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# $Ag_8Cl_2[Se_2P(OEt)_2]_6$: A rare example containing a combination of discrete clusters and chains†

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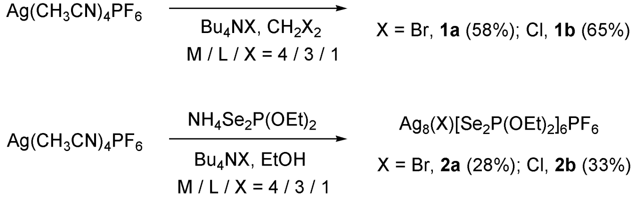
**The novel halide-centered $Ag^{I}_{8}$ cubic clusters containing diethyl diselenophosphato ligands are prepared and their solid state structures, a discrete unit or a one-dimensional chain, are dictated by the counter anions.**

More than a quarter of a century ago, Freeman and Birker reported a remarkable mixed-valence cluster, $Tl_5[Cu^{II}_6Cu^{I}_8(D\text{-}Pen)_{12}Cl]\cdot 55H_2O$.[1] This purple complex was made by the reaction of $CuCl_2$ and D-penicillamine at physiological pH and the structural result was used for the elucidation of the role of D-penicillamine in the chemotherapy for Wilson's disease. The structural characteristics of this mixed-valence cluster can be envisaged as a slightly distorted rhombic dodecahedral copper cage with the chloride position at its center. Later a similar framework has been extended to the isolation of several mixed-valence, mixed-metal clusters such as $[Cu^{II}_6Cu^{I}_8(SC(CH_3)_2COO)_{12}Cl]^{5-}$,[2] $[Cu^{II}_6Cu^{I}_8(SC(CH_3)_2CH_2NH_2)_{12}Cl]^{7+}$,[3] and $[Ni^{II}_6Ag^{I}_8(D\text{-}Pen)_{12}Cl]^{5-}$.[4] Nevertheless a rhombohedral silver cage having a chloride (or bromide) in the center was not known until Mingos and coworkers reported novel silver-alkynyl cage compounds, $[Ag_{14}(C{\equiv}C^tBu)_{12}X]Y$ (X = Cl, Br; Y = OH, $BF_4$).[5] The successful isolation of these cages has been attributed to the anion-templated syntheses[6] and argentophilic Ag···Ag interactions.[7] If we can envisage that the central portion of a regular dodecahedron is a cubic array made up of silver atoms, the question could be asked: Will the chloride (or bromide)-centered discrete $Ag^{I}_{8}$ cubic clusters be isolated? Following the successful characterizations of both halide-centered $Cu^{I}_{8}$ cubic clusters[8] and selenide-centered $M^{I}_{8}$ (M = Cu, Ag) cubes[9] comprising with diselenophosphato ligands, herein we present novel halide-centered $Ag^{I}_{8}$ cubic clusters where their structural characteristics reflect the central portion of the rhombohedral silver cage[5] and the mixed-metal cluster in $[Ag^{I}_8Ni^{II}_6(D\text{-}Pen)_{12}\ Cl]^{5-}$.[2] More intriguingly, the structural analysis for $Ag_8Cl_2[Se_2P(OEt)_2]_6$ is confirmed to be a rare example containing a combination of discrete clusters and chains where two chloride-centered $Ag^{I}_{8}$ cubes are connected by the chloride ion and form a polymeric chain.

Whereas the reaction of $NH_4Se_2P(OEt)_2$, $Ag(CH_3CN)_4PF_6$, and $Bu_4NX$ (X = Cl, Br) in a molar of 3 : 4 : 1 in $CH_2X_2$ afforded the halide-centered discrete $Ag^{I}_{8}$ cubic clusters, $\{Ag_8(X)[Se_2P(OEt)_2]_6\}(PF_6)$; the reaction in alcohol produced one-dimensional chain structures, $\{Ag_8(X)[Se_2P(OR)_2]_6X\}_\infty$ (Scheme 1). All clusters are well characterized by NMR, positive FAB mass spectrometry, and in case of **1a**, and **2b** by single crystal X-ray diffraction.‡ Despite the differences in counter anion, both discrete clusters and one dimensional chain have the same chemical shifts for dsep ligands in the solution NMR studies. Thus these imply that halide-centered discrete $Ag^{I}_{8}$ cubic clusters are present ubiquitously in solution. In addition, an expected molecular ion peak of $Ag_8(X)[Se_2P(OR)_2]_6^+$ for all complexes was identified from the FAB mass spectrum.



