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Novel silver diselenophosphate clusters: structures of $Ag_{10}(\mu_{10}$-Se)$[Se_2P(OEt)_2]_8$ and $\{Ag[Se_2P(OPr^i)_2]\}_6$†

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Two types of clusters, $[Ag(Se_2P(OR)_2)]_n$ (R = Et, $n = \infty$, **1a**; R = Pr^i, $n = 6$, **1b**) and $Ag_{10}(\mu_{10}$-Se)$[Se_2P(OR)_2]_8$ (**2a**, **2b**) were obtained from the reaction of stoichiometric amounts of $Ag(CH_3CN)_4PF_6$ and $NH_4Se_2P(OR)_2$ in $(C_2H_5)_2O$ at −20 °C. These new silver(I) clusters containing diselenophosphate (dsep) ligands were characterized by elemental analysis, NMR spectroscopy, fast-atom bombardment mass spectrometry (FAB-MS) for **2**, and, in the case of **1b**, and **2a**, by X-ray crystallography. The structure of **1b** reveals a hexameric aggregate $\{Ag[Se_2P(OPr^i)_2]\}_6$ where six silver atoms are located at the corners of a pseudohexagonal prism alternating with selenium atoms in two Ag_3Se_3 rings interconnected vertically by the P–Se bridges of the dsep ligands but not by additional Ag–Se bonding. The dsep ligands are organized in a paddle-wheel fashion about an Ag_6Se_6 pseudohexagonal prismatic core. The decasilver clusters **2** contain an encapsulated selenium atom in a distorted, *cis*-bicapped trapezoidal-prismatic geometry and are surrounded by eight dsep ligands having three different types of coordination pattern. Furthermore, the hypercoordinated selenide ion, Se^{2-}, in **2** was unequivocally identified by the solution $^{77}Se\{^1H\}$ NMR spectrum with a chemical shift centered at −1396 ppm.

Introduction

Owing to the ability of chalcogenide dianions (E^{2-}) to coordinate in various ways,[2] a diverse range of soluble transition metal aggregates may be stabilized. A noteworthy example is the structure of $Cu_{72}Se_{36}(PPh_3)_{20}$ in which the selenium coordination numbers range from four to ten.[3] For this and other mega clusters[4] Fenske and his coworkers suggest that the larger the cluster size the higher the average coordination number for chalcogenide atoms leading to more dense metal chalcogenide packing.

Fenske's results have prompted us to investigate the possibility of hypercoordination of chalcogenide ions by medium sized clusters. Furthermore the chemistry of hypercoordinated main group elements by gold atoms has been an active research topic in recent years since the seminal works of Schmidbaur.[5] Following our initial reports of the first selenide-centered Cu^I_8 cubic clusters containing dialkyl diselenophosphate ligands (dsep),[6] a novel nonacoordinate bridging selenido ligand in a tricapped trigonal-prismatic geometry was revealed in the undecacopper cluster of $Cu_{11}(\mu_9$-Se$)(\mu_3$-Br$)_3[Se_2P(OPr^i)_2]_6$.[7] Along this line we discovered that the coordination number of selenium can also be expanded to ten by taking advantage of argentophilic interactions[8] that promote the aggregation of Ag^I centers into various polyhedra, and a hitherto unknown geometry, a distorted *cis*-bicapped trapezoidal prism, was demonstrated. This was found in the decasilver clusters of the type $Ag_{10}(\mu_{10}$-Se)$[Se_2P(OR)_2]_8$ (R = Et, Pr^i), which are the major products from the reaction of stoichiometric amounts of $Ag(CH_3CN)_4PF_6$ and $NH_4Se_2P(OR)_2$ in $(C_2H_5)_2O$.

Experimental

NMR spectra were recorded on a Bruker AC-F200 and Avance-300 Fourier transform spectrometer. 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 performed on VG 70–250S mass spectrometer with nitrobenzyl alcohol as the matrix. Elemental analyses were obtained with a Perkin Elmer 2400 CHN analyzer. $[Ag(CH_3CN)_4]PF_6$ was prepared according to the literature reports.[9] All reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. Commercial CH_2Cl_2 and ROH (R = Et, Pr^i) were distilled from P_4O_{10} and Mg, respectively, before use. Hexanes and diethyl ether were distilled from Na/K.

