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The First Series of Luminescent (μ_4-Chalcogenido)silver(I) Clusters

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The chemistry of transition metal−chalcogen complexes represents an important aspect in structural chemistry.[1] Although the syntheses and structural characterizations of a number of transition metal−chalcogenide clusters have been reported,[2] the occurrence of unsubstituted chalcogenidosilver(I) compounds has been exceptionally rare.[3] Also, photochemical studies of polynuclear silver(I) complexes[4] have been less extensively pursued compared with studies of other d^{10} systems such as those of copper(I) and gold(I). This may be a consequence of the light sensitivity of silver compounds. With our recent interest in luminescent polynuclear chalcogenidocopper(I)[5a,b] and -platinum(II)[5c−e] systems, we believe that an exploration into the structural and photochemical aspects of soluble silver(I) chalcogen complexes represents a very exciting area of research. Herein we report the syntheses and crystal structures of a novel class of luminescent chalcogenidosilver(I) clusters, $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})](OTf)_2$ [E = S (**1**), Se (**2**), Te (**3**)]. The photophysical properties of these clusters were also studied.

Reactions of $[Ag_2(\mu\text{-dppm})_2](OTf)_2$ with Na_2E or Li_2E (E = S, Se, Te) in acetone afforded **1**−**3** as air-stable yellow crystals. The new clusters gave satisfactory elemental analyses and were characterized by positive ESI-MS and NMR spectroscopy. The structures of the silver(I) clusters have also been established by X-ray crystallography.[6]

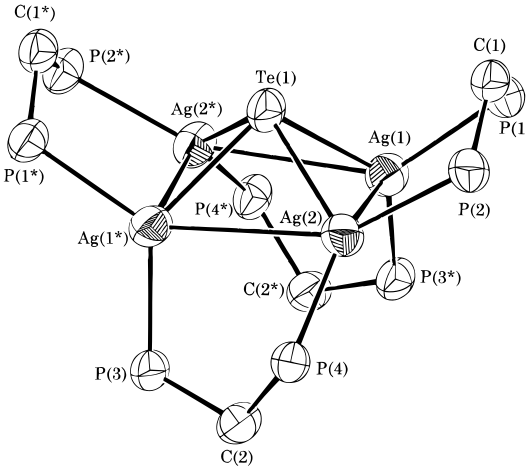

Figure 1. Perspective view of $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-Te})]^{2+}$ with the atomic numbering scheme. The phenyl rings are omitted for clarity. Thermal ellipsoids have been drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg) are as follows. Ag(1)−Ag(2): **1**, 3.038(2), **2**, 3.055(2), **3**, 3.071(1). Ag(1)−Ag(2*): **1**, 3.160(2), **2**, 3.222(2), **3**, 3.357(1). Ag(1)−E(1): **1**, 2.508(3), **2**, 2.613(1), **3**, 2.745(1). Ag(2)−E(1): **1**, 2.513(2), **2**, 2.622(1), **3**, 2.765(1). Ag−P: **1**, 2.422(4)−2.506(4), **2**, 2.427(3)−2.516(3), **3**, 2.430(3)−2.514(3). Ag(1)−Ag(2)−Ag(1*): **1**, 85.79(4), **2**, 85.82(3), **3**, 85.90(3). Ag(2)−Ag(1*)−Ag(2*): **1**, 93.46(4), **2**, 93.60(3), **3**, 93.70(3). Ag(1)−E(1)−Ag(1*): **1**, 114.5(2), **2**, 109.81(8), **3**, 105.98(5). Ag(1)−E(1)−Ag(2): **1**, 74.47(10), **2**, 71.40(5), **3**, 67.75(3). Ag(1)−E(1)−Ag(2*): **1**, 78.0(1), **2**, 75.99(4), **3**, 75.06(3). Ag(2)−E(1)−Ag(2*): **1**, 127.8(2), **2**, 121.59(8), **3**, 116.17(5).

Clusters **1**−**3** were found to be isostructural. Figure 1 depicts the perspective drawing of the complex cation of **3**, $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-Te})]^{2+}$. The four silver(I) ions in a distorted rectangular array are quadruply bridged by an unsubstituted chalcogenido ligand. Similar μ_4 bridging modes of monochalcogenides have been observed in other systems.[2,5a,b,7] However, there have been no examples occurring with silver(I). The Ag−Ag bond distances in **1** [3.038(2), 3.160(2) Å], **2** [3.055(2), 3.222(2) Å], and **3** [3.071(1), 3.357(1) Å] are comparable to those observed in $[Ag_3(\mu\text{-dppm})_3(\mu_3\text{-Br})_2]^+$ [3.192(3)−3.362(3) Å],[8a] $[Ag_2\{OOC-(CH_2)_2-COO\}]_\infty$ [2.938(1) Å],[8b] $[Ag_3\{HC(PPh_2)_3\}_2]^{3+}$ [3.1618(5)−3.2228(9) Å],[4e] and $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+$ [2.943(2)−3.014(2) Å].[4f] However, the Ag−Ag bond distances in all three clusters are shorter than the