$$Ag(CH_3CN)_4PF_6 \xrightarrow[\substack{Bu_4NX,\ CH_2X_2 \\ M/L/X = 4/3/1}]{NH_4Se_2P(OEt)_2} \{Ag_8(X)[Se_2P(OEt)_2]_6X\}_n \quad X = Br,\ \mathbf{1a}\ (58\%);\ Cl,\ \mathbf{1b}\ (65\%)$$

$$Ag(CH_3CN)_4PF_6 \xrightarrow[\substack{Bu_4NX,\ EtOH \\ M/L/X = 4/3/1}]{NH_4Se_2P(OEt)_2} Ag_8(X)[Se_2P(OEt)_2]_6PF_6 \quad X = Br,\ \mathbf{2a}\ (28\%);\ Cl,\ \mathbf{2b}\ (33\%)$$

**Scheme 1**

The compound **1a** crystallized in the *R*(−)3*C* space group and revealed a bromide-centered discrete $Ag_8$ cube surrounded by six dsep ligands and a counter anion, $PF_6^-$. The threefold rotational axis passes through the Ag(1), Br(1), and Ag(4) atoms as revealed in Fig. 1. Eight silver atoms occupy at the corners of the cube with the Ag···Ag lengths in the range of 3.269 ~ 3.549 Å. Restricted by the crystallographic symmetries lack of inversion center, the Br(1) atom does not exactly locate in the center of the cube even though the distances between the Br(1) and two silver atoms on the $C_3$ are almost identical. [2.962(2) and 2.963(3) Å] The rest of the Ag–Br distances are in the range of 2.865(1) ~ 3.012(1) Å and are significantly shorter than those in $[Ag_{14}(C{\equiv}C^tBu)_{12}Br]^+$, which range between 3.148(2) and 3.313(1) Å. The Ag–Br–Ag angles fall in the range 67.53(3)–72.89(4)°. Thus the coordination geometry around the bromide ion is close to cubic which resembles the antifluorite type structure.[10] In addition, each face of the cube is

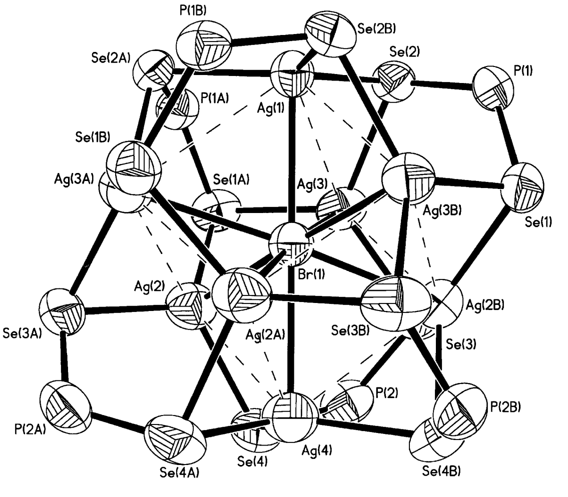


**Fig. 1** The thermal ellipsoid drawing (50% probability) of the cation of **1a**. The ethoxyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Br(1)–Ag(1), 2.962(2); Br(1)–Ag(4), 2.963(3); Br(1)–Ag(3), 3.012(1); Br(1)–Ag(2), 2.865(1); Ag(1)–Se(2), 2.601(1), Ag(4)–Se(4), 2.596(1); Ag(2)–Se(3A), 2.619(2); Ag(2)–Se(1A), 2.615(2); Ag(2)–Se(4) 2.640(2); Ag(3)–Se(2), 2.613(1); Ag(3)–Se(1A), 2.620(2); Ag(3)–Se(3), 2.595(2); Se(1)···Se(2), 3.818; Se(3)···Se(4), 3.809; Ag(2)–Br(1)–Ag(4), 69.64(4); Ag(1)–Br(1)–Ag(3), 72.89(4); Ag(2)–Br(1)–Ag(3) 72.05(3), Ag(2)–Br(1)–Ag(3a) 67.53(3); Ag(2B)–Se(1)–Ag(3B), 82.69(4); Ag(1)–Se(2)–Ag(3), 85.78(4); Ag(3)–Se(3)–Ag(2B), 77.63(4); Ag(2)–Se(4)–Ag(4), 78.96(5), Se(1)–P(1)–Se(2), 123.93(13); Se(3)–P(2)–Se(4), 124.20(15). Symmetry codes: A: −x+y, −x+1, z; B: −y+1, x−y+1, z.

