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Novel Chloride-Centered Discrete Cu^{I}_{8} Cubic Clusters Containing Diselenophosphate Ligands. Syntheses and Structures of $\{Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6\}(PF_6)$ (R = Et, Pr, ^{i}Pr)[1]

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Three clusters **1**–**3**, $Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6(PF_6)$ (R= Et, Pr, ^{i}Pr), were synthesized in high yield from the reaction of $[Cu(CH_3CN)_4](PF_6)$, $NH_4[Se_2P(OR)_2]$, and Bu_4NCl in a molar ratio of 4:3:1 in diethyl ether. FAB mass spectra show *m*/*z* peaks at 2218.10 for **1**, 2386.10 for **2**, and 2387.34 for **3** which are due to molecular cations, $[\mathbf{1}\text{–}PF_6]^+$, $[\mathbf{2}\text{–}PF_6]^+$, and $[\mathbf{3}\text{–}PF_6]^+$, respectively. ^{31}P NMR spectra of **1**–**3** display a singlet at δ 76.48, 76.73, and 69.32 ppm with satellites (J_{PSe} = 652, 653, and 648 Hz), respectively. The ^{77}Se NMR spectra of **1**–**3** exhibit a doublet peak at –21.7, –16.42, and 2.3 ppm, respectively (J_{SeP} = 652 Hz for **1**, 653 Hz for **2**, and 648 Hz for **3**). The X-ray structure (**1**–**3**) consists of a discrete cationic cluster in which eight copper ions are linked by six diselenophosphate ligands and a central μ_8-Cl ion with a noncoordinating PF_6^- anion. The shape of the molecule is a chloride-centered distorted Cu_8 cube in clusters **1** and **2** and a near perfect Cu_8 cube for cluster **3**. The dsep ligand exhibits a tetrametallic tetraconnective (μ_2, μ_2) coordination pattern, and each occupies a square face of the cube. Each copper atom of the cube is coordinated by three selenium atoms with a strong interaction with the central chloride ion. The observed Cu–Cl distances lie in the range 2.649–2.878 Å.

Introduction

The anion coordination chemistry continues to draw considerable attention due to establishing a new realm of supramolecular chemistry,[2] anion assisted synthesis,[3] anionic binding and recognition,[4] and anion template effects.[5] The halide ions are the dominant species being studied to the greatest extent because of its variable coordination modes, and the coordination polyhedra for the halides are planar,[6] tetrahedral,[7] octahedral,[8] and cubic.[9] Molecular cubic clusters encapsulating halide ion are not only extremely rare but also particularly interesting in view of their unusual bonding

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characteristics.[10] Although several mixed-metal, mixed-valence clusters of the type $M^{II}_6M^I_8(\mu_8\text{-}Cl)L_{12}$ are known in the literature,[11] of which copper clusters have been used to elucidate the possible role of D-penicillamine in chemotherapy for Wilson disease,[12] only two halide-centered discrete M_8 cube species, $(\mu_8\text{-}I)Cd_8(SCH_2CH_2OH)_{12}I_3$[9c] and $\{Cu_8(\mu_8\text{-}Br)[S_2P(O^iPr)_2]_6\}PF_6$,[9b] and one chloride-centered polymeric M_8 cube, $\{Cu_8(\mu_8\text{-}Cl)[S_2P(OEt)_2]_6Cl\}_\infty$,[13] have been identified so far. Our initial report of a bromide-centered Cu^I_8 cube having the diselenophosphato ligand (dsep), $\{Cu_8(\mu_8\text{-}Br)[Se_2P(O^iPr)_2]_6\}(PF_6)$, has been communicated.[14]

To extend our research efforts in halide-centered M_8 cubic clusters using dsep, we focus our attention on the chloride ion and uncovered chloride-centered Cu^I_8 cube which is indeed the first chloride-centered discrete Cu^I_8 cube containing the diselenophosphato ligand. Herein, we report the detailed synthesis and characterizations of chloride-centered Cu^I_8 cubic clusters $\{Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6\}(PF_6)$ (**1**−**3**) (R= Et, Pr, ^{i}Pr) both in solid and solution states.

