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Selenium-Centered, Undecanuclear Silver Cages Surrounded by Iodo and Dialkyldiselenophosphato Ligands. Syntheses, Structures, and Photophysical Properties

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Three clusters $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_6]$ (R = Et, **1**; ^iPr, **2**; ^2Bu, **3**) were isolated from the reaction of $[Ag(CH_3CN)_4](PF_6)$, $NH_4[Se_2P(OR)_2]$, and Bu_4NI in a molar ratio of 4:3:1 in CH_2Cl_2 in 47–55% yield. Compounds **1** and **2** can also be synthesized with high yield from the reaction of $Ag_{10}(Se)[Se_2P(OR)_2]_8$ with 8 equiv of Bu_4NI. In the positive fast atom bombardment mass spectra of **1**–**3**, two major peaks that correspond to the intact molecule with the loss of an iodide ion, $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_2\{Se_2P(OR)_2\}_6]^+$, and a diselenophosphate ligand, $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_5]^+$, were identified. Single-crystal X-ray analyses of **2** and **3** reveal an $Ag_{11}Se$ core stabilized by three iodide anions and six diselenophosphato ligands in a tetrametallic tetraconnective (μ_2,μ_2) coordination mode. The central core adopts the geometry of a 3,3,4,4,4-pentacapped trigonal prism with a selenium atom in the center. In addition, weak intermolecular Se···I interactions exist in **2** and form a one-dimensional polymeric chain structure. Furthermore, all compounds exhibit orange-red luminescence in both the solid state and solution.

Introduction

Encapsulation of a main-group element in the transition-metal framework continues to be an active research field in cluster syntheses.[1] The halide ions are dominated species in the encapsulated elements, and the coordination polyhedra for the halides can be planar,[2] tetrahedral,[3] octahedral,[4] and cubic.[5] Molecular cubic clusters encapsulating main-group elements are also interesting in view of their unusual bonding characteristics.[6] Several cubic clusters encapsulating S^{2-}, Cl^-, and Br^- are known for a dithiophosphate ligand.[7] For the corresponding diselenophosphate ligands, our research group has reported selenide-centered cubes, $[Cu_8(\mu_8\text{-}Se)\{Se_2P(O^iPr)_2\}_6]$[8] and $[Ag_8(\mu_8\text{-}Se)\{Se_2P(O^iPr)_2\}_6]$,[9] as well as halide-centered cubes, $[Cu_8(\mu_8\text{-}X)\{Se_2P(OR)_2\}_6](PF_6)$[10] and $[Ag_8(\mu_8\text{-}X)\{Se_2P(OR)_2\}_6](PF_6)$ (X = Cl, Br).[11] Recently, we have reported a novel nonacoordinated selenide in a tricapped

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trigonal-prismatic geometry in a Cu_{11} cluster where 11 copper atoms adopt a pentacapped trigonal-prismatic geometry.[10b,12] Clusters or cages having the geometry of a pentacapped trigonal prism are not common.[13] To extend our research efforts, we turned our attention to the silver element and uncovered a nonacoordinated selenide anion in a tricapped trigonal-prismatic geometry identified in the Ag_{11} cluster. The isolated undecanuclear silver cluster is a remarkable example of a 3,3,4,4,4-pentacapped trigonal-prisimatic silver framework. Besides, weak intermolecular Se···I interactions exist to form a one-dimensional polymeric chain structure in **2**. Se−I interactions are well-known because these complexes exhibit interesting charge-transfer properties.[14] Herein, we report the detailed syntheses, characterizations, and photophysical properties of undecanuclear silver clusters, $[Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3\{Se_2P(OR)_2\}_6]$ (R = Et, **1**; ^{i}Pr, **2**; ^{2}Bu, **3**). These are also the first reported metal clusters with diselenophosphato ligands that exhibit photoluminescent properties in both the solid state and solution.

