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Unprecedented Solution-Stable Silver(I) Ethynediyl Clusters

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In contrast to silver alkynyl compounds containing substituted ethynyl ligands ($RC\equiv C^-$),[1] silver–ethynediyl ($^-C\equiv C^-$, acetylide dianion) coordination receives much less attention[2] because of the explosive nature of Ag_2C_2 and its insolubility, which present serious difficulties in synthesis and characterization. It was found that Ag_2C_2 could be depolymerized in a concentrated aqueous solution containing one or more soluble silver(I) salts.[3] This depolymerization mechanism is not clearly understood, but it is conceivable that argentophilicity provides the driving force to transform polymeric Ag_2C_2 to labile $C_2@Ag_n$ species with cage structures each encapsulating a C_2^{2-} anion. Many interesting compounds containing Ag_2C_2 as a component have been reported, and most of them have polymeric structures with the component $C_2@Ag_n$ cages sharing common vertices or linked by bridging anions.[4] Furthermore, crown ethers have been employed as blocking groups to install protective cordons around the $C_2@Ag_n$ moiety to obtain discrete molecules.[5] Unfortunately, their characterization has been limited in the solid state because all known complexes containing Ag_2C_2 as a constituent decompose quickly when they are dissolved.

Solution-stable examples of gold(I) complexes comprising C_2^{2-} units are known in which the C_2^{2-} anion links a pair of gold atoms by σ-bonding to form a linear molecule [(μ-C≡C)bis{(phosphine)gold(I)}].[6] There are only two known ethynediyl copper(I) complexes, and in these complexes the C_2^{2-} anion coordinates four rectangularly arranged copper atoms in $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C\equiv C)](BF_4)_2$ and a butterfly-shaped tetranuclear copper(I) core in $[Cu_4(\mu\text{-}Ph_2Ppypz)_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C\equiv C)](ClO_4)_2$.[7] However, to the best of our knowledge there is as yet no information on the solution behavior of any silver ethynediyl complex in the literature. Our attempts to prepare a phosphine-protected silver(I) ethynediyl analog by using similar methods for copper and gold were met with no success, probably because the interaction between a phosphine and a silver ion is not strong enough to prevent the attack of ethynediyl, which leads to the formation of the insoluble Ag_2C_2 precipitate. Based on our previous work on the diimine-stabilized silver clusters,[8] we envision that diimines such as 2,2′-bipyridine (bpy) may provide effective protection owing to their chelating nature. Our efforts to isolate molecular ethynediyl silver(I) complexes by using diimine ligands have been successful. This work reports the synthesis, structure, and photophysical properties of the first solution-stable complexes containing Ag_2C_2 as a component, namely, $[Ag_7(C_2)(CF_3CO_2)_5(bpy)_5]\cdot MeCN\cdot 0.5MeOH$ (**1**·MeCN·0.5MeOH) and $[Ag_7(C_2)(CF_3CO_2)_5(phen)_5]\cdot 2CH_2Cl_2$ (**2**·2CH_2Cl_2; phen = phenanthroline).

Complex **1** was obtained in high yield by adding trimethylsilylacetylene ($Me_3SiC\equiv CH$, the precursor of C_2^{2-}) into a methanol solution of $[Ag(bpy)CF_3CO_2]$ that was generated by mixing equivalent amounts of silver trifluoroacetate and bpy. A clear solution was obtained without precipitation of Ag_2C_2. The bpy ligands provides the protection for the silver ions, and the release of C_2^{2-} from $Me_3SiC\equiv CH$ also inhibits the formation of Ag_2C_2. Using Ag_2C_2 directly in the preparation did not result in any reaction because a high silver(I) concentration is necessary to promote the solution of Ag_2C_2 as documented in the literature.[3]

The composition of **1** was confirmed by the analytical data. Although the C_2^{2-} dianion is IR silent, a C≡C band at 1766 cm^{-1} is found in its Raman spectrum in the solid state. The much lower $\tilde{\nu}(C\equiv C)$ frequency is consistent with the longer C≡C bond length associated with π bonding with the silver atoms. A similar C≡C band at 1788 cm^{-1} was reported in $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C\equiv C)](BF_4)_2$.[9] The existence of acetonitrile in **1** was also confirmed by a Raman signal at 2248 cm^{-1}.

