Synthesis and Crystal Structure of a Polynuclear Copper-selenide Cluster $[Cu^{I}_{36}(Cu^{II}Cl)_2Se_{13}(SePh)_{12}(dppe)_6]\cdot 3EtOH$

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Treatment of copper(I) chloride in the presence of the bidentate phosphine ligand $Ph_2PCH_2CH_2$-PPh_2 (dppe) with $Se(SiMe_3)_2$ and $PhSeSiMe_3$ in THF solution afforded a novel polynuclear mixed-valence copper-selenide cluster compound $[Cu^{I}_{36}(Cu^{II}Cl)_2Se_{13}(SePh)_{12}(dppe)_6]\cdot 3EtOH$. A central μ_8-Se atom is surrounded by 14 copper atoms, 2 of which are trigonal-bipyramidally coordinated with terminal Cu–Cl bonds and are thus defined to be copper(II) centers. The 14 copper atoms are also enclosed by another distorted Se_{12} icosahedron to form a $[Se_{13}Cu_{14}]$ central unit in the cluster. The cluster unit core is further extended to the periphery by coordination of the Se_{12} substructure to another 24 copper atoms, 12 of which are ligated by the six dppe ligands.

Key words: Synthesis, Crystal Structure, Copper, Selenium, Cluster Compound

Introduction

The chemistry of transition metal chalcogenide complexes attracts wide interest not only because of their diversity of bonding modes and structural motifs, but also their potential use as precursors for materials with photochemical properties [1 – 3]. Fenske and coworkers reported the syntheses and structural characterization of a series of highly nucleated copper-selenium clusters with monodentate phosphine ligands [4], of which a notable example is the β-Cu_2Se structure $[Cu_{146}Se_{73}(PPh_3)_{30}]$ which has a diameter of about 40 Å and a thickness of 15 Å [5]. As is well known, formation of σ-donor phosphine-stablized and chalcogen-bridged copper clusters with high nuclearities mainly depends upon the reaction conditions, such as the CuX-to-phosphine ratio (X = Cl, Br, OAc), the counterion X of the copper salt, and especially the nature of the phosphine ligand used. Furthermore, it is interesting to note that the driving force of the reactions is the formation of thermodynamically particularly stable silanes $SiMe_3X$ (X = halide, OAc) and can thus be controlled by the choice of X according to the bond strength of the Si–X bond [6]. With this idea in mind, we are interested to extend the study of polynuclear coinage metal-selenide clusters. In this paper, we report a novel polynuclear mixed-valence copper-selenide cluster $[Cu^{I}_{36}(Cu^{II}Cl)_2Se_{13}(SePh)_{12}(dppe)_6]\cdot 3EtOH$ (dppe = $Ph_2PCH_2CH_2PPh_2$, bis(diphenylphosphino)ethane).

Experimental Section

General

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. All reagents, unless otherwise stated, were purchased as analysis grade and were used without further purification. $Se(SiMe_3)_2$ [7] and $PhSeSiMe_3$ [8] were prepared according to the literature methods. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. The magnetic moment of the solid sample was measured by a Sherwood magnetic susceptibility balance at r. t.

Synthesis

Copper(I) chloride (0.11 g, 1.1 mmol) was dissolved along with dppe (0.20 g, 0.5 mmol) in THF (25 mL). Upon addition of $PhSeSiMe_3$ (0.25 mL, 1.0 mmol) and $Se(SiMe_3)_2$ (0.11 mL, 0.5 mmol) at 0 °C, the colorless solution turned to red immediately, and the red solution gradually changed into a dark red solution when the temperature was slowly increased to r. t. The solution was filtered to give a clear dark-red filtrate which was layered with ethanol/diethyl ether (1 : 5). Black block-shaped crystals formed from the solution were characterized as $[Cu^{I}_{36}(Cu^{II}Cl)_2Se_{13}(SePh)_{12}$-

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Table 1. Crystal data, data collection parameters and details of the structure refinement.

