Metal dialkyl diselenophosphates:[1] a rare example of co-crystallization with clusters, $Ag_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$ and $Ag_6[Se_2P(OPr^i)_2]_6$, superimposing in a trigonal lattice†

C. W. Liu,*[a] Iu-Jie Shang,[a] Ju-Chung Wang[b] and Tai-Chiun Keng[b]

[a] *Department of Chemistry, Chung Yuan Christian University, Chung-Li, Taiwan 320, R. O. C.*
E-mail: chenwei@cchp01.cc.cycu.edu.tw
[b] *Department of Chemistry, Soochow University, Taipei, Taiwan 111, R. O. C.*

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A remarkable co-crystallization in which two neutral clusters, $Ag_8(Se)[Se_2P(OPr^i)_2]_6$ and $Ag_6[Se_2P(OPr^i)_2]_6$, superimpose along the three-fold axis in the trigonal lattice and share a common $Ag_6[Se_2P(OPr^i)_2]_6$ unit, is reported.

Molecular cubic clusters encapsulating main-group elements are very rare[2] and they are particularly interesting from the general point of view of bonding.[3] Previously we reported the first discrete selenide-centered Cu^I cubic cluster containing diselenophosphate ligands (dsep), $\{Cu_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6\}$.[4] To extend our research efforts in centered cubic cluster synthesis, herein, we report the synthesis of silver analogues and uncover an extremely rare example of co-crystallization, $Ag_8(Se)[Se_2P(OPr^i)_2]_6$ and $Ag_6[Se_2P(OPr^i)_2]_6$ share a common $Ag_6[Se_2P(OPr^i)_2]_6$ unit and have equal occupancies along the three-fold axis of the trigonal lattice. Co-crystallization of organic compounds is a common phenomenon[5] and recently it has been used to resolve the racemic 1,1′-bi-2-naphthol.[6] In organometallic chemistry many anion–cation pairs[7] as well as two neutral cluster molecules[8] in the same crystal have also been recognized. In inorganic compounds, two or three components can share the same metal core with minute differences in the composition of peripheral ligands. The most recent example is $[NEt_4]_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$, a dimeric molybdenum polyselenide containing a $Mo_2O_2(\mu\text{-}Se)_2$ core, reported by Mak and Guo.[9] To our knowledge, a co-crystallization as revealed in the superposition of Ag_8 and Ag_6 clusters which share a common $Ag_6[Se_2P(OPr^i)_2]_6$ unit is unprecedented.

Treatment of $NH_4Se_2P(OPr^i)_2$ (105 mg, 0.3 mmol) with $Ag(MeCN)_4PF_6$ (62.5 mg, 0.15 mmol) in CH_2Cl_2 (30 mL) at −50 °C resulted in a yellow solution after 12 h of stirring. After evaporation under vacuum, the residue was re-dissolved in 30 mL of hexanes from which a white precipitate was formed within a few minutes at ambient temperature (*ca.* 12% yield based on Ag). Upon dissolving the white precipitate in $CDCl_3$ a singlet at δ 72.7 (J_{PSe} = 654 Hz) flanked with selenium satellites was observed in the ^{31}P NMR spectrum while a doublet at δ 147 (J_{PSe} = 654 Hz) was observed in the ^{77}Se NMR spectrum.‡ These data implied that all dsep ligands are equivalent in solution. In order to understand the detailed structure of the isolated species, a single crystal X-ray diffraction analysis was undertaken and revealed a remarkable co-crystalline structure.§

The crystal structure of $\{Ag_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6\}_{0.5}\{Ag_6[Se_2P(OPr^i)_2]_6\}_{0.5}$ contains $Ag_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6$ and $Ag_6[Se_2P(OPr^i)_2]_6$ with equal occupancy, sharing the same $Ag_6[Se_2P(OPr^i)_2]_6$ unit. They are alternately distributed along the three-fold axis of the trigonal lattice. The thermal ellipsoid drawings (50% probability) of the octanuclear and hexanuclear silver clusters are depicted in Fig. 1 and 2, respectively. The six silver atoms of the latter form a slightly compressed octahedron with S_6 point group symmetry. This octahedron consists of two uncapped, equilateral triangles and six isosceles triangles in which each triangular face is bridged by a diselenophosphate ligand in a 'trimetallic triconnective'[10] (μ_2, μ_1) coordination mode. Silver–silver distances of 4.649(2) and 3.3578(8) Å within the isosceles triangles are observed in the hexanuclear silver cluster. Thus, the mean distance between the two uncapped Ag_3 triangles through which the three-fold axis passes is 2.0175 Å, whereas, that between two *trans* occupied Ag_3 planes is 3.3522 Å. Each silver atom of the octahedron is coordinated to three selenium atoms of three different ligands. The average Ag–Se(dsep) bond length is 2.6209(8) Å and Se–Ag–Se bond angles range from 115.80(2) to 122.62(3)°. In the octanuclear cluster, the eight silver atoms are arranged at the corners of an almost regular cube in which each square face of the cube is bridged by a dsep ligand exhibiting a 'tetrametallic tetraconnective'[10] (μ_2, μ_2) coordination mode. The coordination environment around each silver atom of the cube is very similar to that observed in the octahedron aside from the interaction to the central selenide anion. Hence two different bond lengths, 2.714(2) and 2.8675(6) Å, are observed between the central selenium atom and peripheral silver atoms so that a slightly compressed cube is observed along the three fold axis.

