Silver Clusters

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Unprecedented Efficient Structure Controlled Phosphorescence of Silver(I) Clusters Stabilized by Carba-*closo*-dodecaboranylethynyl Ligands

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Abstract: *$\{Ag_2(12\text{-}C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11})\}_n$ and selected pyridine ligands have been used for the synthesis of photostable Ag^I clusters that, with one exception, exhibit for Ag^I compounds unusual room-temperature phosphorescence. Extraordinarily intense phosphorescence was observed for a distorted pentagonal bipyramidal Ag^I_7 cluster that shows an unprecedented quantum yield of $\Phi = 0.76$ for Ag^I clusters. The luminescence properties correlate with the structures of the central Ag^I_n motifs as shown by comparison of the emission properties of the clusters with different numbers of Ag^I ions, different charges, and electronically different pyridine ligands.*

Silver(I) alkynyl compounds exhibit a diverse chemistry,[1] are versatile starting materials for organic syntheses,[1d] and are increasingly discussed for materials applications, for example, as sensors,[2] because of their physical properties, which include luminescence.[3] In particular, their structural chemistry is versatile because of the formation of Ag^I clusters.[1e,f] In contrast to silver(I) alkynyl compounds, which are often hardly soluble and structurally difficult-to-characterize coordination polymers,[4] well-defined Ag^I clusters with donor ligands (e.g. pyridine[5]), as silver(I) double salts,[1e,f] or with templates[1g,6] are more easily accessible. Self-organization to yield coordination polymers or clusters is mainly due to 1) the flexible coordination of Ag^I ions to more than one alkynyl ligand, 2) bridging alkynyl ligands, and 3) argentophilic interactions.[2,7] Argentophilic interactions are structure-determining dispersive interactions between metal ions with a d^{10} valence electron configuration,[8] with aurophilicity as prototype.[9] Furthermore, argentophilic interactions are important for the physical properties, for example, luminescence.[3,10] Despite the large number of silver(I) alkynyl clusters and related Ag^I clusters, in general, only very few well-defined silver(I) compounds have been studied that exhibit efficient luminescence and especially phosphorescence at room temperature.[1a,3a,11] The low thermal and photolytic stability of many Ag^I compounds often precludes luminescence studies.[1a,3a]

Carba-*closo*-dodecaboranyl ligands show an unusual coordination behavior as demonstrated by the synthesis of the tetrahedral Au^I clusters $[\{12\text{-}(R_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}\}_2]$ (R = Me, Et) that are solely stabilized by aurophilic interactions.[12] The unusual coordination properties are due to the negative charge of the $\{closo\text{-}1\text{-}CB_{11}\}$ cage and the bonding of the C≡C unit to one of the B atoms of the boron cluster. Only a limited number of further coordination compounds with other ligands, in which a $\{closo\text{-}1\text{-}CB_{11}\}$ cluster is either directly bound to a metal atom or via a substituent, are known.[13] Herein, we report on room-temperature phosphorescent Ag^I clusters with $[12\text{-}C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^{2-}$ ligands that are examples for complexes with unprecedented and new properties and that are based on $\{closo\text{-}1\text{-}CB_{11}\}$ clusters.

The reaction of cesium ethynylcarba-*closo*-dodecaborate[14] with silver nitrate in aqueous solutions resulted in $\{Ag_2(12\text{-}C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11})\}_n$ (**1**) as a microcrystalline solid in excellent yield (Scheme 1). The initially neutral mixture became acidic during the reaction because of the nitric acid formed.

$\{Ag_2(12\text{-}C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11})\}_n$ (**1**)
(*colorless precipitate*, 95 %)

Scheme 1. Synthesis of **1**.