Complex	$[\mathrm{Cu^{I}_{36}(Cu^{II}Cl)_2Se_{13}(SePh)_{12}}$-$\mathrm{(dppe)_6}]\cdot 3\mathrm{EtOH}$
Empirical formula	$\mathrm{C_{234}H_{236}O_3Cl_2P_{12}Cu_{38}Se_{24}}$
Formula weight	7927.29
Color, habit	black, block
Crystal size, mm^3	$0.18 \times 0.10 \times 0.08$
Crystal system	rhombohedral
Space group	$R\bar{3}$
a, Å	34.4163(10)
c, Å	19.2212(11)
Volume, Å^3	19716.9(14)
Z	3
Density (calc.), g cm^{-3}	2.00
Absorption coefficient, mm^{-1}	6.6
Temperature, K	150(2)
$F(000)$, e	11490
Radiation	MoK_α (λ = 0.71073 Å)
Reflections collected	68774
Independence reflections	8488
R_int	0.0871
Reflections with $[I \geq 2\sigma(I)]$	4335
Parameters refined	466
$R1/wR2$ (all data)[a]	0.070/0.163
Goodness of fit (GoF)[a]	0.95
Final difference peaks, e Å^{-3}	+1.37/−1.45

[a] $R1 = \Sigma||F_\mathrm{o}| - |F_\mathrm{c}||/\Sigma|F_\mathrm{o}|$; $wR2 = [\Sigma w(|F_\mathrm{o}{}^2| - |F_\mathrm{c}{}^2|)^2 / \Sigma w|F_\mathrm{o}{}^2|^2]^{1/2}$; $w = [\sigma^2(F_\mathrm{o}{}^2) + 0.1016P^2 + 0.0000P]$, where $P = (F_\mathrm{o}{}^2 + 2F_\mathrm{c}{}^2)/3$; GoF = $[\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2/(N_\mathrm{obs} - N_\mathrm{param})]^{1/2}$.

$\mathrm{(dppe)_6}]\cdot 3\mathrm{EtOH}$ (**1**). Yield: 80 mg (35 %). – Anal. for $\mathrm{C_{228}H_{218}Cl_2P_{12}Cu_{38}Se_{24}\cdot 3(C_2H_6O)}$: calcd. C 35.8, H 3.03, Cl 0.90; found C 35.6, H, 3.01, Cl 0.89.

Crystal structure determination

A single crystal of **1** ($0.18 \times 0.10 \times 0.08$ mm^3) was mounted on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 293 K using an ω scan mode. The collected frames were processed with the software SAINT [9]. The data were corrected for absorption using the program SADABS [10]. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [11]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96 and C_{sp^2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters but were not refined. One of the Se-attached phenyl rings was refined isotropically without hydrogen atoms due to heavy disorder. Ethanol solvent molecules in **1** were isotropically refined without hydrogen atoms. Crystal data, data collection parameters and details of the structure refinement are given in Table 1, selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths (Å) and bond angles (deg) for the cluster **1** · 3EtOH.