$NH_4Se_2P(OR)_2$ (R = Et, Pr^i)

The preparation largely followed the method[10] reported by Zingaro *et al.* except using NH_3(g). A typical reaction method is as follows: P_2Se_5 (2.96 g) was suspended in alcohol, then refluxed for 2 h. The color changed from colorless to yellowish during the reaction. The yellowish filtrate was kept in the ice-bath, then bubbled through with NH_3(g) until the solution became grayish. The solvent was evaporated under vacuum, then a large amount of diethyl ether was added to afford white powder of $NH_4Se_2P(OR)_2$ (2.54 g). Thermally unstable, moisture and air-sensitive, colorless powders were obtained in 50–85% yields. Attempts to obtain elemental analyses were hindered by rapid decomposition. The $^{31}P\{^1H\}$ and ^1H NMR (D_2O) were as follows: Et, δ 88 (J_{SeP} = 720 Hz), δ 1.35 (d, $^3J_{HH}$ = 7 Hz, 6H; CH_3), 4.10 (m, 4H; CH_2); Pr^i, δ 82 (J_{SeP} = 720 Hz), δ 1.16 (d, $^3J_{HH}$ = 6 Hz, 12H; CH_3), 4.58 (m, 2H; CH).

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† Metal dialkyl diselenophosphates. Part 5. For preceding paper see ref. 1.

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Reaction of $Ag(CH_3CN)_4PF_6$ and $NH_4Se_2P(OR)_2$

Treatment of $NH_4Se_2P(OEt)_2$ (230mg, 0.78mmol) and $Ag(CH_3CN)_4PF_6$ (330 mg, 0.78 mmol) in $(C_2H_5)_2O$ (20 mL) at −20 °C afforded a brown solution after 24 h of stirring. The solvent was evaporated under vacuum, and the residue was washed with copious amounts of de-ionized H_2O. Then it was extracted with hexanes to afford a yellow solution and white precipitate. Diffusion of diethyl ether into a concentrated yellow solution gave yellow crystals of **2a** (140 mg) in 56% yield. The precipitate was re-dissolved in CH_2Cl_2 and colorless crystals of **1a** (30 mg) were obtained within a few days. Yield (10%). The isopropyl derivatives (**1b** and **2b**) were prepared in a similar way.

1a. Anal. Calc. for $C_4H_{10}AgO_2PSe_2$: C, 12.42; H, 2.61; found: C, 12.46; H, 2.60; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 77.4 (J_{SeP} = 661 Hz); $^{77}Se\{^1H\}$ NMR (38.168 MHz, $CDCl_3$): δ 114.6 (J_{SeP} = 660 Hz); ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (d, $^3J_{HH}$ = 7 Hz, 6H; CH_3), 4.16 (m, 4H; CH_2).

1b. Anal. Calc. for $C_{36}H_{84}Ag_6O_{12}P_6Se_{12}$: C, 17.37; H, 3.40; found: C, 16.90; H, 3.35; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 72.08 (J_{SeP} = 652 Hz); $^{77}Se\{^1H\}$ NMR (38.168 MHz, $CDCl_3$): δ 144.6 (J_{SeP} = 652 Hz); ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (d, $^3J_{HH}$ = 7 Hz, 36H; CH_3), 4.86 (m, 6H; CH).

2a. Anal. Calc. for $C_{32}H_{80}Ag_{10}O_{16}P_8Se_{17}\cdot 1/2(C_2H_5)_2O$: C, 11.92; H, 2.48; found: C, 12.35; H, 2.35; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 81.0 (J_{SeP} = 672 Hz); $^{77}Se\{^1H\}$ NMR (38.168 MHz, $CDCl_3$): δ 77.9 (d, J_{SeP} = 672 Hz, 16Se), −1396.0 (s); ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (t, $^3J_{HH}$ = 11 Hz, 48H; CH_3), 4.17 (m, 32H; CH_2); positive ion FAB-MS: m/z (m/z_{calcd}): 3109.7 (3110.8) $[M - dsep]^+$.

2b. Anal. Calc. for $C_{48}H_{112}Ag_{10}O_{16}P_8Se_{17}$: C, 15.95; H, 3.12; found: C, 15.95; H, 3.10; $^{31}P\{^1H\}$ NMR (81MHz, $CDCl_3$): δ 75.6 (J_{SeP} = 669 Hz); $^{77}Se\{^1H\}$ NMR (38.168 MHz, $CDCl_3$): δ 108.0 (d, J_{SeP} = 668 Hz, 16Se), −1395.4 (s); ^1H NMR (300 MHz, $CDCl_3$): δ 1.34 (d, $^3J_{HH}$ = 7 Hz, 96H; CH_3), 4.86 (m, 16H; CH); positive ion FAB-MS: m/z (m/z_{calcd}): 3307.2 (3306.5) $[M - dsep]^+$.

Crystallography

Single crystals were obtained directly from the reaction products. Data were collected on a Siemens SMART diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and were corrected for Lorentzian, polarization, and Ψ-scan absorption effects. The structure was solved by the use of direct methods and refinement was performed by least-squares methods on F^2 with the SHELXL-97 package,[11] incorporated in SHELXTL/PC V5.10.[12] All non-hydrogen atoms were refined anisotropically. In the structure of **2a**, a silver atom is disordered in two positions (Ag10 and Ag11) and treated in an equal population model. Several ethoxy groups were found disordered and a model with fixed C–C (1.550Å) and O–C (1.450Å) distances was introduced. Data collection and structural refinements are shown in Table 1.