The crystal structure of **1** has been determined and the molecular structure is shown in Figure 1.[10] Compound **1** is a caged molecule comprising seven silver atoms, one C_2^{2-}, five

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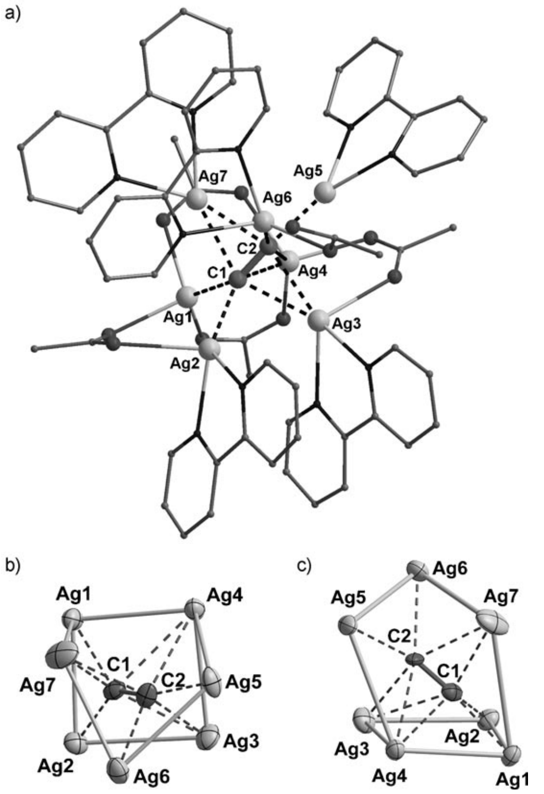

Figure 1. a) The molecular structure of **1**. Hydrogen atoms and Ag···Ag contacts have been omitted for clarity. b) Top view and c) side view of the $C_2@Ag_7$ core in **1**. Selected bond lengths [Å]: C1–C2 1.261(8), C1–Ag1 2.209(6), C1–Ag2 2.132(6), C1–Ag3 2.445(6), C1–Ag4 2.561(6), C1–Ag7 2.440(6), C2–Ag3 2.413(6), C2–Ag4 2.539(6), C2–Ag5 2.089(6), C2–Ag6 2.303(6), C2–Ag7 2.309(6), Ag1···Ag2 2.7894(7), Ag1···Ag4 2.9174(6), Ag2···Ag3 3.0664(7), Ag3···Ag4 2.9190(7), Ag1···Ag7 3.3039(8), Ag4···Ag5 3.1939(7), Ag5···Ag6 2.8935(7), Ag6···Ag7 2.9189(8).

bpy, and five CF_3CO_2. The shape of the cage is not regular, but it could be roughly described as a square antiprism with a missing corner. The polyhedron could also be described as an edge-sharing Ag1–Ag2–Ag3–Ag4 square and a bent Ag1–Ag4–Ag5–Ag6–Ag7 pentagon, which form an envelope structure enclosing the C_2^{2-} fragment. The structural core is illustrated in Figure 1b; four silver atoms Ag1–Ag2–Ag3–Ag4 construct a square and the other three Ag5–Ag6–Ag7 build a triangle. The C_2^{2-} anion is completely encapsulated in the silver cage with C1–C2 bond length of 1.261(8) Å being significantly longer than the C≡C triple bond lengths found in acetylene (1.205 Å),[11] CaC_2 (1.191 Å),[12] and the ternary alkali metal silver acetylides $CsAgC_2$ and $KAgC_2$ [1.217(7) and 1.223(6) Å, respectively].[13] The Ag–C distances lie in the range 2.089(6)–2.561(6) Å. The Ag···Ag distances in the cluster range from 2.7894(4) to 3.3039(8) Å, which are comparable to the interatomic contact of 2.89 Å in silver metal and shorter than twice the van der Waals radii of silver.[14]