Experimental Section

Materials and Measurements. All chemicals were purchased from commercial sources and used as received. Commercial CH_2Cl_2 and ROH were distilled from P_4O_{10} and magnesium, respectively. Hexane and diethyl ether were distilled from sodium. For the photophysical measurements, spectrograde CH_2Cl_2 (Aldrich) was used and distilled over P_4O_{10}. All reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The starting silver(I) complexes, $Ag(CH_3CN)_4(PF_6)$[15] and $[Ag_{10}(Se)\{Se_2P(OR)_2\}_8]$,[16] and the ligands, $NH_4Se_2P(OR)_2$ (R = Et, ^{i}Pr, ^{2}Bu),[17] were prepared according to the literature methods. The elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on Bruker AC-F200 and Advance-300 Fourier transform spectrometers. The $^{31}P\{^1H\}$ NMR is referenced externally against 85% H_3PO_4 ($\delta = 0$ ppm). Positive fast atom bombardment (FAB) mass spectra were carried out on a VG 70-250S mass spectrometer with nitrobenzyl alcohol as the matrix. UV−visible absorption spectra were recorded on a HP 8453 photodiode array spectrometer. Emission spectra were recorded on a Cary Eclipse B10 fluorescence spectrophotometer. The solutions were deoxygenated by purging with N_2 for 10 min and sealed before the measurements. Emission spectra were corrected for instrumental responses. Integrated emission quantum yields Φ_{em} were estimated relative to that of $Ru(bipy)_3^{2+}$ ($\Phi_{em} = 0.02$) as a reference. Excited-state lifetimes were measured by a home-constructed, time-resolved laser spectrometer. The instrument was equipped with a Quanta Ray GCR-170 pulsed Nd:YAG laser. The third harmonic (355 nm, fwhm = 10 ns) was used as an excitation source. Emission signals were focused into an ARC SpectraPro-500 double monochromator. The monochromator output was sent into a photomultiplier tube (Hamamatsu R928). The signal was further amplified by a homemade fast amplifier before being sent into a digitizer (LeCory 9350A). Decay traces were transferred to a personal computer loaded with the commercial software Origin 3.5. All experimental data were fitted by a single-exponential decay.

Preparation of $[Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3\{Se_2P(OR)_2\}_6]$ (R = Et, 1; ^{i}Pr, 2; ^{2}Bu, 3). Except for compound **3**, both compounds **1** and **2** can be prepared by following two general procedures. and a detailed preparation method is given for compound **2** for both methods.

Method a (1−3). $NH_4Se_2P(O^iPr)_2$ (1.58 g, 4.86 mmol) and Bu_4NI (0.60 g, 1.62 mmol) in CH_2Cl_2 (30 mL) at −60 °C were stirred for 30 min, and then $Ag(CH_3CN)_4PF_6$ (2.70 g, 6.47 mmol) was added. The solution mixture was stirred for 24 h at −60 °C under a dinitrogen atmosphere. After filtration, the filtrate was washed with deionized water (150 mL) several times to afford a yellow solution. Then the solvent was evaporated under vacuum, and the residue was washed with hexanes. This was collected by filtration, redissolved in diethyl ether, and dried under vacuum to obtain a yellow powder. Recrystallization from CH_2Cl_2/hexanes gave an orange-yellow crystal, 1.12 g of **2**. Yield: 55%.

Method b (1 and 2). Treatment of $Ag_{10}(Se)[Se_2P(O^iPr)_2]_8$ (655 mg, 0.18 mmol) with Bu_4NI (536 mg, 1.45 mmol) in CH_2Cl_2 (30 mL) resulted in an orange-yellow solution after 24 h of stirring. The filtrates were washed with deionized water several times and then were triturated with a copious amount of diethyl ether to afford yellow precipitates. The yellow powders were washed with hexanes and dried under vacuum. Yield: 90%.

Compound 1. Yield: ~45%, 0.785 g. Elem anal. Calcd for $C_{24}H_{60}Ag_{11}O_{12}P_6Se_{13}I_3\cdot 2Et_2O$: C, 11.08; H, 2.32. Found: C, 10.98; H, 2.35. FAB MS: m/z (m/z_{calcd}) 3193 (3193.6) $(M - I)^+$, 3041 (3041.6) $(M - dsep)^+$. ^1H NMR (CD_2Cl_2): δ 1.35 [t, 18H, OCH_2CH_3, $^3J_{HH} = 7$ Hz], 1.38 [t, 18H, OCH_2CH_3, $^3J_{HH} = 7$ Hz], 4.12 [m, 12H, OCH_2CH_3], 4.26 [m, 12H, OCH_2CH_3]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 83.4 [s, 6P, $J_{PSe} = 667$ Hz].

Compound 2. Yield: ~55%, 1.01 g. Elem anal. Calcd for $C_{36}H_{84}Ag_{11}O_{12}P_6Se_{13}I_3$: C, 12.39; H, 2.43. Found: 12.52; H, 2.49. FAB MS: m/z (m/z_{calcd}) 3360 (3361.7) $(M - I)^+$, 3183 (3181.6) $(M - dsep)^+$. ^1H NMR (CD_2Cl_2): δ 1.17 [d, 36H, $OCH(CH_3)_2$, $^3J_{HH} = 7$ Hz], 1.20 [d, 36H, $OCH(CH_3)_2$, $^3J_{HH} = 7$ Hz], 4.77 [m, 6H, $OCH(CH_3)_2$], 5.14 [m, 6H, $OCH(CH_3)_2$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 78.2 [s, 6P, $J_{PSe} = 660$ Hz].