The Ag^I salt **1** is thermally very stable (260 °C) and it is not sensitive to mechanical shock or light. Two intense C≡C bands are observed in the Raman spectrum of **1** at 1954 and 1915 cm^{-1} (Figure S1 in the Supporting Information). The low wavenumbers confirm the bonding of the ethynyl groups to more than one Ag^I ion: Both are smaller than the wavenumbers found for $[12\text{-}(Me_3PAu)_2C{\equiv}C\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ (1988 cm^{-1}) and in this complex two Au^I fragments are coordinated to a single ethynyl group.[12] Ag···H-B interactions result in a shift of some of the ν(BH) bands of **1** to lower wavenumbers (by 100–200 cm^{-1}) compared to Cs[12-HC≡C-

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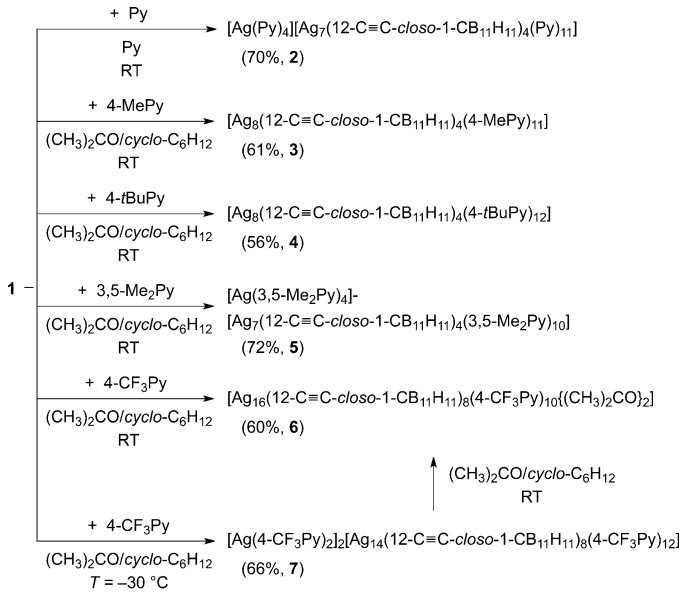
closo-1-$CB_{11}H_{11}$].[14b] The coordination of Ag^I ions to H atoms of {*closo*-1-CB_{11}} cages was observed, previously.[13a,b,15]

The reaction of **1** with pyridine, 4-methylpyridine, 4-*tert*-butylpyridine, and 3,5-lutidine yielded silver(I) clusters with seven or eight Ag^I ions, four [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ anions, and 10–12 molecules of the respective pyridine (Scheme 2). Single crystals of the silver(I) complexes were obtained from pyridine (**2**) or acetone (**3**–**5**).



Scheme 2. Syntheses of Ag^I clusters with carba-*closo*-dodecaboranylethynyl and selected pyridine ligands.

In contrast to the four aforementioned complexes, reaction of **1** with 4-trifluoromethylpyridine (4-CF_3Py) at different temperatures yielded two different Ag^I clusters. [Ag_{16}(12-C≡C-*closo*-1-$CB_{11}H_{11}$)$_8$(4-CF_3Py)$_{10}${$(CH_3)_2CO$}$_2$] (**6**) was formed at room temperature. At −30 °C, [Ag(4-CF_3Py)$_2$]$_2$[Ag_{14}(12-C≡C-*closo*-1-$CB_{11}H_{11}$)$_8$(4-CF_3Py)$_{12}$] (**7**) was obtained and at 15 °C single crystals were grown from acetone/cyclohexane. At 20 °C, **7** was suspended in acetone/cyclohexane and converted into **6** (Scheme 2).

Ag^I clusters stabilized by argentophilic interactions are the central structural motif of the silver(I) alkynyl complexes with the [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ anion and different pyridine ligands (Figure 1 and Figure 2, Table S2). In **2**–**4** and **6** more or less distorted octahedral Ag^I_6 clusters are present and additional Ag^I ions are either bonded to one of the silver atoms of the clusters (**3** and **6**) or bridge an edge of the octahedrons (**2**, **4**, and **6**). In **2** an almost regular octahedron is present whereas the one in **3** is strongly compressed with a short distance of 317.57(5) pm for the apical silver atoms. In the crystal of **4**, one of the silver atoms is disordered over two positions. The main component (95 %) is an open cluster (**4a**) and the minor component (5 %) is a closed octahedron (**4b**; Figure 2). Each octahedron in **2**–**4** is surrounded by four [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ ligands that