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† Electronic supplementary information (ESI) available: analytical data for compounds **1** and **2**. See http://www.rsc.org/suppdata/cc/b3/b300887h/

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capped by a diselenophosphato ligand in a tetrametallic tetraconnective ($\mu_2$, $\mu_2$) coordination pattern.[11] The ligand bite distances average 3.814 Å. Ignoring the interaction between the central Br and peripheral silver atoms, each silver atom is trigonally coordinated by three selenium atoms having averaged Ag–Se bond distances of 2.608(5) Å.

The compound **2b**, a combination of a discrete cluster, $\{Ag_8(Cl)[Se_2P(OEt)_2]_6\}Cl$ (25%), and a polymeric chain, $\{Ag_8(Cl)[Se_2P(OEt)_2]_6Cl\}_\infty$ (75%), crystallizes in the *R*(−)3 space group. Whereas the chloride-centered discrete $Ag_8$ cube is iso-structural with the bromide-centered cube (**1a**) except for the different counter anions, $Cl^-$ and $PF_6^-$, the one-dimensional polymeric chain is formed via the bridging chloride ion, which connects two chloride-centered, elongated $Ag_8$ cubes. Their thermal ellipsoid drawings are displayed in Figure 2. In the discrete unit, two kinds of Ag–Cl distances are exhibited, 2.792(1) and 2.857(12) Å, so are the Ag···Ag distances, 3.255(7) and 3.232(2) Å. All Ag–Cl distances are significantly shorter than those observed in the mixed-metal cluster, $[Ni^{II}_6Ag^{I}_8(D\text{-}Pen)_{12}Cl]^{5-}$ ranging between 2.897(9) and 3.136(4) Å, and the rhombohedral cluster, which range between 3.116(2) and 3.297(1) Å. The Ag–Cl–Ag bond angles fall in the range 70.35(3)–70.71(3)° (70.53° is required for an idealized cubic arrangement). On the other hand, in the supramolecular chain structure two of the Ag···Cl lengths on the $C_3$ axis are extremely long, 3.635 Å, by comparison with the rest of Ag–Cl bond distances, 2.792(1). Thus an elongated cube is revealed. In fact the shortest Ag–Cl distance, 2.711(4), is exhibited on the bridging chlorine atom, Cl(2), and is within those reported.[12] The "bite" distance for dsep ligand is 3.779 Å which is slightly shorter than those in **1a**.

The combination of a discrete $Ag_8$ cube and a supramolecular chain in one structure, to the best of our knowledge, is unprecedented. Both the structures of $Cu_8Cl_2[S_2P(OEt)_2]_6$[13] and $\{Ag_8(S)[S_2P(OEt)_2]_6{\cdot}H_2O\}_\infty$[14] where the chlorine and oxygen of the water molecule are bridging a pair of elongated $Cu_8$ and $Ag_8$ cubes, respectively, also display a polymeric chain along the threefold rotational axis, but no indication of any existing metal framework disorder such as observed in **2b**. Very recently, the reduced rare-earth metal halides, $Ln_{13}Br_{18}B_3$ (Ln = Gd, Tb), were characterized as a combination of discrete and condensed clusters.[15]