Complex **1** is air stable and soluble in common organic solvents such as MeOH and MeCN to give a clear solution. ESIMS did not give satisfactory results owing to the fragmentation that occurred under ESI conditions. However, complex **1** can be recrystallized from the solution, and the product of recrystallization was confirmed to have the same composition as **1**. This observation strongly suggests that **1** is stable in methanol solution, because all previously reported complexes containing Ag_2C_2 components decompose readily to deposit Ag_2C_2 precipitates once dissolved. Because Ag_2C_2 is extremely insoluble, the decomposition is irreversible, that is, once the Ag_2C_2 deposits it will not go back to form **1** again. Because **1** can be recrystallized from solutions, it has to be intact when dissolved.

To test the generality of the synthetic protocol, phen was used in place of bpy and a molecular silver ethynediyl complex **2** was isolated, which has a similar $C_2@Ag_7$ core structure (see the Supporting Information). Complex **2** is also soluble without decomposition. This observation indicates that diimines are a good supporting group owing to the chelating effect.

Note that $Me_3SiC{\equiv}C^-$ remained intact in the preparation of $[Me_3SiC{\equiv}CAgPMe_3]_\infty$,[15] in which $[CpAgPMe_3]$ was used as the precursor and the Cp^- was replaced by the $Me_3SiC{\equiv}C^-$ ligand.

The reaction process of the preparation of **1** goes very fast, and this process could be monitored by watching the luminescence color of the frozen glasses. Immediately after adding $Me_3SiC{\equiv}CH$ to the $[Ag(bpy)CF_3CO_2]$ solution (green emissive at 77 K), the resulting solution was quickly cooled to 77 K and the frozen glass displayed a bright yellow emission.

Complexes **1** and **2** are not emissive at room temperature. At 77 K, the frozen glasses of **1** and **2** (MeCN/MeOH, 1:1) are luminescent, and their emission spectra along with those of bpy and phen are illustrated in Figure 2. It is known that

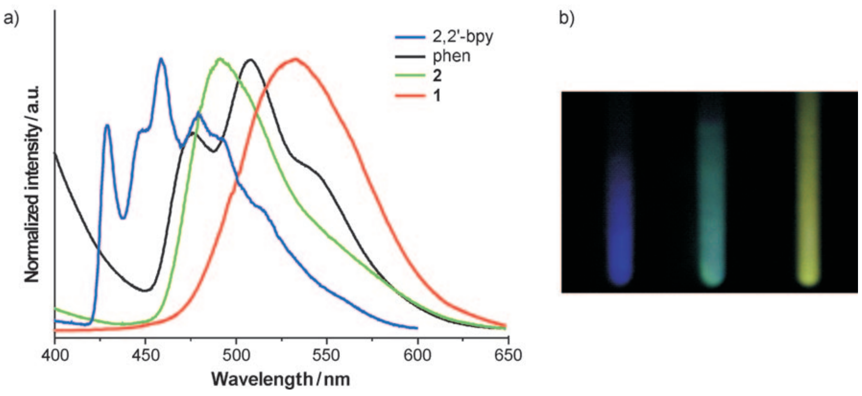

Figure 2. a) Normalized emission spectra of frozen glasses. b) Photograph of the luminescence taken at 77 K. From left to right: frozen glasses of bpy, $[Ag(bpy)CF_3CO_2]$, and **1** irradiated with 365 nm UV light.

the blue emission of bpy originates from a triplet intraligand π–π* excited state. The unstructured yellow emission of **1** is not energetically possible from π–π* excited states of bpy or C_2^{2-}. The d–π*(C_2^{2-}) emissive state should be also ruled out because the π* of C_2^{2-} has a very high energy.[16] We tentatively assign this emission at 532 nm to arise from the MMLCT d–π*(bpy) transition. Although a low-lying MLCT electronic level is not permitted,[17] MMLCT may lie at a low energy level because the Ag^I–Ag^I interactions in the cluster raise the HOMO energy level of d orbitals. The emissive states derived from the $[(C{\equiv}C)^{2-}\rightarrow Ag_7]$ LMCT may be also involved.

