Synthesis and Structure of the Clusters $[\mathrm{Hg_2(\mu{-}SePh)_2(SePh)_2(PPh_3)_2}]$ and $[\mathrm{Hg_3Br_3(\mu{-}SePh)_3}] \cdot 2\,\mathrm{DMSO}$

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Abstract. The compounds $[\mathrm{Hg_2(\mu{-}SePh)_2(SePh)_2(PPh_3)_2}]$ (**I**) and $[\mathrm{Hg_3Br_3(\mu{-}SePh)_3}] \cdot 2$ DMSO (**II**) are formed by reactions of $[\mathrm{Hg(SePh)_2}]$ with $\mathrm{PPh_3}$ in THF(**I**) or with $\mathrm{HgBr_2}$ in DMSO (**II**) at room temperature. X−ray crystallography reveals that the cluster **I** consists of a distorted square built by each two Hg and Se atoms. The Hg atoms have almost tetrahedral co-ordination environments formed by selenium atoms of two (μ-$^{-}$SePh) ligands and Se and P atoms of terminal $^{-}$SePh and $\mathrm{PPh_3}$ ligands. The compound **II** is a six-membered ring with alternating Hg and Se atoms in the chair conformation. Two DMSO molecules occupy positions below and above the $[\mathrm{Hg_3Se_3}]$ ring with the oxygen atoms directed to the centre of the ring.

Keywords: Selenium; Organoselenium compounds; Secondary bonds; Crystal structure

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Inhaltsübersicht. Die Clusterverbindungen $[\mathrm{Hg_2(\mu\text{-}SePh)_2(SePh)_2(PPh_3)_2}]$ (**I**) and $[\mathrm{Hg_3Br_3(\mu\text{-}SePh)_3}] \cdot 2$ DMSO (**II**) entstehen bei Reaktionen von $[\mathrm{Hg(SePh)_2}]$ mit $\mathrm{PPh_3}$ in THF (**I**) bzw. mit $\mathrm{HgBr_2}$ in DMSO (**II**). Die Strukturen der Produkte wurden kristallographisch aufgeklärt. Das Zentrum von $[\mathrm{Hg_2(\mu\text{-}SePh)_2(SePh)_2(PPh_3)_2}]$ besteht aus einem verzerrten Quadrat aus zwei Hg- und zwei Se-Atomen. Die Quecksilberatome sind nahezu tetraedrisch koordiniert. Ihre Koordinationssphäre wird aus den Se-Atomen zweier (μ-$^{-}$SePh)-Liganden und den Se und P-Atomen terminaler $^{-}$SePh- und $\mathrm{PPh_3}$-Einheiten gebildet. Die Verbindung **II** besteht aus einem sechsgliedrigen Ring, in dem alternierend Hg- und Se-Atome angeordnet sind. Oberhalb und unterhalb der Ringebene sind DMSO-Moleküle angeordnet, deren Sauerstoffatome in Richtung der Ringebene weisen.

Introduction

Mercury chalcogenide compounds have found considerable use in industry, especially as low gap semiconductors, in photovoltaic applications, and IR detection devices [1]. Thin films of metal chalcogenides are also of great interest in the field of photovoltaics, where the metal chalcogenide is deposited as films on glass, ceramic, and plastic surfaces from a homogeneous solution by chemical deposition [2]. Thus, the control of the synthesis and molecular structure of metal chalcogenide is of considerable interest in both processes [3]. Compounds such as $[\mathrm{M(ER)_2}]$ (M = Zn, Cd, Hg; E = Se, Te; R = alkyl or aryl), which have all of the constituent of the product incorporated in a single molecule are called "single-source" compounds [4]. These offer advantages such as better control of the reaction stoichiometry and lower reaction temperatures. Additionally, they can be used to generate some ligands for the synthesis "in situ" [5].

