Synthesis and Structure of the new cluster $[Hg_{10}Se_4(SePh)_{12}(PPh_2nPr)_4]$ and its Conversion into $[Hg_{32}Se_{14}(SePh)_{36}]$

Andreas Eichhöfer*[a] **and Emma Tröster**[a]

Keywords: Cluster compounds / Mercury / Selenium / UV/Vis spectroscopy

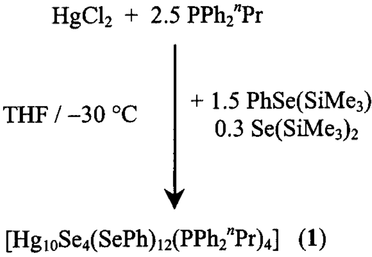
The reaction of $HgCl_2$ and PPh_2nPr with $PhSeSiMe_3$ and $Se(SiMe_3)_2$ in THF at –30 °C results in the formation of yellow octahedral crystals of $[Hg_{10}Se_4(SePh)_{12}(PPh_2nPr)_4]$. The molecular structure of the cluster is similar to structures of other $[M_{10}Se_4(SePh)_{12}(PR_3)_4]$ (M = Cd, Zn; R = organic group) cluster compounds although it is the first of its type with mercury as the group 12 metal atom. Dissolving $[Hg_{10}Se_4(SePh)_{12}(PPh_2nPr)_4]$ in benzene at 10 °C leads to the rapid formation of a dark red solution from which red crystals of the larger cluster $[Hg_{32}Se_{14}(SePh)_{36}]$ could be crystallized in 50% yield upon layering with pentane.

Introduction

Systematic studies of the size-dependent optical and electronic properties of CdSe cluster molecules such as $[NPr_4]^+_2[Cd_4(SePh)_6Cl_4]^{2-}$, $[Cd_{10}Se_4(SePh)_{12}(PPr_3)_4]$, $[Cd_{17}Se_4(SePh)_{24}(PPh_2Pr)_4]^{2+}[Cd_8Se(SePh)_{12}Cl_4]^{2-}$ and $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$ (Ph = phenyl, Pr = *n*-propyl) show that the absorption and low temperature photoluminescence excitation onset of the clusters shifts systematically to the blue in smaller clusters,[1] thus confirming that the quantum confinement effect that is well-known for larger CdSe nanocrystals is also valid in these small molecular systems. The synthesis and structural characterization of group 12/16 cluster molecules has mostly been focused on ZnS,[2] ZnSe,[3] ZnTe,[4] CdS,[5,6] and CdSe[7] compounds. In contrast, chalcogenide cluster compounds with mercury are rare and $[Hg_{32}Se_{14}(SePh)_{36}]$ (**2**) is, to the best of our knowledge, the only example of such a compound containing selenido ligands as well as selenolato ones.[8] Nonetheless, these materials possess interesting properties as bulk or nano-materials. The alloy $Cd_{1-x}Hg_xTe$ is a well-known material for long-wavelength IR detector technologies, and HgTe nanoparticles have been proposed to act as potential amplifiers operating at wavelengths of 1.3 µm and 1.55 µm for telecommunication device.[9,10] Furthermore, optical investigations on small cluster molecules of bulk materials with smaller band gaps have advantages over those which possess larger ones due to the fact that for smaller clusters the mixing of ligand transitions with those of the cluster core are more pronounced in materials with a large band gap. Therefore in order to extend optical investigations on group 12/16 cluster molecules we began to investigate the synthesis and crystallisation of further mercury selenide cluster molecules.

Results and Discussion

The reaction of $HgCl_2$ and PPh_2nPr with $PhSeSiMe_3$ and $Se(SiMe_3)_2$ in THF at −30 °C results in the formation of yellow octahedral crystals of $[Hg_{10}Se_4(SePh)_{12}(PPh_2nPr)_4]$ (**1**; Scheme 1).