Experimental Section

Materials and Measurements. All chemicals and reagents were purchased from commercial sources and used as received. Commercial CH_2Cl_2 and ROH were distilled from P_4O_{10} and Mg, respectively. Hexane and diethyl ether were distilled from Na/K. All the reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The starting copper(I) complex, $Cu(CH_3CN)_4(PF_6)$,[15] and the ligand, $NH_4Se_2P(OR)_2$ (R= Et, Pr, ^{i}Pr),[16] were prepared according to the literature methods. The elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on a Bruker AC-F200 and Advance-300 Fourier transform spectrometers. The $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR are referenced externally against 85% H_3PO_4 ($\delta = 0$) and PhSeSePh ($\delta = 463$), respectively. Positive FAB mass spectra were carried out on a VG 70-250S mass spectrometer with nitrobenzyl alcohol as the matrix.

Preparation of $Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6(PF_6)$ (R = Et, 1; Pr, 2; ^{i}Pr, 3). The compounds **1**−**3** were prepared by following a general procedure. Diethyl ether (50 mL) was added to a Schlenk flask (100 mL) containing $[Cu(CH_3CN)_4](PF_6)$ (1.491 g, 4 mmol), $NH_4[Se_2P(OR)_2]$ (3 mmol), and Bu_4NCl (0.278 g, 1 mmol). The solution mixture was stirred for 12 h at 0 °C under a dinitrogen atmosphere using a Schlenk line. The white precipitate was formed with a change in the solution color from colorless to light yellow during the reaction period. The white residue was obtained by filtration of the reaction mixture, and the residue was redissolved in dichloromethane. The dichloromethane solution was extracted with 500 mL of double distilled water to remove impurities. Solvent was removed by rotary evaporation from the dichloromethane extract which afforded a pure compound.

From the yellow filtrate, another isolated product (8−10%) was the selenium-centered Cu_8 cube, $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6\}$, which is known to form in the reaction of $[Cu(CH_3CN)_4](PF_6)$ and $NH_4\text{-}[Se_2P(OR)_2]$ in diethyl ether medium.[17]

Compound 1. (Yield ~ 82%, 0.968 g.) Anal. Calcd for $C_{24}H_{60}\text{-}ClCu_8F_6O_{12}P_7Se_{12}$: C, 12.20; H, 2.56. Found: C, 13.01; H, 2.58. FAB MS, *m/z* 2218.10 (M^+). ^1H NMR ($CDCl_3$) δ 1.37 [t, 36H, OCH_2CH_3, $J_{HH} = 7$ Hz], 4.16 [m, 24H, OCH_2CH_3]; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 76.48 [s, 6P, $P(OR)_2$, $J_{PSe} = 652$ Hz], −143.0 (septet, PF_6^-, $J_{PF} = 712$); $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ −21.7 [d, 12Se, $Se_2P(OR)_2$, $J_{SeP} = 652$ Hz].

Compound 2. (Yield ~ 80%, 1.012 g.) Anal. Calcd for $C_{36}H_{84}ClCu_8F_6O_{12}P_7Se_{12}$: C, 17.08; H, 3.34. Found: 16.94; H, 3.28. FAB MS, *m/z* 2386.10 (M^+). ^1H NMR ($CDCl_3$) δ 0.98 (t, 36H, $OCH_2CH_2CH_3$, $J_{HH} = 7$ Hz), 1.74 [m, 24H, $OCH_2CH_2CH_3$], 4.05 [m, 24H, $OCH_2CH_2CH_3$]; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 76.73 [s, 6P, $P(OR)_2$, $J_{PSe} = 653$ Hz], −143.0 (septet, PF_6^-, $J_{PF} = 712$); $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ −16.4 [d, 12Se, $Se_2P(OR)_2$, $J_{SeP} = 653$ Hz].

Compound 3. (Yield ~ 75%, 0.949 g.) Anal. Calcd for $C_{36}H_{84}\text{-}ClCu_8F_6O_{12}P_7Se_{12}$: C, 17.08; H, 3.34. Found: C, 17.31; H, 3.33. FAB MS, *m/z* 2387.34 (M^+). ^1H NMR ($CDCl_3$) δ 1.36 [d; 72H, $OCH(CH_3)_2$, $J_{HH} = 6$ Hz], 4.78 [m; 12H, $OCH(CH_3)_2$]; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 69.32 [s, 6P, $P(OR)_2$, $J_{PSe} = 648$ Hz], −143.0 (septet, PF_6^-, $J_{PF} = 712$); $^{77}Se\{^1H\}$ NMR ($CDCl_3$) δ 2.3 [d, 12Se, $Se_2P(OR)_2$, $J_{SeP} = 648$ Hz].