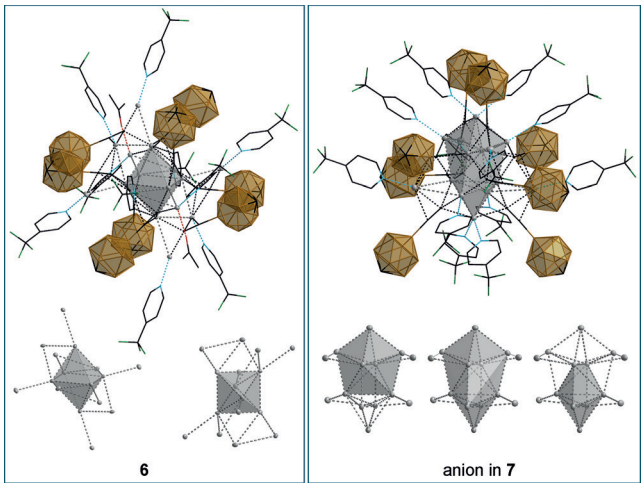


Figure 1. The Ag^I clusters in **6** and **7** (H atoms are omitted for clarity).

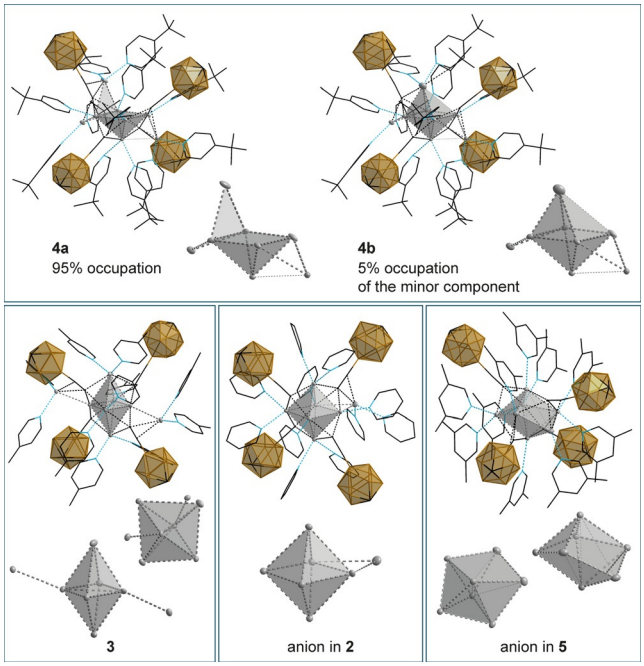


Figure 2. Molecular structures of the Ag^I clusters in the crystals of **2**–**5** (H atoms are omitted for clarity; one of the silver atoms in **4** is disordered, the open main **4a** (95 %) and the closed minor component **4b** (5 %) are depicted).

are capping one of the faces of the octahedrons. In some cases, this μ_3-η^1-coordination of the [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ ligands is expanded by another π-bonded Ag^I ion to a μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$-coordination. The Ag^I_6 octahedron in **6** is coordinated by eight [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ ligands and further 10 Ag^I ions are connected to the central Ag^I octahedron via argentophilic interactions (Figure 1). In addition, the coordination sphere of the resulting Ag^I_{16} clusters contains 10 4-CF_3Py and two acetone molecules. The coordination of the [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ ligands varies from μ_3-η^1,η^1,η^2 to μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$. So far, only a few analogous silver(I) alkynyl clusters with an Ag^I_6 octahedron and four face capping

alkynyl ligands have been described,[16] for example, $[Ag_6\{\mu_3\text{-}C{\equiv}CC{\equiv}CRe(Me_2bpy)(CO)_3\}_4(\mu\text{-dppm})_4][PF_6]_2$[16a] and $[Ag_{12}(C{\equiv}CtBu)_6(bpy)_4(CF_3CO_2)_6]$ (Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine, bpy = 2,2′-bipyridine).[16b] Higher nuclear silver(I) alkynyl clusters that contain a distorted octahedral Ag^I_6 motif are also rare.[17] However, some related distorted octahedral Ag^I_6 clusters with other ligands were described.[18]

Compound **5** is composed of $[Ag(3,5\text{-}Me_2Pyr)_4]^+$ ions and anionic, distorted pentagonal bipyramidal Ag^I_7 clusters with four [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ and 10 lutidine ligands. The coordination of the alkynyl ligands in **5** is similar to the ones discussed for the other Ag^I_6 clusters. The double negatively charged Ag^I_{10} cluster in **7** is a distorted decahedron, which alternatively can be interpreted as two interpenetrating pentagonal bipyramids (Figure 1). Compound **7** reveals parallels to anion **5** with respect to charge, cluster geometry, and lack of additional Ag^I ions that are bonded to the cluster.

