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A μ_9-Iodide in a Tricapped Trigonal-Prismatic Geometry

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Supporting Information

ABSTRACT: Two luminescent, undecanuclear silver complexes $[Ag_{11}(\mu_9\text{-I})(\mu_3\text{-I})_3\{E_2P(O^iPr)_2\}_6](PF_6)$ [E = S (yellow), **1**; Se (orange), **2**], containing the first μ_9-iodine inscribed at the center of a pentacapped trigonal-prismatic silver skeleton, were reported.

The chemistry of hypercoordination or hypervalency for the main-group elements continues to be an active research field because of the unusual bonding characteristics that they exhibit[1] and their role in anion-templated synthesis.[2] Until now, no discrete molecules containing a μ_9-iodide have been reported.[1] In high oxidation state, iodine can bind from six to eight atoms.[3−7] In the formal 1− oxidation state, it can also bind up to six,[8,9] and even eight,[10,11] Lewis acidic centers. On the other hand, a few discrete chloride (or bromide)-centered M_8 (Ag^I_8 and Cu^I_8) cubic clusters are also known.[12] Generally, the anion coordination chemistry put forward prospects for supramolecular chemistry,[13] anion-assisted synthesis,[14] anionic binding and recognition,[15] and catalysis.[8,16]

Among mixed metal−halide functional materials, silver halides are some of the most attractive for not only their versatile coordination modes but also their potential applications in various fields.[17] Furthermore, whereas the coordination mode for the metal halides can be planar, tetrahedral, octahedral, and cubic,[18] the tricapped trigonal-prismatic geometry has never been observed in any halides. Indeed, it was quite unusual for main-group elements until we reported the first μ_9-selenide in $Cu_{11}(\mu_9\text{-Se})(\mu_3\text{-X})_3\{Se_2P(OR)_2\}_6$ (X = Br, I; R = Et, ^{i}Pr, Pr).[19] Thus, as part of our ongoing studies on the encapsulation of main-group elements by transition metals, recently we described full characterization of μ_9-selenide-encapsulated Ag^I_{11} clusters, $Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-X})\{Se_2P(OR)_2\}_6$ (X = Br, I; R = Et, ^{i}Pr, ^{2}Bu),[20] within a pentacapped trigonal-prismatic cluster topology. However, neither discrete M^I_8 clusters nor M^I_{11} clusters with an encapsulated iodide could be isolated. Thus, we have begun to investigate the use of convenient halide sources, and herein we report the syntheses, characterizations, and photophysical properties of the first μ_9-iodide undecanuclear silver clusters, $[Ag_{11}(\mu_9\text{-I})(\mu_3\text{-I})_3\{E_2P(O^iPr)_2\}_6](PF_6)$ (E = S, **1**; Se, **2**).

The reaction of $[Ag(CH_3CN)_4](PF_6)$ with $(NH_4)[E_2P(O^iPr)_2]$ (E = S, Se) in an 11:6 ratio for 1 h in a methanol solvent followed by the addition of 4 equiv of Bu_4NI led to the isolation of air- and moisture-stable discrete iodide-centered Ag^I_{11} clusters, $[Ag_{11}(\mu_9\text{-I})(\mu_3\text{-I})_3\{E_2P(O^iPr)_2\}_6](PF_6)$ (E = S, **1**; Se, **2**) in approximately equal yields.[21] The formulations of **1** and **2** were well characterized by elemental analysis, electrospray ionization mass spectrometry, and multinuclear NMR (^{1}H, ^{31}P, and ^{77}Se) spectroscopy.[21] The detailed molecular structure was unequivocally established by X-ray crystallographic analysis.[22] The ^{31}P NMR spectrum of **1** and **2** displays singlets (two sets of Se satellites, J_{PSe} = 645 and 646 Hz for **2**) at 103 and 74 ppm, respectively. Furthermore, the appearance of two doublets at 8.7 and 91.4 ppm in the $^{77}Se\{^1H\}$ NMR of **2** indicates magnetic nonequivalence of the Se atoms of the dsep ligands, and this is the characteristic for molecules having an idealized C_{3h} symmetry (vide infra).[19,20] As a result, two chemical shifts for the methine protons of each isopropyl group are identified in the ^{1}H NMR spectra of both compounds. The patterns of the mass spectra are similar for both clusters **1** and **2** (Figures S1 and S2 in the Supporting Information). For example, in compound **2**, a peak at m/z 3536 corresponds to the intact iodide-centered cluster cation. Also appearing in the mass spectrum is a peak at m/z 3719, which can be attributed to the replacement of one capping iodide by a dsep ligand, giving $[Ag_{11}I_3\{Se_2P(O^iPr)_2\}_7]^+$.