Safety Note. *Selenium and its derivatives are toxic! These materials should be handled with great caution.*

X-ray Crystallographic Procedures. The crystal structures of $Cu_8(\mu_8\text{-}Cl)[Se_2P(OEt)_2]_6(PF_6)\cdot 1/2CHCl_3$ ($\mathbf{1}\cdot{}^1/_2CHCl_3$), $Cu_8(\mu_8\text{-}Cl)\text{-}[Se_2P(OPr)_2]_6(PF_6)$ (**2**), and $Cu_8(\mu_8\text{-}Cl)[Se_2P(O^iPr)_2]_6(PF_6)$ (**3**) were obtained by the single-crystal X-ray diffraction technique. Crystals were mounted on the tips of glass fibers with epoxy resin. Data were collected on a Siemens SMART CCD (charged coupled device) diffractometer. For all the crystals, data were measured with ω scans of 0.3° per frame for 90 s. A total of 1271 frames were collected with a maximum resolution of 0.84 Å. Cell parameters were retrieved with SMART software[18] and refined with SAINT

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Table 1. Selected Crystallographic Data for $Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6(PF_6)$ (R= Et, **1**; Pr, **2**; ^{i}Pr, **3**)

	1·1/2CHCl$_3$	**2**	**3**
formula	$C_{24.5}H_{60.5}Cl_{2.5}Cu_8F_6O_{12}P_7Se_{12}$	$C_{36}H_{84}ClCu_8F_6O_{12}P_7Se_{12}$	$C_{36}H_{84}ClCu_8F_6O_{12}P_7Se_{12}$
fw	2422.48	2531.11	2531.11
space group	$R\bar{3}c$	$R\bar{3}$	$C2/c$
a, Å	17.705(2)	21.683(3)	24.324(1)
b, Å	17.705(2)	21.683(3)	13.150(1)
c, Å	73.576(10)	13.865(4)	24.972(1)
α, deg	90	90	90
β, deg	90	90	91.463(1)
γ, deg	120	120	90
V, Å^3	19975(4)	5645(2)	7985(1)
Z	12	3	4
ρ_{calcd}, g cm^{-3}	2.417	2.234	2.106
λ(Mo Kα), Å	0.71073	0.71073	0.71073
μ, mm^{-1}	9.392	8.262	7.789
T, K	293(2)	298(2)	293(2)
R1^a	0.0436	0.0683	0.0506
wR2^b	0.0906	0.1705	0.1079

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

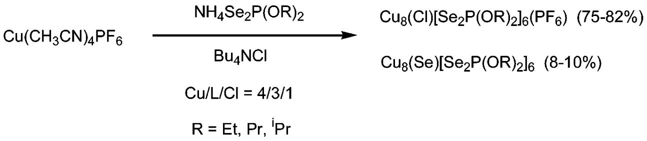
software[19] on all observed reflections ($I > 10\sigma(I)$). Data reduction was performed with SAINT, which corrects for Lorentz and polarization effects. An empirical absorption correction was applied for **1**−**3**. The structure was solved by the use of direct methods, and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[20] incorporated in SHELXTL/PC V5.10.[21] Selected crystal data for the compounds (**1**−**3**) are summarized in Table 1.

Compound 1·$^1/_2$CHCl$_3$. Crystals suitable for X-ray diffraction were grown from $CHCl_3$ layered with hexane. A colorless crystal (0.58 × 0.40 × 0.06 mm^3) was mounted in the manner described, and data were collected. A total of 19888 reflections were collected, of which 3902 were unique ($R_{int} = 0.0304$) and 2913 were observed with $I > 2\sigma(I)$. Hydrogen atoms were added except the solvent molecule in the calculation. The final cycle of the full-matrix least-squares refinement was based on 2913 observed reflections, and 219 parameters, and converged with unweighted and weighted agreement factors of R1 = 0.0436 and wR2 = 0.0906, respectively. The largest residual peak and hole are 0.724 e/Å^3 and −0.478 e/Å^3.

Compound 2. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexane. A colorless crystal (0.50 × 0.40 × 0.20 mm^3) was mounted, and data were collected. A total of 4167 reflections were collected, of which 2109 were unique ($R_{int} = 0.0378$) and 1492 were observed with $I > 2\sigma(I)$. The C−C distance is fixed at 1.54(0.05) Å for one of the *n*-propyl groups. H-atoms were added. The final cycle of the full-matrix least-squares refinement was based on 1492 observed reflections, 2 restraints, and 125 parameters, and converged with unweighted and weighted agreement factors of R1 = 0.0683 and wR2 = 0.1705, respectively. The largest residual peak and hole are 1.864 e/Å^3 and −1.266 e/Å^3.