Scheme 1

Figure 1 shows the X-ray crystal structure of the $[Hg_{10}Se_{16}P_4]$ cluster core. The compound crystallizes in the tetragonal space group $I4_1/a$. The core of the cluster, which comprises four HgSe adamantane cages, is a macrotetrahedral fragment of the sphalerite structure, which is also found in HgSe.[11] The tetrahedron with the four phosphane atoms at the apex positions displays edge lengths of 1221.4−1293.4 pm. The Hg atoms Hg1−Hg3 have distorted tetrahedral environments, coordinated by the Se atoms of the μ_2-$SePh^-$ (Se2, Se3, Se4) and the μ_3-Se^{2-} (Se1) atoms as well as the P atoms of the PPh_2nPr (P1) ligands [Se−Hg−Se: 92.17−130.73(5); P−Hg−Se: 103.31−112.98(7)°]. The Hg−SePh bond lengths range

---

[a] Institut für Nanotechnologie, Forschungszentrum Karlsruhe,
Postfach 3640, 76021 Karlsruhe, Germany
Fax: (internat.) +49-(0)7247/82-6368
E-mail: eichhoefer@int.fzk.de

from 262.09 to 277.69(12) pm and the Hg−Se bond lengths from 256.03 to 262.81(10) pm; these distances are similar to those in HgSe (262 pm).[11] The value for the Hg−P1 bond length of the four outer Hg1 atoms coordinated by the PPh_2nPr ligands is 257.5(3) pm. The structure is therefore similar to structures of other $[M_{10}Se_4(SePh)_{12}(PR_3)_4]$ (M = Cd, Zn; R = organic group)[3,7] cluster compounds although it is the first of this type with mercury as the group 12 metal atom.

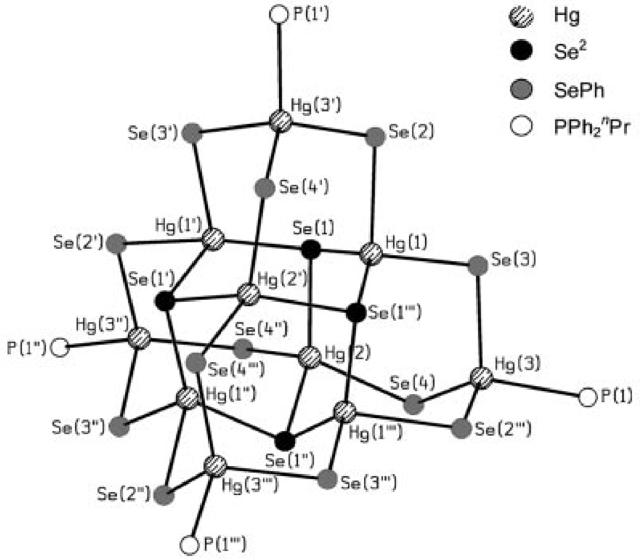


Figure 1. The $Hg_{10}Se_{16}P_4$ cluster core as a section of the molecular structure of **1**; Hg atoms (hatched circles), Se^{2-} atoms (black), $SePh^-$ (grey), P atoms (open circles); C and H atoms are omitted for clarity

Filtration of **1** at −30 °C and subsequent drying under vacuum results in a yellow powder which is stable under nitrogen at room temperature. A reflectance spectrum of microcrystalline **1** between two quartz plates (Figure 2, straight line) displays an absorption onset at 475 nm and two shoulders at approximately 410 nm and 382 nm. If **1** is dissolved in benzene at 10 °C one observes the rapid formation of a deep red solution and a small amount of black precipitate. The UV/Vis absorption spectrum of the supernatant solution (Figure 2, dashed line) displays the bands characteristic of the larger cluster $[Hg_{32}Se_{14}(SePh)_{36}]$ (**2**).[8] Upon concentration at room temperature yellow crystals of $Hg(SePh)_2$ are formed in the red solution. Layering of the filtered solution with pentane yields red crystals of **2**, sometimes accompanied by a small amount of $[Hg(SePh)_2]$. Both compounds were characterized by the determination of the lattice parameters and comparison to literature data {$[Hg(SePh)_2]$,[12] **2**: hexagonal, $a = b = 22.863$, $c = 53.390$ Å, $V = 24256$ Å^3 [8]} and **2** also by elemental analysis. Additionally the UV/Vis absorption spectrum of the red crystalline powder is in perfect agreement with the published one of **2**.[8] The black precipitate displays the three main reflections $2\theta_{111} = 25.4°$, $2\theta_{220} = 42.1°$ and $2\theta_{311} = 49.8°$ of cubic HgSe in its powder diffraction pattern.[13] Following these observations the schematic reaction equation in Scheme 2 can be established.