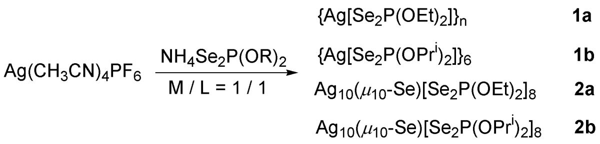
CCDC reference numbers 175725 and 175726.

See http://www.rsc.org/suppdata/dt/b1/b111095k/ for crystallographic data in CIF or other electronic format.

Results and discussion

In sharp contrast to the wide-ranging studies of phospho-1,1-dithiolato metal complexes, the corresponding selenium analogues do not receive much attention. This is partly due to the difficulty in synthesis and thermal instability of the diselenophosphate ligand. However we have found that the ammonium salts of the ligands are much easier to handle within a short period of time than the potassium salts reported previously.[10] Thus pure, colorless powders of $NH_4Se_2P(OR)_2$ can be obtained by bubbling anhydrous $NH_{3(g)}$ into the $HSe_2P(OR)_2$ at 0 °C. A single resonance flanked by a pair of selenium satellites in the $^{31}P\{^1H\}$ NMR spectrum together with the typical proton signals of the alkyl groups with exact integration ratios indicates the purity of the ligands.

Two types of clusters, $[Ag(Se_2P(OR)_2)]_n$ (R = Et, $n = \infty$, **1a**; R = Pr^i, n = 6, **1b**) and $Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OR)_2]_8$ (**2a**, **2b**) were obtained from the reaction of stoichiometric amounts of $Ag(CH_3CN)_4PF_6$ and $NH_4Se_2P(OR)_2$ in $(C_2H_5)_2O$ at −20 °C (Scheme 1). These new silver(I) diselenophosphate clusters were characterized by elemental analysis, NMR spectroscopy, fast-atom bombardment mass spectrometry (FAB-MS) for **2**, and, in the case of **1b**, and **2a**, by X-ray crystallography. All silver clusters are air stable, and, as crystalline solids, show no appreciable sensitivity to light.



Scheme 1

The single crystal X-ray diffraction analysis (Fig. 1) of **1b** reveals a hexameric aggregate $\{Ag[Se_2P(OPr^i)_2]\}_6$. Six silver atoms are located at the corners of a pseudohexagonal prism alternating with selenium atoms in two Ag_3Se_3 rings interconnected vertically by the P–Se bridges of the dsep ligands but not by additional Ag–Se bondings. The dsep ligands are organized in a paddle-wheel fashion about an Ag_6Se_6 pseudohexagonal prismatic core. The shortest Ag–Ag distances between the rings are in the range of 3.047(1)–3.152(2) Å, within twice the van der Waals radius of the silver atom. The Ag–Se bond distances are in the range of 2.594(1)–2.678(1) Å. The Ag–μ_2-Se–Ag and Se–P–Se angles are averaged at 104.23(4)° and 116.49(9)°, respectively. The Ag_6Se_{12} core revealed in **1b**, with idealized D_{3d} symmetry, displays a distinct geometrical arrangement compared to that of $Ag_6[Se_2P(OPr^i)_2]_6$, a S_6 point group symmetry, found in part of the co-crystallization structure of $\{Ag_8(\mu_8\text{-}Se)[Se_2P(OPr^i)_2]_6\}_{0.5}\{Ag_6[Se_2P(OPr^i)_2]_6\}_{0.5}$.[13] Indeed the structure is similar to that[14] of $Ag_6[S_2P(OPr^i)_2]_6$. The selected bond

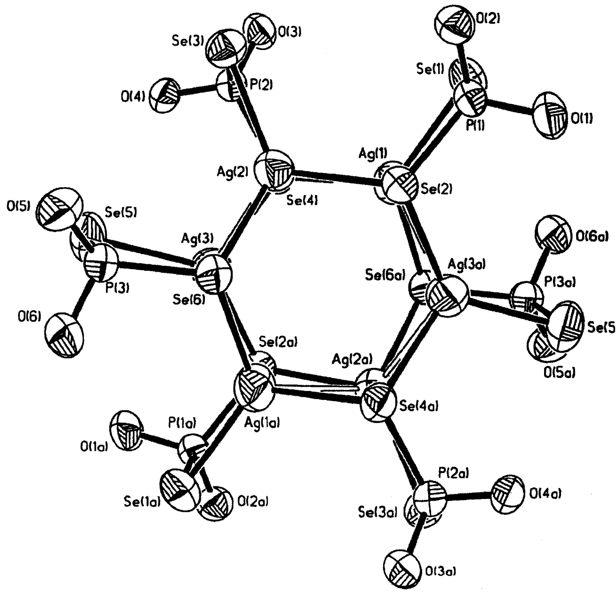


Fig. 1 The thermal ellipsoid drawing (50%) of $\{Ag[Se_2P(OPr^i)_2]\}_6$ down the C_3 axis of symmetry with isopropyl groups removed for clarity.

