Synthesis and Structures of Silver–Selenide Cluster Complexes $[Ag_4(SeiPr)_4(dppm)_2]$, $[Ag_8(SeEt)_8(dppp)]_\infty$, $[Ag_{28}Se_6(SenBu)_{16}(dppp)_4]$, and $[Ag_{124}Se_{57}(SePtBu_2)_4Cl_6(tBu_2P(CH_2)_3PtBu_2)_{12}]$**

Dieter Fenske* and Timo Langetepe

Dedicated to Professor Jochen Strähle
on the occasion of his 65th birthday

The specific synthesis of nanometer-sized clusters and colloids is of particular interest because of the electronic and optical properties of this type of substances.[1, 2] Colloids as well as ligand-stabilized sections of metals[3] and semiconductor clusters[4] have been intensively studied. As result of the quantum size effect, the clusters show a dependence of the band gap on the particle size. In the last few years, we have been working on the synthesis of cluster complexes whose core is formed, for example, by transition metal chalcogenides.[5] This core is protected by a shell of ligands from self-aggregation, which would lead to the thermodynamically stable binary phase.[6]

One approach to the preparation of metal chalcogen bridged cluster complexes is the reaction of transition metal salts, or their phosphane complexes with silylated chalcogenide compounds of the general type $E(SiMe_3)_2$ or $RESiMe_3$ (R = alkyl or aryl; E = S, Se, Te). The driving force of the reaction is the formation of $XSiMe_3$ (X = Cl, Br, OAc, etc). In this way we have prepared and characterized a large number of cluster compounds, examples of which are given in Scheme 1.

$[Cu_{146}Se_{73}(PPh_3)_{30}]$[7]

$[Ag_{172}Se_{40}(SenBu)_{92}(dppp)_4]$[8] (dppp = 1,3-bis(diphenylphosphanyl)propane)

$[Ag_{38}Te_{13}(TetBu)_{12}(dppe)_6]$[9]

$[Au_{18}Se_8(dppe)_6]Cl_2$[10] (dppe = 1,2-bis(diphenylphosphanyl)ethane)

$[Zn_{16}Te_{13}(TePh)_6(tmeda)_5]$[11] (tmeda = tetramethylethylenediamine)

$[Cd_{32}S_{14}(SR)_{36}(OH_2)_4]$[12] (R = $CH_2CH(OH)CH_3$)

Scheme 1.

These compounds are usually obtained in a high yield. It shows that the used reactants and the reaction conditions are crucial for the observed composition of the isolated cluster complexes. However, several species are propably present in an equilibrium existing in the reaction mixture, from which that with the lowest solubility will crystallize. Therefore it is not surprising, that even a slight change in the reaction conditions may cause the formation of novel, yet unknown cluster structures. Herein, we describe the synthesis and crystal structures of **1**–**4**.

$[Ag_4(SeiPr)_4(dppm)_2]$ **1**

$[Ag_8(SeEt)_8(dppp)]_\infty$ **2**

$[Ag_{28}Se_6(SenBu)_{16}(dppp)_4]$ **3**

$[Ag_{124}Se_{57}(SePtBu_2)_4Cl_6(tBu_2PCH_2)_3PtBu_2)_{12}]$ **4**

Reaction of silver thiocyanate, bis(diphenylphosphanyl)methane (dppm), and $iPrSeSiMe_3$ in diethyl ether gave the complex **1** [Eq. (1)]. The analogous reaction with silver benzoate gave the same reaction product, however, in lower yields. Reaction of silver benzoate, dppp, and $EtSeSiMe_3$ in a mixture of 1,4-cyclooctadiene (COD) and toluene [Eq. (2)] led to the formation of an orange solution, from which small yellow crystals of **2** have been isolated.

$$AgSCN + \tfrac{1}{2}dppm + iPrSeSiMe_3 \xrightarrow[Et_2O]{-60\,^\circ C} \underset{\mathbf{1}}{[Ag_4(SeiPr)_4(dppm)_2]} \quad (1)$$

$$AgO_2CPh + \tfrac{1}{4}dppp + EtSeSiMe_3 \xrightarrow[PhMe/COD]{-40\,^\circ C} \underset{\mathbf{2}}{[Ag_8(SeEt)_8(dppp)]_\infty} \quad (2)$$