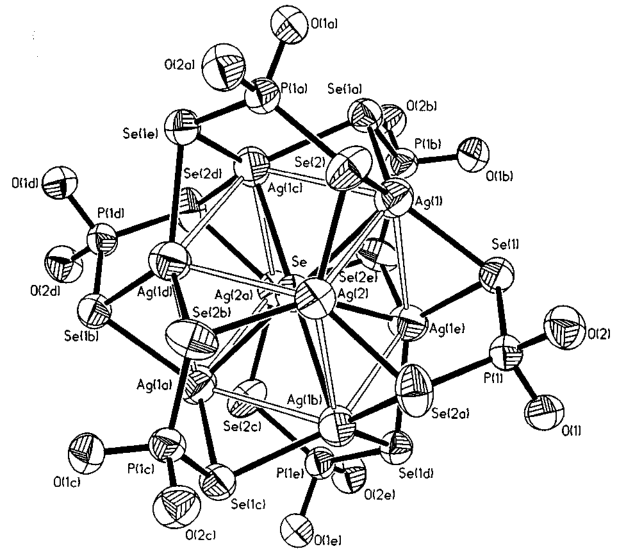

Fig. 1 Thermal ellipsoid drawing (50% probability) of $Ag_8(Se)[Se_2P(OPr^i)_2]_6$. The isopropyl groups are omitted for clarity. Selected bond lengths(Å) and angles(°): Se–Ag(2) 2.714(2), Se–Ag(1) 2.8675(5), Se(1)–Ag(1) 2.6236(8), Se(1)–Ag(1e) 2.6330(9), Se(2)–Ag(1) 2.6062(9), Se(2)–Ag(2) 2.5349(9), Ag(1)–Ag(2) 3.1800(12), Ag(1)–Ag(1e) 3.3578(8), Se(1)–P(1) 2.174(2), P(1)–O(1) 1.575(5), P(1)–O(2) 1.576(5); Ag(2a)–Se–Ag(1) 110.595(12), Ag(2)–Se–Ag(1) 69.403(12), Ag(1)–Ag(2)–Ag(1b) 93.94(4), Ag(1c)–Ag(1)–Ag(1e) 87.62(2), Ag(2)–Ag(1)–Ag(1c) 89.13(2).

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† Dedicated to Professor John P. Fackler, Jr. on the occasion of his 65th birthday.

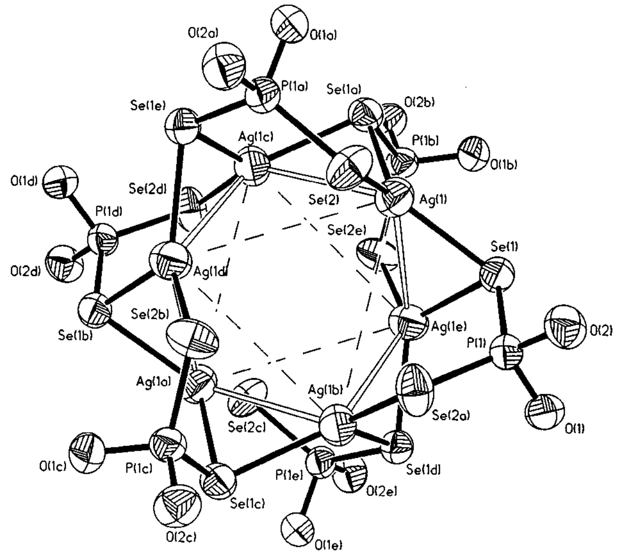

Fig. 2 Thermal ellipsoid drawing (50% probability) of $Ag_6[Se_2P(OPr^i)_2]_6$. The isopropyl groups are omitted for clarity. Selected bond lengths(Å) and angles(°): Ag(1)–Ag(1b) 4.649(2); Se(1)–Ag(1)–Se(2) 122.62(3), Se(1)–Ag(1)–Se(1a) 115.80(2), Se(2)–Ag(1)–Se(1a) 117.37(3), Se(1)–P(1)–Se(2a) 121.33(7).

Consequently a 0.1778 Å difference is seen in the Ag–Ag bond distances [3.3578(8) *vs.* 3.1800(12) Å]. The central selenide atom, in conjunction with the twelve selenium atoms of the ligands, forms a body-centered icosahedron. To our knowledge this geometry has never previously been observed in silver clusters.