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Table 1. Selected Crystallographic Data of **2** and **3**

	2	**3**
formula	$C_{36}H_{84}Ag_{11}I_3O_{12}P_6Se_{13}$	$C_{48}H_{108}Ag_{11}I_3O_{12}P_6Se_{13}$
fw	3488.60	3656.91
space group	$P2_1/n$	$P2_1/c$
a, Å	14.908(1)	23.398(7)
b, Å	23.342((1)	14.386(4)
c, Å	24.831(2)	30.173(9)
α, deg	90	90
β, deg	91.337(1)	99.347(4)
γ, deg	90	90
V, Å^3	8638(1)	10022(5)
Z	4	4
ρ_{calcd}, g cm^{-3}	2.682	2.424
λ(Mo Kα), Å	0.71073	0.71073
μ, mm^{-1}	9.136	7.881
T, K	298(2)	293(2)
R1[a]	0.0657	0.0562
wR2[b]	0.1236	0.1448

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

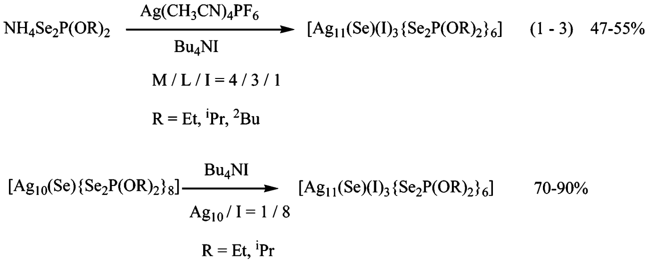
Compound 3. Yield: ~55%, 1.06 g. Elem anal. Calcd for $C_{48}H_{108}Ag_{11}O_{12}P_6Se_{13}I_3$: C, 15.77; H, 2.98. Found: C, 15.41; H, 2.88; FAB MS: m/z (m/z_{calcd}) 3529.9 (3529.7) (M − I)$^+$, 3323.2 (3321.6) (M − dsep)$^+$. ^{1}H NMR (CD_2Cl_2): δ 0.92 [m, 36H, OCH(CH$_3$)CH$_2$CH_3], 1.36 [m, 36H, OCH(CH_3)CH$_2$CH$_3$], 1.46 [m, 24H, OCH(CH$_3$)CH_2CH$_3$], 4.55 [m, 6H, OCH(CH$_3$)CH$_2$CH$_3$], 5.0 [m, 6H, OCH(CH$_3$)CH$_2$CH$_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 77.4 [s, 6P, P(OR)$_2$, J_{PSe} = 664 Hz], 77.1 [s, 6P, P(OR)$_2$, J_{PSe} = 659 Hz].

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

X-ray Crystallographic Procedures. The structures of **2** and **3** were obtained by the single-crystal X-ray diffraction technique. Crystals were mounted on the tips of glass fibers with an epoxy resin. Data were collected on a Siemens SMART CCD (charged-coupled device) diffractometer for compound **2**. Cell parameters were retrieved with *SMART* software[18] and refined with *SAINT* software[19] on all observed reflections [$I > 10\sigma(I)$]. Data reduction was performed with *SAINT*, which corrects for Lorentz and polarization effects and ψ-scan absorption. For compound **3**, data were collected at 293 K on a CCD 1000 and were corrected for Lorentz, polarization, and SADABS absorption effects. The structures of **2** and **3** were solved by the use of direct methods, and refinement was performed by least-squares methods on F^2 with the *SHELXL-97* package,[20] incorporated in *SHELXTL*/PC version 5.10.[21] Selected crystal data for compounds **2** and **3** are summarized in Table 1.

2. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexane. An orange-yellow crystal (0.44 × 0.36 × 0.24 mm) was mounted in the manner described above, and data were collected. A total of 23 382 reflections were collected, of which 12 367 were unique (R_{int} = 0.0385) and 8644 were observed with $I > 2\sigma(I)$. Hydrogen atoms were not included. A total of 10 carbon atoms out of 36 were disordered. Bond distances were constrained for disordered atoms and atoms connected to them during the structural refinement. These constraints are d(C−C) = 1.550 Å, d(O−C) = 1.450 Å, and d(O−C) = 2.50 Å. The final cycle of the full-matrix least-squares refinement was based on 8644 observed reflections, 26 restraints, and 715 parameters and converged with unweighted and weighted agreement factors of R1 = 0.0657 and wR2 = 0.1236, respectively. The largest residual peak and hole are +1.095 and −0.892 e/Å^3.