In summary, diimines have been proved to be good stabilizing ligands that prevent $C_2@Ag_7$ clusters from decomposition in solution. Complexes **1** and **2** represent a new type of luminescent complex containing $C_2@Ag_n$ clusters, which join the large family of luminescent coinage metal acetylides.

Experimental Section

General methods: All manipulations were carried out in the air, and compounds **1** and **2** are air stable.

Synthesis of 1·CH_3CN·0.5 CH_3OH: 2,2′-bpy (0.071 g, 0.455 mmol) was added into a solution of $AgCF_3CO_2$ (0.100 g, 0.454 mmol) in MeCN/MeOH (2 mL; v/v = 1:1), the resulting solution was stirred for 5 min at room temperature to give a light-yellow solution. Then (trimethylsilyl)-acetylene (0.023 g, 0.232 mmol) was added slowly into this solution, which was stirred for another 5 min. After adding Et_2O (0.5 mL) the solution was set aside at 4 °C. After 12 h, crystals of **1**·CH_3CN·0.5CH_3OH were obtained (yield: 0.065 g, 59.9 %). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 8.64$ (d, 2H), 8.14 (d, 2H), 7.89 (t, 2H), 7.30 ppm (t, 2H); IR (KBr): $\tilde{\nu} = 1688\ cm^{-1}$ (s; C=O); Raman (powder,): $\tilde{\nu} = 1766\ cm^{-1}$(s; C≡C); elemental analysis calcd (%) for $[Ag_7(bpy)_5C_2(CF_3CO_2)_5{\cdot}CH_3CN]$: C 35.04; H 1.90; N 6.59; found: C 34.97; H 1.89; N 6.45.

Synthesis of 2·2 CH_2Cl_2: 1,10-Phen (0.080, 0.405 mmol) was added into a solution of $AgCF_3CO_2$ (0.095, 0.432 mmol) in CH_2Cl_2/MeOH (2 mL, v/v = 1:1), and the resulting solution was stirred for about 5 min at room temperature to give a light-yellow solution. Then (trimethylsilyl)acetylene (0.031 g, 0.316 mmol) was added slowly into the solution, which was stirred for a further 1 h. Slow evaporation of the solution afforded colorless crystals (yield: 0.047 g, 31.3 %). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 9.11$ (dd, 2H), 8.62 (d, 2H), 8.05 (s, 2H), 7.86 ppm (dd, 2H); IR (KBr): $\tilde{\nu} = 1594\ cm^{-1}$ (s, C=O); Raman (powder): $\tilde{\nu} = 1779\ cm^{-1}$ (s, C≡C); elemental analysis calcd (%) for $[Ag_7(phen)_5C_2(CF_3CO_2)_5{\cdot}(CH_2Cl_2)_2]$: C 36.80; H 1.84; N 5.80; found: C 36.30; H 1.89; N 5.75.

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[1] a) M. D. Janssen, K. Köhler, M. Herres, A. Dedieu, W. J. J. Smeets, A. L. Spek, D. M. Grove, H. Lang, G. van Koten, *J. Am. Chem. Soc.* **1996**, *118*, 4817; b) H. Lang, K. Köhler, S. Blau, *Coord. Chem. Rev.* **1995**, *143*, 113; c) D. M. P. Mingos, R. Vilar, D. Rais, *J. Organomet. Chem.* **2002**, *641*, 126–133.

[2] T. C. W. Mak, X.-L. Zhao, Q.-M. Wang, G.-C. Guo, *Coord. Chem. Rev.* **2007**, *251*, 2311–2333.

[3] R. Vestin, E. Ralf, *Acta Chem. Scand.* **1949**, *3*, 101.