The reaction of silver laureate, dppp, and $nBuSeSiMe_3$ in dichloromethane at −20 °C, led to the formation of small red crystals of **3** [Eq. (3)]. These crystals are very sensitive. They already decompose at temperatures above −10 °C into unknown substances. Evidently, the reaction conditions, especially the solvent, play an important role, since the reaction of the same starting compounds in a mixture of toluene and chloroform gave the largest known silver cluster $[Ag_{172}Se_{40}(SenBu)_{92}(dppp)_4]$.[8] Reaction of silver laureate with 1,3-bis(di-*tert*-butylphosphanyl)propane ($tBu_2P(CH_2)_3PtBu_2$) and $tBuSeSiMe_3$ in dichloromethane at −20 °C, small black crystals of **4** were formed [Eq. (4)].

$$AgO_2CC_{11}H_{23} + \tfrac{1}{4}dppp + nBuSeSiMe_3 \xrightarrow[CH_2Cl_2]{-80\,^\circ C} \underset{\mathbf{3}}{[Ag_{28}Se_6(SenBu)_{16}(dppp)_4]} \quad (3)$$

$$AgO_2CC_{11}H_{23} + \tfrac{1}{2}tBu_2P(CH_2)_3PtBu_2 + tBuSeSiMe_3 \xrightarrow[CH_2Cl_2]{-20\,^\circ C} \underset{\mathbf{4}}{[Ag_{124}Se_{57}(SePtBu_2)_4Cl_6(tBu_2P(CH_2)_3PtBu_2)_{12}]} \quad (4)$$

The molecular structures of **1**–**4** were determined by single-crystal X-ray structural analysis.[13]

Complex **1** crystallizes in the form of yellow cubes in the acentric space group $P2_1$ with two formula units in the asymmetric unit. The molecular structure of one of the two independent molecules of **1** is shown in Figure 1a. The bond lengths and angles of the two independent clusters are identical, within standard deviation. The complex is based on an Ag_4 tetrahedron, whose four edges are bridged by selenium atoms of the SeiPr ligands. Ag–Ag distances range from 305.8(2) to 335.1(2) pm, indicating nonbonding metal–metal interactions. Assuming a formal charge of −1 for the selenolate ligands, all silver atoms are charged +1. The Ag-

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[*] Prof. Dr. D. Fenske, T. Langetepe
Institut für Anorganische Chemie der Universität
Engesserstrasse, Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-8440
E-mail: dieter.fenske@chemie.uni-karlsruhe.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 195) and the Fonds der Chemischen Industrie. dppm = bis(diphenylphosphanyl)methane, dppp = 1,3-bis-(diphenylphosphanyl)propane.

