correction	Gaussian	Gaussian
Max. and min. transmission	0.8041 and 0.4616	0.3783 and 0.1797
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	12 587/360/548	12 606/360/548
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.045	1.010
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0633, <i>wR</i> <sub>2</sub> = 0.1486	<i>R</i> <sub>1</sub> = 0.0539, <i>wR</i> <sub>2</sub> = 0.1287
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1336, <i>wR</i> <sub>2</sub> = 0.1811	<i>R</i> <sub>1</sub> = 0.1270, <i>wR</i> <sub>2</sub> = 0.1702
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.511 and -1.417	1.341 and -0.871

and **2**, respectively, suggesting that one  $\text{PPh}_3$  and 3.5  $\text{SePh}_2$  are cleaved for a theoretical weight loss of 58.6% and 57.2% for **1** and **2**, respectively. This TGA interpretation was confirmed by mass spectra of the volatile compounds in a separate experiment. The volatile products of thermolysis of compounds **1** and **2** at 350 °C under nitrogen flow were collected in a cold trap, dissolved in ethylacetate and analyzed by CG-MS. For both compounds only two peaks in CG at different restraint times were observed: 7.4 and 11.5 min. The first CG peak showed two principal peaks in mass spectroscopy located between  $m/e$  152–155 and 231–233 which can be assigned to the fragmentation product  $\text{SePh}$  ( $m/e = 155$ ) and parent compound  $\text{SePh}_2$  ( $m/e = 233$ ), respectively. The second CG peak showed four principal peaks in MS located between  $m/e$  150–152, 180–182, 197–199 and 273–278, identified to be  $\text{Ph}_2$  ( $m/e = 154$ ),  $\text{PPh}_2$  ( $m/e = 181$ ),  $\text{O}=\text{PPh}_2$  ( $m/e = 201$ ), and  $\text{O}=\text{PPh}_3$  ( $m/e = 278$ ). These mass spectra results suggest that  $\text{PPh}_3$  is oxidized to  $\text{O}=\text{PPh}_3$  during sample handling. The TGA interpretation is in good agreement with mass spectra of the volatiles of the thermolysis, and the respective X-ray structure analyses, of **1** and **2**.

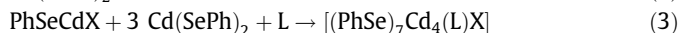
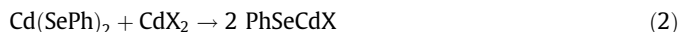
The molecular structures of **1** and **2** are similar to the clusters  $[(\text{PhSe})_7\text{Hg}_4(\text{L})\text{X}]_n$  ( $\text{L} = \text{Py}, \text{DMF}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) which we have investigated previously [7,8]. The reactions to form **1** and **2** for  $\text{M} = \text{Cd}$  should be very similar to those for  $\text{M} = \text{Hg}$ . In **1** and **2**, we propose that the one-pot syntheses of the clusters occurs with the initial formation of the intermediate  $\text{PhSeCdX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ), Eq. (2), and the global reaction in Eq. (3), where  $\text{L} = \text{PPh}_3$ .

compounds decompose in a two-step process between 25 and 350 °C with an observed weight loss of 54.2% and 52.0% for **1**