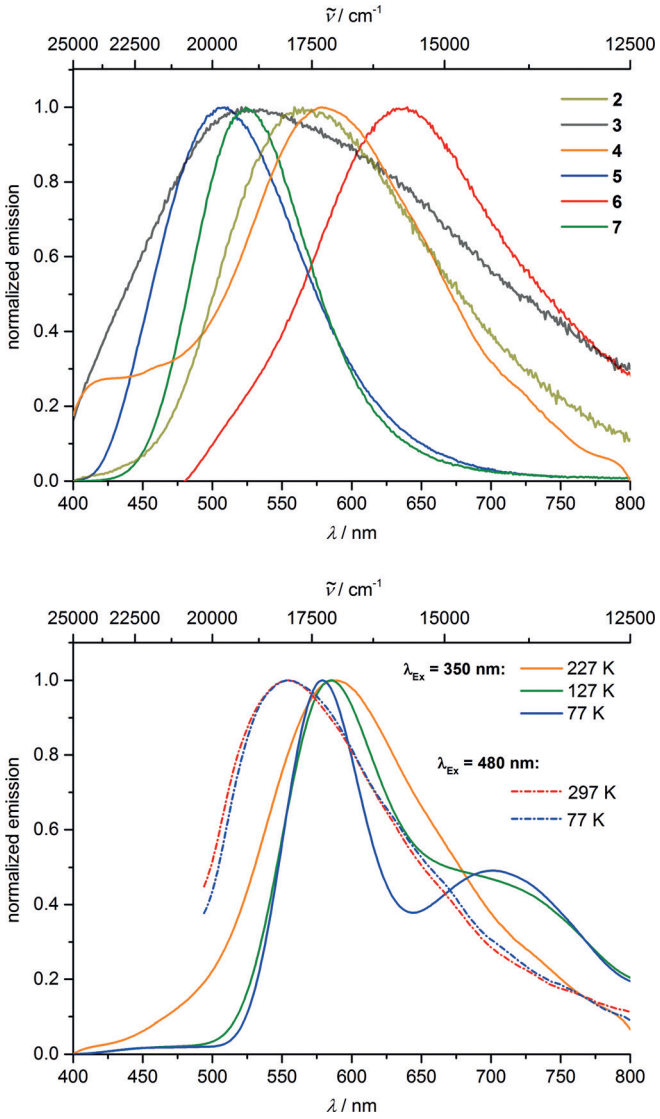


Figure 3. Top: Phosphorescence of **2**–**7** in the solid state at 297 K under argon. Bottom: Excitation-wavelength-dependent fluorescence (–•–•) and phosphorescence (——) of **4** at different temperatures.

Table 1: Selected photophysical data of **2**–**6** and of **7** in crystalline and powdery samples under argon, respectively.

Compound	T [K]	λ_{Em} [nm]	Φ	τ [µs]
2	297	559	0.14	1
	77	544	–	18
3	297	521	0.02	0.2 (55), 0.8 (35), 3.5 (10)
	77	525	–	17 (76), 41 (23), 113 (1)
4	297	521,[a] 579[b]	0.09,[a] <0.01[b]	0.3 (54), 2.1 (36), 5.1 (10) ns,[a] –[b]
	77	579, 702	–	19,[c] 38[d]
6	297	640	<0.01	–
7	297	524	0.05	0.8 (62), 4.5 (38)
5	297	511	0.76	1.9 (40), 6.9 (60)

[a] Fluorescence data: excitation at 480 nm. [b] Phosphorescence data: excitation at 350 nm. [c] λ_{Em} = 579 nm. [d] λ_{Em} = 702 nm.