Mercury selenides form interesting compounds by interaction with lanthanide chalcogenates [6] or based on $[\mathrm{Hg(SeR)_2}]$ units [7] as has been shown for reactions of $\mathrm{HgCl_2}$ with $\mathrm{P}^t\mathrm{Bu_3}$ and $\mathrm{PhSeSiMe_3}$ which yield the mercury clusters $[\mathrm{Hg_6(SePh)_{12}(P}^t\mathrm{Bu_3)_2}]$ and $(\mathrm{HP}^t\mathrm{Bu_3})_2[\mathrm{Hg_6(SePh)_{14}}]$ constituted by similar Hg-Se cages with distorted tetrahedral coordination around mercury atoms [7b]. $[\mathrm{Hg(ER)_2}]$ (E=S, Se) reacts with equimolar amounts of $\mathrm{HgCl_2}$ in pyridine to yield metallacyclic compounds of the type $[\mathrm{Hg_4Cl_4(\mu{-}ER)_4(py)_n}]$ (E=S, R= ^{t}Bu, n=2 [8]; E=Se, R= Et, n=4; E=Se, R= ^{t}Bu, n=4 [9]) and we found that the corresponding tellurides afford under similar conditions the clusters $[\mathrm{Hg_6(\mu{-}Br)_2Br_2(\mu_2{-}TePh)_8(py)_2}]$, $[\mathrm{Hg_3X_3(\mu{-}TePh)_3}] \cdot 2$ DMSO (X=Cl, Br, I) [10], and $[\mathrm{Hg_8(\mu{-}}n\mathrm{{-}C_3H_7Te)_{12}(\mu_2{-}Br)Br_3}]$ [11]. The presence of the co-ordinating solvents and the sterical requirements of the organic residues bonded to the chalcogen atoms are considered to be limiting parameters in the linking mode of the ligands and the size of the clusters. Although the structure of $[\mathrm{Hg(SePh)_2}]$ has been recently reported [12], its reactivity is only scarcely explored. This is probably due to the tend-

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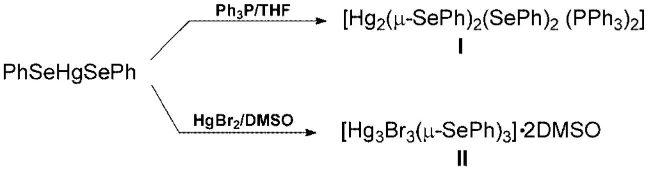
ency of the compound to deposite mercury and to form $(SePh)_2$. However, bearing in mind the stabilizing effect of DMSO or other donor solvents to mercury chalcogenides, here we verify the influence of the nature of the chalcogen atom on the reactivity following a similar procedure as has previously been used for the synthesis of tellurium−mercury clusters [10, 11].

Results and Discussion

In clear contrast to the tellurium analogue, the reactivity of $[Hg(SePh)_2]$ is limited by its tendency to deposit mercury under formation of $(SePh)_2$. The mercury(II) cation is stabilized by addition of a slight excess of selenolate to form the anionic complex $[Hg(SePh)_3]^-$ [12]. The reaction of $[Hg(SePh)_2]$ with triphenylphosphine affords $[Hg_2(\mu-SePh)_2(SePh)_2(PPh_3)_2]$ (**I**) (Scheme I). The compound is air-stable and soluble in DMSO, dioxane and diethylether. As its tellurium analogue, $[Hg(SePh)_2]$ reacts with $HgBr_2$ in DMSO to form a 6-membered ring system, $[Hg_3Br_3(\mu-SePh)_3] \cdot 2$DMSO (**II**). However, **I** does not form metallacyclic species when it reacts with the Lewis acids HgX_2 but forms the known compounds PhSeHgX [13].