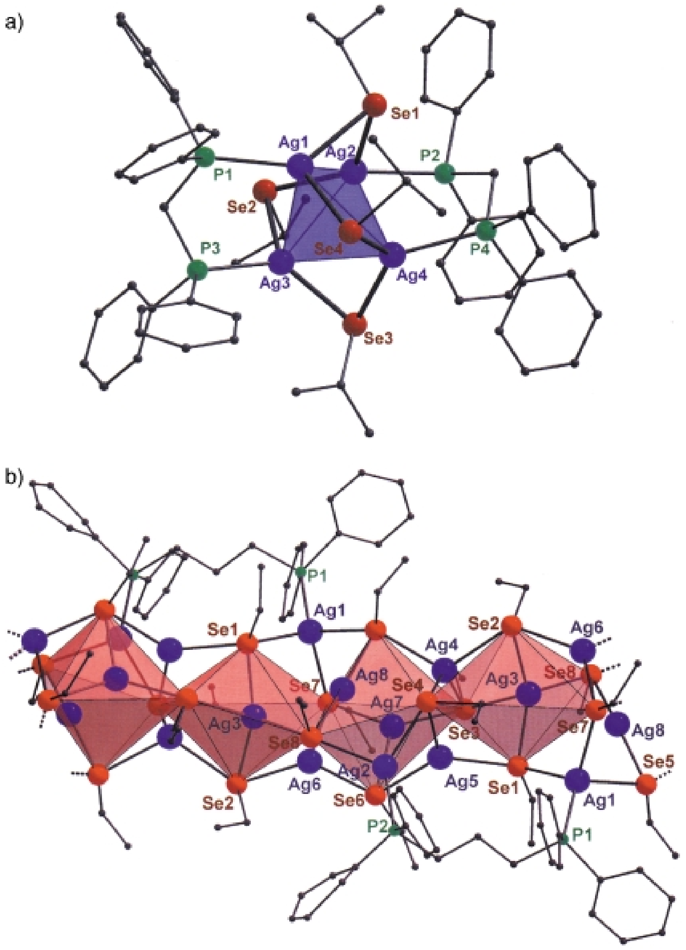

Figure 1. a) Molecular structure of **1** in the crystal(color code: Ag: blue, Se: red, P: green, C: gray). Selected distances [pm] and angles [°]: Ag1-Ag2 335.1(2), Ag3-Ag4 311.3(2), Ag1-Se4 264.5(2), Ag3-Se2 265.4(2), Ag4-Se3 263.9(3), Ag4-Se4 251.7(3), Ag1-P1 250.2(5); Ag2-Ag1-Ag3 56.1(1), Ag2-Ag1-Ag4 58.1(1), Ag3-Ag1-Ag4 59.9(1), Ag2-Se2-Ag3 71.2(1). b) Section of the structure of the polymeric compound **2** in the crystal (color code as in a). The linked Se_6 octahedrons in the polymeric chain, are represented as polyhedrons. Selected distances [pm] and angles [°]: Ag3-Ag4 291.1(3), Ag6-Ag8 332.5(4), Ag1-Se1 268.0(2), Ag1-Se5 274.7(7), Ag1-Se7 260.8(4), Ag3-Se1 262.6(3), Ag3-Se2 280.3(2), Ag3-Se3 284.7(3), Ag3-Se8 273.0(3), Ag4-Se2 280.3(3), Ag6-Se2 255.9(3), Ag8-Se5 250.9(4), Ag8-Se8 252.2(4), Ag1-P1 240.6(6), Ag2-P2 241.3(6); P2-Ag2-Se4 137.8(2), P2-Ag2-Se8 122.7(2), Se4-Ag2-Se8 98.0(2), Se1-Ag3-Se3 87.4(1), Se3-Ag4-Se4 129.5(2), Se1-Ag5-Se4 107.9(1), Se1-Ag5-Se6 135.9(2), Se4-Ag5-Se6 115.4(1), Se5-Ag8-Se8 164.2(2), Ag4-Se3-Ag7 68.5(1), Ag2-Se8-Ag3 151.8(2).

Se-Ag angles at the selenium atoms Se1–Se4 are 71.2(1)–80.6(1)°. The Ag–Se bond lengths are 251.7(3)–265.4(2) pm, which is a typical range for μ_2-bridging selenolate ligands between silver atoms. All silver atoms show distorted trigonal-planar coordination geometry (sum of angles: 352.6–358.4°), coordinated to two selenium atoms and one phosphorus atom of a dppm ligand (Ag–P distances: 242.0(4)–250.5(4) pm).

Complex **2** (Figure 1 b) crystallizes in the monoclinic space group *C*2/*c* with eight formula units per unit cell. Complex **2** is a polymeric compound, formed by a strand of distorted edge-sharing Se_6 octahedrons (Se–Se distances: 378.6(4)–553.9(5) pm). All eight $(SeEt)^-$ ligands act as μ_3 bridges between silver atoms. The Ag–Se bond lengths range between 250.9(4) and 284.7(3) pm. All silver atoms in **2** show different coordination modes. Ag1 is surrounded tetrahedrally by three selenium atoms (Se1, Se5, Se7) that form the face of an octahedron, and one phosphorus atom (P1) of a dppp ligand. Ag2 binds two corners of the Se_6 octahedron (Se4, Se8) and the other phosphorus atom of the dppp ligand (P2), and thus shows a distorted trigonal-planar coordination geometry (sum of angles: 358.6°). Ag3 and Ag4 are surrounded by four selenium atoms leading to the formation of a distorted tetrahedron. While Ag4 is located between two neighboring Se_3 faces (Se2, Se3, Se4; Se3, Se4, Se5), Ag3 lies within a Se_6 octahedron and binds to Se1, Se2, Se3, and Se8. The Se-Ag-Se angles range between 87.4(1) and 129.5(2)°. Three silver atoms show a trigonal-planar coordination geometry, each binding to three selenium atoms (sum of angles: 359.2° (Ag5), 360.0° (Ag6), and 354.4° (Ag7)). Ag5 and Ag6 are coordinated to two selenium atoms that form the top of the Se octahedrons (Se1, Se6 and Se2, Se6, respectively) and one more selenium atom each of an equatorial plane (Se4 and Se7, respectively). Silver atom Ag7, however, centers an Se_3 octahedral face (Se3, Se6, Se7). Ag8 has the smallest coordination number of all silver atoms. It is bound linearly to two selenium atoms above an an edge of an octahedron (Se5 and Se8, angle Se5-Ag8-Se8: 164.2(2)°). The Ag–Ag distances of 291.1(3) to 332.5(4) pm do not indicate binding interactions. The low steric protection of the Ag–Se core of the polymer is noticeable.