The solid-state structures of compounds **1** and **2** are analogous to $Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-X})_3\{Se_2P(OR)_2\}_6$ (X = Br, I; R = Et, ^{i}Pr, ^{2}Bu),[20] and the $Ag_{11}I$ core, which is similar to $Ag_{11}Se$, is stabilized by three iodides and six dichalcogenophosphate ligands, where 11 Ag atoms adopt a slightly distorted five-capped trigonal-prismatic geometry with an iodide in the center (Figure 1a). Six Ag atoms (Ag2, Ag3, Ag5, Ag2A, Ag3A, and Ag5A) occupy vertices of a trigonal prism, the five faces of which are further capped by an additional five Ag atoms (Ag4, Ag4A, Ag1, Ag6, and Ag7). Thus, 11 Ag atoms constitute a pentacapped trigonal prism (Figure 1b). The $Ag_{11}I$ core exhibits an idealized D_{3h} symmetry with a pseudo-C_3 axis passing through both Ag4 atoms, each capped triangular face of the prism, and the central iodide. Six Ag_4 butterflies, whose hinges are the edges of two triangular faces, are each capped by one dichalcogenophosphate ligand, and all of the phosphate ligands are connected to silver metals through sulfur (or selenium) in a tetrametallic tetraconnective (μ_2,μ_2) pattern (Figure 1a).[12,23] The other three Ag_4 butterflies, whose hinges are parallel to C_3, are each capped by a triply bridging iodide over an alternating set of three of the six triangular faces. The Ag−E (E = S, Se) bond distances are in the ranges 2.491(4)−2.543(4) and 2.585(2)−2.690(2) Å for compounds **1** and **2**,

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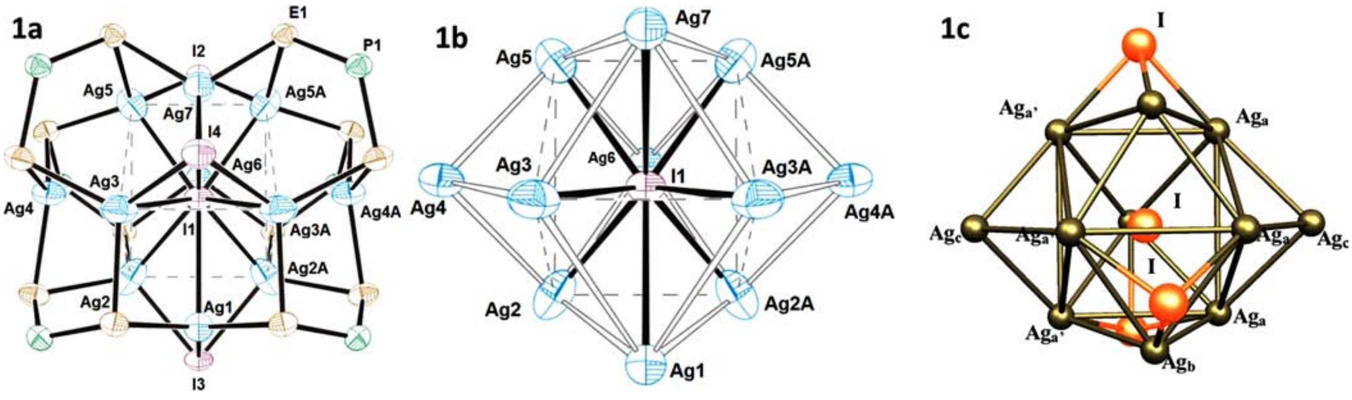

Figure 1. (1a) Molecular structures of **1** (E = S) and **2** (E = Se) (isopropoxy groups are omitted for clarity). Select interatomic distances (Å) of **1** {**2**}: Ag−S 2.491(4)−2.543(4), Ag−Se 2.585(2)−2.690(2), P−S 1.986(6)−2.030(6), P−Se 2.154(5)−2.197(5), Ag−μ_3-I 2.752(2)−2.786(3) {2.747(3)−2.825(2)}, I1−Ag1 3.152(2) {3.224(3)}, I1−Ag2 3.252(2) {3.059(3)}, I1−Ag3 3.152(2) {3.202(2)}, I1−Ag5 3.317(2) {3.069(2)}, I1−Ag6 3.195(3) {3.264(3)}, I1−Ag7 3.224(2) {3.324(2)}. (1b) $Ag_{11}I$ core unit of clusters **1** and **2**. (1c) $Ag_{11}(\mu_9\text{-I})(I_3)$ core of the optimized structure of $[Ag_{11}(\mu_9\text{-I})(\mu_3\text{-I})_3\{Se_2P(OH)_2\}_6]^+$ in its C_{3h} ground state.