Table 1 Experimental data for the X-ray diffraction studies of compounds **1b** and **2a**

	1b	**2a**·1/2Et$_2$O
Formula	$C_{36}H_{84}Ag_6O_{12}P_6Se_{12}$	$C_{34}H_{85}Ag_{10}O_{16.5}P_8Se_{17}$
FW	2489.59	3426.80
T/°C	20	25
Space group	$P\bar{1}$	$C2/c$
a/Å	11.866(2)	49.153(3)
b/Å	12.484(2)	14.9447(9)
c/Å	14.572(3)	25.3060(15)
α/°	109.50(3)	—
β/°	104.69(3)	107.872(1)
γ/°	100.48(3)	—
V/Å^3	1882.3(6)	17692.0(2)
Z	1	8
μ/mm^{-1}	7.501	9.348
Measured/independent reflections/R_{int}	9119/6318/0.0478	24371/12086/0.0430
Final $R1^a$ ($wR2^b$)	0.047 (0.1143)	0.0714 (0.1703)

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

Table 2 Selected bond lengths (Å) and angles (°) for compound **1b** (e.s.d.s in parentheses)

Ag(1)–Se(1)	2.594(1)	Ag(1)–Se(6a)	2.617(2)
Ag(1)–Se(4)	2.648(1)	Ag(1)–Ag(2)	3.093(1)
Ag(1)–Ag(3a)	3.152(2)	Ag(2)–Se(3)	2.609(2)
Ag(2)–Se(6)	2.619(1)	Ag(2)–Se(2)	2.678(1)
Ag(2)–Ag(3)	3.047(1)	Ag(3)–Se(5)	2.595(2)
Ag(3)–Se(2a)	2.606(2)	Ag(3)–Se(4)	2.668(1)
Ag(3)–Ag(1a)	3.152(2)	Se(1)–P(1)	2.122(2)
Se(2)–P(1)	2.205(2)	Se(2)–Ag(3a)	2.606(2)
Se(3)–P(2)	2.138(2)	Se(4)–P(2)	2.183(2)
Se(5)–P(3)	2.120(3)	Se(6)–P(3)	2.186(2)
Se(6)–Ag(1a)	2.617(2)		
Se(1)–Ag(1)–Se(6a)	126.71(4)	Se(1)–Ag(1)–Se(4)	124.43(5)
Se(6a)–Ag(1)–Se(4)	95.25(5)	Se(3)–Ag(2)–Se(6)	129.09(4)
Se(3)–Ag(2)–Se(2)	122.34(5)	Se(6)–Ag(2)–Se(2)	93.91(4)
Se(5)–Ag(3)–Se(2a)	132.94(5)	Se(5)–Ag(3)–Se(4)	116.25(5)
Se(2a)–Ag(3)–Se(4)	100.32(4)	P(1)–Se(1)–Ag(1)	89.03(6)
P(1)–Se(2)–Ag(3a)	105.04(6)	P(1)–Se(2)–Ag(2)	111.54(7)
Ag(3a)–Se(2)–Ag(2)	103.90(5)	P(2)–Se(3)–Ag(2)	89.15(7)
P(2)–Se(4)–Ag(1)	110.87(7)	P(2)–Se(4)–Ag(3)	105.02(6)
P(3)–Se(5)–Ag(3)	89.95(7)	P(3)–Se(6)–Ag(1a)	105.09(8)
P(3)–Se(6)–Ag(2)	103.88(7)	Ag(1a)–Se(6)–Ag(2)	106.67(4)
Se(1)–P(1)–Se(2)	116.58(9)	Se(3)–P(2)–Se(4)	116.20(9)
Se(5)–P(3)–Se(6)	116.70(10)	Ag(1)–Se(4)–Ag(3)	102.12(5)

Symmetry transformations used to generate equivalent atoms: a $-x + 1, -y + 1, -z + 2$.

distances and angles are listed in the Table 2. Although the detailed structure of **1a** is not available to date, it is very likely to be iso-structural with the dithiophosphinato silver complex, $[AgS_2P(C_2H_5)_2]_\infty$, a polymeric species.[15]