Complex **3** crystallizes in the monoclinic space group *C*2/c and contains four formula units and 20 molecules of dichloromethane per unit cell. The molecular structure of **3** ($\bar{1}$ symmetry) is shown in Figure 2. Six of the 22 selenium atoms are "naked" selenido ligands (Se1, Se2, Se3, and symmetry-equivalent positions) and form a distorted octahedron. The edge lengths of this polyhedron (463.0(2)–531.1(2) pm) indicate these are nonbonding interactions. The 16 selenium atoms of the Se*n*Bu groups form a layer-type substructure together with the selenido ligands, in which Se3, Se4, Se6, Se7, Se8, Se9, and Se11 as well as Se1, Se2, Se5, and Se10 and symmetry equivalents form the layers. The silver atoms show different coordination modes. Four silver atoms, Ag5, Ag6, and symmetry-equivalent sites are surrounded by selenium atoms, forming distorted tetrahedral angles (92.8(1)–128.1(1)°). 14 further silver atoms (Ag7, Ag8, Ag9, Ag10, Ag11, Ag12, Ag13, and symmetry equivalents) are trigonal-planarly coordinated to selenium atoms (sum of angles: 356.6–359.9°). However, some of the angles deviate clearly from 120° (93.4(1)–165.4(1)°). Ag14/Ag14′ bind to two selenium atoms Se2/Se3′ or Se2′/Se3, respectively. The remaining eight silver atoms (Ag1, Ag2, Ag3, Ag4 and symmetry-equivalent positions) are each coordinated by one phosphorus atom and selenium atoms of the Se*n*Bu ligands and show tetrahedral (Ag1) or trigonal-planar coordination geometry (Ag2, Ag3, Ag4).

Complex **4** crystallizes in the monoclinic space group *P*2$_1$/c with four molecules per unit cell. The spherical cluster molecule (Figure 3) contains 124 silver and 61 selenium atoms and has a size of approximately 3 nm. Additionally six chlorine atoms are found as ligands. Four of them (Cl3–Cl6) are μ_3-bridging on the cluster surface with Ag–Cl bond lengths of between 257.4(4) and 290.3(8) pm. Two further chlorine atoms (Cl1, Cl2) only bridge two silver atoms with Ag–Cl distances of 256.6(9) to 278.3(9) pm (Figure 4). The Ag-Cl-Ag angles lie between 60.2(2) and 95.2(2)°. All chloro ligands probably come from the solvent (dichloromethane).

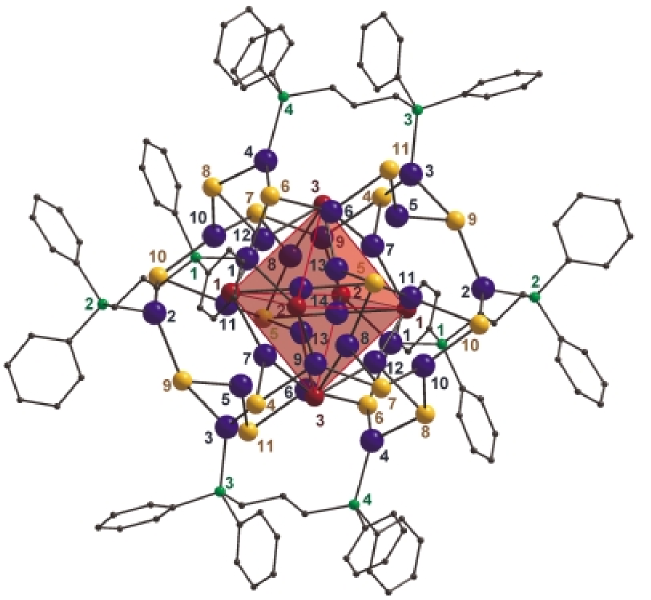

Figure 2. Molecular structure of **3** in the crystal (*n*-butyl groups are omitted for clarity; color code: Ag: blue, Se (selenide ligands): dark red, Se (selenato ligands): orange, P: green, C: gray). The atom number is given and the corresponding atom type can be deduced from the color. Selected distances [pm] and angles [°]: Ag1-Ag5 286.5(1), Ag3-Ag5 299.6(1), Ag6-Ag12 321.6(2), Ag6-Se1 256.4(2), Ag7-Se6 257.9(2), Ag9-Se5 261.5(2), Ag9-Se6 310.8(2), Ag11-Se10 287.7(2), Ag1-P1 243.3(3), Ag13-P4 241.9(2); P1-Ag1-Se2 107.3(1), P3-Ag2-Se4 123.9(1), P3-Ag2-Se9 116.0(1), Se4-Ag2-Se9 116.3(1), Se6-Ag6-Se8 98.5(1), Se6-Ag7-Se8 127.1(1), Se6-Ag8-Se7 93.4(1), Se7-Ag8-Se8 101.1(1), Se3-Ag12-Se8 154.4(1), Ag6-Se1-Ag13 76.0(1), Ag1-Se3-Ag11 162.0(1), Ag3-Se3-Ag12 111.5(1), Ag6-Se6-Ag9 56.3(1).