respectively. The distances (3.602 and 3.709 Å for **1** and **2**, respectively) of capping atoms Ag4 and Ag4A on triangular faces of the prism from the central iodide I1 are much longer than the other nine I−Ag distances (3.152−3.298 Å for **1** and 3.059−3.324 Å for **2**), which lie in the range of Ag−I distances reported in the literature.[24] As a result, a novel μ_9-iodide in tricapped trigonal-prismatic geometry is revealed in the title compounds, and a clear view of the $Ag_{11}I$ core unit of both clusters (**1** and **2**) is shown in Figure 1b. Both Ag_{11} cages are also larger than those with a selenide in the center.[20] Thus, the silver skeleton in clusters **1** and **2** is more expanded because of the presence of a larger iodide at the center.

In order to understand the bonding in **1** and **2**, density functional theory calculations at the PBE0/Def2-TZVP level[25] have been performed on the model $[Ag_{11}(\mu_9\text{-I})(\mu_3\text{-I})_3\{Se_2P(OH)_2\}_6]^+$. Geometry optimization led to a C_{3h} true minimum similar to the X-ray structures of **1** and **2** (Figure 1c). The existence of nine bonding contacts involving the central iodide is attested by Ag_a−I and Ag_b−I distances of 3.301 and 3.273 Å, respectively, whereas the Ag_c−I distance is longer (4.079 Å). This is confirmed by the corresponding Ag−I Wiberg indices, which are 0.123 (Ag_a), 0.121 (Ag_b), and 0.024 (Ag_c). It is worth noting that the sum of the Ag−$I_{central}$ Wiberg indices (1.149) is similar to the sum of the Ag−$I_{capping}$ ones (1.124). The corresponding sums of the Mulliken overlap populations, 0.238 and 0.373, respectively, do not contradict this trend. The natural-bond-order charge of the central iodide (−0.66) is also consistent with a significant covalent component of the overall ionocovalent bonding although less than that in the non-acoordinated selenide analogue.[20]

Photophysical data for both complexes in the solid and solution states at 298 and 77 K are summarized in Table 1, and spectra at room temperature in solution are shown in Figure 2. The complexes display yellow (**1**) and orange (**2**) luminescence under UV irradiation with emission lifetimes in the microsecond range. Complexes **1** and **2** exhibit intense absorptions at 388 and 397 nm, respectively, with extinction coefficients larger than 10^4 dm^3 mol^{-1} cm^{-1}, indicating a charge-transfer transition. Additionally, a similar low-energy absorption band was also found in the analogous compound $[Ag_{11}(\mu_9\text{-Se})(\mu_3\text{-I})_3\{Se_2P(O^iPr)_2\}_6]$ (390 nm).[20] No significant shift while the central anion Se^{2-} was replaced by I^- is revealed. Previously, the theoretical investigations on selenide-centered Ag_{11} clusters affirmed that the low-energy absorptions as well as emissions were due to transitions from an orbital mostly of a selenophosphate ligand/central Se atom character to an orbital of silver character (ligand-to-metal charge transfer, LMCT), and a significant structural distortion associated with the loss of σ_h was revealed in the first excited triplet state due to the second-order Jahn−Teller effect.[20] Halides appear to have no effect in the spin-forbidden triplet excited state, and the great similarity in the absorption, excitation, and emission spectra

Table 1. Photophysical Data for 1 and 2

compd	state (T/K)	λ_{abs}/nm (ε/dm^3 mol^{-1}cm^{-1})	λ_{ex}/nm	λ_{em}/nm	lifetime (μs)
1	CH_2Cl_2(298)	388 (11000)	414	572	
	CH_2Cl_2 glass (77)		377	590	
	solid (298)		389	565	2.9, 0.8
	solid (77)		379	598	
2	CH_2Cl_2(298)	397 (13000)	438	600	
	CH_2Cl_2 glass (77)		420	636	
	solid (298)		438	592	1.7
	solid (77)		426	653	