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(6) Crystal data for **1**: $[Ag_4SP_8C_{100}H_{88}]^{2+}, 2CF_3SO_3^-\cdot 2H_2O$ ($C_{102}H_{92}O_8F_6P_8S_3Ag_4$): M_r = 2335.28, monoclinic, *C*2/*c* (No. 15), a = 29.07(1) Å, b = 16.44(8) Å, c = 24.301(9) Å, β = 115.57(2)°, V = 10477(29) Å^3, Z = 4, D_c = 1.480 g cm^{-3}, T = 298 K. Convergence for 296 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.009F_o^2)^2]$ for 4289 reflections with $I > 3\sigma(I)$, was reached at R = 0.064 and R_w = 0.073. Crystal data for **2**: $[Ag_4SeP_8C_{100}H_{88}]^{2+}, 2CF_3SO_3^-\cdot 2H_2O$ ($C_{102}H_{92}O_8F_6P_8S_2SeAg_4$); M_r = 2382.18, monoclinic, *C*2/*c* (No. 15), a = 29.017(8) Å, b = 16.466(4) Å, c = 24.389(3) Å, β = 115.54(2)°, V = 10513(4) Å^3, Z = 4, D_c = 1.505 g cm^{-3}, T = 298 K. Convergence for 551 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.015F_o^2)^2]$ for 4171 reflections with $I > 3\sigma(I)$, was reached at R = 0.055 and R_w = 0.064. Crystal data for **3**: $[Ag_4TeP_8C_{100}H_{88}]^{2+}, 2CF_3SO_3^-\cdot 2H_2O$ ($C_{102}H_{92}O_8F_6P_8S_2TeAg_4$); M_r = 2430.82, monoclinic, *C*2/*c* (No. 15), a = 29.038(3) Å, b = 16.360(5) Å, c = 24.628(3) Å, β = 115.807(7)°, V = 10532(3) Å^3, Z = 4, D_c = 1.533 g cm^{-3}, T = 298 K. Convergence for 551 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.023F_o^2)^2]$ for 4904 reflections with $I > 3\sigma(I)$, was reached at R = 0.056 and R_w = 0.068.

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Table 1. Photophysical Data for **1**−**3**

cluster	abs[a] λ/nm (ϵ/dm^3 mol^{-1} cm^{-1})	medium (T/*K*)	emission λ/nm (τ_o/μs)
1	246 sh[b] (91 745)	solid (298)	516 (1.0 ± 0.1)
	400 sh (970)	solid (77)	536
		$(CH_3)_2CO$ (298)	628 (1.2 ± 0.1)
		CH_3CN (298)	628 (1.5 ± 0.2)
2	256 sh (53 985)	solid (298)	527 (0.9 ± 0.1)
	402 sh (1445)	solid (77)	552
		$(CH_3)_2CO$ (298)	570 (1.3 ± 0.1)
		CH_3CN (298)	572 (3.4 ± 0.3)
3	254 sh (67 075)	solid (298)	574 (3.1 ± 0.2)
	440 sh (1475)	solid (77)	588
		$(CH_3)_2CO$ (298)	615 (1.4 ± 0.1)
		CH_3CN (298)	626 (3.3 ± 0.3)

[a] All UV−vis absorption spectra were recorded in acetonitrile solutions. [b] The absorption shoulders were determined from the derivatives of the UV−vis absorption spectra.

sum of van der Waals radii (3.40 Å).[8c] The Ag−E bond lengths [Ag−S in **1**, 2.508(3)−2.513(3) Å; Ag−Se in **2**, 2.613(1)−2.622(1) Å; Ag−Te in **3**, 2.745(1)−2.765(1) Å] are similar to those observed in related systems.[3,9] The saddle-like orientation of the four dppm ligands is attributable to the steric requirements of the bulky phenyl rings. The Ag−P bond distances in **1** [2.422(4)−2.506(4) Å], **2** [2.427(3)−2.516(3) Å], and **3** [2.430(3)−2.514(3) Å] are comparable to those observed in other silver(I) phosphine complexes.[4e,f, 8a]

The electronic absorption spectra of **1**−**3** in CH_3CN reveal a high-energy absorption shoulder at *ca*. 250 nm and a lower energy absorption in the 350−460 nm region. Excitation of the complexes in solid states and fluid solutions with $\lambda > 350$ nm results in long-lived green to orange luminescence. The photophysical data are summarized in Table 1. The excited-state lifetimes of the clusters are in the microsecond range, suggesting that the emissions are associated with a spin-forbidden transition. In view of the σ-donating capability of chalcogenides, the transitions associated with the emissions are believed to originate predominantly from a ligand-to-metal charge-transfer LMCT $[(E^{2-}) \rightarrow Ag_4]$ excited state, and probably with mixing of a metal-centered (d−s/d−p)Ag(I) state. Similar assignments have also been suggested for other luminescent polynuclear d^{10} chalcogenido,[5a,b] thiolato,[4c,d,10a−e] and halo[4d,10f] systems. The energies of the solid-state luminescence of the clusters at 298 K follow the order **1** (516 nm) > **2** (527 nm) > **3** (574 nm), which corresponds to the changes in the ionization potentials of the chalcogens.[11] Despite the fact that a similar trend was not observed for the complexes in fluid solutions, it is unlikely that decomposition or structural changes have occurred, as evidenced by positive ESI-MS and NMR spectroscopic data. The assignment of the excited states of these silver(I) clusters as admixtures of LMCT $[(E^{2-}) \rightarrow Ag_4]$ and the MC (d−s/d−p) state of Ag(I) is further supported by MO calculations.[12]

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Supporting Information Available: Text giving details of the syntheses, characterizations, and structure solutions of **1**−**3**, perspective drawings of the complex cations of **1** and **2**, and tables of crystal data, atomic coordinates, isotropic thermal parameters, anisotropic displacement parameters, and complete bond distances and angles for **1**−**3** (50 pages). Ordering information is given on any current masthead page.

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