Crystals of **I** suitable for X-ray analysis could be obtained from the reaction mixture. An ellipsoid representation [14] of the molecular structure is shown in Figure 1. The structure can be described as constituted by two mercury atoms which are asymmetrically bridged by two $^-$SePh ligands. The co-ordination spheres of the Hg atoms are completed by two terminal $^-$SePh and PPh_3 ligands. The asymmetric unit of the structure contains a half molecule of **I** and inversion symmetry centre completes the four-membered ring, with alternating Hg and Se atoms. The co-ordination around the mercury atom is a distorted $HgPSe_3$tetrahedron, main distortions are due to the Se(1)-Hg(1)-Se(2) and Se(2)-Hg(1)-Se(2)#1 angles of 121.51(2) and 95.06(2)°, respectively. The Hg−P bond (2.5563(14) Å) is in the expected range [15], but the Hg−Se bond lengths (2.544(1)−2.819(1) Å) are clearly longer than those found in $[Hg(SePh)_2]$ (2.471(2) Å) and $[Hg((SePh)_3]^-$ (2.600(2)-2.536(1) Å) [12]. More bond lengths and angles are contained in Table 1. The strong asymmetry of the phenylselenolato bridges is obvious when compared with the structure of $[Hg(SeMe)_2]_n$, which also contains a four-membered ring formed by $^-$SeMe bridges between two Hg atoms and where the Hg-Se bond lengths range between 2.614(2) and 2.764(2) Å) [9]. Furthermore, the Hg-Hg distance in **I** (3.4985(4) Å) is intermediate between the two values observed in the methyl derivative (3.538(1) and 4.070(2) Å) but clearly shorter than in $[Hg(SePh)_2]$ (4.672(1) Å) [12].

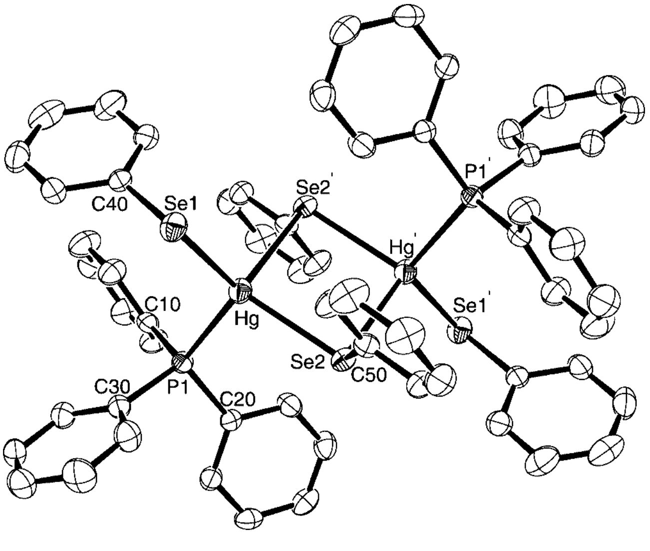


Fig. 1 Ellipsoid representation of the molecular structure of $[Hg_2(\mu-SePh)_2(SePh)_2(PPh_3)_2]$ (**I**).

Table 1 Selected bond lengths /Å and angles /° for $[Hg_2(\mu-SePh)_2(SePh)_2(PPh_3)_2]$ (**I**).

Hg-Se(1)	2.544(1)
Hg-P(1)	2.556(1)
Hg-Se(2)	2.657(1)
Hg-Se(2)′	2.819(1)
Se(2)-Hg′	2.819(7)
Se(1)-Hg-P(1)	118.27(4)
Se(1)-Hg-Se(2)	121.51(2)
P(1)-Hg-Se(2)	103.33(3)
Se(1)-Hg-Se(2)′	109.15(2)
P(1)-Hg-Se(2)′	106.34(4)
Se(2)-Hg-Se(2)′	95.06(2)
Hg-Se(2)-Hg′	84.94(2)