Scheme 1



3. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexane. An orange-yellow crystal (0.20 × 0.15 × 0.10 mm) was mounted, and data were collected. A total of 84 596 reflections were collected, of which 30 178 were unique (R_{int} = 0.0616) and 6681 were observed with $I > 2\sigma(I)$. Hydrogen atoms were added. The final cycle of the full-matrix least-squares refinement was based on 6681 observed reflections, 1 restraint, and 407 parameters and converged with unweighted and weighted agreement factors of R1 = 0.0562 and wR2 = 0.1448, respectively. The largest residual peak and hole are +1.410 and −1.327 e/Å^3.

Results and Discussion

Syntheses and Characterizations. Clusters [$Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_6$] (R = Et, **1**; ^{i}Pr, **2**; ^{2}Bu, **3**) were isolated from the reaction of $Ag(CH_3CN)_4PF_6$, $NH_4Se_2P(OR)_2$, and Bu_4NI in a molar ratio of 4:3:1 in CH_2Cl_2 at −60 °C (Scheme 1). The yields of the isolated product were 45%, 55%, and 55% for **1**−**3**, respectively. The clusters **1** and **2** were also obtained in much higher yield (70−90%) from the reaction of [$Ag_{10}(Se)\{Se_2P(OR)_2\}_8$] with 8 equiv of Bu_4NI in CH_2Cl_2 at ambient temperature. The reaction can be followed by the ^{31}P NMR studies, and the spectra were listed in the Supporting Information. The ^{31}P{^{1}H} NMR spectra of **1** and **2** display a singlet at 83.4 and 78.2 ppm accompanied by satellites 667 and 660 Hz, respectively. These results are slightly different from those of its isostructural, undecanuclear copper clusters,[10b,12] whose ^{31}P NMR patterns display a single resonance flanked with two sets of satellites arising from the inequivalence of the two selenium environments. However, two distinct sets of chemical shifts for the alkyl group were clearly identified in the ^{1}H NMR spectra for clusters **1** and **2**. The discrepancy further implies that two alkyl groups within one diselenophosphate (dsep) ligand cannot be interchanged by any symmetry elements (vide infra). Surprisingly, compound **3** exhibits two chemical shifts in the ^{31}P{^{1}H} NMR spectrum at 77.4 and 77.1 ppm with satellites 664 and 659 Hz, respectively, presumably due to the chiral center at the 2-butyl group of the dsep ligand in the cluster. Overall, the NMR data suggest that all six dsep ligands are equivalent in solution. Elemental analyses are in good agreement with the molecular formulation of clusters **1**−**3**. In the positive FAB mass spectra of **1**−**3**, two major peaks that correspond to the intact molecule with the loss of

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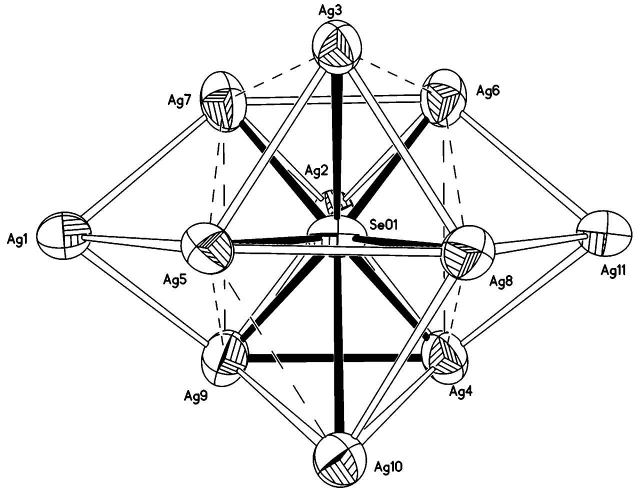

Figure 1. $Ag_{11}Se$ core unit of cluster **2**. The Ag−Ag distances that are longer than 3.4 Å are represented by the dashed lines.