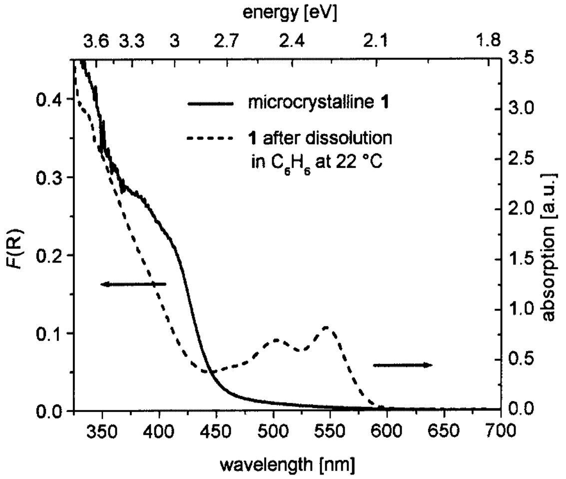


Figure 2. Reflectance spectra of **1** as a microcrystalline powder between two quartz plates (straight line) and UV/Vis absorption spectra of **1** after dissolution in C_6H_6 at 22 °C (dashed line)

$$\begin{array}{c}[Hg_{10}Se_4(SePh)_{12}(PPh_2{}^nPr)_4]\ \mathbf{(1)}\\ \Big\downarrow\ C_6H_6\,/\,22\ °C\\ [Hg_{32}Se_{14}(SePh)_{36}]\ \mathbf{(2)}\\ +\\ Hg(SePh)_2 + HgSe\end{array}$$

Scheme 2

The conversion of the smaller cluster to the larger one is not induced by light as confirmed by experiments in benzene in the dark. This is in contrast to the experiment of Corrigan et al. who observed the formation of $[Cu_{50}(TePh)_{20}Te_{17}(PEtPh_2)_8][PEtPh_3]$ from $[Cu_6(TePh)_6(PEtPh_2)_5]$ by a light-induced conversion of tellurolate to telluride.[14] Furthermore we could not find any proof for the formation of $SePh_2$ in the reaction solutions similar to the formation of $TePh_2$ in Corrigan's experiment. In the present case temperature seems to play an important role for the induction of the conversion. Because of the high melting point of benzene (5 °C) the progress of the reaction could only be followed in other solvents. Compound **1** is not soluble in toluene at −60 °C. Upon warming, the solution gradually becomes coloured; it is pale yellow at −45 °C, yellow-orange at −15 °C and then becomes turbid at 0 °C with the formation of a black precipitate. The UV/Vis absorption spectrum of the supernatant pale red solution displays the bands typical for **2**. Upon layering with pentane only a few tiny crystals of **2** could be grown. In THF **1** is hardly soluble at −60 °C leading to a pale yellow solution. Upon warming, this solution also gradually turns dark remaining yellow up to −30 °C changing to brown at −10 °C and finally becoming black and turbid at room temperature. This solution shows a strong band at 256 nm probably originating from transitions related to the phenyl ligands, followed by a continuous decay to 800 nm with no indication of the formation of **2**. These results indicate that the solvent used has also an important influence on the formation of **2**.

Although **2** consists of a core built up from Hg−Se adamantane cages its formation cannot be explained in terms of a direct condensation reaction of the $[Hg_{10}Se_4(SePh)_{12}]$ cluster cores of **1**. Because the outer Se−Ph ligands cannot act as bridging ligands inside the cluster cage of **2** larger rearrangements of the cluster core in **1** must take place which could also include the temporary formation of other cluster compounds. These larger rearrangements are also suggested by the formation of $Hg(SePh)_2$ and HgSe, which indicate partial decomposition of **1** during the reorganisation to **2**. The driving force of the conversion reaction could therefore be the complete formation of bulk HgSe and $Hg(SePh)_2$. Accordingly, heating a benzene solution for several hours results in a pale yellow solution with a black precipitate. However the additional formation of elemental mercury and the proof of the formation of $SePPh_2nPr$ by GC-MS and ^{31}P NMR spectroscopy suggests that the decomposition process is a more complex one as is also suggested by the yield of approximately 50% for **2** with respect to the theoretical yield based on the reaction in Scheme 2.

