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Facile Self-Assembly Synthesis and Characterization of Diselenophosphinato Octanuclear Cu^{I} Clusters Inscribed in a Twelve-Vertex Selenium Polyhedron

Ping-Kuei Liao,[a] De-Ren Shi,[a] Jian-Hong Liao,[a] C. W. Liu,*[a] Alexander V. Artem'ev,[b] Vladimir A. Kuimov,[b] Nina K. Gusarova,[b] and Boris A. Trofimov*[b]

The self-assembly synthesis and structural characterization of the first representatives of diselenophosphinato octanuclear Cu^I clusters inscribed in a twelve-vertex selenium polyhedron are reported herein. An extremely facile (room temp., THF, 1 h) reaction between $[Cu(MeCN)_4](PF_6)$ and ammonium diselenophosphinate, $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ (**1**), in a 4:3 molar ratio resulted in the self-assembly of copper(I) cluster $[Cu_8\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)_2$ (**2**) containing an empty Cu$_8$ cubic core. Meanwhile, when the reactants were allowed to react in the presence of appropriate anion sources, new anion-centered octanuclear copper(I) clusters self-assembled. Thus, the interaction of $[Cu(MeCN)_4](PF_6)$ with diselenophosphinate **1** in the presence of $[Cs_4(P_2Se_6)(H_2O)_4]$ as Se^{2-} source under the same conditions gave neutral selenide-centered octanuclear copper cluster $[Cu_8(Se)\{Se_2P-$ $(CH_2CH_2Ph)_2\}_6]$ (**3**). Three novel anion-centered Cu$_8$ clusters of general formula $[Cu_8(X)\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)$ [X = H (**4**), Cl (**5**), or Br (**6**)] were synthesized in high yields by self-assembly reactions between $Cu[(MeCN)_4]PF_6$ and diselenophosphinate **1** in the presence of the corresponding anion sources (NaBH$_4$ for H$^-$, Bu$_4$NCl for Cl$^-$, and $[Bu_4N]Br$ for Br$^-$) under exceptionally mild conditions (room temp., THF, 4 h). X-ray diffraction studies showed structures **3**, **5**, and **6** to consist of an anion-centered cubic Cu$_8$ core capped by six diselenophosphinate ligands, whereas cluster **4** contains a tetracapped tetrahedral Cu$_8$ cage with an interstitial hydride anion. In all the clusters, each of the six diselenophosphinate ligands exhibits a tetrametallic tetraconnective (μ_2,μ_2) coordination pattern.

Introduction

The synthesis of metal clusters has long captivated chemists because of their wide variety of applications, for example, in molecular recognition, catalysis, gas storage, and the stabilization of reactive materials and unstable species through cavity confinement.[1] The most facile and convenient approach to the synthesis of metal clusters is based on the application of self-assembly processes between metal ions and appropriate multimodal ligands.[2] The latter facilitate control over cluster formation and stabilize cages through the chelating and bridging sites. The last decade has seen a considerable expansion of research in the chemistry of diselenophosphates $[(RO)_2PSe_2^-$, "dsep"] because of the use of these compounds as versatile anionic ligands for the self-assembly synthesis of remarkable multinuclear metal clusters.[3] Thus, Liu and co-workers have reported

the self-assembly reactions of diselenophosphates with group 11 metals, that is, Cu^I,[4–12] Ag^I,[13–19] and Au^I,[20] to furnish original clusters possessing remarkable structures. For instance, the interaction between $[Cu(MeCN)_4](PF_6)$ and ammonium diselenophosphates, $[NH_4][Se_2P(OR)_2]$ (R = Pr, iPr), proceeds under mild conditions to deliver dicationic octanuclear copper(I) clusters $[Cu_8\{Se_2P-$ $(OR)_2\}_6](PF_6)_2$ consisting of a discrete empty Cu$_8$ cubic core linked by six diselenophosphate ligands with a noncoordinating PF$_6^-$ anion.[12] The anion-centered octanuclear copper(I) clusters of general formula $[Cu_8(X)\{Se_2P-$ $(OR)_2\}_6](PF_6)_n$ (X = H$^-$ and F$^-$,[12] Cl$^-$,[8] Br$^-$,[9] S^{2-},[12] and Se^{2-};[4] n = 0 or 1) were prepared by the reaction of $[Cu(MeCN)_4](PF_6)$ with $[NH_4][Se_2P(OR)_2]$ in the presence of a source of the corresponding anions.

Surprisingly, the structural cognates of diselenophosphates, diselenophosphinates (R$_2$PSe$_2^-$, "dsepi"), have virtually been neglected in cluster synthesis. To the best of our knowledge, just a few syntheses of clusters incorporating diselenophosphinate ligands have been reported. In 2006, O'Brien and co-workers synthesized tetranuclear copper(I) cluster $[Cu_4(Se_2Pi\text{Pr}_2)_4]$ by the reaction of CuCl$_2$ with bis(diisopropylselenophosphanyl) selenide, $(i\text{Pr}_2\text{PSe})_2$Se, which acted as a source of $[i\text{Pr}_2\text{PSe}]^-$ anions.[21] More recently, the silver(I) complex $[Ag(Se_2Pi\text{Pr}_2)]$ was prepared by

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the reaction of AgNO$_3$ with [Et$_3$NH][Se$_2$PiPr$_2$].[22] Although no data for the structure of the silver(I) complex was given, based on the results of an investigation of reactions between [Ag(MeCN)$_4$](PF$_6$) and [NH$_4$][Se$_2$P-(OR)$_2$],[13–19] one can surmise that the [Ag(Se$_2$PiPr$_2$)] complex has a cluster structure.

At the same time, a number of simple diselenophosphinates are now accessible,[23] because they can be easily prepared from available secondary phosphanes, elemental selenium, and bases, for example, alkali-metal hydroxides,[24] ammonia,[25] amines,[26] and alkaloids.[27] Note that owing to differences in the steric and electronic properties of diselenophosphates and diselenophosphinates, one can anticipate that the reactivity of the latter in cluster synthesis may be significantly different to that of the former. Consequently, the reactions involving diselenophosphinates may lead to unusual outcomes, unlike the known reactions involving diselenophosphates. Thus, the synthesis and investigation of (diselenophosphinato)metal clusters represent an important fundamental and practical problem in coordination chemistry.

The purpose of this work was the synthesis of the first representatives of octanuclear copper(I) clusters containing diselenophosphinate ligands. To pursue this goal, we investigated for the first time the self-assembly reaction between [Cu(MeCN)$_4$](PF$_6$) and ammonium diselenophosphinate, [NH$_4$][Se$_2$P(CH$_2$CH$_2$Ph)$_2$] (**1**), as well as their interactions in the presence of anion sources, for example, [Cs$_4$(P$_2$Se$_6$)(H$_2$O)$_4$] (for Se^{2-}), NaBH$_4$ (for H$^-$), [Bu$_4$N]Cl (for Cl$^-$), and [Bu$_4$N]Br (for Br$^-$).

Results and Discussion

### Synthesis of the Diselenophosphinate Ligand

Ammonium bis(2-phenethyl)diselenophosphinate (**1**) was synthesized in 89% yield by an original three-component reaction between accessible bis(2-phenethyl)phosphane, elemental selenium, and ammonia[25] (Scheme 1).
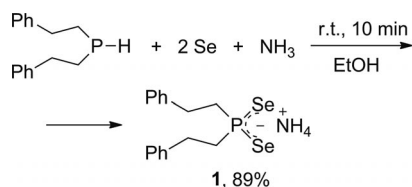
Scheme 1. Three-component synthesis of diselenophosphinate **1**.

Synthesis of (Diselenophosphinato)copper(I) Clusters

[Cu(MeCN)$_4$](PF$_6$) readily reacted with the ammonium diselenophosphinate **1** in a 4:3 molar ratio under mild conditions (ambient temperature, THF, 1 h) to afford the self-assembled product **2**, an octanuclear cubic copper cluster, in 87% isolated yield (Scheme 2).
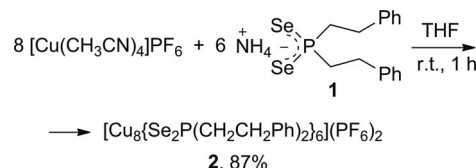
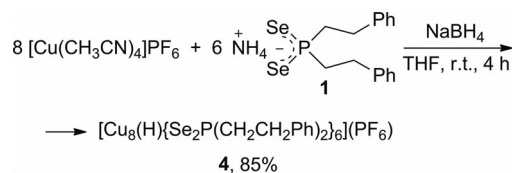Scheme 2. Self-assembly synthesis of empty Cu$_8$ cubic cluster **2**.