Table 2. Selected Bond Distances (Å) and Angels (deg) for **2**

Ag3−Se01	3.091(2)	Ag9−Se01−Ag4	73.63(7)
Ag4−Se01	2.727(3)	Ag4−Se01−Ag6	87.80(8)
Ag5−Se01	2.766(3)	Ag6−Se01−Ag8	91.09(8)
Ag6−Se01	2.745(3)	Ag8−Se01−Ag7	135.44(6)
Ag7−Se01	2.764(3)	Ag5−Se01−Ag3	61.86(5)
Ag8−Se01	2.749(3)	Ag4−Se01−Ag3	144.08(10)
Ag9−Se01	2.696(3)	Se12−Ag1−Se1	118.91(8)
Ag4−I1	2.941(2)	Se12−Ag1−Se10	118.85(8)
Ag3−I2	2.774(2)	Se1−Ag1−Se10	119.69(8)
Ag5−I2	2.925(2)	Se3−Ag3−Se2	94.75(7)
Ag2−I3	2.789(2)	Se5−Ag4−Se8	103.02(8)
Ag1−Ag5	3.119(2)	Se11−Ag5−Se1	107.31(8)
Ag2−Ag4	3.285(2)	Ag10−I1−Ag9	63.95(5)
Ag3−Ag5	3.023(2)	Ag4−I1−Ag9	66.97(6)
Ag4−Ag9	3.250(3)	Ag3−I2−Ag8	65.41(5)
Ag5−Ag8	3.279(2)	Ag8−I2−Ag5	68.32(6)
Ag6−Ag7	3.217(3)	Ag2−I3−Ag6	65.52(5)
Ag8−Ag10	3.367(2)	Ag6−I3−Ag7	67.03(6)
Ag1−Se1	2.594(2)	Ag1−Se1−Ag5	72.70(7)
Ag2−Se8	2.622(2)	Ag3−Se2−Ag7	80.60(7)
Ag3−Se2	2.674(2)	Ag3−Se3−Ag6	79.79(7)
Ag4−Se5	2.673(3)	Ag11−Se4−Ag8	70.57(7)
Ag5−Se11	2.663(2)	Ag10−Se6−Ag8	78.07(7)
Ag6−Se7	2.656(3)	Ag11−Se7−Ag6	72.67(7)
Ag7−Se10	2.666(3)	Ag10−Se11−Ag5	81.17(7)
Ag8−Se4	2.709(3)	Ag1−Se12−Ag9	70.69(7)
Ag9−Se12	2.675(3)	Ag1−Se10−Ag7	71.81(7)
Ag10−Se6	2.649(3)	Se1−P1−Se2	119.8(2)
Ag11−Se4	2.584(2)	Se3−P2−Se4	120.6(2)
P−Se(av)	2.157	Se6−P3−Se5	121.4(2)
Se···Se(av)	3.757	Se8−P4−Se7	122.9(2)

an iodide ion, $[Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_2\{Se_2P(OR)_2\}_6]^+$, and a dsep ligand, $[Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3\{Se_2P(OR)_2\}_5]^+$, were identified.

Surprisingly, only a negligible amount of decanuclear Ag clusters, $Ag_{10}(Se)[Se_2P(OR)_2]_8$,[16] could be detected in the reaction mentioned above. However, if the reaction were performed with the molar ratio of 3:3:2 (M/L/I), the decanuclear silver clusters were isolated in ~35% yield in addition to the undecanuclear silver clusters. None of the iodo-centered Ag_8 cubic clusters could be isolated. This result further implies that the size of the iodo anion is too large to locate in the center of the Ag_8 cube.

Structure of $Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3[Se_2P(OR)_2]_6$ (R = ^{i}Pr, 2; ^{2}Bu, 3). The general structural features of clusters **2** and **3** are similar. A total of 11 silver atoms adopt the geometry of a 3,3,4,4,4-pentacapped trigonal prism with a nonacoordinated selenium atom in the center. The core unit $Ag_{11}Se$ of cluster **2** is shown in Figure 1. Selected bond lengths and angles of cluster **2** are given in Table 2.