Symmetry transformations used to generate equivalent atoms: ′ −x+2, −y+1, −z+1

The X-ray crystallographic analysis of **II** shows that the structure is isotypic with the tellurium analogues $[Hg_3X_3(\mu-TePh)_3] \cdot 2$ DMSO (X = Cl, Br,) [10], and it consists of molecules based on six-membered rings with alternating Hg and Se atoms in a chair conformation (Fig. 2) and a terminal bromine atom co-ordinates to each mercury atom. The Hg−Se distances (Table 2) are shorter than the corresponding values for the bridging $^-$SePh unit in **I** (*vide supra*) and the phenylselenolato ligand in **II** forms almost symmetric bridges. The Hg−Br distances are close to those found in $[Hg_3Br_3(\mu-TePh)_3] \cdot 2$ DMSO [10]. Considering only the interactions noted above, the coordination around the mercury atom would be trigonal-planar. However, as observed in the tellurium derivatives, there are two dimethylsulfoxide molecules occupying positions on either side of the Hg_3Se_3 ring with the oxygen atoms oriented to

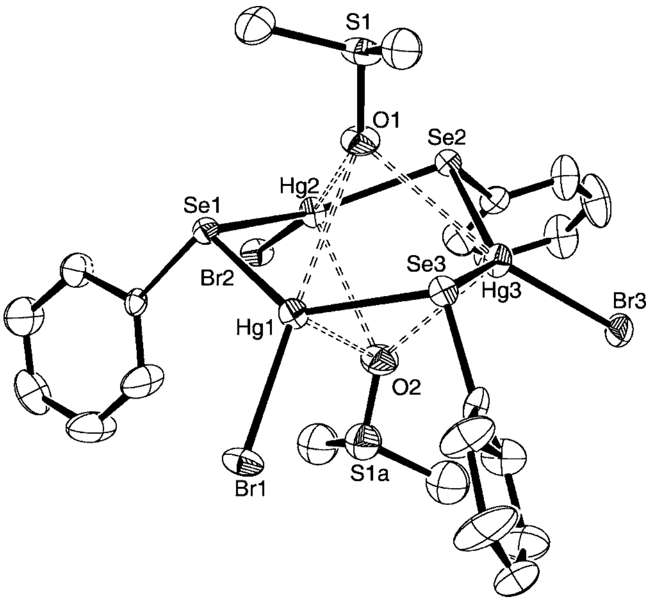


Fig. 2 Ellipsoid representation of $[Hg_3Br_3(\mu{-}SePh)_3] \cdot 2$ DMSO (**II**). Weak O···Hg interactions (distances of about 3 Å) are indicated as dashed lines.

the centre of the ring. The Hg-O distances are shorter than the sum of their van der Waals radii [16]. The mercury atoms interact weakly with the bromine atoms of the neighbouring molecules [Hg(1)···Br(1)′ = 3.134(2), Hg(2)···Br(2)″ = 3.164(2), Hg(3)···Br(3)‴ = 3.329(2) Å (symmetry operations: (′) x+1, −y+1, −z; (″) −x+1, −y+1, −z+1; (‴) −x+1, −y, −z+1). If all weak interactions are considered, the resulting co-ordination polyhedron around the mercury atom can be described as a strongly distorted octahedron, while the co-ordination around the selenium atom is trigonal-pyramidal with Hg-Se-Hg angles around 95°.

Experimental Section

Triphenylphosphine (Aldrich) and mercury(II) bromide (Fluka) were used as received. $[Hg(SePh)_2]$ was synthezised by a reported method [12]. Melting points were determined on a Micro Química APF 301 apparatus and were uncorrected.

Table 2 Bond lengths /Å and angles /° for $[Hg_3Br_3(\mu{-}SePh)_3] \cdot 2$ DMSO (**II**).