Compound 3. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexane. A colorless crystal (0.4 × 0.4 × 0.5 mm^3) was mounted, and data were collected. A total of 11908 reflections were collected, of which 5924 were unique ($R_{int} = 0.0304$) and 4886 were observed with $I > 2\sigma(I)$. H-atoms were added. Both O(12) and O(13) atoms connected to P(1) and C(14) are disordered, and site occupancy factors are refined to 44% and 56%, respectively. Three F atoms of the PF_6 anion are also disordered in four positions, and a site occupancy factor of 0.75 is treated. The final cycle of the full-matrix least-squares refinement was based on 4886 observed reflections, and 371 parameters, and converged with unweighted and weighted agreement factors of R1 = 0.0506 and wR2 = 0.1079, respectively. The largest residual peak and hole are 0.994 e/Å^3 and −0.760 e/Å^3.

Scheme 1



Results and Discussion

General Synthesis Aspects. The compounds $Cu_8(\mu_8\text{-}Cl)[Se_2P(OEt)_2]_6(PF_6)$ (**1**), $Cu_8(\mu_8\text{-}Cl)[Se_2P(OPr)_2]_6(PF_6)$ (**2**), and $Cu_8(\mu_8\text{-}Cl)[Se_2P(O^iPr)_2]_6(PF_6)$ (**3**) were prepared (Scheme 1) from the reaction of $[Cu(CH_3CN)_4](PF_6)$, $(NH_4)[Se_2P(OR)_2]$ (R= Et, Pr, ^{i}Pr), and Bu_4NCl in a molar ratio of 4:3:1 in diethyl ether at 0 °C. The yields of the isolated products were 82%, 80%, and 75% for **1**, **2**, and **3**, respectively, with 8−10% of the selenium-centered Cu_8 cube, $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OR)_2]_6\}$. Compounds **1**−**3** can also be prepared in CH_2Cl_2.

The cluster synthesis reported here is more reasonable than the formation of $\{Cu_8(Cl)[S_2P(OEt)_2]_6Cl\}_\infty$ which was isolated from the reaction of $CuCl_2$ and $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2[\mu\text{-}SOP(OEt)_2][S_2P(OEt)_2]_3(O)_2$ in a fortuitous fashion.[13]

Compounds **1**−**3** are well characterized by elemental analysis, FAB-MS, multinuclear NMR (^{1}H, ^{31}P, and ^{77}Se), and X-ray diffraction techniques. Elemental analyses of the compounds are in good agreement with the molecular formulation of clusters **1**−**3**. Positive fast-atom bombardment mass spectra (FAB-MS) of **1**−**3** in nitrobenzyl alcohol show the molecular cation, [**1**−PF$_6$]$^+$, [**2**−PF$_6$]$^+$, and [**3**−PF$_6$]$^+$, respectively. The observed *m*/*z* peaks in the positive FAB mass spectra are 2218.10 for **1** ($M_{calcd} = 2217.91$), 2386.10 for **2** ($M_{calcd} = 2386.24$), and 2387.34 for **3** ($M_{calcd} = 2386.24$), providing further evidence in support of the structural assignment for **1**−**3**. $^{31}P\{^1H\}$ NMR spectra of **1**−**3** display a singlet at δ 76.48, 76.73, and 69.32 ppm with satellites ($J_{PSe} = 652$ Hz, 653 Hz and 648 Hz), respectively, whereas the free ligands $NH_4[Se_2P(OR)_2]$ show a singlet at δ 88.0, 88.0, and 82.0 ppm ($J_{PSe} = 720$) with their respective ethyl, propyl, and isopropyl derivatives. The ∼11−13 ppm chemical shift from free dsep ligands to clusters (**1**−**3**) indicates the cluster formation and remains intact in the solution state. ^{1}H NMR spectra exhibit chemical shifts at δ 1.37 and 4.16 ppm for the CH_2CH_3 group of dsep ligand in **1**, 0.98, 1.74, and 4.05 ppm for the $CH_2CH_2CH_3$ group of dsep in **2**, and 1.36 and 4.78 ppm for the $CH(CH_3)_2$ group of dsep in **3**. The $^{77}Se\{^1H\}$ NMR spectra of **1**−**3** show a doublet peak at −21.7, −16.42, and 2.3 ppm, respectively ($J_{SeP} = 652$ Hz for **1**, 653 Hz for **2**, and 648 Hz for **3**). These