Cluster **2** crystallizes in the monoclinic space group $P2_1/n$. A pseudo 3-fold axis passes through Ag1, Se01, and Ag11 atoms. A group of six silver atoms, Ag4, Ag8, Ag6, Ag5, Ag7, and Ag9, form an idealized trigonal prism, of which each rectangular and triangular face is further capped by an additional silver atom. The edges of the trigonal prism are in the range of 3.734−3.921 Å, while the heights (Ag4−Ag9, Ag8−Ag5, and Ag6−Ag7) are on average 3.249 Å. Shorter Ag−Ag distances are observed between the capping atoms and the prism; they are in the range of 3.023−3.463 Å. Alternatively, the undecanuclear silver cage can be delineated as a combination of nine Ag_4 butterflies, where the wing-tip positions are represented by five capping silver atoms, with each edge and height of the trigonal prism being hinges. The Ag−Se01 distances are quite diverse. Three of them, Ag3−Se01, Ag2−Se01, and Ag10−Se01 (3.091, 3.157, and 3.144 Å, respectively), are relatively long. However, they are much shorter than the sum of their van der Waals radii of 3.72 Å.[22] The rest of the Ag−Se01 bond lengths are in the range of 2.696(3)−2.766(3) Å and are comparable to the Ag−μ_5-Se distances [2.656(4)−2.898(4) Å] found in $Ag_{11}(\mu_5\text{-Se})(\mu_4\text{-Et}_2NCS_2)_3(\mu_3\text{-Et}_2NCS_2)_6$.[13c] The Ag−Se01−Ag angles are in the range of 61.85−144.10°. The central core is further stabilized by three iodides and six dsep ligands. The Ag_4 butterflies containing a silver atom on the C_3 axis are each capped by a dsep ligand having a tetrametallic tetraconnective (μ_2,μ_2) coordination pattern (Figure 2a).[23] The Ag−μ_2-Se distances lie in the range between 2.584 and 2.709 Å, and the Ag−μ_2-Se−Ag angles range between 70.57 and 81.17°. The P−Se distances average 2.158 Å. The Se···Se "bite" distances average 3.757 Å and are slightly shorter than those (3.805−3.818 Å) found in the Ag_8 cube.[11] The remaining three, where hinge positions are the heights of the prism, are each capped by a triply bridging iodide atom over an alternating set of three of the six triangular faces (Figure 2b). The average Ag−I bond distance is 2.880 Å. The Ag−I−Ag angles are in the range of 63.95−68.32°. Thus, two distinct coordination environments around silver atoms are observed: two on the C_3 axis are trigonally coordinated by three selenium atoms and the rest are tetragonally coordinated by three selenium atoms, two from desp ligands and one central selenide, and one iodine atom. Overall, because of the existence of three alternating triply bridging iodides, the idealized D_{3h} symmetry of the $Ag_{11}Se$ unit observed in Figure 1 is lowered to C_{3h}. Hence, all the dsep ligands are related to each other by the virtual $3/m$ symmetry.

Interestingly, there also exist weak intermolecular interactions between two selenium atoms of one cluster and the capping iodine atom of the adjacent molecule, forming a chainlike supramolecular structure. A packing diagram viewed down the pseudo C_3 axis is displayed in Figure 3.

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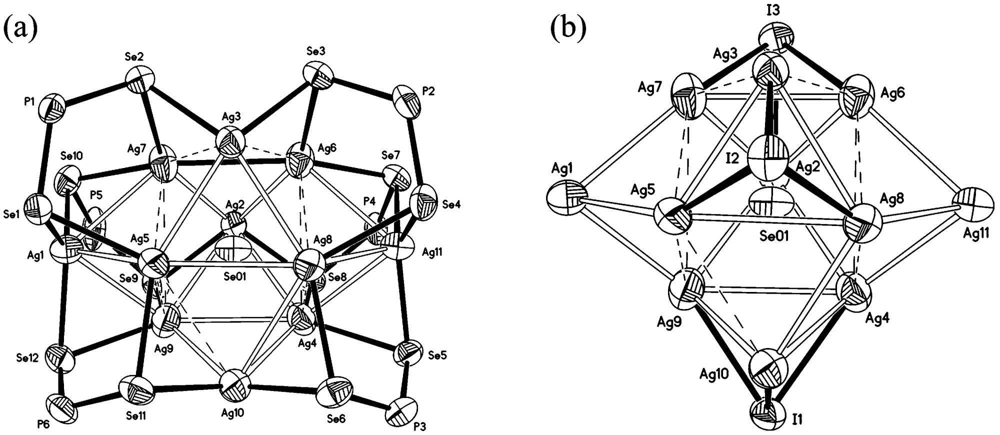

Figure 2. (a) Thermal ellipsoid drawing (30% probability level) of the $Ag_{11}Se$ core with the addition of six diisopropyldiselenophosphate ligands. The isopropoxyl groups are omitted for clarity. (b) Drawing of the $Ag_{11}Se$ core with the addition of three iodo ligands.