An X-ray crystallographic study of the yellow crystals of **2a** established the stoichiometry $Ag_{10}SeL_8$·1/2Et$_2$O and the core structure, $Ag_{10}Se$, is illustrated in Fig. 2. The coordination geometry about the central Se(1) atom can be best described as a distorted *cis*-bicapped trapezoidal prism where two unequal, trapezoidal planes are defined by Ag(1)–Ag(2)–Ag(6)–Ag(9) and Ag(3)–Ag(4)–Ag(10)–Ag(7) and the heights (Agl–Ag3, Ag9–Ag7, Ag2–Ag4, Ag6–Agl0) of the prism are on average 3.060(3)Å with the remaining Ag(5) and Ag(8) atoms oriented in a *cis* position and acting as the two capping atoms. The edges of the trapezoidal planes are long, in the range of 2.977(3)–5.331 Å and 3.094(2)–3.915 Å, respectively. The angle Ag(5)–Se(1)–Ag(8) is 77.99(8)°. A pseudo two-fold axis going through the central Se(1) atom and bisecting the edges of Ag(6)–Ag(9) and Ag(3)–Ag(4) is present so that the two capping silver atoms are related by an idealized C_2 axis. Although the bond lengths of Ag(2)–Se(1), Ag(6)–Se(1) and Ag(7)–Se(1) (3.177, 3.172, 3.187 Å, respectively) are relatively long, they are much shorter than the sum of the van der Waals radii of 3.72Å.[16] The rest of Ag–Se(1) bond distances range from 2.631(2) to 2.923(2)Å and are comparable to those previously reported.[4] The $Ag_{10}Se$ core is further stabilized by the eight dsep ligands. As depicted in the Fig. 3 a total of three kinds of ligand bridging modes are observed: four (P1, P3, P4, P5) are tetrametallic tetraconnective bridging (μ_2, μ_2)[17] which are located on the four uncapped Ag_4 planes; three (P6, P7, P2) display a trimetallic triconnective (μ_2, μ_2) coordination pattern situated on the triangular faces defined by the Ag2–Ag5–Ag6, Agl–Ag5–Ag9, and Ag6–Ag8–Agl0 triangles; the last one (P8) bridges across the Ag7–Ag8 edge. *It is worth noting that the existence of three different bridging patterns of the dsep ligand simultaneously in one cluster is*

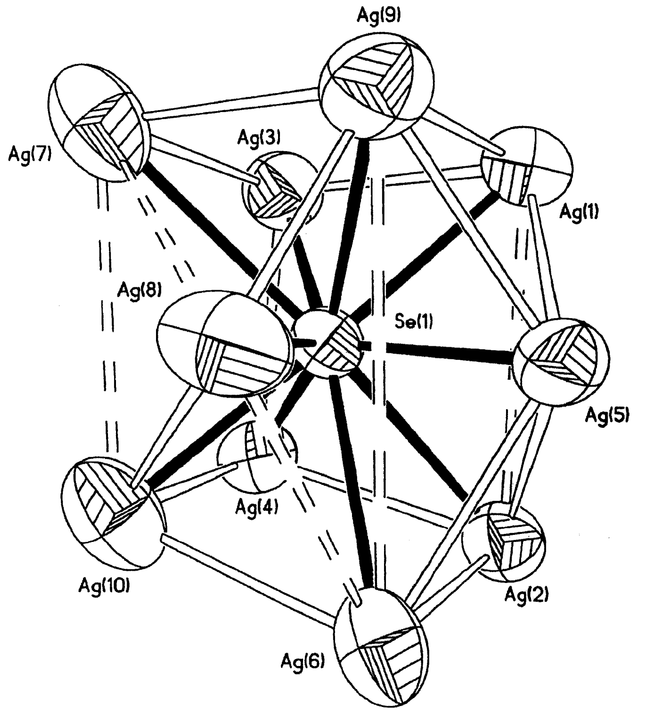


Fig. 2 Core structure of the cluster **2a**. The distances which are longer than the sum of the van der Waals radii are represented by broken lines. Selected bond lengths [Å]: Ag(1)–Se(1) 2.906(2), Ag(2)–Se(1) 3.177(3), Ag(3)–Se(1) 2.920(2), Ag(4)–Se(1) 2.934(2), Ag(5)–Se(1) 2.631(2), Ag(6)–Se(1) 3.172(3), Ag(7)–Se(1) 3.187(3), Ag(8)–Se(1) 2.792(2), Ag(9)–Se(1) 2.921(2), Ag(10)–Se(1) 2.744(4). Ag(1)–Ag(3) 3.025(2), Ag(7)–Ag(9) 3.142(3), Ag(2)–Ag(4) 3.040(2), Ag(6)–Ag(10) 3.026(5), Ag(1)–Ag(9) 2.977(3), Ag(2)–Ag(6) 2.979(2), Ag(3)–Ag(7) 3.094(2), Ag(4)–Ag(10) 3.175(4), Ag(3)–Ag(4) 2.985(2), Ag(5)–Ag(1) 2.963(2), Ag(5)–Ag(2) 3.378(2), Ag(5)–Ag(6) 3.236(2), Ag(5)–Ag(9) 3.144(2), Ag(8)–Ag(9) 2.956(3), Ag(8)–Ag(10) 3.106(4), Ag(7) ··· Ag(10) 3.915, Ag(1) ··· Ag(2) 4.001, Ag(9) ··· Ag(6) 5.331, Ag(8) ··· Ag(7) 3.621, Ag(8) ··· Ag(6) 3.580.