Se(1)-Hg(1)	2.536(2)
Se(1)-Hg(2)	2.577(2)
Se(2)-Hg(2)	2.533(2)
Se(2)-Hg(3)	2.571(2)
Se(3)-Hg(3)	2.547(2)
Se(3)-Hg(1)	2.563(2)
Hg(1)-Br(1)	2.609(2)
Hg(1)-Br(1)′	3.134(2)
Hg(2)-Br(2)	2.606(2)
Hg(3)-Br(3)	2.575(2)
Br(1)-Hg(1)′	3.134(2)
Hg(1)-Se(1)-Hg(2)	95.42(5)
Hg(2)-Se(2)-Hg(3)	95.11(5)
Hg(3)-Se(3)-Hg(1)	96.27(5)
Se(1)-Hg(1)-Se(3)	132.03(5)
Se(1)-Hg(1)-Br(1)	120.17(5)
Se(3)-Hg(1)-Br(1)	107.65(5)
Se(1)-Hg(1)-Br(1)′	93.72(5)
Se(3)-Hg(1)-Br(1)′	89.54(5)
Br(1)-Hg(1)-Br(1)′	90.17(5)
Se(2)-Hg(2)-Se(1)	130.58(5)
Se(2)-Hg(2)-Br(2)	121.63(6)
Se(1)-Hg(2)-Br(2)	107.79(6)
Se(3)-Hg(3)-Se(2)	128.63(5)
Se(3)-Hg(3)-Br(3)	121.25(6)
Se(2)-Hg(3)-Br(3)	110.06(6)
Hg(1)-Br(1)-Hg(1)′	89.83(5)

Symmetry transformations used to generate equivalent atoms: ′ −x, −y, −z+1

Table 3 Crystal data and structure refinements.

	I	**II**
Empirical formula	$C_{60}H_{50}Hg_2P_2Se_4$	$C_{22}H_{27}Br_3Hg_3O_2S_2Se_3$
Formula weight	1549.96	525.01
T / K	293(2)	293(2)
Wavelength/ Å	0.71073 Å	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a / Å	9.829(2)	10.155(2)
b / Å	11.669(6)	14.053(3)
c / Å	14.092(2)	14.404(3)
α / °	64.86(1)	61.04(1)
β / °	77.66(1)	72.67(1)
γ / °	72.86(1)	89.53(1)
V / Å^3	1390.8(8)	1694.0(6)
Z	1	2
ρ_{calc} / g cm^3	1.851	2.874
μ / mm^{-1}	8.224	20.464
Crystal size/mm^3	0.3 · 0.13 · 0.13	0.13 · 0.12 · 0.10
θ range / °	2.18−25.47	2.47−24.97
Limiting indices	$-11 \leq h \leq 11$ $-14 \leq k \leq 12$ $-17 \leq l \leq 0$	$-12 \leq h \leq 12$ $0 \leq k \leq 16$ $-14 \leq l \leq 17$
Refl. Collected	5367	6203
Refl. Unique (R_{int})	5141 (0.0189)	5940 (0.0618)
Refl. Observed [$I > 2\sigma(I)$]	3970	4288
Goodness-of-fit on F^2	1.023	1.023
R1 (observed data)	0.0250	0.0480
*w*R2 (all data)	0.0562	0.0880
Largest peak/hole / e Å^3	0.532/ −0.671	1.897/ −1.869

X-ray data collection, structures solution and refinement.

The X-ray data have been collected at an automated CAD4 diffractometer (Enraf Nonius). The structures were solved by direct methods (SHELXS−97 [17]). All refinements were made by full−matrix least−squares on F^2 with anisotropic displacement parameters for all non hydrogen atoms (SHELXL−97 [17]). Hydrogen atoms positions for **I** have been taken from the Fourier map and refined, and for **II** they have been calculated for idealized positions and treated with the 'riding model' option of SHELXL. Crystal data and some relevant structure refinement parameters are listed in Table 3. Further details of the crystal structure determination are available free of charge via *www.ccdc.cam.ac.uk/conts/retrieving.html* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) as Supplementary publication Nos. CSD 220807 ($[Hg_2(\mu{-}SePh)_2(SePh)_2(PPh_3)_2]$), CSD 220808 ($[Hg_3Br_3(\mu{-}SePh)_3]$ · 2 DMSO).