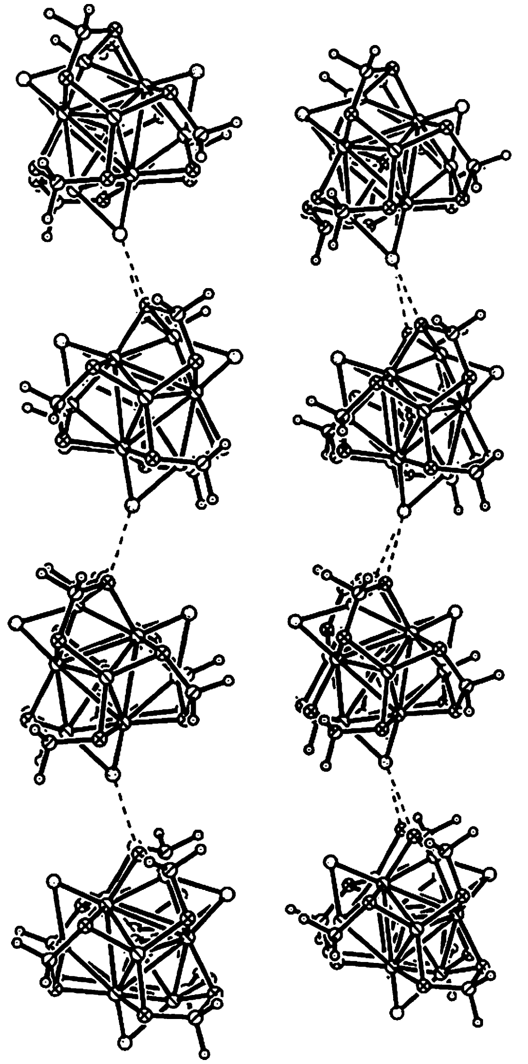

Figure 3. Molecular packing viewed down the pseudo C_3 axis reveals that a chainlike supramolecular structure is formed through weak intermolecular Se$\cdots$I contacts.

The interatomic distances between Se and I (4.015 and 3.997 Å) are slightly shorter than the sum of their van der Waals radii, 4.15 Å, and can be considered a weak secondary soft–soft interaction.[24]

Cluster **3** crystallizes in the monoclinic space group $P2_1/c$ and is isostructural with compound **2**. The edges of the trigonal prism are in the range of 3.614–3.978 Å, while the heights (Ag7–Ag9, Ag3–Ag8, and Ag2–Ag6) are on average 3.274 Å. Shorter Ag–Ag distances are also observed between the capping atoms and the prism (2.967–3.342 Å). The Ag–Se01 distances are between 2.700 and 3.134 Å, and the Ag–Se01–Ag angles are in the range of 61.16–149.20°. The Ag–μ_2-Se distances lie in the range between 2.580 and 2.693 Å, and the Ag–μ_2-Se–Ag angles range between 69.89 and 83.93°. The P–Se distances average 2.157 Å, and the Se–P–Se angle ranges between 119.75 and 120.78°. The Se$\cdots$Se "bite" distances average 3.737 Å. The average Ag–I bond distance is 2.887 Å. The Ag–I–Ag angles are in the range of 61.78–69.62°.

Clusters or cages having the geometry of a pentacapped trigonal prism are not common; examples containing main-group elements as capping atoms are $Ni_6(\mu_3\text{-}Se)_2(\mu_4\text{-}Se)_3(PPh_3)_6$[13a] and $[Cu_6(\mu_3\text{-}I)_2(\mu_4\text{-}I)_3I_6]^{5-}$.[13b] The undecanuclear silver clusters containing diethyldithiocarbamate ligands of the type $Ag_{11}(\mu_5\text{-}E)(\mu_4\text{-}Et_2NCS_2)_3(\mu_3\text{-}Et_2NCS_2)_6$ ($E = S^{2-}$, Se^{2-})[13c–e] are known where central S^{2-} or Se^{2-} is connected to five silver atoms in a trigonal-bipyramidal geometry. Our group has reported $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3[Se_2P(OR)_2]_6$ (R = Pr, ^iPr) and $Cu_{11}(\mu_9\text{-}Se)(\mu_3\text{-}Br)_3[Se_2P(OR)_2]_6$ (R = Et, Pr, ^iPr).[10b,12]

Absorption Spectra and Luminescence Properties. Electronic absorption spectra of compounds **1**–**3** were measured in dichloromethane at room temperature (Table 3). All compounds exhibited an intense absorption band in the ultraviolet region with a shoulder at around 316 nm (Figure 4). Presumably, these are ligand-based transitions overlapped with the transition of the $Ag{-}Se_2P(OR)_2$ moiety because the potassium salt of diethyldiselenophosphate absorbs at ~273 nm[17] and Ag-dsep at ~320 nm.[25] Besides, a lower-energy absorption band near 400 nm is observed. This band is also revealed in the decanuclear silver clusters of the type $[Ag_{10}(Se)\{Se_2P(OR)_2\}_8]$.[26] Thus, it is unlikely that this band is due to the iodo-to-metal charge transfer.