Table 3 Significant lengths (Å) and angles (°) for compound **2a** (e.s.d.s in parentheses)

Ag(1)–Se(16)	2.617(3)	Ag(1)–Se(4)	2.715(2)
Ag(1)–Se(2)	2.750(2)	Ag(2)–Se(4)	2.617(2)
Ag(2)–Se(3)	2.648(2)	Ag(2)–Se(6)	2.683(2)
Ag(3)–Se(10)	2.630(3)	Ag(3)–Se(2)	2.642(2)
Ag(3)–Se(8)	2.672(2)	Ag(4)–Se(6)	2.625(2)
Ag(4)–Se(13)	2.649(3)	Ag(4)–Se(8)	2.704(2)
Ag(5)–Se(15)	2.557(3)	Ag(5)–Se(17)	2.766(3)
Ag(6)–Se(9)	2.608(2)	Ag(6)–Se(7)	2.639(2)
Ag(6)–Se(3)	2.652(2)	Ag(7)–Se(11)	2.584(3)
Ag(7)–Se(10)	2.648(2)	Ag(7)–Se(5)	2.655(3)
Ag(8)–Se(14)	2.588(3)	Ag(8)–Se(9)	2.801(3)
Ag(9)–Se(5)	2.558(3)	Ag(9)–Se(17)	2.698(3)
Ag(10)–Se(13)	2.557(4)	Ag(10)–Se(7)	2.638(6)
Ag(10)–Se(12)	2.734(4)	Se(2)–P(3)	2.155(5)
Se(3)–P(6)	2.144(5)	Se(4)–P(1)	2.157(5)
Se(5)–P(3)	2.169(5)	Se(6)–P(5)	2.160(5)
Se(7)–P(5)	2.106(5)	Se(8)–P(1)	2.161(6)
Se(9)–P(2)	2.149(5)	Se(10)–P(4)	2.155(5)
Se(11)–P(8)	2.157(6)	Se(12)–P(2)	2.130(5)
Se(13)–P(4)	2.146(5)	Se(14)–P(8)	2.100(7)
Se(15)–P(6)	2.116(5)	Se(16)–P(7)	2.103(6)
Se(17)–P(7)	2.119(7)	Se(4) ··· Se(8)	3.771
Se(9) ··· Se(12)	3.680	Se(2) ··· Se(5)	3.778
Se(13) ··· Se(10)	3.760	Se(7) ··· Se(6)	3.704
Se(15) ··· Se(3)	3.663	Se(16) ··· Se(17)	3.637
Se(14) ··· Se(11)	3.706		
Ag(5)–Se(1)–Ag(10)	123.83(10)	Ag(5)–Se(1)–Ag(8)	77.99(8)
Ag(10)–Se(1)–Ag(8)	68.25(10)	Ag(5)–Se(1)–Ag(1)	64.47(5)
Ag(10)–Se(1)–Ag(1)	170.47(9)	Ag(8)–Se(1)–Ag(1)	120.20(7)
Ag(11)–Se(1)–Ag(1)	154.15(9)	Ag(5)–Se(1)–Ag(3)	126.82(7)
Ag(10)–Se(1)–Ag(3)	108.65(9)	Ag(8)–Se(1)–Ag(3)	134.57(8)
Ag(1)–Se(1)–Ag(3)	62.55(5)	Ag(5)–Se(1)–Ag(9)	68.69(6)
Ag(10)–Se(1)–Ag(9)	124.36(12)	Ag(8)–Se(1)–Ag(9)	62.26(6)
Ag(1)–Se(1)–Ag(9)	61.34(6)	Ag(3)–Se(1)–Ag(9)	89.84(6)
Ag(5)–Se(1)–Ag(4)	129.83(7)	Ag(10)–Se(1)–Ag(4)	67.96(9)
Ag(8)–Se(1)–Ag(4)	136.17(8)	Ag(1)–Se(1)–Ag(4)	103.36(6)
Ag(3)–Se(1)–Ag(4)	61.30(5)	Ag(9)–Se(1)–Ag(4)	151.06(7)
P(3)–Se(2)–Ag(3)	99.52(13)	P(3)–Se(2)–Ag(1)	109.21(13)
Ag(3)–Se(2)–Ag(1)	68.24(6)	P(6)–Se(3)–Ag(2)	103.23(14)
P(6)–Se(3)–Ag(6)	103.63(2)	Ag(2)–Se(3)–Ag(6)	68.42(6)
P(1)–Se(4)–Ag(2)	102.06(13)	Se(14)–P(8)–Se(11)	121.0(3)
P(1)–Se(4)–Ag(1)	103.84(14)	Ag(2)–Se(4)–Ag(1)	97.22(7)
P(3)–Se(5)–Ag(9)	107.93(15)	P(3)–Se(5)–Ag(7)	101.28(14)
Ag(9)–Se(5)–Ag(7)	74.17(8)	P(5)–Se(6)–Ag(4)	101.11(15)
P(5)–Se(6)–Ag(2)	102.07(12)	Ag(4)–Se(6)–Ag(2)	69.90(6)
P(5)–Se(7)–Ag(10)	121.33(16)	P(5)–Se(7)–Ag(6)	102.32(14)
Ag(10)–Se(7)–Ag(6)	70.12(10)	P(1)–Se(8)–Ag(3)	100.73(13)
P(1)–Se(8)–Ag(4)	104.42(13)	Ag(3)–Se(8)–Ag(4)	67.46(6)
P(2)–Se(9)–Ag(6)	99.97(13)	P(2)–Se(9)–Ag(8)	82.25(14)
Ag(6)–Se(9)–Ag(8)	82.83(7)	P(4)–Se(10)–Ag(3)	105.31(2)
P(4)–Se(10)–Ag(7)	105.13(14)	Ag(3)–Se(10)–Ag(7)	71.78(7)
P(8)–Se(11)–Ag(7)	99.50(18)	P(2)–Se(12)–Ag(10)	106.04(17)
P(4)–Se(13)–Ag(10)	126.10(19)	P(4)–Se(13)–Ag(4)	100.40(16)
Ag(10)–Se(13)–Ag(4)	75.18(11)	P(8)–Se(14)–Ag(8)	98.47(18)
P(6)–Se(15)–Ag(5)	95.41(16)	P(7)–Se(16)–Ag(1)	115.55(18)
P(7)–Se(17)–Ag(9)	91.27(17)	P(7)–Se(17)–Ag(5)	95.15(15)
Ag(9)–Se(17)–Ag(5)	70.21(7)	Se(4)–P(1)–Se(8)	121.8(2)
Se(12)–P(2)–Se(9)	118.7(2)	Se(2)–P(3)–Se(5)	121.84(18)
Se(13)–P(4)–Se(10)	121.9(2)	Se(7)–P(5)–Se(6)	120.48(19)
Se(15)–P(6)–Se(3)	118.6(2)	Se(16)–P(7)–Se(17)	119.0(2)