[4] For examples, see: a) G.-C. Guo, G.-D. Zhou, Q.-G. Wang, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 652–654; *Angew. Chem. Int. Ed.* **1998**, *37*, 630–632; b) G.-C. Guo, G.-D. Zhou, T. C. W. Mak, *J. Am. Chem. Soc.* **1999**, *121*, 3136; c) Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 7594.

[5] Q.-M. Wang, T. C. W. Mak, *Angew. Chem.* **2001**, *113*, 1164–1167; *Angew. Chem. Int. Ed.* **2001**, *40*, 1130–1133.

[6] a) T. E. Müller, D. M. P. Mingos, D. J. Williams, *J. Chem. Soc., Chem. Commun.* **1994**, 1787; b) J. Vicente, M. T. Chicote, M. D. Abrisqueta, P. G. Jones, *Organometallics* **1997**, *16*, 5628; c) J. Vicente, M. T. Chicote, M. D. Abrisqueta, P. G. Jones, *Organometallics* **2000**, *19*, 2629.

[7] a) V. W.-W. Yam, W. K.-M. Fung, K.-K. Cheung, *Angew. Chem.* **1996**, *108*, 1213–1215; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1100–1102; b) H.-B. Song, Q.-M. Wang, Z.-Z. Zhang, T. C. W. Mak, *Chem. Commun.* **2001**, 1658–1659.

[8] M.-L. Chen, X.-F. Xu, Z.-X. Cao, Q.-M. Wang, *Inorg. Chem.* **2008**, *47*, 1877–1879.

[9] V. W.-W. Yam, K. K.-W. Lo, W. K.-M. Fung, C.-R. Wang, *Coord. Chem. Rev.* **1998**, *171*, 17–41.

[10] Crystal data for **1**·MeCN·0.5 MeOH; $C_{62}H_{40}N_{10}O_{10}F_{15}Ag_7{\cdot}MeCN{\cdot}0.5\,MeOH$; $a = 13.5611(3)$, $b = 35.9534(9)$, $c = 14.5774(2)$ Å; $\beta = 98.003(2)°$; $V = 7038.2(3)$ Å^3; monoclinic; space group $P2_1/n$; $Z = 4$; $T = 173(2)$ K; 57569 reflections measured; 23093 unique ($R_{int} = 0.0470$); final $R1 = 0.0591$; $wR2 = 0.1212$ for 12378 observed reflections [$I > 2\sigma(I)$]. Crystal data for **2**·2 CH_2Cl_2; $C_{72}H_{40}N_{10}O_{10}F_{15}Ag_7{\cdot}2\,CH_2Cl_2$; $a = 13.8448(7)$, $b = 23.8692(15)$, $c = 24.4745(13)$ Å; $\beta = 91.716(5)°$; $V = 8084.3(8)$ Å^3; monoclinic; space group $P2_1/c$; $Z = 4$; $T = 123(2)$ K; 27563 reflections measured; 12265 unique ($R_{int} = 0.1086$); final $R1 = 0.1204$; $wR2 = 0.2910$ for 8512 observed reflections [$I > 2\sigma(I)$]. CCDC-778340 (**1**) and CCDC-778341 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] G. Herzberg, J. W. T. Spinks, *Z. Phys.* **1934**, *91*, 386.

[12] M. Atoji, *J. Chem. Phys.* **1961**, *35*, 1950.

[13] W. Kockelmann, U. Ruschewitz, *Angew. Chem.* **1999**, *111*, 3697–3700; *Angew. Chem. Int. Ed.* **1999**, *38*, 3492–3495.

[14] J. Emsley, *The Elements*, Clarendon, Oxford, **1989**, p. 174.

[15] C. Brasse, P. R. Raithby, M.-A. Rennie, C. A. Russell, A. Steiner, D. S. Wright, *Organometallics* **1996**, *15*, 639–644.

[16] C.-M. Che, H.-Y. Chao, V. M. Miskowski, Y. Li, K.-K. Cheung, *J. Am. Chem. Soc.* **2001**, *123*, 4985–4991.

[17] A. Barbieri, G. Accorsi, N. Armaroli, *Chem. Commun.* **2008**, 2185–2193.

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