Preparation of $[Hg_2(\mu-SePh)_2(SePh)_2(PPh_3)_2]$ *(**I**)*:

$[Hg(SePh)_2]$ (0.512 g, 1 mmol) and PPh_3 (0.262 g, 1 mmol) were dissolved in THF and heated under reflux for 1 h. Pure $[Hg_2(\mu-SePh)_2(SePh)_2(PPh_3)_2]$ was obtained as pale yellow crystals upon slow evaporation of the resulting solution under nitrogen. Yield: 0.472 g, 61 %. M.p. 124°C. Anal. Found: C, 41.25; H, 3.1 %. Calcd. for $C_{60}H_{50}Hg_2P_2Se_4$: C, 42.19; H, 2.95 %.

Preparation of $[Hg_3Br_3(\mu-SePh)_3] \cdot 2$ *DMSO (**II**):* $[Hg(SePh)_2]$ (0.52 g, 1 mmol) and $HgBr_2$ (0.360 g, 1 mmol) were dissolved in 10 ml of DMSO and the mixture was stirred for 3 h at room temperature. The solution was over-layered with ethyl acetate (5 ml) to give after 3 days pale yellow crystals. Yield: 1.0 g, 68 %. M.p. 208 °C. Anal. Found: C, 17.7; H, 1.5 %. Calc.: C, 16.5; H, 1.1 %.

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References

[1] C. J. Warren, R. C. Haushalter, A. B. Bocarsly, *J. Alloys Comp.* **1995**, *229*, 175.
[2] M. T. S. Nair, P. K. Nair, R. A. Zingaro, E. A. Mayers, *J. Appl. Phys.* **1994**, *75*, 1557.
[3] I. Dance, K. Fisher, *Prog. Inorg. Chem.* **1994**, *41*, 637.
[4] A. H. Cowley, R. A. Jones, *Angew. Chem.* **1989**, *101*, 1235; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1208.
[5] E. S. Lang, C. C. Gatto, U. Abram, *Z. Anorg. Allg. Chem.* **2002**, *628*, 335.
[6] M. Bernardini, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **1995**, *34*, 5327.
[7] (a) S. Behrens, M. Bettenhausen, A. C. Devenson, A. Eichhöfer, D. Fenske, A. Lohde, H. Woggon, *Angew. Chem.* **1996**, *108*, 2360; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2215. (b) M. Bettenhausen, D. Fenske, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1245.
[8] A. J. Canty, C. L. Raston, A. H. White, *Aust. J. Chem*. **1978**, *31*, 677. See also for the 4-metylpyridine derivative: A. J. Canty, C. L. Raston, A. H. White, *Aust. J. Chem.* **1979,** *72,* 311.
[9] A. P. Arnold, A. J. Canty, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1982**, 607.
[10] E. Schulz Lang, R. A. Zan, C. C. Gatto, R. A. Burrow, E. M. Vázquez-López, *Eur. J. Inorg. Chem.* **2002**, 331.
[11] E. S. Lang, C. Peppe, R. A. Zan, U. Abram, E. M. Vázquez-López, B. Krumm, O. P. Ruscitti, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2815.
[12] E. Schulz Lang, M. M. Dias, U. Abram, E. M. Vázquez-López, *Z. Anorg. Allg. Chem.* **2000**, *626*, 784 and references cited therein.
[13] A. Fredga, *Chem. Ber.* **1939**, *71b*, 286.
[14] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[15] N. A. Bell, T. D. Dee, M. Goldstein, P. J. McKenna, I. W. Nowell, *Inorg. Chim. Acta* **1988**, *71*, 135.
[16] A. Bondi, *J. Phys. Chem.* **1964**, *15*, 383.
[17] G. M. Sheldrick, *SHELXS97 and SHELXL97 − Programmes for the solution and refinement of crystal structures*, University of Göttingen (Germany), **1997**.