Notably, when the reactants were allowed to react in a 1:2 molar ratio under the above conditions, cluster **2** was also formed. This result is quite unusual taking into account the known data on the reaction of [Cu(MeCN)$_4$]-(PF$_6$) with a two-fold excess of the "dsep" ligand, [(RO)$_2$-PSe$_2$]$^-$, which gives rise to the neutral selenide-centered cluster [Cu$_8$(Se){Se$_2$P(OR)$_2$}$_6$].[4] The observed discrepancy in chemical behavior of [R$_2$PSe$_2$]$^-$ and [(RO)$_2$PSe$_2$]$^-$ is likely due to differences in the energies of the P–Se bonds in these anionic ligands. In the "dsep" ligand, [(RO)$_2$PSe$_2$]$^-$, the P–Se bond is more labile and hence can be severed easily. This allows the [(RO)$_2$PSe$_2$]$^-$ ligand to be employed as the Se^{2-} source in the reaction of [Cu(MeCN)$_4$](PF$_6$) with 2 equiv. of NH$_4$Se$_2$P(OiPr)$_2$ to fabricate selenide-centered cluster [Cu$_8$(Se){Se$_2$P(OiPr)$_2$}$_6$].[4]

The diselenophosphinate analogue of the latter, the neutral selenide-centered octanuclear copper cluster [Cu$_8$(Se){Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$] (**3**), was successfully synthesized in 56% yield by the self-assembly reaction of [Cu(MeCN)$_4$](PF$_6$), ammonium diselenophosphinate **1**, and [Cs$_4$(P$_2$Se$_6$)(H$_2$O)$_4$] as Se^{2-} source (Scheme 3).
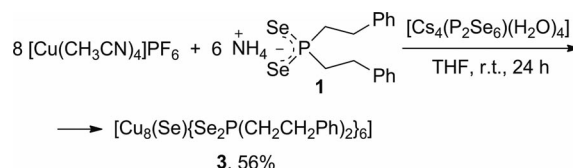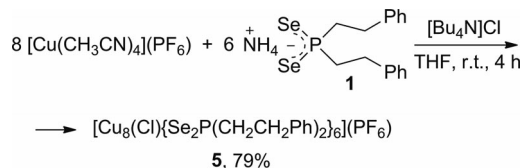

Scheme 3. Self-assembly synthesis of selenide-centered cubic Cu$_8$ cluster **3**.

In the light of the data obtained (Scheme 3), an important question to be answered is the dependence of the reaction course (Scheme 2) on the presence of other anions distinct from the Se^{2-} anion. To address this issue we investigated the reaction between [Cu(MeCN)$_4$](PF$_6$) and ammonium diselenophosphinate **1** in the presence of various anion sources, such as sodium borohydride (for H$^-$), tetrabutylammonium chloride (for Cl$^-$), and tetrabutylammonium bromide (for Br$^-$). In the light of previous studies by Liu and co-workers,[8,9,12] it might be expected that if, in this reaction, appropriate anion sources were introduced, anion-centered Cu$_8$ clusters will be formed. Indeed, the three-component reaction between [Cu(MeCN)$_4$](PF$_6$), ammonium diselenophosphinate **1**, and NaBH$_4$ in an 8:6:1 molar ratio proceeded under mild conditions (ambient temperature, THF, 4 h) to give the novel hydride-centered octanuclear copper(I) cluster **4** in 85% isolated yield (Scheme 4).

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Scheme 4. Self-assembly synthesis of hydride-centered Cu$_8$ cluster **4**.

The self-assembly reaction between $[Cu(MeCN)_4](PF_6)$ and ammonium diselenophosphinate **1** in the presence of $[Bu_4N]Cl$ (its molar ratio is 8:6:1) proceeded readily at ambient temperature (THF, 4 h) to form a new chloride-centered Cu$_8$ cube **5** in 79% isolated yield (Scheme 5).

Scheme 5. Self-assembly synthesis of chloride-centered Cu$_8$ cubic cluster **5**.

Similarly, the first bromide-centered diselenophosphinato Cu$_8$ cubic cluster **6** was synthesized in high yield (75%) by the self-assembly interaction of $[Cu(MeCN)_4](PF_6)$ with ammonium diselenophosphinate **1** in the presence of $[Bu_4N]Br$ (its molar ratio is 8:6:1; Scheme 6).
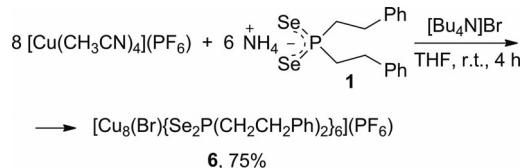
Scheme 6. Self-assembly synthesis of bromide-centered Cu$_8$ cubic cluster **6**.

Notably, the coordination properties of ammonium diselenophosphinate **1** in the reactions studied are very similar to those of ammonium diselenophosphates. This is quite unusual taking into account the fact that the electronic and steric properties of diselenophosphinates and diselenophosphates are significantly different.

Note that the self-assembly reactions investigated are extremely facile, proceed under essentially mild conditions (room temp., without catalyst, 1 h), and are highly selective: Only one cluster is formed.

The newly synthesized compounds **2–6** were fully characterized by X-ray single-crystal crystallography, multinuclear NMR (^1H, ^{31}P and ^{77}Se) spectroscopy, and ESI-MS techniques. The elemental analyses gave good agreement with the molecular structures of these clusters.

Cyclic voltammetry of the copper clusters **2–6** as well as ammonium diselenophosphinate **1** showed that these compounds are extremely unstable under electrochemical conditions. Three irreversible anodic peaks were identified for **1**, and all the copper clusters displayed similar irreversible oxidation peaks (see Table S1 in the Supporting Information).

Indeed, during the cyclic voltammetry experiments, the clusters **2–6** underwent decomposition, precipitating black powders on platinum electrodes. This indicates that ligand oxidation is followed by rapid decomposition of the clusters.

NMR Studies

In the ^{31}P NMR spectra, each of the clusters **2–6** exhibit a singlet accompanied by selenium satellites originating from the diselenophosphinate moieties. In contrast to their diselenophosphate analogues, the observed resonance frequencies of the anion-encapsulated species (except the hydride-centered **4**) are shifted upfield in the ^{31}P NMR spectrum in comparison with **2** (see the Exp. Sect.). However, the ^{77}Se NMR chemical shifts are found to be quite sensitive to the encapsulated anion and hence to the Cu···Cu distances. Note that the signal is significantly shifted downfield in the empty cluster **2** compared with in the other clusters. Thus, a doublet at $\delta = -7.7$ ppm was observed for the empty cluster **2**, whereas the doublets for **3**, **4**, **5**, and **6** are at $\delta = -139.3$, -106.2, -114.3, and -135.8 ppm, respectively. The same effect was observed in the case of the Cu$_8$–diselenophosphate clusters.[12] Thus, all the P and Se atoms in **2–6** are equivalent in solution. Furthermore, the $^1J_{PSe}$ coupling constants are appreciably smaller for **2–6** than for the phosphate analogues by around 130–150 Hz.[12] The smaller coupling constants J_{PSe} for **2–6** compared with the precursor **1** ($J_{PSe} = 616$ Hz)[25] indicate that the P–Se bond order has decreased and is consistent with that of a typical P–Se single bond.

Accordingly, the ^1H NMR spectra display a set of chemical shifts corresponding to the methylene protons of the PCH_2CH_2Ph units for all of the compounds in the series. Furthermore, in the ^1H NMR spectrum of complex **4**, the most characteristic signal is that of the interstitial hydride, which appears as a broad peak centered at $\delta = -1.93$ ppm, which integrates to 1 H, relative to 24 protons of the CH_2P groups (the corresponding resonance for the hydride in $[Cu_8(\mu_4\text{-}H)\{Se_2P(OiPr_2)\}_6](PF_6)$ is observed at $\delta = -0.58$ ppm).[12] Because the size of the copper core around the hydride ion is almost identical to that in $[Cu_8(\mu_4\text{-}H)\{Se_2P(OiPr_2)\}_6](PF_6)$,[12] the difference in the chemical shift of the hydride ion could be related to the different electron-donating ability between the $iPrO$ and CH_2CH_2Ph donors on the PSe_2^- moiety. Thus, this peak could correspond to the hydride resonance.