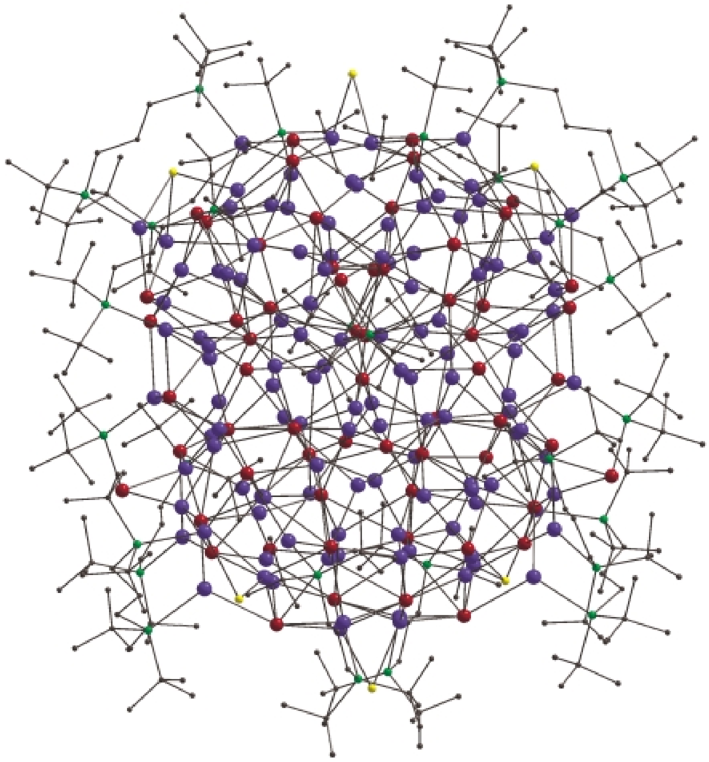

Figure 3. Molecular structure of **4** in the crystal (color code: Ag: blue, Se: dark red, P: green, Cl: yellow, C: gray)