In summary we have shown that the new cluster $[Hg_{10}Se_4(SePh)_{12}(PPh_2nPr)_4]$ (**1**) is a metastable compound that converts to $Hg(SePh)_2$, HgSe and the larger cluster $[Hg_{32}Se_{14}(SePh)_{36}]$ (**2**) in benzene at room temperature. This is therefore an interesting example of controlled cluster growth in solution induced by thermal energy and suggests also the possible use of these clusters as precursor compounds in the synthesis of nanoparticles. Whether the treatment of **2** with other solvents such as THF and toluene leads to the formation of different cluster compounds and whether this conversion reaction is also valid for cluster compounds with composition $[M_{10}E_4(EPh)_{12}(PR_3)_4]$ (M = Zn, Cd; E = Se, Te; R = organic group) is the focus of current investigations.

Experimental Section

General: Standard Schlenk techniques were employed throughout the syntheses using a double-manifold vacuum line with high purity dry nitrogen. Tetrahydrofuran and benzene were dried over sodium/benzophenone, pentane with $LiAlH_4$ and distilled under nitrogen. Anhydrous $HgCl_2$ was purchased from Aldrich. $PhSeSiMe_3$ [15] and $Se(SiMe_3)_2$ [16] were prepared according to standard literature procedures.

X-ray powder diffraction patterns (XRD) were measured on a STOE STADI P diffractometer (Cu-K_α radiation, Ge monochromator, Debye−Scherrer geometry) in sealed glass capillaries.

Absorption spectra of cluster molecules in solution were measured on a Varian Cary 500 spectrophotometer in quartz cuvettes. Solid-state reflectance spectra were measured on micron-sized crystalline powders between quartz plates with a Labsphere integrating sphere.

Synthesis of 1: $HgCl_2$ (0.18 g, 0.66 mmol) was dissolved in 30 mL of THF and PPh_2nPr (0.30 mL, 1.33 mmol) was added. Then $PhSeSiMe_3$ (0.19 mL, 0.99 mmol) was added at 0 °C and the resulting clear yellow solution stirred overnight at room temperature. Addition of $Se(SiMe_3)_2$ (0.045 mL, 0.2 mmol) at −60 °C led to the formation of a pale yellow solution from which $[Hg_{10}Se_4(SePh)_{12}(PPh_2nPr)_4]$ (**1**) could be crystallized at −30 °C (60% yield). $C_{132}H_{128}Hg_{10}P_4Se_{16}$ (5107.6): calcd. C 31.04, H 2.53; $C_{132}H_{128}Hg_{10}P_4Se_{16}\cdot 6C_4H_8O$: calcd. C 33.8, H 3.02; found C 31.60, H 2.44%. Most of the solvent molecules in the crystal therefore evaporate upon drying under vacuum (10^{-3} mbar). Suitable crystals for X-ray diffraction were obtained by warming the reaction solution to 0 °C and recooling to −35 °C.

Synthesis of 2: Compound **1** (0.18 g, 0.035 mmol) was dissolved in 20 mL of benzene at 10 °C to give a dark red solution with a small amount of black precipitate of HgSe. After two days at room temperature the solution was concentrated to 10 mL. Yellow platelet-like crystals of $Hg(SePh)_2$ grow together with a small amount of red crystals of **2**. These were filtered after two days and subsequent layering of the clear red solution with benzene/pentane led to the formation of red crystals of **2** (yield 49% calculated for Scheme 2). $C_{216}H_{180}Hg_{32}Se_{40}$ (12353.1): calcd. C 19.74, H 1.38; found C 21.87, H 1.58. The deviations in the C H analysis probably indicate the presence of $Hg(SePh)_2$ in the red crystalline powder.