In addition, the formation of complexes **3–6** has been further verified by mass spectrometry. In the ESI mass spectra, each of the anion-encapsulated compounds exhibit a highest fragment peak that corresponds to the adduct cation formulated as $[Cu_8(X)\{Se_2P(CH_2CH_2Ph)_2\}_6]^{n+}$ (X = H, Cl, Br, $n = 1$; X = Se, $n = 0$), which confirms their existence.

Crystal Structure Descriptions

The empty cluster **2** and three anion-centered octanuclear clusters **3–6** were characterized by single-crystal X-

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Table 1. Data collection and refinement parameters for **2**–**6**.

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{96}H_{108}Cu_8F_{12}P_8Se_{12}$	$C_{96}H_{108}Cu_8P_6Se_{13}$	$C_{96}H_{109}Cu_8F_6P_7Se_{12}$	$C_{96}H_{108}ClCu_8F_6P_7Se_{12}$	$C_{96}H_{108}BrCu_8F_6P_7Se_{12}$
Formula mass [g/mol]	3193.42	2982.44	3049.46	3083.90	3128.36
Space group	$R\bar{3}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	15.5760(18)	12.861(3)	12.7457(4)	12.8257(9)	12.8724(16)
b [Å]	15.5760(18)	15.607(3)	15.5865(5)	15.6496(11)	15.6710(19)
c [Å]	42.647(5)	16.085(3)	15.9682(5)	16.0142(11)	16.038(2)
α [°]	90.00	61.430(9)	63.0140(10)	64.618(2)	64.049(3)
β [°]	90.00	83.800(10)	83.372(2)	84.645(2)	84.080(3)
γ [°]	120.00	77.498(10)	76.689(2)	77.075(2)	76.822(2)
V [Å^3]	8960.4(18)	2768.2	2750.69	2830.46	2832.4(6)
Z	3	1	1	1	1
$D_{calcd.}$ [g/cm^3]	1.775	1.789	1.841	1.809	1.834
μ [mm^{-1}]	5.217	5.906	5.639	5.504	5.829
Temperature [K]	296(2)	296(2)	296(2)	296(2)	296(2)
Reflections collected	18209	48905	43309	25157	23617
Independent reflections	3803 (R_{int} = 0.0571)	9708 (R_{int} = 0.0624)	9509 (R_{int} = 0.0576)	9975 (R_{int} = 0.0314)	9967 (R_{int} = 0.0414)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0515, 0.1378	0.0559, 0.1563	0.0734, 0.1694	0.0645, 0.1899	0.0767, 0.2323
R_1, wR_2 (all data)	0.0735, 0.1483	0.1155, 0.1888	0.1357, 0.1996	0.0862, 0.2076	0.1009, 0.2573
Goodness of fit	1.090	1.019	1.055	1.046	1.049
Largest diff peak and hole [e/Å^3]	1.006 and –0.679	1.634 and –1.138	1.780 and –0.907	1.349 and –0.927	2.682 and –1.943

ray diffraction. The empty cubic cluster **2** crystallizes in the trigonal $R\bar{3}$ space group, whereas the anion-centered clusters **3**–**6** crystallize in the triclinic $P\bar{1}$ space group, the selenide-, chloride-, and bromide-centered clusters **3**, **5**, and **6** being structurally similar. Selected crystallographic data for **2**–**6** are listed in Table 1. The structures **2**–**6** consist of a discrete cluster in which eight copper ions are linked by six face-capped bis(2-phenethyl)diselenophosphinate ligands and a central anion (for **3**–**6**) with a noncoordinating PF_6^- anion (for **2** and **4**–**6**). Such self-assembly leads to greater symmetry in the clusters **2**–**6** in comparison with their diselenophosphate analogues $[Cu_8(\mu\text{-}X)\{Se_{2(}P(OR)_2\}_6]^{n+}$, probably because of the nature of the six bulky diselenophosphinate ligands. The average Cu⋯Cu distances decrease in the following order: Empty cluster **2** (3.260 Å) > Br-centered cluster **6** (3.192 Å) > Cl-centered cluster **5** (3.150 Å) > Se-centered cluster **3** (2.943 Å) > hydride-centered cluster **4** (2.917 Å). In this connection, the size of the metallic core may be varied by changing both the radius and the charge of the encapsulated ion. The same tendency has been shown for $[Cu_8(\mu\text{-}X)\{Se_2P(OiPr)_2\}_6]^{n+}$.[12] The longer the radius of the interstitial anion, the larger the Se–P–Se angle in the clusters: 115.94(16)° for **4**, 117.57(7)° for **2**, 119.57(12)° for **5**, 120.33(16)° for **6**, and 120.52(12)° for **3**. The bulky $[Cu_8(X)\{Se_2P(CH_2CH_2Ph)_2\}_6]^{n+}$ clusters are the sterically most encumbered copper cubic clusters so far synthesized.

Compound 2

The shape of the cluster is a near perfect Cu_8 cube stabilized by six monoanionic seleno ligands in a tetrametallic tetracoordinative (μ_2,μ_2) fashion through their 12 selenium atoms. According to the X-ray diffraction data, the core of

the molecule (Figure 1) has a structure very similar to the structure of $[Cu_8\{Se_2P(OiPr)_2\}_6]^{2+}$ described previously.[12] The bulky phenylethyl groups at the P atom appear to have no significant effect on any of the bond lengths and angles
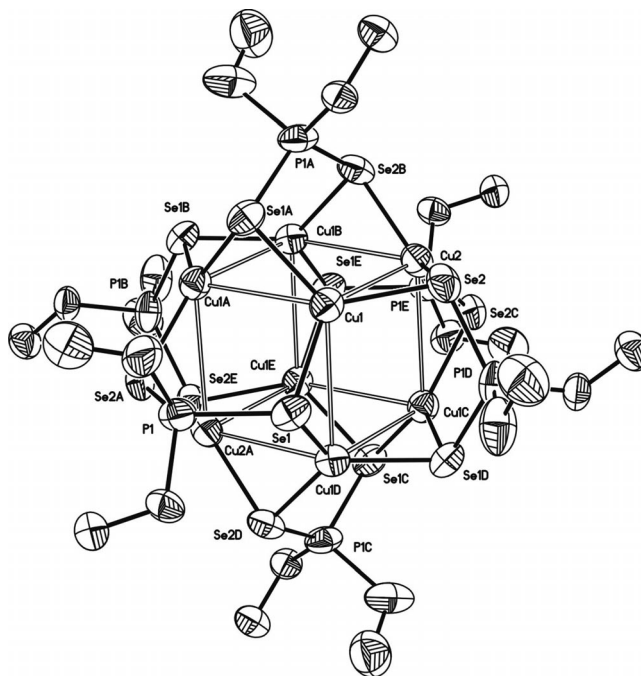

Figure 1. Perspective view of the dication $[Cu_8\{Se_2P(CH_2CH_2Ph)_2\}_6]^{2+}$ (**2**; 30% thermal ellipsoid) with hydrogen atoms and phenyl groups omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)⋯Cu(2) 3.237(1), Cu(1)⋯Cu(1A) 3.282(1), Se(1)–Cu(1) 2.3463(10), Se(1A)–Cu(1) 2.3435(11), Cu(1)–Se(2) 2.3469(10), Cu(2)–Se(2) 2.3498(8), Cu(2)–Se(2B) 2.3498(8), Cu(2A)–Se(2A) 2.3499(8), Se(1)–P(1) 2.192(2), Se(2)–P(1) 2.201(2); Cu(1)–Se(1)–Cu(1) 88.84(4), Cu(1)–Se(2)–Cu(2) 87.14(4), Se(1)–P(1)–Se(2A) 117.57(7).