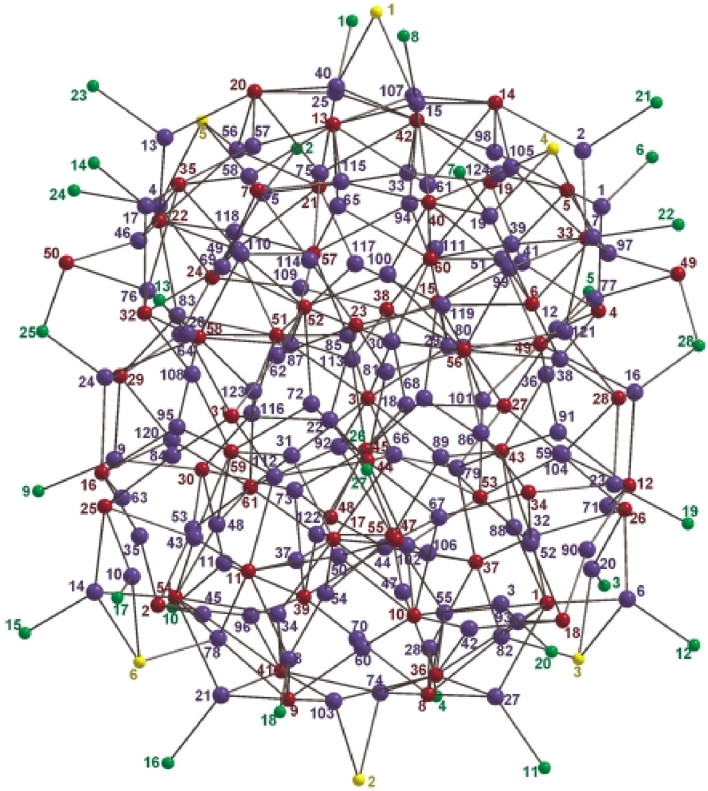

Figure 4. Cluster core of **4** in same orientation as in Figure 3 (with same color code), without carbon and hydrogen atoms. Selected distances [pm] and angles [°]: Ag41-Ag51 337.9(4), Ag74-Ag103 271.9(4), Ag85-Se3 270.1(3), Ag92-Se3 277.2(3), Ag111-Se38 249.1(4), Ag121-Se56 310.1(4), Ag5-Cl5 290.3(8), Ag40-Cl1 256.6(9) Ag74-Cl2 278.3(9), Ag78-Cl6 257.4(8), Ag2-P21 250.0(11), Ag18-P26 245.8(7), Ag21-P16 244.2(8), Ag24-P25 242.6(8), Se48-P26 224.0(8), Se50-P25 227.2(8); Ag27-Se8-Ag55 54.8(1), Ag89-Se3-Ag87 175.9(2), Se17-Ag37-Se11 170.1(2), Se5-Ag51-Se15 136.3(2), Se48-Ag73-Se39 82.5(8), Se14-Ag98-Se5 128.0(2), P20-Ag3-Se10 132.7(2), P24-Ag4-Se24 129.4(2), P27-Ag22-Se44 104.0(2), P27-Se47-Ag67 103.0(2), P28-Se49-Ag77 98.1(2), Ag24-P25-Se50 115.3(3), Ag18-P26-Se48 116.1(3), Cl5-Ag4-P24 107.7(3), Cl5-Ag4-Se24 118.1(2), Cl1-Ag40-Se20 127.7(2), Cl1-Ag40-Se42 95.7(2), Ag40-Cl1-Ag107 64.1(2), Ag74-Cl2-Ag103 60.2(2), Ag20-Cl3-Ag82 95.2(2).

A more exact description of the structure of **4** is exceptionally difficult since there is no similarity to the cluster structures known until now. The most significant structural feature is a slightly twisted Frank–Kasper polyhedron surrounding the central atom Se3. Its 16 selenium atoms (Se15, Se17, Se43, Se44, Se45, Se46, Se51, Se52, Se53, Se55, Se56, Se57, Se58, Se59, Se60, Se61) show distances of 493.2–536.0 pm to Se3 (Figure 5). The Se–Se distances within this polyhedron range between 434.9 and 506.0 pm. The next shell is formed by the 44 selenium atoms of the remaining 40 selenido and four $(SeP\mathit{t}Bu_2)^-$ ligands. They are placed at distances of 770.8 to 938.7 pm around Se3 and form a strongly

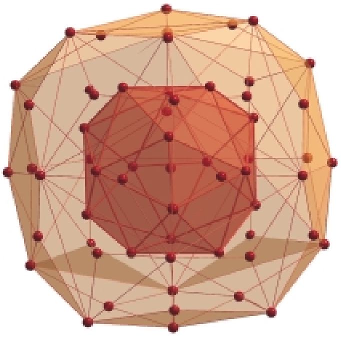

Figure 5. Selenium substructure of **4**. The central atom Se3 is surrounded by the Se_{16} Frank–Kasper polyhedron (red) in the first coordination sphere and by the Se_{44} polyhedron in the second coordination sphere (orange).

distorted deltahedron of 84 $\mathit{\Delta}_3$ faces (Se–Se distances: 380.1 to 599.4 pm) that can be discribed on the basis of a growth of the Se_{16} Frank–Kasper polyhedron.[14] Twelve of the 28 tetrahedral holes of the Se_{16} deltahedron centered about Se3 are occupied by silver atoms, that, however, show a distorted coordination. A further 80 silver atoms are situated between the Se_{16} polyhedron and the Se_{44} polyhedron, and display different coordination modes. Apart from the occupation of tetrahedral holes, silver atoms show the coordination number two or three. Finally, 32 silver atoms are located on the cluster surface, and either obtain a distorted tetrahedral or trigonal-planar coordination.

The selenido ligands in **4** act as $\mu_3, \mu_4, \mu_5, \mu_6, \mu_7$, or μ_8 bridges between the silver atoms. All Ag–Se bond lengths lie in the range between 249.1(4) and 310.1(3) pm and the angles Ag-Se-Ag range between 54.8(1) and 175.9(1)°. If we assume $57\,Se^{2-}$, six Cl^{1-}, and four $(SeP\mathit{t}Bu_2)^-$ ligands are present, all silver atoms are formally charged 1+. Consequently the nonbonding Ag–Ag distances range between 271.9(4) and 337.9(4) pm. The $(SeP\mathit{t}Bu_2)^-$ ligands coordinated on the cluster surface are each bound to two silver atoms through the selenium atoms and to another silver atom through the phosphorus atoms. Evidently, the formation of this ion might be the result of a decomposition reaction.