Cu(1)-Se(1)	2.478(1)	Cu(1)-Se(3)	2.586(1)
Cu(1)-Se(4)$^{\#1}$	2.470(1)	Cu(2)-Se(1)$^{\#4}$	2.442(2)
Cu(2)-Se(2)	2.520(2)	Cu(2)-Se(3)	2.674(1)
Cu(3)-Se(1)$^{\#4}$	2.378(1)	Cu(3)-Se(2)$^{\#2}$	2.402(2)
Cu(3)-Se(3)	2.443(1)	Cu(4)-Se(2)	2.448(1)
Cu(4)-Se(3)	2.389(1)	Cu(4)-Se(4)	2.417(1)
Cu(5)-Se(3)$^{\#4}$	2.439(1)	Cu(5)-Se(3)$^{\#5}$	2.641(1)
Cu(5)-Se(4)	2.613(2)	Cu(5)-Se(5)	2.612(1)
Cu(6)-Se(3)$^{\#3}$	2.652(3)	Cu(6)-Se(4)$^{\#3}$	2.337(3)
Cu(6)-Se(4)$^{\#4}$	2.381(3)	Cu(6)-Se(5)	2.885(3)
P(1)-Cu(1)-Se(4)$^{\#1}$	108.35(8)	P(1)-Cu(1)-Se(1)	115.07(7)
Se(4)$^{\#1}$-Cu(1)-Se(1)	126.53(5)	P(1)-Cu(1)-Se(3)	107.79(7)
Se(4)$^{\#1}$-Cu(1)-Se(3)	102.34(5)	Se(1)-Cu(1)-Se(3)	92.85(5)
P(2)-Cu(2)-Se(1)$^{\#4}$	123.77(8)	P(2)-Cu(2)-Se(2)	121.61(9)
Se(1)$^{\#4}$-Cu(2)-Se(2)	96.51(5)	P(2)-Cu(2)-Se(3)	103.91(8)
Se(1)$^{\#4}$-Cu(2)-Se(3)	98.76(5)	Se(2)-Cu(2)-Se(3)	109.94(5)
Se(1)$^{\#4}$-Cu(3)-Se(2)$^{\#2}$	139.27(6)	Se(1)$^{\#4}$-Cu(3)-Se(3)	107.43(5)
Se(2)$^{\#2}$-Cu(3)-Se(3)	107.42(5)	Se(3)-Cu(4)-Se(4)	122.19(5)
Se(3)-Cu(4)-Se(2)	123.15(5)	Se(4)-Cu(4)-Se(2)	109.59(5)
Se(3)$^{\#4}$-Cu(5)-Se(5)	106.94(5)	Se(5)-Cu(5)-Se(4)	102.22(4)
Se(5)-Cu(5)-Se(3)$^{\#5}$	101.20(4)	Se(4)-Cu(5)-Se(3)$^{\#5}$	97.11(4)
Se(4)$^{\#3}$-Cu(6)-Se(3)$^{\#3}$	114.8(1)	Se(4)$^{\#4}$-Cu(6)-Se(3)$^{\#3}$	102.9(1)
Se(4)$^{\#4}$-Cu(6)-Se(5)	100.7(1)	Cu(3)$^{\#2}$-Se(1)-Cu(2)$^{\#2}$	73.76(5)
Cu(3)$^{\#2}$-Se(1)-Cu(1)	71.88(5)	Cu(2)$^{\#2}$-Se(1)-Cu(1)	123.42(5)
Cu(3)$^{\#4}$-Se(2)-Cu(4)	65.63(4)	Cu(3)$^{\#4}$-Se(2)-Cu(2)	117.56(5)
Cu(4)-Se(2)-Cu(2)	64.25(4)	Cu(4)-Se(3)-Cu(5)$^{\#2}$	71.18(4)
Cu(4)-Se(3)-Cu(3)	106.65(5)	Cu(5)$^{\#2}$-Se(3)-Cu(3)	66.11(4)
Cu(4)-Se(3)-Cu(1)	116.73(5)	Cu(5)$^{\#2}$-Se(3)-Cu(1)	132.98(5)
Cu(3)-Se(3)-Cu(1)	136.21(5)	Cu(4)-Se(3)-Cu(5)$^{\#1}$	107.67(4)
Cu(5)$^{\#2}$-Se(3)-Cu(5)$^{\#1}$	68.46(5)	Cu(3)-Se(3)-Cu(5)$^{\#1}$	107.98(5)
Cu(1)-Se(3)-Cu(5)$^{\#1}$	65.08(4)	Cu(4)-Se(3)-Cu(6)$^{\#3}$	58.91(6)
Cu(5)$^{\#2}$-Se(3)-Cu(6)$^{\#3}$	78.03(8)	Cu(3)-Se(3)-Cu(6)$^{\#3}$	144.14(9)