(compare **2** and $[Cu_8\{Se_2P(OiPr)_2\}_6]^{2+}$). Compound **2** is the second example after $[Cu_8\{S_2PPh_2\}_6]^{2+}$ to show an empty cationic cubic copper framework stabilized by six dichalcogenophosphinate ligands. The copper atoms are located at the corners of a nearly perfect cube [Cu···Cu···Cu angles lie between 88.92(5) and 90.50(5)°], the inversion center of which is at the center of the cube. In contrast, $[Cu_8\{S_2PPh_2\}_6]^{2+}$ has a less symmetrical Cu8 cage [Cu···Cu···Cu angles in the range 87.82(4)–92.97(4)°]. Each Cu atom in **2** is trigonally coordinated by three Se atoms from three independent "dsepi" ligands. Twelve selenium atoms from six "dsepi" ligands are located in the vertices of a slightly distorted icosahedron, and an idealized T_h point group symmetry is exhibited. Thus, the six P atoms and 12 Se atoms from the ligands are symmetry-related, as is indicated by the results of the ^{31}P and ^{77}Se NMR studies (see above). The ligand "bite" average distances are 3.758(1) Å. The Cu···Cu edge distances are slightly longer than those in $[Cu_8\{Se_2P(OiPr)_2\}_6]^{2+}$ [3.216(1)–3.220(1) Å].[12] The Cu···Cu distances in $[Cu_8\{S_2PPh_2\}_6]^{2+}$ lie in the range 3.1275(16)–3.2861(14) Å.[28] The P–Se bonds are almost all equal in length [2.192(2) and 2.201(2) Å], and the Cu–Se distances [2.3435(11)–2.3499(8) Å] are normal and comparable to those reported for the empty cube covered by "dsep".[12] The dihedral angle between the phenyl rings in the diselenophosphinate moieties in **1** is 21.55°, whereas for the phosphane sulfide complex $[Cu_8(S_2PPh_2)_6]^{2+}$ this value is 75.0°.[28]

Compound 3

The selenide-centered octanuclear copper cluster also shows the metal centers in a cubic geometry (Figure 2). The neutral compound **3** is isostructural with the chloride- and bromide-centered clusters **5** and **6** (see below). Each copper ion is strongly bonded to the central μ_8-Se ion, and all the "dsepi" ligands in **3** adopt a tetrametallic tetraconnective (μ_2,μ_2) bridging mode. The Cu–Cu–Cu angle is close to 90° [average 90.2(3)°]. The 12 Se atoms of the ligands are arranged in a nearly regular icosahedron. Each copper atom of the cube is coordinated to three selenium atoms of three different ligands. At the same time, the Cu···Cu distances along the edges range from 2.9140(16) to 2.9764(18) Å and are even shorter than in the chloride-centered **5** by approximately 0.2 Å (see below), which suggests a greater symmetrical, cubic contraction of the central Cu8 framework induced by the Se[2–] anion, in agreement with the data obtained for their diselenophosphate analogue $[Cu_8(Se)\{Se_2P(OiPr)_2\}_6]$.[4] The other set of Cu–Se bond lengths and Se···Se bite distances are consistent with those observed in related systems,[12] the latter being longer by 0.2 Å than in the precursor $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ (**1**).[26] The average "bite distance" is 3.807(2) Å, and the Se–Cu–Se bond angles range from 114.27 to 117.07°. However, the P–Se distances [2.186(3)–2.194(3) Å] are longer than those in **2** and **4** in contrast to the phosphate analogues.[12] The average Cu–Se(dsepi) bond length is 2.447 Å.

The central selenide atom in conjunction with the 12 selenium atoms of the ligands forms a body-centered icosahedron. The bond lengths between the central selenide and the peripheral copper atoms range from 2.5448(13) to 2.5519(12) Å and are slightly longer than those of $[Cu_8(\mu_8\text{-}Se)\{Se_2P(OiPr)_2\}_6]^{2+}$ [2.506(3)–2.577(5) Å].[4]
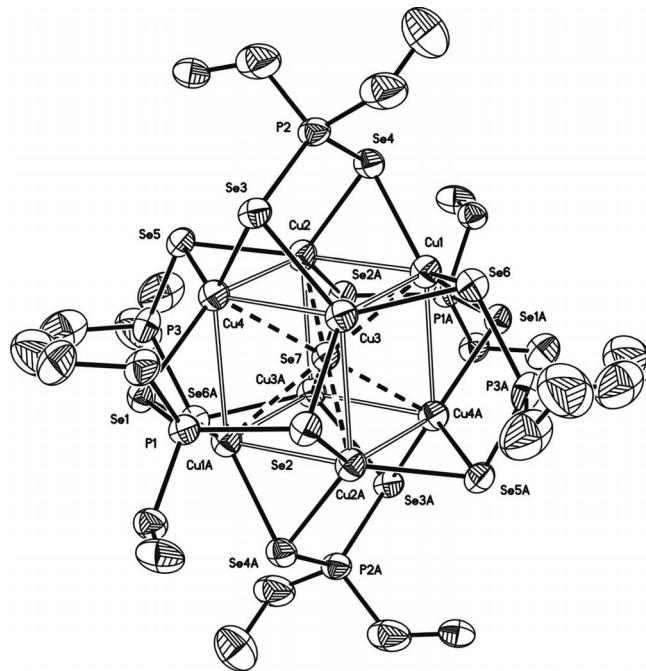
Figure 2. Perspective view of $[Cu_8(\mu_8\text{-}Se)\{Se_2P(CH_2CH_2Ph)_2\}_6]$ (**3**; 30% thermal ellipsoid) with hydrogen atoms and phenyl groups omitted for clarity. Ranges of selected bond lengths [Å] and angles [°]: Cu···Cu 2.9140(16)–2.9764(18), Cu–Se$_{cent}$ 2.5448(13)–2.5518(12), Se–Cu 2.4399(15)–2.4668(17), Se–P 2.186(3)–2.194(3), P–C 1.715(17)–1.939(19); Cu–Se–Cu 72.50(5)–75.04(5), Cu–Cu–Cu 89.34(5)–90.59(5), Se–P–Se 120.04(12)–120.30(12), C–P–C 101.0(8)–107.2(5).

Compound 4

Although this is the first example of a hydride-centered copper(I) diselenophosphinate cluster, the related copper(I) diselenophosphate cage $[Cu_8(H)\{Se_2P(OR)_2\}_6]^+$ (R = Et, iPr) is known.[12] Single-crystal X-ray diffraction analysis revealed the monocationic octanuclear copper framework in **4** (Figure 3), which contains a tetracapped tetrahedral metallic core with T_d symmetry surrounded by six "dsepi" ligands along with an interstitial hydride anion and the counteranion PF_6^-. In the crystal structure, the copper atoms are disordered in two orientations. A total of 16 copper atoms, each with 50% occupancy, form two cubes, one inside the other, like those observed in $[Cu_8(H)\{Se_2P(OiPr)_2\}_6]^+$.[12] Thus, only four copper atoms are present in each cube. The cluster is a three-dimensional framework comprising a hub of eight copper atoms with the geometry of a slightly distorted tetracapped tetrahedron containing an encapsulated hydride anion linked to four Cu atoms, Cu1, Cu4, Cu2A, and Cu3A (abbreviated as Cu$_v$), in a four-

fold coordination mode. These four copper atoms comprise the inner tetrahedron, and each triangular face of this tetrahedron is capped by Cu1B, Cu2′, Cu3′, and Cu4B (abbreviated as Cu_{cap}). The capping Cu atoms are almost in the same plane as the three Se atoms coordinated to them. The Cu_v–Cu_v distances through the edges of the tetrahedron lie in the range 2.866(4)–2.958(5) Å, which are shorter by 0.1 Å than those of $[Cu_8(H)\{Se_2P(OiPr)_2\}_6]^+$,[12] However, the distances between the copper atoms at the vertex and the capping Cu atoms (Cu_v–Cu_{cap}) vary from 2.712(5) to 2.759(5) and are shorter than those of the Cu_v–Cu_v distances. These distances are slightly shorter than those observed in $[Cu_8(H)\{Se_2P(OiPr)_2\}_6]^+$,[12] which suggests comparatively better packing in **4**. All of the Cu–Cu distances are shorter than those identified in the empty-caged octanuclear copper cluster **2**. All the "dsepi" ligands show a tetrametallic tetraconnective binding mode to coordinate a Cu_4 butterfly formed by two Cu_{cap} and two Cu_v atoms, whereas the hinge position is the edge of the tetrahedron, and the wingtips are two capping Cu atoms. The average dihedral angle of the Cu_4 butterflies (ca. 152°) is almost identical to that in $[Cu_8(H)\{Se_2P(OiPr)_2\}_6]^+$.[12] Unlike its precursor **2**, which displays an almost identical Cu–Se bond length of around 2.3414 Å, two kinds of Se–Cu distances, namely, Cu_v–Se and Cu_{cap}–Se, each averaging 2.574(04) and 2.294(7) Å, are revealed in **4**, the shorter distance being associated with the wingtip Cu_{cap}. The average intraligand

Se···Se bite distance is 3.7096(7) Å in **4**, shorter than in its precursor **2** by only 0.0685 Å. The P–Se distances lie in the range 2.180(3)–2.195(4) Å and are slightly longer than those observed in $[Cu_8(H)\{Se_2P(OiPr)_2\}_6]^+$.[12] Because the hydride ion cannot be determined reliably by X-ray diffraction, the relevant metric data for Cu–H have not been reported herein.