No characteristic details of the Ag_2Se phases are visible in the structure of **4**.[15] This is astonishing, since we have previously shown that the formation of Ag_2Se substructures in molecular cluster complexes depends on the size of the cluster.[8] For example, a transition to the structure of α-Ag_2Se is found in selenido- and selenolato-bridged silver clusters, depending on the number of silver atoms. In smaller clusters such as $[Ag_{30}Se_8(Se\mathit{t}Bu)_{14}(P\mathit{n}Pr_3)_8]$ and $[Ag_{90}Se_{38}(Se\mathit{t}Bu)_{14}(PEt_3)_{22}]$ no relationship to the structure of binary Ag_2Se is observed. However, for the compounds $[Ag_{112}Se_{32}(Se\mathit{n}Bu)_{48}(P\mathit{t}Bu_3)_{12}]$, $[Ag_{114}Se_{34}(Se\mathit{n}Bu)_{46}(P\mathit{t}Bu_3)_{14}]$, and $[Ag_{172}Se_{40}(Se\mathit{n}Bu)_{92}(dppp)_4]$ the structural transition becomes clear. Which other factors influence the point at which this structural transition occurs are currently under investigation.

Experimental Section

1: A suspension of AgSCN (1.21 mmol, 200 mg) and $Ph_2P(CH_2)PPh_2$ (0.60 mmol, 230 mg) in diethyl ether (10 mL) was treated with $\mathit{i}PrSeSiMe_3$ (1.21 mmol, 0.25 mL) at −60 °C. The resulting yellow solution was stirred for two hours and stored for three weeks at −20 °C. After another week at room temperature, small yellow crystals of **1** grew together with a microcrystalline solid (yield 45 %).

2: A suspension of AgO_2CPh (1.14 mmol, 260 mg) and $Ph_2P(CH_2)_3PPh_2$ (0.28 mmol, 120 mg) in toluene (10 mL) and COD (0.14 mL) was treated with $EtSeSiMe_3$ (1.14 mmol, 0.22 mL) at −40 °C. After the mixture had been stirred for two hours, the orange solution was warmed up to room temperature. After one week, a brown precipitate was formed. It was separated, and the solution was again stored for one week. Within this time, small yellow needles of **2** crystallized in low yield (30 %).

3: A suspension of $AgO_2CC_{11}H_{23}$ (1.04 mmol, 320 mg) and $Ph_2P(CH_2)_3PPh_2$ (0.26 mmol, 110 mg) in dichloromethane (10 mL) was treated with $\mathit{n}BuSeSiMe_3$ (1.04 mmol, 0.23 mL) at −80 °C. The red solution was slowly warmed up to −20 °C over three days and stored at this temperature. Red needles of **3** appeared in 45 % yield.

4: A suspension of $AgO_2CC_{11}H_{23}$ (0.91 mmol, 280 mg) and $\mathit{t}Bu_2P(CH_2)_3P\mathit{t}Bu_2$ (0.46 mmol, 310 mg) in dichloromethane (10 mL) was treated with $\mathit{t}BuSeSiMe_3$ (0.91 mmol, 0.25 mL) at −20 °C. The red solution was then stirred for two hours and stored for three weeks at −20 °C. After another week at room temperature, small black crystals of **4** grew together with a microcrystalline solid in a low yield (20 %).

The Ag, P, C, H analysis of **1**–**4** correspond to the stated formulas.