An octahedral metal skeleton is commonly observed in hexanuclear silver clusters containing chalcogenide-donor ligands such as in $\{Ag_6(S_2CNPr^n{}_2)_6\}$,[11] $\{Ag_6[S(O)-(CNPr^n)_2]_6\}$,[12] $\{Ag_6[S_2P(OPr^i)_2]_6\}$[13] and $[NMe_4]_6-[Ag_6(i\text{-MNT})_6]$ [i-MNT = $S_2CC(CN)_2{}^{2-}$].[14] All six bridging sulfur atoms in these clusters are located on the two uncapped Ag_3 triangles while the terminally coordinated sulfur (or oxygen) atoms are in the belt positions of an octahedron.[13] Thus the Ag_6S_{12} (or $Ag_6S_6O_6$) core in these clusters has an idealized D_{3d} point group symmetry.[13] The S_6 point group symmetry found in the $Ag_6[Se_2P(OPr^i)_2]_6$ cluster results from the differences in bridging selenium atom positions in comparison with the bridging sulfur atom positions in $Ag_6[S_2P(OPr^i)_2]_6$.[13] On the other hand, an octanuclear silver cluster with cubic geometry is extremely rare. Examples prior to the title compound are $[Ag_8(i\text{-MNT})_6]^{4-}$,[15] and $[Ag_9(SCH_2CH_2S)_6]^{3-}$,[16] where a silver atom resides inside an extremely distorted Ag_8 cube. Furthermore, the title complex is the first discrete silver homocubane containing an encapsulated chalcogenide anion. Previously only one example[17] of a chloride-centered Ag_8 cuboidal structure was known found in the central portion of a mixed-valence, mixed-metal cluster $[Ag^I{}_8Ni^{II}{}_6\{SCMe_2CH(NH_2)CO_2\}_{12}Cl]^{5-}$.

Since the ligand bridging mode between Ag_8 and Ag_6 clusters is different, two chemical shifts should be observed in the ^{31}P NMR spectrum. Instead a single resonance flanked with selenium satellites is observed over the temperature range 300–180 K. Since the true bond connectivities are virtually identical for the phosphorus center in these two clusters and the spatial orientation magnetically is also virtually identical for all phosphorus positions, the chemical shifts are not expected to be very different. Although this possibility can not be ruled out, the fast ligand dissociation in solution or extreme lability of Ag–Se bond is the most likely reason for the single signal. This is further corroborated by the absence of one-bond coupling to $^{107/109}Ag$ nuclei of the title complex in the ^{77}Se NMR spectrum in which only a doublet arising from the coupling to ^{31}P nuclei is observed. In fact, it has been reported from multinuclear NMR studies that silver complexes of group 16 donor ligands are much more labile than their group 15 analogues in solution.[18]

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Notes and references

‡ $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ72.7(J_{SeP} 654 Hz); ^1H NMR ($CDCl_3$), δ 1.37 [d, 72H, $CH(CH_3)_2$], 4.88 [m, 12H, $CH(CH_3)_2$]; $^{77}Se\{^1H\}$ NMR ($CDCl_3$), δ 147 (J_{SeP} 654 Hz). Anal. Calc. for $C_{36}H_{84}Ag_7O_{12}P_6Se_{12.5}$: C, 16.40; H, 3.19. Found: C, 16.97; H, 3.16%.

§ *Crystal data*: $C_{36}H_{84}Ag_7O_{12}P_6Se_{12.5}$, $[(C_{36}H_{84}Ag_8O_{12}P_6Se_{13})_{0.5}-(C_{36}H_{84}Ag_6O_{12}P_6Se_{12})_{0.5}]$, M = 2636.94; trigonal, space group $R\bar{3}$, a = 22.7866(12), b = 22.7866(12), c = 12.8738(9) Å , γ = 120°, V = 5788.9(6) Å^3, Z = 3, D_c = 2.269 Mg m^{-3}, $F(000)$ = 3720, μ = 7.800 mm^{-1}, T = 298(2) K.

The structure was solved by direct methods using the SHELXTL-PLUS software package,[19] and refined by full-matrix least squares on F^2. The site occupancies of Ag(2) and Se in special positions were initially set to unity. The U_{eq} of these two atoms are 0.128(1) and 0.118(2) which is nearly twice that of the averaged U_{eq} of other Ag and Se atoms. In addition, an unreasonably, high $wR2$ of 0.2996 was obtained. Therefore the site occupancy factors of Ag(2) and Se were tied and refined as a free variable. Final convergence resulted in site occupancies of 0.5. In addition, two carbon atoms of isopropyl groups were also found to be disordered and refined isotropically as an equal population model. Refinement converged to $R1 = 0.0382$ [$I > 2\sigma(I)$], $wR2 = 0.0992$ (all data) and GOF = 1.069 based on 114 variables and 2228 reflections. CCDC 182/1241. See http://www.rsc.org/suppdata/cc/1999/995/ for crystallographic files in .cif format.

1 See ref. 4 for preceeding paper.
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