**Table 2**  
Selected interatomic distances [Å] and angles [°] for **1** and **2**.

Bond lengths for <b>1</b>		Bond lengths for <b>2</b>	
Cd(1)–Cl	2.473(3)	Cd(1)–Br	2.5546(14)
Cd(1)–Se(1)	2.6639(15)	Cd(1)–Se(2)	2.6435(13)
Cd(1)–Se(3)	2.6418(14)	Cd(1)–Se(3)	2.6775(14)
Cd(1)–Se(5)	2.6489(15)	Cd(1)–Se(4)	2.6576(13)
Cd(2)–P	2.602(3)	Cd(2)–P	2.614(3)
Cd(2)–Se(4)	2.6180(15)	Cd(2)–Se(1)	2.6172(14)
Cd(2)–Se(5)	2.6121(15)	Cd(2)–Se(4)	2.6140(12)
Cd(2)–Se(6)	2.6358(16)	Cd(2)–Se(6)	2.6381(14)
Cd(3)–Se(1)	2.6318(14)	Cd(3)–Se(3)	2.6256(13)
Cd(3)–Se(2)	2.6400(14)	Cd(3)–Se(5)	2.6421(13)
Cd(3)–Se(6)	2.6643(16)	Cd(3)–Se(6)	2.6671(14)
Cd(3)–Se(7A)	2.6447(17)	Cd(3)–Se(7A)	2.6400(18)
Cd(3)–Se(7B)	2.658(6)	Cd(3)–Se(7B)	2.668(4)
Cd(4)–Se(2)	2.6144(14)	Cd(4)–Se(1)	2.6605(14)
Cd(4)–Se(3)	2.6307(15)	Cd(4)–Se(2)	2.6341(13)
Cd(4)–Se(4)	2.6582(15)	Cd(4)–Se(5)	2.6151(13)
Cd(4)–Se(7A)	2.6572(16)	Cd(4)–Se(7A)	2.6418(17)
Cd(4)–Se(7B)	2.686(6)	Cd(4)–Se(7B)	2.706(4)
Bond angles for <b>1</b>		Bond angles for <b>2</b>	
Cl–Cd(1)–Se(3)	107.37(9)	Br–Cd(1)–Se(2)	109.88(5)
Cl–Cd(1)–Se(5)	107.54(9)	Br–Cd(1)–Se(4)	106.92(5)
Cl–Cd(1)–Se(1)	109.48(9)	Br–Cd(1)–Se(3)	109.31(5)
P–Cd(2)–Se(5)	106.75(9)	P–Cd(2)–Se(4)	107.09(7)
P–Cd(2)–Se(4)	104.33(9)	P–Cd(2)–Se(1)	104.97(8)
P–Cd(2)–Se(6)	110.19(11)	P–Cd(2)–Se(6)	109.32(8)
Se(1)–Cd(3)–Se(2)	128.55(5)	Se(3)–Cd(3)–Se(7A)	106.65(5)
Se(1)–Cd(3)–Se(7A)	105.38(5)	Se(3)–Cd(3)–Se(5)	127.68(5)
Se(1)–Cd(3)–Se(7B)	124.12(15)	Se(3)–Cd(3)–Se(6)	111.27(4)
Se(1)–Cd(3)–Se(6)	110.29(4)	Se(3)–Cd(3)–Se(7B)	121.28(10)
Se(2)–Cd(4)–Se(3)	120.16(5)	Se(5)–Cd(4)–Se(2)	119.72(4)
Se(2)–Cd(4)–Se(7A) <sup>''</sup>	104.84(5)	Se(5)–Cd(4)–Se(7A) <sup>''</sup>	105.66(5)
Se(2)–Cd(4)–Se(4)	116.54(5)	Se(5)–Cd(4)–Se(1)	116.29(5)
Se(2)–Cd(4)–Se(7B) <sup>''</sup>	87.11(13)	Se(5)–Cd(4)–Se(7B) <sup>''</sup>	88.88(10)

Symmetry transformations used to generate equivalent atoms: (')  $-x+1/2, y-1/2, -z+1/2$  (")  $-x+1/2, y+1/2, -z+1/2$ .



The choice of the reaction conditions is crucial for the use of  $\text{M}(\text{EPh})_2$  ( $\text{M} = \text{metal}$ ,  $\text{E} = \text{Se}$ ,  $\text{Te}$ ) and  $\text{MX}_2$  ( $\text{X} = \text{halogen}$ ) as starting reagents to obtain clusters by redistributions reactions. The use of adequate ligands or coordinating solvents is necessary to stabilize the metal halide and  $[\text{M}(\text{EPh})_2\text{L}]$  building blocks in solution ( $\text{L} = \text{coordinating solvent or phosphine ligand}$ ). The new interactions formed by the  $[\text{M}(\text{EPh})_2\text{L}]$  building blocks and metal halides in solution can be considered the driving force of these reactions.