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[13] X-ray structure analysis: STOE-IPDS ($Mo_{K\alpha}$ radiation); data collection and refinement (SHELXS-97, SHELXL-97); empirical absorption correction (Habitus). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-167634 (**1**), CCDC-167635 (**2**), CCDC-167636 (**3**), and CCDC-167637 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). **1**: $C_{62}H_{72}Ag_4P_4Se_4$, monoclinic, space group $P2_1$ (no. 4), $Z=4$, cell dimensions (190 K): $a=1340.0(3)$, $b=1646.0(3)$, $c=2969.0(6)$ pm, $\beta=102.4(1)^\circ$, $V=6396\times10^6$ pm^3, $\mu(Mo_{K\alpha})=3.620$ mm^{-1}, $2\Theta_{max}=56.18^\circ$, 52315 reflections, 28623 independent reflections, 23755 reflections with $I>2\sigma(I)$, 1234 parameters (Ag, Se, P, and C anisotropic). Absolute structural parameter 0.50(2). Max. electron density 1.6 e Å^{-3}; $R_1=0.08$; $wR_2=0.20$; GooF = 1.070. **2**: $C_{50}H_{65}Ag_8P_2Se_8$, monoclinic, space group $C2/c$ (no. 15), $Z=8$, cell dimensions (190 K): $a=2616.1(5)$, $b=1804.9(4)$, $c=2728.8(6)$ pm, $\beta=90.59(3)^\circ$, $V=12884\times10^6$ pm^3, $\mu(Mo_{K\alpha})=6.979$ mm^{-1}, $2\Theta_{max}=52.04^\circ$, 7177 reflections, 5677 independent reflections, 4883 reflections with $I>2\sigma(I)$, 488 parameters (Ag, Se, P, and C anisotropic). Max. electron density 1.0 e Å^{-3}; $R_1=0.08$; $wR_2=0.19$; GooF = 0.991. **3**: $C_{172}H_{248}Ag_{28}P_8Se_{22}\cdot5\,CH_2Cl_2$, monoclinic, space group $C2/c$ (no. 15), $Z=4$, cell dimensions (190 K): $a=3355.0(7)$, $b=3016.0(6)$, $c=2473.0(5)$ pm, $\beta=90.33(3)^\circ$, $V=25023\times10^6$ pm^3, $\mu(Mo_{K\alpha})=7.935$ mm^{-1}, $2\Theta_{max}=52.12^\circ$, 49340 reflections, 23253 independent reflections, 19051 reflections with $I>2\sigma(I)$, 1179 parameters (Ag, Se, P, anisotropic, C, Cl isotropic). Max. electron density 3.1 e Å^{-3}; $R_1=0.05$; $wR_2=0.15$; GooF = 1.047. **4**: $C_{260}H_{576}Ag_{124}Cl_6P_{28}Se_{61}$, monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, cell dimensions (190 K): $a=3746.3(7)$, $b=4662.6(11)$, $c=3361.8(10)$ pm, $\beta=90.28(2)^\circ$, $V=58721\times10^6$ pm^3, $\mu(Mo_{K\alpha})=7.935$ mm^{-1}, $2\Theta_{max}=41.62^\circ$, 89967 reflections, 53085 independent reflections, 32780 reflections with $I>2\sigma(I)$, 3180 parameters (Ag, Se, P, Cl anisotropic, C isotropic). Max. electron density 5.0 e Å^{-3}; $R_1=0.08$; $wR_2=0.22$; GooF = 1.047.
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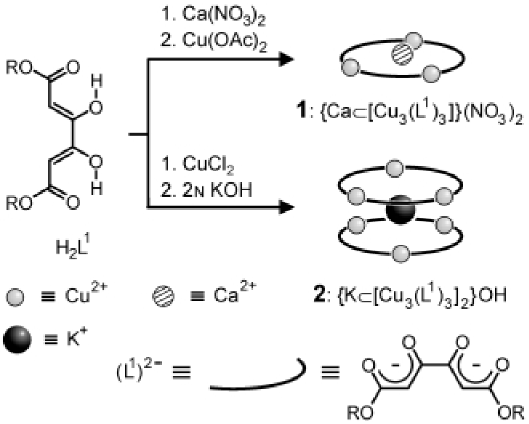
Hybrid Metallacoronates or One-Dimensional Oxo-Bridged Metal Strings by Self-Assembly—Coordination Number Controlled Product Formation[**]

Rolf W. Saalfrank,[*] Harald Maid, Nicolai Mooren, and Frank Hampel

Dedicated to Professor Kenneth N. Raymond
on the occasion of his 60th birthday

Recent developments in the field of design and synthesis of supramolecular inorganic structures that exhibit novel properties have provided exciting new prospects.[1] We have reported on the template-mediated self-assembly of three-membered copper coronate **1** and sandwich complex **2**, starting from dialkyl ketipinates H_2L^1 (Scheme 1).[2] A common feature of these complexes is that the incapsulated alkali or alkaline-earth metal ions are coordinated to the inner carbonyl oxygen donors. Compared to the ketipinate dianions $(L^1)^{2-}$, the hybrid dianions $(L^2)^{2-}$ or $(L^3)^{2-}$ of the glycolate- or catecholate-bridged bis-1,3-diketones, owing to their extra oxygen donors, should be even better ligands[3–6] for the design of metallacoronates. To test this hypothesis, we prepared a solution of bis-1,3-diketone H_2L^2 and a twentyfold excess of alkali metal acetates (M = K, Rb, Cs) in methanol, and added this mixture dropwise to a solution of copper(II)acetate in methanol. Green crystals were obtained in each case



Scheme 1. Synthesis and schematic representation (without coordinating solvent molecules) of metallacoronate **1** and metallasandwich complex **2**.

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[*] Prof. Dr. R. W. Saalfrank, Dr. H. Maid, Dipl.-Chem. N. Mooren, Dr. F. Hampel
Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax: (+49) 9131-852-1165
E-mail: saalfrank@organik.uni-erlangen.de

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