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cu_8(\mu_8\text{-}Cl)[Se_2P(OR)_2]_6(PF_6)$ (R= Et, **1**; Pr, **2**)[a]

	1·$^1/_2$CHCl$_3$		
Cl(1)−Cu(1)	2.775(1)	Cu(1)−Se(1)−Cu(2)	85.10(5)
Cl(1)−Cu(2)	2.744(1)	Cu(2B)−Se(2)−Cu(3)	82.84(4)
Cl(1)−Cu(3)	2.649(1)	Cu(2)−Se(3)−Cu(3)	79.03(4)
Cl(1)−Cu(4)	2.718(3)	Cu(4)−Se(4)−Cu(3A)	80.06(5)
Cu(1)−Se(1)	2.392(7)	Se(1)−Cu(1)−Se(1A)	119.13(2)
Cu(2)−Se(1)	2.389(1)	Se(4)−Cu(4)−Se(4A)	118.06(2)
Cu(2)−Se(2A)	2.399(1)	Se(1)−Cu(2)−Se(3)	120.95(5)
Cu(2)−Se(3)	2.369(1)	Se(1)−Cu(2)−Se(2A)	116.87(5)
Cu(3)−Se(2)	2.407(1)	Se(3)−Cu(2)−Se(2A)	117.99(5)
Cu(3)−Se(3)	2.395(1)	Se(2)−Cu(3)−Se(3)	118.88(5)
Cu(3)−Se(4B)	2.408(1)	Se(2)−Cu(3)−Se(4B)	115.68(4)
Cu(4)−Se(4)	2.365(1)	Se(3)−Cu(3)−Se(4B)	118.06(5)
P−Se (av)	2.178(2)	Cu(3)−Cl(1)−Cu(4)	69.77(6)
Se····Se (av)	3.808	Cu(3)−Cl(1)−Cu(2)	68.38(3)
Se−P−Se(av)	121.85(9)	Cu(3A)−Cl(1)−Cu(2)	72.23(3)
	2		
Cl(1)−Cu(1)	2.674(2)	Cu(1)−Cl(1)−Cu(1A)	70.34(3)
Cl(1)−Cu(2)	2.878(2)	Cu(2)−Cl(1)−Cu(1B)	70.75(3)
Cu(1)−Se(1)	2.388(2)	Se(1)−P(1)−Se(2)	122.09(15)
Cu(1)−Se(2B)	2.400(2)	Cu(1)−Se(1)−Cu(2)	84.82(9)
Cu(1)−Se(2A)	2.387(2)	Cu(1E)−Se(2)−Cu(1D)	80.11(8)
Cu(2)−Se(1)	2.383(1)	Se(1)−Cu(1)−Se(2B)	117.34(8)
Cu(2)−Se(1B)	2.383(1)	Se(1)−Cu(1)−Se(2A)	118.07(8)
Cu(2)−Se(1D)	2.383(1)	Se(2A)−Cu(1)−Se(2B)	118.12((7)
P−Se (av)	2.172(4)	Se(1)−Cu(2)−Se(1B)	119.67(2)
Se(1)···Se(2)	3.801		

[a] With esd's in the parentheses.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Cu_8(\mu_8\text{-}Cl)[Se_2P(O^iPr)_2]_6(PF_6)$, **3**[a]