unprecedented and it has never been identified in any metal dialkyl dithiophosphates (dtp).[17] Thus, the two capping silver atoms associated with Ag9 are each trigonally coordinated by the three Se atoms, with the remaining silver atoms in a distorted tetrahedral environment, if the Ag–Ag interactions are not taken into consideration. The significant distances and angles are listed in the Table 3.

The Ag-μ_2Se–Ag angles deserve further mention. Most are in the range of 67.46(6)–74.17(8)° except Ag2–Se4–Ag1 and Ag6–Se9–Ag8, which are 97.22(7)° and 82.83(7)°, respectively. These can be rationalised by the lengths of the edges of the cluster in which 11 of 20 edges are bridged by selenium atoms. The Ag2–Ag1 distance is 4.001(2) Å and that of Ag6–Ag8 is 3.580 Å; these are both much longer than 3.40 Å which is twice the van der Waals radius of silver atom. The Se–P–Se angles are in the range of 118.6(2)–121.9(2) and are comparable with the "bite distance" of the dsep ligands ranging from 3.663 to 3.778 Å. Surprisingly these distances are similar despite the existence of three different types of bridging ligands.

According to repulsion theory which emphasizes the importance of the repulsion between the electron clouds rather than chemical bonding on the stereochemistry of coordination, the two most favorable arrangement of ten atoms around a central atom with two-fold symmetry are the bicapped square antiprism and the *cis*-bicapped cube (sphenocorona).[18] Remarkable examples of the former, besides those frequently observed in lanthanide and actinide metal complexes, are $[Rh_{10}P(CO)_{22}]^{3-}$,[19] $[Rh_{10}As(CO)_{22}]^{3-}$,[20] $[Ni_{10}C(CO)_{18}]^{2-}$,[21] and $[Rh_{10}S(CO)_{22}]^{2-}$ for