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Table 3. Photophysical Data for $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_6]$ (R = Et, **1**; ^iPr, **2**; ^2Bu, **3**)

compd	state (T/K)	λ_{max}/nm^a	λ_{max}/nm^b (τ_0/ns)	Stokes shift/cm^{-1}	λ_{max}/nm^c (ϵ/dm^3 mol^{-1} cm^{-1})	k_r	k_{nr}	quantum yield^d Φ_{em}
1	CH_2Cl_2 (298)	447	616 (56)	6137	399 (21 802)	1.78×10^4	1.78×10^7	0.000 997
	CH_2Cl_2 (77)	443	650					
	solid (298)	440	599 (258)					
	solid (77)	423	625					
2	CH_2Cl_2 (298)	446	617 (55)	6214	398 (16 125)	3.90×10^4	1.81×10^7	0.002 187
	CH_2Cl_2 (77)	439	650					
	solid (298)	423	627 (1309)					
	solid (77)	422	642					
3	CH_2Cl_2 (298)	450	618 (62)	6040	399 (19 490)	4.31×10^4	1.61×10^7	0.002 671
	CH_2Cl_2 (77)	421	647					
	solid (298)	393	616 (820)					
	solid (77)	422	624					

^{a} Excited at λ_{max}^{em}. ^{b} Emission. ^{c} Absorption. ^{d} Emission quantum yield measured at 298 K with reference to $Ru(bpy)_3^{2+}$, $\Phi_{em} = 0.02$.

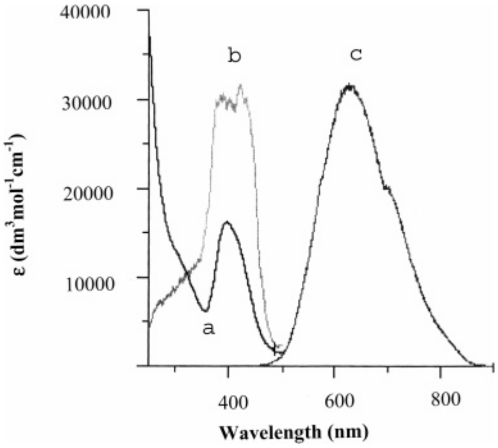

Figure 4. (a) Electronic absorption spectrum, (b) excited spectrum, and (c) emission spectrum of $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(O^iPr)_2\}_6]$ at 298 K.

Therefore, it is likely that the low-energy band can be assigned to the central selenide-to-metal charge transfer (LMCT; $Se^{2-} \rightarrow Ag^I$), which is close to the 438 nm reported in $Ag_{11}(\mu_5\text{-}Se)(\mu_4\text{-}Et_2NCS_2)_3(\mu_3\text{-}Et_2NCS_2)_6$.[13c] Attempts to detect the solvatochromatic behavior of these clusters failed because of their poor solubility in organic solvents other than CH_2Cl_2.

Luminescence studies of the compounds were done in the solid state and solution at room temperature as well as at 77 K. Excitation of clusters at $\lambda > 400$ nm produced orange luminescence. The photophysical data are summarized in Table 3, and spectra at 298 K for cluster **2** are shown in Figure 4. Table 3 also lists radiative (k_r) and nonradiative (k_{nr}) decay rate constants of the photoexcited state as calculated from the relationship $k_r = \phi_{em}/\tau_0$ and $k_{nr} = (1 - \phi_{em})/\tau_0$.

The emission bands centered at 616, 617, and 618 nm for **1**−**3**, respectively, in CH_2Cl_2 solutions are structureless and exhibit a slight red shift of ~30 nm of the emission maximum at 77 K. A general trend is also identified at the solid-state emission. The Stokes shift observed for the emission of **1**−**3** is ca. 6100 cm^{-1}, coupled with a long emissive lift time (1.3 μs for **2**), suggesting that it is from a spin-forbidden triplet emissive state. The excitation spectrum of **2** at 298 K in CH_2Cl_2 ($\lambda_{em} = 617$ nm) exhibits good overlap with the low-energy absorption band, indicating that the emission may arise from the central selenide-to-silver charge transfer. On the basis of the good σ-donating capability of the chalcogenide ion, the transitions are assigned to originate predominantly from a LMCT ($Se^{2-} \rightarrow Ag$) triplet excited state. Certainly, the probability of the mixing with a metal-centered (d−s/d−p) silver(I) state cannot be ruled out. Similar assignments have also been suggested in several polynuclear d^{10} metal chalcogenido systems.[27] It is of interest to realize that $Ag_{11}(\mu_5\text{-}Se)(\mu_4\text{-}Et_2NCS_2)_3(\mu_3\text{-}Et_2NCS_2)_6$ only luminesces in the solid state.

Conclusion

Undecanuclear silver clusters, $[Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_6]$ (R = Et, ^iPr, ^2Bu), possessing a 3,3,4,4,4-pentacapped trigonal-prismatic silver framework, were isolated. The central core, $Ag_{11}Se$, having a nonacoordinated selenium atom in a tricapped trigonal-prismatic geometry, was further stabilized by three iodides and six dsep ligands. Besides, weak intermolecular Se···I interactions exist and form a one-dimensional polymeric chain structure for **2**. The compound exhibits photoluminescent properties in both the solid state and solution.

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

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