Cu(1)-Se(3)-Cu(6)$^{\#3}$	70.52(8)	Cu(5)$^{\#1}$-Se(3)-Cu(6)$^{\#3}$	55.77(7)
Cu(4)-Se(3)-Cu(2)	62.62(4)	Cu(5)$^{\#2}$-Se(3)-Cu(2)	98.89(4)
Cu(3)-Se(3)-Cu(2)	68.68(4)	Cu(1)-Se(3)-Cu(2)	126.66(5)
Cu(5)$^{\#1}$-Se(3)-Cu(2)	166.66(5)	Cu(6)$^{\#3}$-Se(3)-Cu(2)	118.99(7)
Cu(6)$^{\#3}$-Se(4)-Cu(6)$^{\#2}$	74.41(16)	Cu(6)$^{\#3}$-Se(4)-Cu(4)	63.12(8)
Cu(6)$^{\#2}$-Se(4)-Cu(4)	116.58(9)	Cu(6)$^{\#3}$-Se(4)-Cu(1)$^{\#5}$	142.8(1)
Cu(6)$^{\#2}$-Se(4)-Cu(1)$^{\#5}$	77.11(8)	Cu(4)-Se(4)-Cu(1)$^{\#5}$	111.11(5)
Cu(4)-Se(4)-Cu(7)	99.69(5)	Cu(1)$^{\#5}$-Se(4)-Cu(7)	116.59(4)
Cu(6)$^{\#3}$-Se(4)-Cu(5)	77.82(9)	Cu(6)$^{\#2}$-Se(4)-Cu(5)	59.21(8)
Cu(4)-Se(4)-Cu(5)	67.15(4)	Cu(1)$^{\#5}$-Se(4)-Cu(5)	67.11(4)
Cu(7)-Se(4)-Cu(5)	77.13(6)	Cu(5)$^{\#5}$-Se(5)-Cu(5)$^{\#4}$	66.44(2)
Cu(5)$^{\#5}$-Se(5)-Cu(5)	113.56(2)	Cu(5)-Se(5)-Cu(5)$^{\#2}$	66.44(2)
Cu(5)-Se(5)-Cu(5)$^{\#3}$	180	Cu(5)-Se(5)-Cu(7)	75.01(2)
Cu(5)-Se(5)-Cu(7)$^{\#3}$	104.99(2)	Cu(7)-Se(5)-Cu(7)$^{\#3}$	180
Cu(5)$^{\#4}$-Se(5)-Cu(6)$^{\#4}$	111.13(6)	Cu(5)-Se(5)-Cu(6)$^{\#4}$	108.77(7)
Cu(5)$^{\#1}$-Se(5)-Cu(6)$^{\#4}$	68.87(6)	Cu(7)$^{\#3}$-Se(5)-Cu(6)$^{\#4}$	145.18(6)
Cu(5)$^{\#5}$-Se(5)-Cu(6)$^{\#1}$	126.75(6)	Cu(5)$^{\#4}$-Se(5)-Cu(6)$^{\#1}$	68.87(6)
Cu(5)-Se(5)-Cu(6)$^{\#1}$	71.23(7)	Cu(5)$^{\#2}$-Se(5)-Cu(6)$^{\#1}$	53.25(6)
Cu(5)$^{\#3}$-Se(5)-Cu(6)$^{\#1}$	108.77(7)	Cu(6)$^{\#4}$-Se(5)-Cu(6)$^{\#1}$	180
Cu(5)$^{\#5}$-Se(5)-Cu(6)$^{\#2}$	68.87(6)	Cu(5)$^{\#4}$-Se(5)-Cu(6)$^{\#2}$	71.23(7)
Cu(5)-Se(5)-Cu(6)$^{\#2}$	53.25(6)	Cu(5)$^{\#3}$-Se(5)-Cu(6)$^{\#2}$	126.75(6)
Cu(5)-Se(5)-Cu(6)	111.13(6)	Cu(5)$^{\#2}$-Se(5)-Cu(6)	108.77(7)
Cu(5)$^{\#3}$-Se(5)-Cu(6)	68.87(6)	Cu(7)-Se(5)-Cu(6)	145.18(6)
Cu(6)$^{\#4}$-Se(5)-Cu(6)	120.7(1)	Cu(6)$^{\#1}$-Se(5)-Cu(6)	59.3(1)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+y-1, -x+1, z$; $^{\#2}$ $-y+1, x-y+2, z$; $^{\#3}$ $-y+1, x-y+1, z$; $^{\#4}$ $-x+y, -x+1, z$; $^{\#5}$ $-y+1, x-y+2, z$.