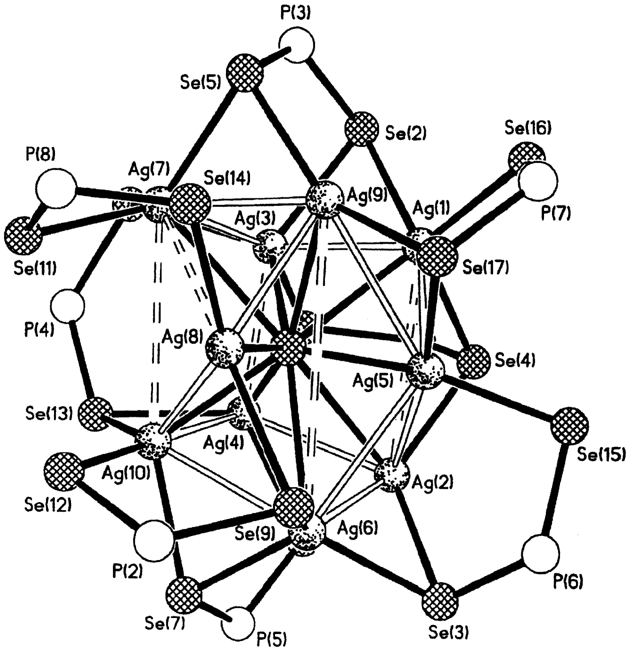


Fig. 3 Molecular structure of $Ag_{10}(\mu_{10}\text{-}Se)[Se_2P(OEt)_2]_{10}$. Shaded, cross-hatched, and white spheres represent Ag, Se, and P atoms, respectively; ethoxy groups have been omitted for clarity.

main group elements.[22] A representative of the latter is $K_4[U(C_2O_4)_4]\cdot 4H_2O$.[23] However, to the best of our knowledge the latter has never occurred for any main group element. The coordination geometry about the selenide anion reported in **2a** is indeed a distorted *cis*-bicapped cube.

The formation process of clusters **2** is not clear, but the polyhedral geometry may be the result of the compound maximizing metal ligand contacts and minimizing repulsions. The distorted *cis*-bicapped trapezoidal prismatic arrangement of the silver atoms around the central selenium ion may result from the nature of the bridging dialkyldiselenophosphate ligands which are bound in three different ways.

Spectroscopy

From the crystal structure determination of **2a** three different types of dsep ligands would be expected in the solution NMR spectra; instead only one ^{31}P NMR signal flanked with selenium satellites was found for **2** (**2a**: δ 81.0, J_{SeP} = 672 Hz; **2b**: δ 75.6, J_{SeP} = 669 Hz) at ambient temperature. Thus a variable temperature ^{31}P NMR experiment was performed. However, no change in the ^{31}P NMR signal was detected upon cooling to −80 °C. This suggests labile of Ag–Se bonding[24] and that the ligand bridging patterns mentioned above might not present in solution. This assumption is further supported by the solution ^{77}Se NMR spectra in which a doublet for the ligand (J_{SeP} = 672 and 668 Hz for **2a** and **2b**, respectively) was identified at room temperature despite the existence of several inequivalent selenium atoms. However, the central selenide ion in **2** was unequivocally proved by the solution $^{77}Se\{^1H\}$ NMR with a chemical shift centered at δ −1396. (Fig. 4) The chemical shift for Se^{2-} sites surrounded by four and seven Ag^+ ions in β-Ag_7PSe_6,[25] an archetype of the argyrodite family,[26] was reported at −817.2 and −1273.9 ppm, respectively, at 293 K by Taulelle *et al.*[27] and Eckert *et al.*[28] using a magic angle spinning (MAS) technique. Since the different isotropic shifts (δ_{iso}) were attributed to the number of silver atoms surrounding selenium where the electronic transfer from the s orbital of silver to the p orbital of selenium leads to the shielding of selenium,[27] the data reported here are convincing given the number of silver atoms surrounding the selenide ion in **2**, which seems to have the most negative ^{77}Se chemical shift reported so far.[29]

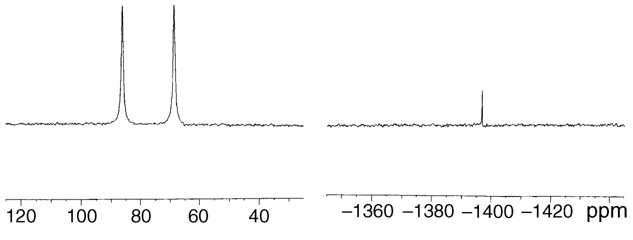


Fig. 4 $^{77}Se\{^1H\}$ NMR spectrum ($CDCl_3$) of cluster **2a**.

In conclusion, cluster nuclearities of six, and ten silver atoms were characterized along with a decacoordinated bridging selenido ligand in a distorted, *cis*-bicapped trapezoidal prismatic geometry. Both clusters exhibit a considerable Ag^I–Ag^I argentophilic interaction. Although the compositions and structures of **1** are not new and parallel the corresponding sulfur system, clusters **2** have never been identified in any silver complexes containing sulfur-donor ligands and this result further indicates that the structural chemistry of diselenophosphato metal complexes is more diverse than its lighter congener, namely dithiophosphates.[17] Surprisingly the reaction of clusters **2** with eight equivalents of Bu_4NI affords the undecasilver cluster, $Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OR)_2]_6$, which exhibits photoluminescence both in solid and solution states. This will be the subject of a subsequent report.

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