Cu(1)−Se(1)	2.391(2)	Cu(1)−Se(4)−Cu(2)	83.58(5)
Cu(1)−Se(4)	2.394(2)	Cu(1)−Se(5)−Cu(3A)	82.19(5)
Cu(1)−Se(5)	2.388(1)	Cu(4)−Se(6)−Cu(2A)	83.14(5)
Cu(2)−Se(2)	2.385(1)	Se(1)−Cu(1)−Se(5)	120.00(6)
Cu(2)−Se(4)	2.387(1)	Se(1)−Cu(1)−Se(4)	116.83(6)
Cu(2)−Se(6A)	2.384(1)	Se(4)−Cu(1)−Se(5)	117.81(6)
Cu(3)−Se(2)	2.384(1)	Se(4)−Cu(2)−Se(2)	117.76(5)
Cu(3)−Se(5A)	2.391(1)	Se(4)−Cu(2)−Se(6A)	118.07(6)
Cu(3)−Se(3A)	2.387(2)	Se(2)−Cu(2)−Se(6A)	119.89(5)
Cu(4)−Se(6)	2.375(2)	Se(2)−Cu(3)−Se(3A)	118.58(5)
Cu(4)−Se(1)	2.368(1)	Se(2)−Cu(3)−Se(5A)	118.63(6)
Cu(4)−Se(3A)	2.377(2)	Se(3A)−Cu(3)−Se(5A)	118.14(6)
Cl(1)−Cu(1)	2.691(1)	Se(1)−Cu(4)−Se(6)	118.03(6)
Cl(1)−Cu(2)	2.726(1)	Se(1)−Cu(4)−Se(3A)	118.24(6)
Cl(1)−Cu(3)	2.743(1)	Se(6)−Cu(4)−Se(3A)	118.57(6)
Cl(1)−Cu(4)	2.715(1)	Cu(1)−Cl(1)−Cu(4)	69.75(4)
P−Se (av)	2.177(2)	Cu(1A)−Cl(1)−Cu(2A)	72.03(3)
Se····Se (av)	3.812	Cu(4)−Cl(1)−Cu(2A)	70.95(3)
Se−P−Se (av)	122.17(11)	Cu(4)−Cl(1)−Cu(3)	70.42(3)
Cu(1)−Se(1)−Cu(4)	81.03(5)	Cu(1A)−Cl(1)−Cu(3)	70.61(3)
Cu(2)−Se(2)−Cu(3)	81.53(5)	Cu(2)−Cl(1)−Cu(3)	69.41(3)
Cu(3A)−Se(3)−Cu(4A)	82.68(5)		

[a] With esd's in the parentheses.

NMR (^{1}H, ^{31}P, and ^{77}Se) data suggest that all the dsep ligands are equivalent in solution and the geometry of the compounds **1**−**3** remains the same both in the solid state and in the solution phase.

Crystal Structures. The clusters **1**−**3** are characterized by the single-crystal X-ray diffraction technique. The structure consists of a discrete cationic cluster in which eight copper ions are linked by six face-capped diselenophosphate ligands and a central μ_8-Cl ion with a noncoordinating PF_6^- anion. Selected bond lengths and angles are given in Tables 2 and 3. Compounds **1**−**3** are structurally similar with slight elongation along the C_3 in **1** and **2** but crystallize in different space groups. The shape of the molecule is a chloride-centered distorted Cu_8 cube in case of compounds **1** and **2** and a near perfect Cu_8 cube for compound **3**. The copper atoms are arranged at the corner of the cube. Each selenium atom of the dsep ligand bridges two copper atoms. Thus, dsep ligand exhibits a tetrametallic tetraconnective (μ_2, μ_2) coordination pattern,[22] and each occupies a square face of the cube. Each copper atom of the cube is coordinated by three selenium atoms of three different ligands. In addition to the trigonal planar geometry around the copper atom, there is a strong interaction with the central chloride ion. A comparison of the structural data among the chloride-centered $(Cu^I)_8$ cubic clusters is given in Table 4.

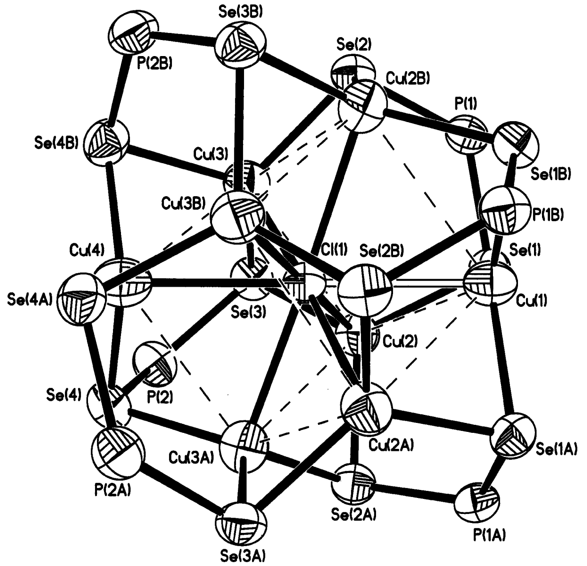

Figure 1. Thermal ellipsoid drawing (50% probability level) of the cation of cluster $Cu_8(\mu_8\text{-}Cl)[Se_2P(OEt)_2]_6(PF_6)\cdot{}^1/_2CHCl_3$ with atom-numbering scheme. The ethoxyl groups are omitted for clarity.