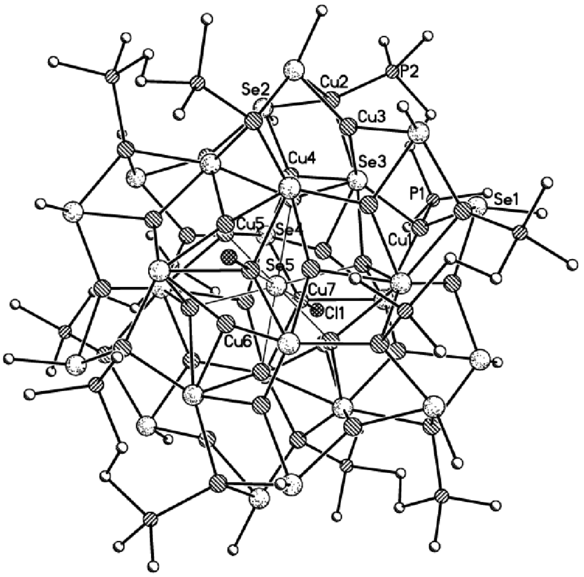

Fig. 1. Molecular structure of the cluster unit in $[\mathrm{Cu^I}_{36}(\mathrm{Cu^{II}Cl})_2\mathrm{Se}_{13}(\mathrm{SePh})_{12}(\mathrm{dppe})_6] \cdot 3\mathrm{EtOH}$ in the solid state. Phenyl rings and hydrogen atoms are omitted for clarity.

CCDC 686866 contains 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.

Results and Discussion

Reaction of a 2 : 1 mixture of CuCl and $\mathrm{Ph_2PCH_2CH_2PPh_2}$ with $\mathrm{PhSeSiMe_3}$ and $\mathrm{Se(SiMe_3)_2}$ in THF yielded, after layering the solution with ethanol/diethyl ether, black crystals of **1** in a few days (Eq. 1).

$$\mathrm{CuCl} + 0.5\,\mathrm{dppe} \xrightarrow[\mathrm{Se(SiMe_3)_2}]{\mathrm{PhSeSiMe_3}} [\mathrm{Cu^I}_{36}(\mathrm{Cu^{II}Cl})_2\mathrm{Se}_{13}(\mathrm{SePh})_{12}(\mathrm{dppe})_6] \tag{1}$$