Crystallographic Data for $1\cdot 6C_4H_8O$: M_r = 5514.91, tetragonal, space group $I4_1/a$ (No. 88), $a = b = 23.059(3)$, $c = 37.757(8)$ Å, $V = 20077$ Å^3, $Z = 4$, $D_c = 1.825$ g·cm^{-3}, μ(Mo-K_α) = 10.59 mm^{-1}. The data collection was carried out on a STOE IPDS II diffractometer using graphite-monochromated Mo-K_α (l = 0.71073 Å) radiation at 170 K. The structure solution and full-matrix least square refinement based on F^2 were performed with the SHELX-97 program package,[17] giving a final $R1$ value of 0.0466 for 406 parameters and 7061 unique reflections with $I \geq 2\sigma(I)$ and a $wR2$ value of 0.1588 for all 37265 reflections.

CCDC-178317 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

---

[1] V. Soloviev, A. Eichhöfer, D. Fenske, U. Banin, *J. Am. Chem. Soc.* **2001**, *123*, 2354−2364.

[2] B. Ali, I. G. Dance, D. C. Craig, M. L. Scudder, *J. Chem. Soc., Dalton Trans.* **1998**, 1661−1667; M. D. Nyman, M. J. Hampden-Smith, E. N. Duesler, *Inorg. Chem.* **1996**, *35*, 802−803.

[3] A. Eichhöfer, D. Fenske, H. Pfistner, M. Wunder, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1909−1914.

[4] H. Pfistner, D. Fenske, *Z. Anorg. Allg. Chem.* **2001**, *627*, 575−582.

[5] G. S. H. Lee, K. J. Fisher, D. C. Craig, M. L. Scudder, I. G. Dance, *J. Am. Chem. Soc.* **1990**, *112*, 6435−6437; G. S. H. Lee, D. C. Craig, I. Ma, M. L. Scudder, T. D. Bailey, I. G. Dance, *J. Am. Chem. Soc.* **1988**, *110*, 4863−4864; I. G. Dance, A. Choy, M. L. Scudder, *J. Am. Chem. Soc.* **1984**, *106*, 6285−6295.

[6] T. Vossmeyer, G. Reck, L. Katsikas, E. T. K. Haupt, B. Schulz, H. Weller, *Science* **1995**, *267*, 1476−1479; T. Vossmeyer, G. Reck, B. Schulz, L. Katsikas, H. Weller, *J. Am. Chem. Soc.* **1995**, *117*, 12881−12882.

[7] S. Behrens, M. Bettenhausen, A. Eichhöfer, D. Fenske, *Angew. Chem.* **1997**, *109*, 2874−2876; *Angew. Chem. Int. Ed. Engl.* **1997**, *24*, 2797; S. Behrens, D. Fenske, *Ber. Bunsenges. Phys. Chem.* **1997**, *101*, 1588−1592.

[8] S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, A. Lohde, U. Woggon, *Angew. Chem.* **1996**, *108*, 2360−2363; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2215−2218.

[9] A. Rogach, S. Kershaw, M. Burt, M. Harrison, A. Kornowski, A. Eychmüller, H. Weller, *Adv. Mater.* **1999**, *11*, 552−555.

[10] M. Harrison, S. Kershaw, A. Rogach, A. Kornowski, A. Eychmüller, H. Weller, *Adv. Mater.* **2000**, *12*, 123−125.

[11] Landolt-Börnstein, Gruppe III: Kristall und Festkörperphysik, Band 17: Halbleiter (Gesamtherausgabe: O. Madelung), Springer, Berlin, **1982**, p. 236.

[12] E. Schulz Lang, M. Müller Dias, U. Abram, E. M. Vázquez-López, *Z. Anorg. Allg. Chem.* **2000**, *626*, 784−788.

[13] J. W. Early, *Am. Mineral.* **1950**, *35*, 337−364.

[14] J. F. Corrigan, D. Fenske, *Angew. Chem.* **1997**, *109*, 2070−2072; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1981−1983.

[15] N. Miyoshi, H. Ishii, K. Kondo, S. Mui, N. Sonoda, *Synthesis* **1979**, 301−304.

[16] H. Schmidt, H. Ruf, *Z. Anorg. Allg. Chem.* **1963**, *321*, 270−273.

[17] G. M. Sheldrick SHELX-97, Program for X-ray crystal structure determination and refinement, Göttingen University, Germany, **1997**.

Received March 22, 2002
[I02153]