Compounds 5 and 6

The X-ray structures of the chloride- (**5**) and bromide-centered (**6**) cubic copper clusters consist of a discrete cationic cluster in which eight copper ions lie at the corners of a cube and are linked to the Se donor atoms of six "dsepi" ligands adopting the same coordination pattern as that in the phosphate analogue $[Cu_8(\mu_8-X)\{Se_2P(OR)_2\}_6]^+$ (X = Cl, Br).[8] Each copper ion is weakly bonded to the central halide ion, whereas PF_6^- is a noncoordinating anion (Figures 4 and 5). The Cu···Cu distances in **5** [3.134(2)–3.162(2) Å] are approximately 0.1 Å shorter than those in **2**, which indicates that contraction of the Cu_8 cubic core induced by the chloride ion has occurred. However, these distances in $[Cu_8(\mu_8-Cl)\{S_2PPh_2\}_6]^{2+}$ are even smaller than those in **5**,[28] and the Cu···Cu distances in **6** [3.176(2)–3.207(2) Å] are slightly longer than those in **5**. The geometry around each Cu ion bonded to three selenium atoms is trigonal-planar. The shape of the molecule is a halide-centered, near perfect Cu_8
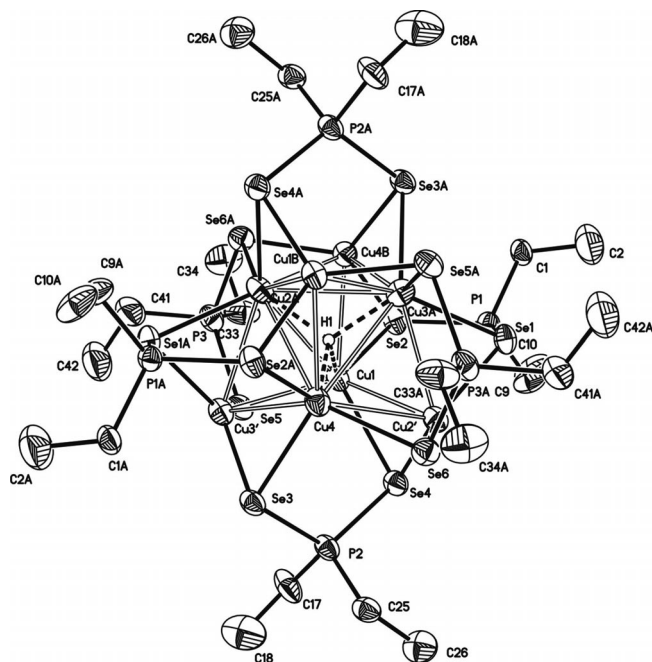

Figure 3. Perspective view of the cation $[Cu_4(\mu_4-H)(\mu_3-Cu)_3\{Se_2P(CH_2CH_2Ph)_2\}_6]^+$ (30% thermal ellipsoid) in **4** with hydrogen atoms and phenyl groups omitted for clarity. Ranges of selected bond lengths [Å] and angles [°]: Cu_v–Cu_v 2.866(4)–2.958(5), Cu_v–Cu_{cap} 2.712(5)–2.759(5), Cu_v–Se 2.542(4)–2.573(4), Cu_{cap}–Se 2.277(3)–2.316(4), Se···Se (bite) 3.709–3.710, Se–P 2.180(3)–2.195(4), P–C 1.799(12)–1.842(14); Se–P–Se 115.82(16)–116.17(14), C–P–C 106.2(6)–113.7(9). Cu_v = Cu atoms at the vertex of the tetrahedron; Cu_{cap} = Cu atoms capping the tetrahedron face.
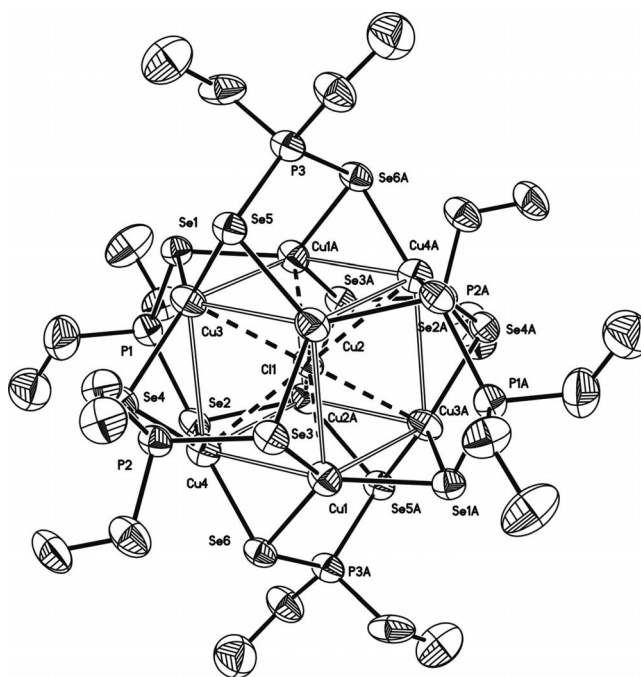
Figure 4. Perspective view of the cation $[Cu_8(\mu_8-Cl)\{Se_2P(CH_2CH_2Ph)_2\}_6]^+$ (30% thermal ellipsoid) in **5** with hydrogen atoms and phenyl groups omitted for clarity. Ranges of selected bond lengths [Å] and angles [°]: Cu···Cu 3.134(2)–3.162(2), Cu–Cl 2.6974(13)–2.7464(13), Se–Cu 2.3763(15)–2.3953(15), Se–P 2.191(3)–2.196(3), P–C 1.795(12)–1.871(14); Cu–Se–Cu 82.00(5)–83.36(5), Cu–Cu–Cu 89.25(5)–90.88(5), Se–P–Se 119.20–119.77, C–P–C 107.8(7)–112.7(8).