In this work, we have extended the use of  $\text{Hg}(\text{EPh})_2$  ( $\text{E} = \text{Se}$ ,  $\text{Te}$ ) [4–11] as a precursor for the preparation of clusters to  $\text{Cd}(\text{SePh})_2$ , offering a complementary methodology in the place of silyl reagents [15–20]. Because this approach should be extensible to the synthons of the general formula  $\text{M}(\text{ER})_n$  for which a great many examples have been reported [21,22], we predict that a systematic methodology for the synthesis of binary and ternary clusters would be possible.

### 3. Experimental

#### 3.1. General

All reactions were carried out under dry argon gas. Solvents were purified and dried by standard procedure and freshly distilled prior to use [23]. Cadmium chloride, cadmium bromide tetrahydrate and triphenylphosphine were purchased from Sigma Aldrich®.  $\text{Cd}(\text{SePh})_2$  was synthesized according to a literature procedure [24].

#### 3.2. Preparation of **1**

A mixture of  $\text{CdCl}_2$  (0.018 g, 0.1 mmol),  $\text{Cd}(\text{SePh})_2$  (0.042 g, 0.1 mmol),  $\text{PPh}_3$  (0.052 g, 0.2 mmol) and 8 mL of MeOH was heated at 130 °C for 1 h. in a 12 mL stainless steel sealed reactor. The reactor was slowly cooled down to room temperature (4 h) to obtained white crystals suitable for X-ray analysis. Yield: 0.047 g, 89% based on  $\text{Cd}(\text{SePh})_2$ . Melting point: 177–180 °C. IR (KBr): 3051 [ $\nu(\text{C}-\text{H})$ ]; 1573, 1473, 1434 [ $\delta_{\text{ip}}(\text{C}=\text{C})$ ]; 1068 [phenyl ring breathing]; 1019 [ $\delta(\text{C}=\text{C}-\text{H})$ ]; 731 [ $\delta_{\text{op}}(\text{C}=\text{C}-\text{H})$ ]; 688, 462 [ $\delta_{\text{op}}(\text{C}=\text{C}-\text{C})$ ]  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{60}\text{H}_{50}\text{Cd}_4\text{ClPSe}_7$ : C, 39.17; H, 2.74. Found: C, 39.15; H, 2.59%.

#### 3.3. Preparation of **2**

The procedure is similar to that described for the preparation of **1**, except  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$  (0.034 g, 0.1 mmol) was used instead of  $\text{CdCl}_2$  (0.018 g, 0.1 mmol). White crystals suitable for X-ray analysis were obtained. Yield: 0.051 g, 93% based on  $\text{Cd}(\text{SePh})_2$ . Melting point: 173–176 °C. IR (KBr): 3051 [ $\nu(\text{C}-\text{H})$ ]; 1573, 1473, 1435 [ $\delta_{\text{ip}}(\text{C}=\text{C}-\text{C})$ ]; 1068 [phenyl ring breathing]; 1019 [ $\delta(\text{C}=\text{C}-\text{H})$ ]; 731 [ $\delta_{\text{op}}(\text{C}=\text{C}-\text{H})$ ]; 688, 462 [ $\delta_{\text{op}}(\text{C}=\text{C}-\text{C})$ ]  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{60}\text{H}_{50}\text{Cd}_4\text{BrPSe}_7$ : C, 38.24; H, 2.67. Found: C, 38.51; H, 2.58%.

#### 3.4. Crystal structure determination

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized  $\text{Mo K}\alpha$  radiation. The crystal structure of **1** and **2** were solved by direct methods using *SHELXS-97* [25]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with *SHELXL-97* [25] on full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions.

#### 3.5. Thermogravimetric measurements

Thermogravimetric measurements were carried out on a Shimadzu DTG-60 apparatus. The experiments were performed in the temperature range from 25 to 700 °C with a heating rate of 10 °C  $\text{min}^{-1}$  for each sample. The average sample size was 10 mg and the nitrogen flow-rate was 50 mL  $\text{min}^{-1}$ .

#### Acknowledgment

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#### Appendix A. Supplementary material

CCDC 708536 and 708537 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.027.

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