Compound **1** is crystallized with a solvated $CHCl_3$ molecule in trigonal space group $R\bar{3}c$. Four copper atoms are found in the asymmetric unit where the 3-fold rotational axis pass through Cu(1), Cl(1), and Cu(4). (Figure 1) Due to the absence of the inversion center, the Cl(1) atom does not locate exactly in the center of the cluster. Hence, the Cu−Cl distances span the range 2.649−2.775 Å with one longer Cu(1)−Cl(1) bond, 2.775 Å, on the C_3, whereas the Cu−Cl distances lie in the range 2.60−3.30 Å in the reported $Cu^I_8(\mu_8\text{-}Cl)$ clusters (Table 4). The average Cu−Cu distance is 3.13 Å, shorter than all the reported $(Cu^I)_8$ cubic clusters.[11c−e] The Se−Cu bond distances lie in the range 2.365−2.408 Å with an average of 2.391 Å, which is slightly shorter than that observed (2.447 Å) for the selenium-centered Cu_8 cube.[17] The average P−Se distance is 2.178 Å. The average Se···Se bite distance is 3.808 Å, and the average Se−P−Se angle is 121.85°. The Se−Cu−Se angle ranges from 115.68° to 120.95°. The Cu−Cl−Cu angles lie in the range 68.38° to 72.23° with an average of 70.13°, whereas in the perfect cube, this angle is 70.53°.

Cluster **2** crystallizes in the trigonal space group $R\bar{3}$. Two copper atoms are located in the asymmetric unit with the C_3 rotational axis through Cu(2) and Cl(1) atoms (Figure 2).

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(22) Haiduc, I.; Sowerby, D. B.; Lu, S.-F. *Polyhedron* **1995**, *14*, 3389.

Table 4. Selected Structural Data for Chloride-Centered Cu^I_8 Cubic Clusters

compd	d_{av} Cu···Cu (range)	$\angle_{av}$ Se−Cu−Se/ S−Cu−S	av Se···Se/S···S bite distance	d_{av} Cu−Se/ Cu−S	d Cu−(μ_8-Cl) range	ref
$\{Cu_8[Se_2P(OEt)_2]_6(\mu_8\text{-Cl})\}^+$	3.13 (3.03−3.23)	118	3.81	2.39	2.65−2.77	*b*
$\{Cu_8[Se_2P(OPr)_2]_6(\mu_8\text{-Cl})\}^+$	3.15 (3.08−3.22)	119	3.80	2.39	2.67−2.88	*b*
$\{Cu_8[Se_2P(O^iPr)_2]_6(\mu_8\text{-Cl})\}^+$	3.14 (3.09−3.19)	118	3.81	2.38	2.69−2.74	*b*
$\{Cu_8[S_2P(OEt)_2]_6(\mu_8\text{-Cl})\}^+$	3.23 (3.02−3.44)	118	3.50	2.30	2.60−3.30	13
$\{(Cu^I)_8(Cu^{II})_6[SC(Me)_2CH_2NH_2]_{12}(\mu_8\text{-Cl})\}^{7+}$	3.31 (3.26−3.34)	120	3.35	2.28	2.85−2.88	11c
$\{(Cu^I)_8(Cu^{II})_6[SC(Me)_2COO]_{12}(\mu_8\text{-Cl})\}^{5-}$	3.35 (3.33−3.38)	120	3.39	2.28	2.89−2.92	11d
$\{(Cu^I)_8(Cu^{II})_6(\text{D-Pen})_{12}(\mu_8\text{-Cl})\}^{5-c}$	3.30 (3.24−3.37)	120	3.38	2.27	2.75−2.92	11e

[a] Distances in angstroms, angles in degrees; *d* = distance. [b] This work. [c] D-Pen = D-penicillaminato.