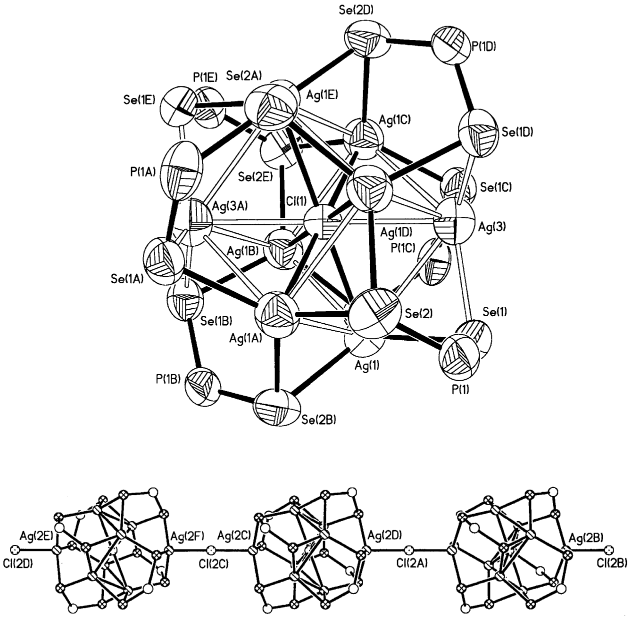

**Fig. 2** Top: The thermal ellipsoid drawing (50% probability) of the cation of **2b**. The ethoxyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cl(1)–Ag(1) 2.792(1), Cl(1)–Ag(3) 2.857(12), Ag(1)–Se(1) 2.589(2), Ag(1)–Se(2B) 2.605(2), Ag(1)–Se(2C) 2.607(2), Ag(3)–Se(1) 2.631(2), Se(1)···Se(2) 3.779, Ag(1)–Cl(1)–Ag(3) 70.35(3), Ag(1)–Cl(1)–Ag(1B) 70.71(3), Ag(1)–Se(1)–Ag(3) 77.2(2), Ag(1A)–Se(2)–Ag(1D) 76.63(6), Se(1)–P(1)–Se(2) 123.42(17). Symmetry codes: A: y+1, −x+y+1, −z; B: x−y, x−1, −z; C: −y+1, x−y−1, z; D: −x+2, −y, −z; E: −x+y+2, −x+1, z; F: −x+2, −y, −z+1. Bottom: The supramolecular chain structure of **2b**. Hatched, cross–hatched, dotted, and white spheres represent Ag, Se, Cl, and P atoms, respectively; the ethoxyl groups have been omitted for clarity. Ag(2)–Cl(2) 2.711(4)Å.

In conclusion, this study represents the syntheses and structures of novel halide-centered octametallic silver complexes containing the dsep ligands, in which solid state structures are dictated by the counter anions. Besides, in the cluster **2b** one of the silver atoms on the $C_3$ is disordered in two positions and results in a rare example containing a combination of discrete clusters and chains.

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## Notes and references

‡ Crystal and structure refinement parameters, **1a**·$0.5H_2O$: $C_{24}H_{61}Ag_8BrF_6O_{12.5}P_7Se_{12}$, $T$ = 298 K, *R*3(−)*C*, $Z$ = 12, $a$ = 18.046(1), $c$ = 75.366(12) Å, $V$ = 21256(4) Å$^3$, $R_1$ = 0.0536 [$I > 2\sigma(I)$], $wR_2$ = 0.1583 (all data). **2b**: $C_{24}H_{60}Ag_8Cl_2O_{12}P_6Se_{12}$, $T$ = 293 K, R(−)3, $Z$ = 3, $a$ = 21.008(3), $c$ = 12.694(2) Å, $V$ = 4851.8(1)Å$^3$, $R_1$ = 0.0612 [$I > 2\sigma(I)$], $wR_2$ = 0.1749 (all data). Data ($\theta$ = 2.40–25.04°, **1a**; $\theta$ = 1.94–25.00°, **2b**) were collected on a Siemens SMART (**1a**) and P4 (**2b**) using graphite monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation. Structures were solved by direct methods and refined against all data using SHELXTL 5.0. In **1a**, one of the ethoxyl chains, O1–C3–C1, is found disordered. A model with fixed C–C (1.55 Å) and O–C (1.45 Å) distances was introduced. In **2b** the Ag(2) atom was found disordered in two special positions and the final convergence resulted in site occupation factor of 0.75 and 0.25 for Ag(2) and Ag(3), respectively. Ignoring the disordered model, the $wR_2$ is 0.2173 (all data). CCDC 202721 and 202722. See http://www.rsc.org/suppdata/cc/b3/b300887h/ for crystallographic data in .cif or other electronic format.

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