cube in which the Cu–X–Cu angles fall in the range 70.28(4)–70.90(4)° for **5** and 70.17(4)–70.77(5)° for **6**, which are comparable to the value expected (70.53°) for a perfect centered cube. However, the average Cu–Se distances [2.385(5) Å for **5** and 2.392(2) Å for **6**] are slightly longer than those in **2**. In **5**, the central chloride ion surrounded by eight copper atoms in cubic arrangement and inscribed into an Se$_{12}$ icosahedron exhibits long Cu–Cl distances in the range 2.697(2)–2.746(1) Å, which compares with 2.6613(5)–2.6804(9) Å for [Cu$_8$(μ_8-Cl){S$_2$PPh$_2$}$_6$]$^{2+}$.[28] The average Cu–Br bond length in **6** is 2.7645(7) Å. All the P–Se bonds in **5** are almost equal in length [2.191(3)–2.196(3) Å], but a little longer than those in the reported Cl-centered cube covered by "dsep",[8] whereas the P–Se bonds in **6** range from 2.185(4) to 2.202(4) Å.
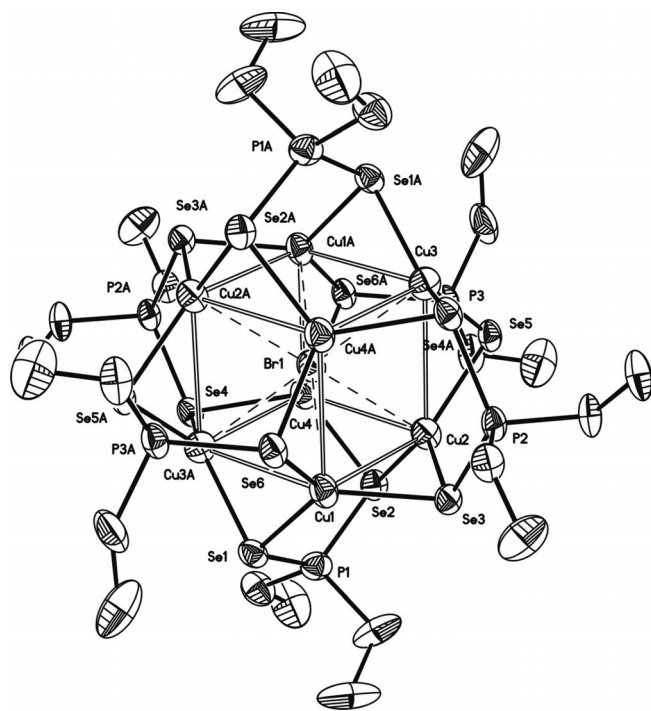

Figure 5. Perspective view of the cation [Cu$_8$(μ_8-Br){Se$_2$P-(CH$_2$CH$_2$Ph)$_2$}$_6$]$^+$ (30% thermal ellipsoid) in **6** with hydrogen atoms and phenyl groups omitted for clarity. Ranges of selected bond lengths [Å] and angles [°]: Cu···Cu 3.176(2)–3.207(2), Cu–Br 2.7341(16)–2.7859(16), Se–Cu 2.3836(18)–2.4028(19), Se–P 2.185(4)–2.202(4), P–C 1.812(16)–1.851(15); Cu–Se–Cu 83.01(6)–84.26(6), Cu–Cu–Cu 89.19(6)–91.00(6), Se–P–Se 120.01(14)–120.52(16), C–P–C 108.6(6)–111.7(9).

Conclusions

The first representatives of octanuclear copper(I) clusters containing diselenophosphinate ligands have been synthesized in high yields. The self-assembly reaction between [Cu(MeCN)$_4$](PF$_6$) and ammonium diselenophosphinate proceeded under exceptionally mild conditions (ambient temperature, 1 h) to afford empty cubic cluster [Cu$_8${Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$](PF$_6$)$_2$ in almost quantitative yield. Meanwhile, the introduction of an Se^{2-} source, for

example, [Cs$_4$(P$_2$Se$_6$)(H$_2$O)$_4$], into this reaction resulted in the self-assembly of neutral selenide-centered cubic copper cluster [Cu$_8$(μ_8-Se){Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$]. Similarly, the three-component self-assembly reaction involving [Cu(Me-CN)$_4$](PF$_6$), ammonium diselenophosphinate, and sources of hydride, chloride, or bromide anions, for example, NaBH$_4$, Bu$_4$NCl, or Bu$_4$NBr, under the same conditions (ambient temperature, THF) furnished three anion-centered Cu$_8$ clusters, [Cu$_4$(μ_4-H)(μ_3-Cu)$_4${Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$](PF$_6$), [Cu$_8$(μ_8-Cl){Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$](PF$_6$), and [Cu$_8$(μ_8-Br){Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$](PF$_6$), respectively. Structural investigation of all the clusters (except for the hydride-centered one) revealed a cubic Cu$_8$ core inscribed within an Se$_{12}$ icosahedron formed by six diselenophosphinate ligands, each of which is coordinated to the copper core in a tetrametallic tetraconnective (μ_2,μ_2) coordination pattern. The dicationic cluster [Cu$_8${Se$_2$P(CH$_2$CH$_2$Ph)$_2$}$_6$](PF$_6$)$_2$ contains an empty copper cube Cu$_8$ stabilized by six diselenophosphinate ligands. The chloride-, bromide-, and selenide-centered octanuclear copper clusters are isostructural and show an anion-centered Cu$_8$ cube, whereas the hydride-centered cluster contains a tetracapped tetrahedral Cu$_8$ cage of T_d symmetry with an interstitial hydride anion. The data obtained testify to the fact that the diselenophosphinate ligands in reactions with copper(I) cations are very similar to their phosphate analogues, that is, diselenophosphates, (RO)$_2$PSe$_2^-$, despite the significant differences in their electronic and spatial properties. The results contribute to the coordination chemistry of diselenophosphinates as well as to the synthesis of metal clusters by self-assembly reactions.

Experimental Section

Caution: Selenium and its derivatives are toxic! These materials should be handled with great caution.

Materials and Methods: Solvents were purified by applying standard procedures prior to use. All reactions were carried out under nitrogen by using standard Schlenk techniques. Ammonium bis(2-phenethyl)diselenophosphinate (**1**) was prepared from available bis(2-phenethyl)phosphane, elemental selenium, and ammonia.[24] [Cu(MeCN)$_4$](PF$_6$)[29] and [Cs$_4$(P$_2$Se$_6$)(H$_2$O)$_4$][30] were prepared according to the reported methods. Other chemicals were purchased from commercial sources and used as received. Melting points were determined with a Fargo MP-2D apparatus. The microanalyses were performed with an Elementar varioEL III-CHNS elemental analyzer. ^{1}H NMR spectra were recorded with a Bruker Avance DPX300 spectrometer (300 MHz). Chemical shifts are expressed with respect to residual protonated solvents, which served as the internal standard. ^{31}P and ^{77}Se NMR spectra were recorded with a Bruker Avance DPX300 NMR spectrometer (121.5 and 57.2 MHz, respectively) and referenced to 85% H$_3$PO$_4$ (δ = 0 ppm) and PhSe-SePh (δ = 463 ppm), respectively. The chemical shifts (δ) and coupling constants (J) are reported in ppm and Hz, respectively. ESI-MS data were recorded with an orbitrap mass spectrometer. The cyclic voltammograms were recorded with a CH Instruments 611C electrochemical analyzer by using a glassy carbon working electrode, Pt wire auxiliary electrode, and Ag/AgNO$_3$ reference electrode (0.33 V ± 10 mV vs. SCE) and standardized by the redox couple ferricinium/ferrocene. [Bu$_4$N][ClO$_4$] (0.2 M) was used as the sup-

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porting electrolyte, and CH_2Cl_2/CH_3CN (2:1, v/v) or THF was used for the samples. Electrochemical solutions were degassed with N_2 and maintained under a positive pressure for the duration of the experiment.

$[Cu_8\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)_2$ (2): $[Cu(MeCN)_4](PF_6)$ (0.047 g, 0.126 mmol) and $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ **1** (0.040 g, 0.096 mmol) were dissolved in THF (40 mL). The mixture was stirred at ambient temperature for 1 h to give a dark-blue solution. The latter was concentrated to dryness under vacuum, and the residue was washed with MeOH and dried under vacuum to afford cluster **2** as a dark-blue powder. Yield: 0.044 g (87 %). M.p. 180 °C (decomp.). ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): $\delta = 2.96$ (m, 24 H, CH_2Ph), 3.17 (m, 24 H, PCH_2), 7.34 (m, 60 H, Ph) ppm. ^{31}P NMR (121.5 MHz, THF, 25 °C): $\delta = 43.0$ (s, $^1J_{PSe} = 500$ Hz, 6 P, PSe_2), −143.0 (sept, $^1J_{PF} = 712$ Hz, PF_6) ppm. ^{77}Se NMR (57.2 MHz, THF, 25 °C): $\delta = -7.7$ (d, $^1J_{PSe} = 503$ Hz, 12 Se, PSe_2) ppm. $C_{96}H_{108}Cu_8F_{12}P_8Se_{12}$ (3193.42): calcd. C 36.10, H 3.41; found C 35.94, H 4.02.