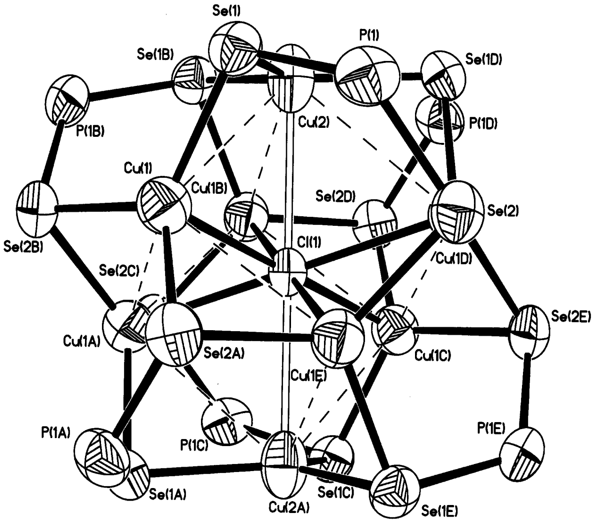

Figure 2. Thermal ellipsoid drawing (50% probability level) of the cation of cluster $Cu_8(\mu_8\text{-Cl})[Se_2P(OPr)_2]_6(PF_6)$ showing atom-numbering scheme. The propoxyl groups are omitted for clarity.

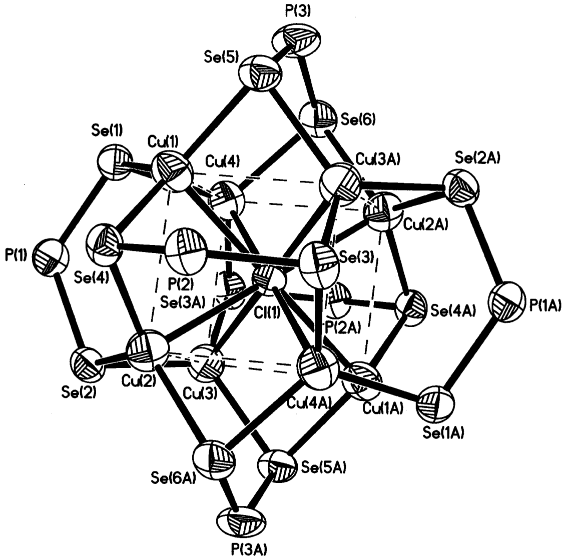

Figure 3. Thermal ellipsoid drawing (50% probability level) of the cation of cluster $Cu_8(\mu_8\text{-Cl})[Se_2P(O^iPr)_2]_6(PF_6)$ with atom-labeling scheme. The isopropoxyl groups are omitted for clarity.

The average Cu−Cu distance is 3.15 Å which is comparable to cluster **1**. In the structure of cluster **2**, six Cu−Cl bonds have the same distance, 2.674 Å, with two longer Cu−Cl bonds along the C_3 having a distance of 2.878 Å. The Se−Cu distances range between 2.383 and 2.400 Å. The P−Se distances are in the range 2.169−2.176 Å with an average of 2.172 Å. The Se···Se bite distance is 3.801 Å, and the Se−P−Se angle is 122.1°. The Se−Cu−Se angles range from 117.34° to 119.67°. The average of the Cu−Cl−Cu angles is 70.34°.

Compound **3** crystallizes in the monoclinic space group *C*2/*c*. Four copper atoms are found in the asymmetric unit with the Cl(1) atom located in the center of inversion (Figure 3). The average Cu−Cu distance is 3.14 Å. The Cu−Cl bond lengths lie in the range 2.691−2.743 Å with an average of 2.72 Å. The Cu−Se distances vary from 2.368 to 2.394 Å. The P−Se distances range from 2.165 to 2.184 Å. The average Se···Se bite distance is 3.811 Å, and the average Se−P−Se angle is 122.17°. The Se−Cu−Se angles range from 116.83° to 120.0°. The Cu−Cl−Cu angles lie in the range 69.41−72.03°, and the average is 70.53°.

There are two more examples with the chloride ion positioned in the center of the M_8 cage. The structure of $[(\mu_2\text{-Cl})Cd_8(SCH_2CH_2OH)_{12}Cl_3]$ which has an oblate Cd_8 hexahedron (compressed along the C_3 rotational axis) is reported by Dance et al.[9d] Besides the two normal Cd−Cl bond lengths which averaged 2.69 Å, the other six cadmium atoms are further distant at 3.58 Å. The central chloride ion is coordinated to only four cadmium atoms[7a] in the cluster of $[ClCd_8\{SCH(CH_2CH_2)_2N(H)Me\}_{16}]^{15+}$, and the Cd−Cl distances averaged 2.51 Å. Both $\{Ag_8(Cl)[Se_2P(OR)_2]_6\}(PF_6)$ and $\{Ag_8(Cl)[Se_2P(OR)_2]_6Cl\}_\infty$ have been characterized, and the details will be the subject of a subsequent report.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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