Compound **1** is a high-nuclearity mixed-valence copper-selenide cluster (Fig. 1). Similar clusters $[\mathrm{Cu}_{38}\mathrm{Se}_{13}(\mathrm{SePh})_{12}(\mathrm{dpp}R)_6]$ (R = e, ethane; b, butane) were reported by Fenske and coworkers [12]. The neutral cluster **1** crystallizes in the trigonal space group $R\bar{3}$ with a crystallographic C_3 axis passing through the terminal Cu(7), Cl(1) and central Se(5) atoms. The central selenium atom (Se5) binds to eight copper atoms [6 × Cu(5) and 2 × Cu(7)] in a slightly distorted dodecahedron to form an unusual selenide bridging μ_8-Se. The Cu–μ_8-Se bond lengths ranging from 2.612(1) to 2.688(2) Å are comparable to those in the related copper-selenide clusters. However, the distance of 2.885(3) Å for Cu(6)–Se(5) is considered mainly non-bonding. Although there is no obvious difference of all Cu–Se bond lengths in the mixed-valence copper cluster, individual valence states of copper in **1** may be inferred from the coordination geometries: eighteen trigonal and eighteen tetrahedral copper atoms are Cu(I) while two trigonal-bipyamidal copper atoms are considered to be Cu(II). Indicative are angles Se(4)–Cu(7)–Se(4a) (a: $-y+1$, $x-y+2$, z) = 116.02(3)° and Se(5)–Cu(7)–Cl(1) = 180° along with the terminal Cu(7)–Cl(1) bond length (2.068(8) Å) involving the Cu(II) atoms. Magnetic susceptibility measurement of solid samples of **1** at r. t. indicated an affective magnetic moment $\mu_{\mathrm{eff}} = 1.21\ \mu_{\mathrm{B}}$. This value may be indicative of Cu(II) in solid **1**. The complex gave no obvious EPR signal at r. t. A further indication is that the NMR spectroscopy of **1** shows broadened peaks typical for paramagnetic compounds. Additional proof of a Cu(II)-Cl species may be taken from the microanalytic determination of the chloride content to be 0.89 % which is in good agreement with the molecular formula $\mathrm{C_{234}H_{236}O_3Cl_2P_{12}Cu_{38}Se_{24}}$ for cluster **1**.

In cluster **1**, the central selenium atom Se(5) is surrounded by a distorded icosahedron of twelve copper atoms, which is enclosed by another distorted $\mathrm{Se_{12}}$ icosahedron. Six edges and six faces of the $\mathrm{Cu_{12}}$ icosahedron are bridged by the selenide ligands to form the $\mathrm{Se_{12}}$ polyhedron. The cluster core is then extended to the periphery by coordination of the $\mathrm{Se_{12}}$ substructure by another twentyfour copper atoms, twelve of which are ligated by the six dppe ligands. All twentyfour of these copper atoms are also bridged by twelve μ_3-SePh groups, which are positioned at the cluster surface between the phosphine ligands. There are two different types of tetrahedral copper atoms in **1**: six Cu(1) and six Cu(2) are bonded to two capped selenium atoms, one bridging selenium atom of μ_3-SePh and one phosphorus atom with Cu–Se bond lengths in the range of 2.4417(15)–2.6744(15) Å; whereas six Cu(5) are coordinated to four capped selenium atoms with Cu–Se bond lengths in the range of 2.4385(14)–2.6414(13) Å. There are three different types of trigonal copper atoms in **1**: six Cu(3) are bonded to one capped selenium atom and two bridging selenium atoms of μ_3-SePh with Cu–Se distances in the range of 2.3780(14)–2.4428(14) Å; six Cu(4) are coordinated to two capping selenium atoms and one bridging selenium atom of μ_3-SePh with Cu–Se bond lengths in the range of 2.3890(13) – 2.4482(14) Å; six Cu(6) are coordinated to three capping selenium atoms with Cu–Se distances in the range of 2.337(3) – 2.652(3) Å. The large range of the Cu(I)–Cu(I) contacts in cluster **1** (2.476(3) – 3.024(3) Å) is comparable to those found in $[Cu_{36}Se_{13}(SePh)_{12}(dppb)_6]$ (b = butane) (2.511(3) – 2.943(4) Å) [12] and $[Cu_{38}Se_{13}(SePh)_{12}(dppp)_6]$ (p = propane) (2.305(4) – 3.040(3) Å) [13]. The coordination mode of the dppe ligands in **1** is μ_2-bridging with an average Cu–P bond length of 2.239(3) Å.

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