$[Cu_8(\mu_8\text{-}Se)\{Se_2P(CH_2CH_2Ph)_2\}_6]$ (3): $[Cu(MeCN)_4](PF_6)$ (0.047 g, 0.126 mmol) and $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ (**1**; 0.040 g, 0.096 mmol) were dissolved in THF (40 mL). The mixture was stirred at ambient temperature for 1 h to form the dark-blue solution. $[Cs_4(P_2Se_6)(H_2O)_4]$ (0.018 g, 0.0158 mmol) was added to this solution, which was stirred for 24 h. The dark-blue solution turned yellow. This yellow solution was then filtered to remove any solid, and the filtrate was concentrated to dryness to give a yellow solid. This solid was washed sequentially with MeOH, and the resulting solid was dried under vacuum to obtain cluster **3** as a yellow powder. Yield: 0.026 g (56 %). M.p. 221 °C (decomp.). ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): $\delta = 2.75$ (m, 24 H, CH_2Ph), 3.08 (m, 24 H, PCH_2), 7.26 (m, 60 H, Ph) ppm. ^{31}P NMR (121.5 MHz, THF, 25 °C): $\delta = 39.2$ (s, $^1J_{PSe} = 520$ Hz, 6 P, PSe_2) ppm. ^{77}Se NMR (57.2 MHz, THF, −40 °C): $\delta = -139.3$ (d, $^1J_{PSe} = 519$ Hz, 12 Se, PSe_2) ppm. MS (ESI): calcd. for $[Cu_8(Se)\{Se_2P(CH_2CH_2Ph)_2\}_6 + H^+]$ 2983.6; found 2983.1. $C_{96}H_{108}Cu_8F_6P_7Se_{13}$ (3049.46): calcd. C 38.66, H 3.65; found C 38.79, H 3.87.

$[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_4\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)$ (4): $[Cu(MeCN)_4](PF_6)$ (0.047 g, 0.126 mmol) and $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ (**1**; 0.040 g, 0.096 mmol) were dissolved in THF (40 mL). The mixture was stirred at ambient temperature for 1 h to form a dark-blue solution. $NaBH_4$ (0.6 mg, 0.0158 mmol) was added, and the mixture was stirred for 3 h. The dark-blue solution turned yellow and was concentrated to dryness under vacuum. The residue was washed sequentially with MeOH and CH_2Cl_2, and the resulting solid was dried under vacuum to give cluster **4** as a yellow powder. Yield: 0.041 g (85 %). M.p. 213 °C (decomp.). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = -1.93$ (br. s, 1 H, μ_4-H) 2.62 (m, 24 H, CH_2Ph), 2.99 (m, 24 H, PCH_2), 7.23 (m, 60 H, Ph) ppm. ^{31}P NMR (121.5 MHz, CDCl$_3$, 25 °C): $\delta = 47.5$ (s, $^1J_{PSe} = 509$ Hz, 6 P, PSe_2), −143.0 (sept, $^1J_{PF} = 712$ Hz, PF_6) ppm. ^{77}Se NMR (57.2 MHz, CDCl$_3$, 25 °C): $\delta = -106.2$ (d, $^1J_{PSe} = 500$ Hz, 12 Se, PSe_2) ppm. MS (ESI): calcd. for $[Cu_8(H)\{Se_2P(CH_2CH_2C_6H_5)_2\}_6]^+$ 2904.6; found 2904.2. $C_{96}H_{109}Cu_8F_6P_7Se_{12}$ (3049.46): calcd. C 37.81, H 3.60; found C 38.11, H 4.15.

$[Cu_8(\mu_8\text{-}Cl)\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)$ (5): $[Cu(MeCN)_4](PF_6)$ (0.047 g, 0.126 mmol) and $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ (**1**; 0.040 g, 0.096 mmol) were placed in a 100 mL Schlenk flask, and THF (40 mL) was added. The mixture was stirred at ambient temperature for 1 h to form a dark-blue solution. $[Bu_4N]Cl$ (4.4 mg, 0.016 mmol) was added, and the mixture was stirred for 3 h. The dark-blue solution turned yellow and was concentrated to dryness under vacuum. The residue was washed sequentially with MeOH

and CH_2Cl_2, and the resulting solid was dried under vacuum to obtain cluster **5** as a yellow powder. Yield: 0.038 g (79 %). M.p. 232 °C (decomp.). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 2.64$ (m, 24 H, CH_2Ph), 3.01 (m, 24 H, PCH_2), 7.25 (m, 60 H, Ph) ppm. ^{31}P NMR (121.5 MHz, CDCl$_3$, 25 °C): $\delta = 38.5$ (s, $^1J_{PSe} = 522$ Hz, 6 P, PSe_2), −143.0 (sept., $^1J_{PF} = 712$ Hz, 1 P, PF_6) ppm. ^{77}Se NMR (57.2 MHz, CDCl$_3$, 25 °C): $\delta = -114.3$ (d, $^1J_{PSe} = 521$ Hz, 12 Se, PSe_2) ppm. MS (ESI): calcd. for $[Cu_8(Cl)\{Se_2P(CH_2CH_2Ph)_2\}_6]^+$ 2939.1; found 2940.0. $C_{96}H_{108}Cl_1Cu_8F_6P_7Se_{12}$ (3083.90): calcd. C 37.39, H 3.53; found C 37.05, H 3.52.

$[Cu_8(\mu_8\text{-}Br)\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)$ (6): $[Cu(MeCN)_4](PF_6)$ (0.047 g, 0.126 mmol) and $[NH_4][Se_2P(CH_2CH_2Ph)_2]$ (**1**; 0.040 g, 0.096 mmol) were placed in a 100 mL Schlenk flask, and THF (40 mL) was added. The mixture was stirred at ambient temperature for 1 h to form a dark-blue solution. $[Bu_4N]Br$ (5.1 mg, 0.016 mmol) was added, and the mixture was stirred for 3 h. The dark-blue solution turned yellow and was concentrated to dryness under vacuum. The residue was washed sequentially with MeOH, and the resulting solid was dried under vacuum to obtain cluster **6** as a yellow powder. Yield: 0.037 g (75 %). M.p. 211 °C (decomp.). ^{1}H NMR (300 MHz, [D$_6$]acetone, 25 °C): $\delta = 2.75$ (m, 24 H, CH_2Ph), 3.11 (m, 24 H, PCH_2), 7.33 (m, 60 H, Ph) ppm. ^{31}P NMR (121.5 MHz, THF, 25 °C): $\delta = 39.0$ (s, $^1J_{PSe} = 519$ Hz, 6 P, PSe_2), −143.0 (sept, $^1J_{PF} = 712$ Hz, 1 P, PF_6) ppm. ^{77}Se NMR (57.2 MHz, THF, 25 °C): $\delta = -135.8$ (d, $^1J_{PSe} = 522$ Hz, 12 Se, PSe_2) ppm. MS (ESI): calcd. for $[Cu_8(Br)\{Se_2P(CH_2CH_2Ph)_2\}_6]^+$ 2983.5; found 2981.1. $C_{96}H_{108}Br_1Cu_8F_6P_7Se_{12}$ (3128.48): calcd. C 36.86, H 3.48; found C 36.88, H 3.48.

X-ray Diffraction Analysis: Single crystals suitable for X-ray diffraction were grown by diffusing hexane into a THF solution of the compounds. Crystals were mounted on the tip of glass fibers with epoxy resin. X-ray diffraction analyses of the crystals were performed with a Bruker APEX-II CCD diffractometer (Mo-K_α radiation, $\lambda = 0.71073$ Å). Absorption corrections for the area detector were performed by using the SADABS program.[31] Structures were solved by direct methods and refined by least-squares methods on F^2 by using the SHELXL-97 package[32] incorporated in SHELXTL/PC V5.10.55.[33] Hydrogen atoms on the 2-phenethyl groups were placed at idealized positions. CCDC-865369 (for **2**), -865372 (for **3**), -865370 (for **4**), -865371 (for **5**) and -890915 (for **6**) contain the supplementary crystallographic data for clusters **2**–**6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Redox potentials for complexes **1**–**6**, cyclic voltammograms for ligand **1** and clusters **4** and **5**.