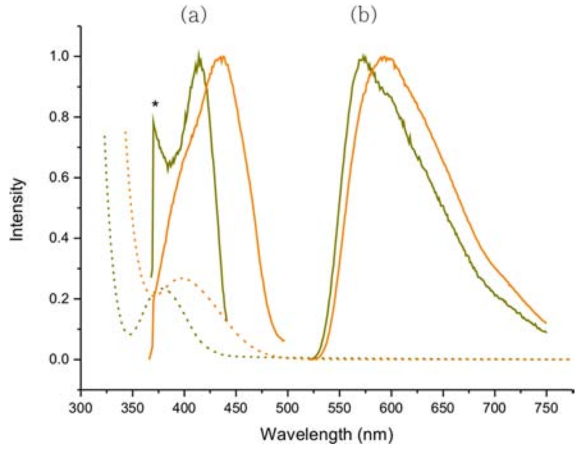

Figure 2. Normalized spectra of **1** (green) and **2** (orange). Electronic absorption spectrum (dashed line), (a) excitation spectrum, and (b) emission spectrum in CH_2Cl_2 at 298 K. (An asterisk denotes an instrumentation artifact.)

between $Ag_{11}(\mu_9\text{-}Se)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_6$ and $[Ag_{11}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{Se_2P(OR)_2\}_6](PF_6)$ suggests that the LMCT transition could be solely due to the Se atoms of a diselenophosphate. In addition, a blue shift observed in both absorption and emission spectra of **1** relative to **2** is in line with the energy of lone-pair orbitals of sulfur lower than those of selenium. Thus, the emission origin can be plausibly assigned as the chalcogen-to-silver charge transfer (LMCT) in the iodide-centered Ag_{11} clusters.

In conclusion, we have demonstrated two luminescent undecanuclear silver clusters containing an unusual μ_9-iodide in a tricapped trigonal-prismatic coordination environment. This rational synthetic methodology may open an avenue to tuning the phosphorescence wavelength by incorporating other transition metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file in CIF format [CCDC 857707 (**1**) and 857708 (**2**)] and computational details and Cartesian coordinates of $[Ag_{11}(\mu_9\text{-}I)(\mu_3\text{-}I)_3\{Se_2P(OH)_2\}_6]^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(21) **1**. Anal. Calcd for $C_{36}H_{84}Ag_{11}F_6I_4O_{12}P_7S_{12}$: C, 13.86; H, 2.71. Found: C, 13.87; H, 2.89. ESI-MS: *m/z* 2973 (M^+). ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, 72H, CH_3), 4.94 (m, 6H, CH), 5.09 (m, 6H, CH). ^{31}P NMR (121 MHz, CDCl3): δ 103.2 (s, 6P), −143.3 (septet, PF_6, $^1J_{PF}$ = 712 Hz). **2**. Anal. Calcd for $C_{36}H_{84}Ag_{11}F_6I_4O_{12}P_7Se_{12}$: C, 11.74; H, 2.30. Found: C, 11.88; H, 2.57. ESI-MS: *m/z* 3536.4 (M^+). ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, 36H, CH_3), 1.47 (d, 36H, CH_3), 4.93 (m, 6H, CH), 5.13 (m, 6H, CH). ^{31}P NMR (121 MHz, $CDCl_3$): δ 74.0 (s, 6P, $^1J_{PSe}$ = 645 Hz, $^1J_{PSe}$ = 646 Hz), −143.3 (septet, PF_6, $^1J_{PF}$ = 712 Hz). ^{77}Se NMR (57 MHz, $CDCl_3$): δ 8.7 (d, 6Se, $^1J_{SeP}$ = 650 Hz), 91.4 (d, 6Se, $^1J_{SeP}$ = 650 Hz).

(22) Crystal data for **1**: $C_{36}H_{84}Ag_{11}F_6I_4O_{12}P_7S_{12}$, $M = 3118.71$, $T = 296(2)$ K, orthorhombic, *Pbcm*, $a = 13.2137(8)$ Å, $b = 20.9757(11)$ Å, $c = 33.2416(18)$ Å, $V = 9213.5(9)$, $\mu = 4.068$, $Z = 4$. Final *R* indices [$I > 2\sigma(I)$]: R1 = 0.0644, wR2 = 0.1945. Crystal data for **2**: $C_{37.50}H_{87}Ag_{11}F_6I_4O_{12.50}P_7Se_{12}$, $M = 3710.55$, $T = 296(2)$ K, orthorhombic, *Pbcm*, $a = 13.3742(17)$ Å, $b = 21.242(3)$ Å, $c = 33.657(6)$ Å, $V = 9562(2)$, $\mu = 8.227$, $Z = 4$. Final *R* indices [$I > 2\sigma(I)$]: R1 = 0.0562, wR2 = 0.1418.

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(25) Computational details are provided in the Supporting Information.