The dianion in **7** is coordinated by 12 4-CF_3Py ligands and surrounded by two $[Ag(4\text{-}CF_3Py)_2]^+$ ions. The coordination of the eight [12-C≡C-*closo*-1-$CB_{11}H_{11}$]$^{2-}$ ligands is μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ or μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$. To our knowledge, neither pentagonal bipyramidal Ag^I_7 nor decahedral Ag^I_{10} clusters with alkynyl ligands have been described, previously.[1e,f]

The silver(I) carba-*closo*-dodecaboranylethynyl clusters **2**–**7** exhibit luminescence (Figure 3, Table 1, and Supporting Information), which is identical for crystalline and powder samples in color and intensity upon irradiation with UV light. The structural diversity of this new class of emissive materials results in emission energies that cover the full range of the visible spectrum. Remarkably, all compounds are phosphorescent at room temperature with µs-lifetimes and unprecedented quantum yields of up to 0.76 for Ag^I clusters.[3a,11b,c,19] Compound **4** is an interesting exception as it shows excitation wavelength dependent fluorescence at λ_{Em} = 521 nm with ns-lifetimes and a quantum yield of Φ = 0.09 or weak phosphorescence at λ_{Em} = 579 nm. The identity of the low-energy emission was confirmed by lifetime measurements at 77 K, which showed two thermally non-equilibrated triplet states at λ_{Em} = 579 nm and λ_{Em} = 702 nm with τ = 19 und 38 µs, respectively. This behavior is rationalized by the disordered Ag^I_6 cluster that contains an open main and a distorted octahedral minor component (Figure 2).

Presumably, the very rare and unusually strong room-temperature phosphorescence[3a,11c] is caused by argentophilic interactions. The beneficial influence of metallophilic interactions on the photophysical properties of d^{10} coinage-metal compounds was demonstrated for Au^I and Cu^I, earlier, enabling small radiative rate constants and mechanochromic luminescence.[8b,9d,20] In most cases, the dominant emitting triplet state is assumed to be of cluster-centered (^{3}CC) nature as a consequence of a $M_n(d\sigma^*\rightarrow s\sigma)$ excitation, although ^{3}LMMCT (ligand-to-metal-to-metal charge transfer) and ^{3}MMLCT (metal-to-metal-to-ligand CT) are possible, as well, resulting in a geometric distortion and strengthening of the metal–metal bonds.[8b,20h,21] Although less often observed due to the inherent photoinstability, metallophilic interactions can also be responsible for the emission properties of Ag^I compounds,[22] as has been demonstrated, for example, for silver(I) complexes on the basis of excimer formation.[10,22c–e]

For the photostable compounds **2**–**7**, the luminescence mechanism can be assumed to be similar to the ^{3}CC emission found for Cu^I clusters.[3a,11b,20h,21] Thus, the differences in the emission properties correlate with the structural motifs of the central Ag^I clusters. The open Ag^I_6 octahedron in **4** results in fluorescence (see above) whereas the closed octahedron allows for the formation of a weakly emissive triplet state (Table 1). The phosphorescence of the 4-methylpyridine derivative **3** with an axially compressed octahedron and the significantly higher phosphorescence quantum yield of $\Phi = 0.14$ for **2** that has an almost regular octahedron are in agreement with a ^{3}CC-dominated emission. The most efficient triplet emission with an unprecedented quantum yield[3a,11b,c,19] of $\Phi = 0.76$ was observed for **5** containing a distorted pentagonal bipyramidal central Ag^I_7 cluster. This observation indicates that the Ag^I ions attached to the central cluster by $Ag^I\cdots Ag^I$ interactions as in **2**–**4** and **6** have no or only little influence on its emission properties. The nature of the central structural motif determines the efficiency of the phosphorescence and not the number of Ag^I ions or the electronic nature of the pyridine ligand as evident from a comparison of the luminescence properties of **2**–**5** to those of **6** and **7**.

The photostable Ag^I alkynyl compounds **2**–**7** are composed of different central Ag^I clusters and show for this class of compounds unusual room temperature phosphorescence. In addition, **4** exhibits excitation-wavelength-dependent fluorescence. Alkynyl **5** is the only compound in this series containing isolated distorted pentagonal bipyramidal Ag^I clusters and resulting in an unprecedented quantum yield of 0.76 for Ag^I clusters, in general. This case study on the above mentioned six Ag^I clusters, which differ in structure, charge, and pyridine ligands, shows that the luminescence properties of this new class of emitting materials can be structurally controlled. Currently, we are developing synthetic routes to further coinage-metal(I) clusters with [12-C≡C-*closo*-1-$CB_{11}H_{11}]^{2-}$ and related ligands, aiming at a detailed understanding of the structure–property relationship for the photophysical properties of these clusters that are based on metallophilic interactions.

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