[1] For reviews, see: a) D. M. P. Mingos, D. J. Wales (Eds.), *Introduction to Cluster Chemistry*, Prentice Hall, New Jersey, **1990**; b) D. Fenske in *Clusters and Colloids – From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**; c) P. Braunstein,

611 L. A. Oro, P. R. Raithby, *Metal Clusters in Chemistry*, Wiley-VCH, Weinheim, **2000**.

[2] a) J. M. Lehn, *Science* **2002**, *295*, 2400–2403; b) G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91–121; c) E. Zangrando, M. Casanova, E. Alessio, *Chem. Rev.* **2008**, *108*, 616 4979–5013, and references cited therein; d) C.-A. Palma, M. Cecchini, P. Samorì, *Chem. Soc. Rev.* **2012**, *41*, 3713–3730.

[3] For reviews, see: a) C. W. Liu, *Phosphorus Sulfur Silicon, Relat. Elem.* **2005**, *180*, 923–933; b) T. S. Lobana, J.-C. Wang, C. W. Liu, *Coord. Chem. Rev.* **2007**, *251*, 91–110; c) C. W. Liu, J. D. 621 Woollins in *Selenium and Tellurium Chemistry: From Small Molecules to Biomolecules and Materials* (Eds.: J. D. Woollins, R. Laitinen), Springer, Berlin and Heidelberg, **2011**, pp. 303–320.

[4] C. W. Liu, H.-C. Chen, J.-C. Wang, T.-C. Kang, *Chem. Commun.* **1998**, 1831–1832. 626

[5] C. W. Liu, C.-M. Hung, H.-C. Chen, J.-C. Wang, T.-C. Keng, K.-M. Guo, *Chem. Commun.* **2000**, 1897–1898.

[6] C. W. Liu, H.-C. Chen, J.-C. Wang, T.-C. Keng, *Angew. Chem.* **2001**, *113*, 2404; *Angew. Chem. Int. Ed.* **2001**, *40*, 2342–2344.

[7] C. W. Liu, C.-M. Hung, J.-C. Wang, T.-C. Keng, *J. Chem. Soc., Dalton Trans.* **2002**, 3482–3488. 631

[8] C. W. Liu, C.-M. Hung, B. K. Santra, H.-C. Chen, H.-H. Hsueh, J.-C. Wang, *Inorg. Chem.* **2003**, *42*, 3216–3220.

[9] C. W. Liu, C.-M. Hung, B.-K. Santra, Y.-H. Chu, Z. Lin, J.-C. Wang, *Inorg. Chem.* **2004**, *43*, 4306–4314. 636

[10] Y.-J. Hsu, C.-M. Hung, Y.-F. Lin, B.-J. Liaw, T. S. Lobana, S.-Y. Lu, C. W. Liu, *Chem. Mater.* **2006**, *18*, 3323–3329.

[11] C.-M. Hung, I.-H. Chu, B. K. Santra, B.-J. Liaw, J.-C. Wang, C. W. Liu, *J. Chin. Chem. Soc.* **2006**, *53*, 825–830.

[12] C. W. Liu, B. Sarkar, Y.-J. Huang, P.-K. Liao, J.-C. Wang, J.-Y. 641 Saillard, S. Kahlal, *J. Am. Chem. Soc.* **2009**, *131*, 11222–11233.

[13] C. W. Liu, I.-J. Shang, J.-C. Wang, T.-C. Keng, *Chem. Commun.* **1999**, 995–996.

[14] C. W. Liu, I.-J. Shang, C.-M. Hung, J.-C. Wang, T.-C. Keng, *J. Chem. Soc., Dalton Trans.* **2002**, 1974–1979. 646

[15] C. W. Liu, C.-M. Hung, H.-C. Haia, B.-J. Liaw, L.-S. Liou, Y.-F. Tsai, J.-C. Wang, *Chem. Commun.* **2003**, 976–977.

[16] C. W. Liu, H.-C. Haia, C.-M. Hung, B. K. Santra, B.-J. Liaw, Z. Lin, J.-C. Wang, *Inorg. Chem.* **2004**, *43*, 4464–4470.

[17] C. W. Liu, I.-J. Shang, J.-C. Fu, B.-J. Liaw, J.-C. Wang, I.-J. 651 Chang, *Inorg. Chem.* **2006**, *45*, 2335–2340.

[18] C. W. Liu, H.-W. Chang, B. Sarkar, J.-Y. Saillard, S. Kahlal, Y.-Y. Wu, *Inorg. Chem.* **2010**, *49*, 468–475.

[19] C. W. Liu, C.-S. Feng, R.-J. Fu, H.-W. Chang, J.-Y. Saillard, S. Kahlal, J.-C. Wang, I.-J. Chang, *Inorg. Chem.* **2010**, *49*, 4934– 656 4941.

[20] H.-J. You, C.-S. Fang, J.-L. Lin, S.-S. Sun, C. W. Liu, *Inorg. Chem.* **2010**, *49*, 7641–7643.

[21] C. Q. Nguyen, A. Adeogun, M. Afzaal, M. A. Malik, P. O'Brien, *Chem. Commun.* **2006**, 2182–2184. 661

[22] A. Panneerselvam, C. Q. Nguyen, M. A. Malik, P. O'Brien, J. Raftery, *J. Mater. Chem.* **2009**, *19*, 419–427.

[23] A. V. Artem'ev, N. K. Gusarova, S. F. Malysheva, B. A. Trofimov, *Org. Prep. Proced.* **2011**, *43*, 381–449.

[24] A. V. Artem'ev, S. F. Malysheva, N. K. Gusarova, B. A. Trofimov, *Synthesis* **2010**, 2463–2467. 666

[25] A. V. Artem'ev, S. F. Malysheva, N. K. Gusarova, N. A. Belogorlova, B. A. Trofimov, *Synthesis* **2010**, 1777–1780.

[26] A. V. Artem'ev, N. K. Gusarova, S. F. Malysheva, P. B. Kraikivskii, N. A. Belogorlova, B. A. Trofimov, *Synthesis* **2010**, 671 3724–3730.

[27] N. K. Gusarova, A. V. Artem'ev, S. F. Malysheva, S. V. Fedorov, O. N. Kazheva, G. G. Alexandrov, O. A. Dyachenko, B. A. Trofimov, *Tetrahedron Lett.* **2010**, *51*, 1840–1843.

[28] N. Assavathorn, R. P. Davies, A. J. P. White, *Polyhedron* **2008**, 676 *27*, 992–998.

[29] G. J. Kubas, *Inorg. Synth.* **1979**, *19*, 90–92.

[30] A. Rothenberger, C. D. Malliakas, M. G. Kanatzidis, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1374–1379.

[31] Included within: *SAINT V4.043: Software for the CCD Detec-* 681 *tor System*, Bruker Analytical, Madison, WI, **1995**.

[32] G. M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, **1997**.

[33] *SHELXL 5.10 (PC Version): Program Library for Structure Solution and Molecular Graphics*, Bruker Analytical, Maidson, 686 WI, **1998**.

FULL PAPER

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Copper Clusters

691 The first diselenophosphinato octanuclear Cu^I clusters inscribed in a twelve-vertex selenium polyhedron have been synthesized by exploiting the self-assembly reaction between [Cu(MeCN)$_4$](PF$_6$) and ammonium

696 diselenophosphinate, [NH$_4$][Se$_2$P(CH$_2$-CH$_2$Ph)$_2$], as well as their interactions in the presence of anion sources, for example,

701 [Cs$_4$(P$_2$Se$_6$)(H$_2$O)$_4$], NaBH$_4$, [Bu$_4$N]Cl, and [Bu$_4$N]Br.

706
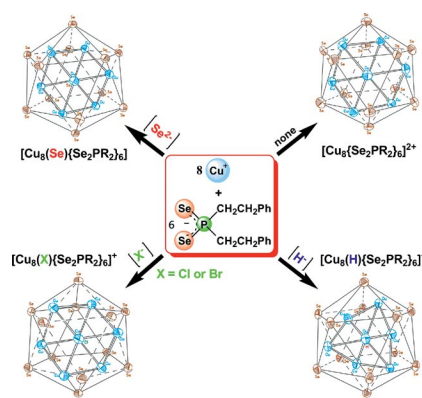
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V. A. Kuimov, N. K. Gusarova,
B. A. Trofimov* **1–10**

Facile Self-Assembly Synthesis and Characterization of Diselenophosphinato Octanuclear Cu^I Clusters Inscribed in a Twelve-Vertex Selenium Polyhedron

Keywords: Cluster compounds / Copper / Selenium / Self-assembly / Solid-state structures