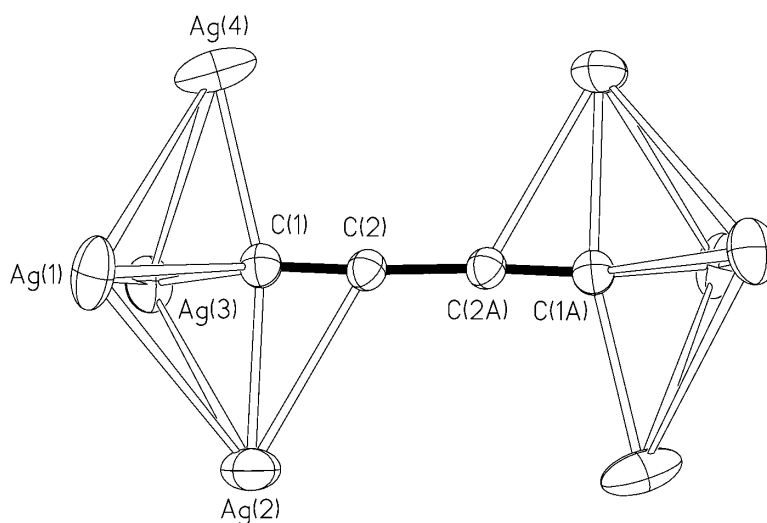


Silver(I) 1,3-Butadiynediide and Two Related Silver(I) Double Salts Containing the C²⁻ Dianion

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J. Am. Chem. Soc., **2004**, 126 (22), 6852-6853 • DOI: 10.1021/ja049772b • Publication Date (Web): 14 May 2004

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Silver(I) 1,3-Butadiynediide and Two Related Silver(I) Double Salts Containing the C_4^{2-} Dianion

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We have carried out a systematic investigation on the synthesis and structural characterization of a series of double, triple, and quadruple salts of the highly explosive silver acetylide, Ag_2C_2 , in which the C_2^{2-} dianion is trapped inside a polyhedral Ag_n cage.¹ In recent years, many research groups have reported a growing number of transition metal complexes containing the linear $M-(C\equiv C-C\equiv C)-R$ moiety,² in which R may be $SiMe_3$,³ a pyridyl derivative,⁴ or a metal center bearing other ligands.⁵ Herein we report the first synthesis of silver(I) 1,3-butadiynediide, Ag_2C_4 , **1**, and the crystal structures of two novel hydrated double salts $Ag_2C_4 \cdot 6AgNO_3 \cdot nH_2O$ [$n = 2$ (**2**); 3 (**3**)].

The reaction of $Li-C\equiv C-C\equiv C-Li$ (generated in situ from hexachloro-1,3-butadiene and nBuLi)⁶ with $AgNO_3$ in a 1:2 molar ratio in THF under an inert atmosphere of nitrogen at room temperature for 12 h gave a dark gray precipitate containing Ag_2C_4 and $AgCl$ (50 wt %, confirmed by powder X-ray diffraction), which can be washed off with saturated aqueous ammonia (35%). **CAUTION!** Crude Ag_2C_4 (contaminated with ~25 wt % of metallic silver) is a light-gray amorphous powder (mp 130 °C, dec) that behaves like its lower homologue Ag_2C_2 (mp 138 °C, dec), being insoluble in most solvents and highly explosive in the dry state when subjected to heating or mechanical shock. Raman (cm^{-1}): 2153 (w, $\Delta\nu_s C\equiv C$) and 1982 (w, $\Delta\nu_a C\equiv C$) for irradiating laser line 514.5 nm.

Transparent, dark-yellow blocks of the double salt $Ag_2C_4 \cdot 6AgNO_3 \cdot 3H_2O$ **3** were obtained from the crystallization of crude Ag_2C_4 in a concentrated aqueous solution of $AgNO_3$. To study the influence of the silver-to-nitrate molar ratio, and at the same time to suppress the deposition of black metallic silver during crystal growth, 2 M HNO_3 was used to dissolve Ag_2C_4 in the presence of $AgNO_3$ and $AgBF_4$, the latter being employed to increase the concentration of the silver(I) ion, leading to yellow prismatic crystals of the double salt $Ag_2C_4 \cdot 6AgNO_3 \cdot 2H_2O$ **2**.

In the crystal structure of $Ag_2C_4 \cdot 6AgNO_3 \cdot 2H_2O$ **2**,⁷ the C_4^{2-} ion is located at an inversion center, each terminal carbon atom being capped by a butterfly-shaped Ag_4 basket. The resulting barbell-like $[Ag_4C_4Ag_4]$ aggregate has quasi- C_{2h} symmetry with a mirror plane passing through atoms $Ag(2)$, $Ag(4)$, $Ag(2A)$, and $Ag(4A)$, as shown in Figure 1a. The $Ag(2)$ atom is π -bonded to the adjacent carbon-carbon triple bond at $Ag(2)-C(2) = 2.633(8)$ Å, longer than the σ -type $Ag-C$ bonds in the range 2.161(8)–2.338(8) Å. The triple and single bond lengths in C_4^{2-} are 1.216(11) and 1.383(16) Å, respectively, in good agreement with those observed in other 1,3-butadiyne-1,4-diyl complexes (1.218^{3a,8a} and 1.210;^{8b} 1.384 Å^{8a}). The $Ag \cdots Ag$ distances within the Ag_4 basket range from 2.880(1) to 3.069(1) Å, suggesting the existence of significant $Ag \cdots Ag$ interactions.⁹

The asymmetric unit contains aqua ligand O(1W) and three independent nitrate groups, which may be conveniently referred to by naming their nitrogen atoms. As shown in Figure 1b, the

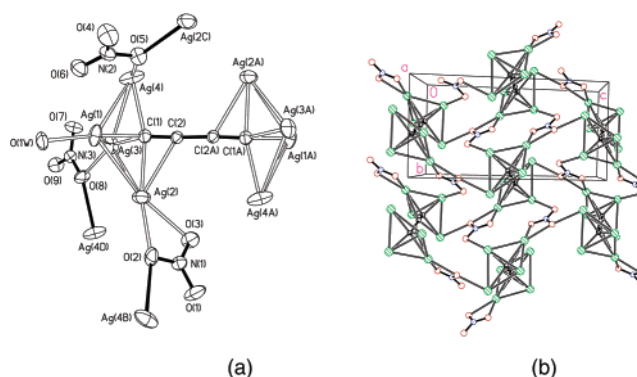


Figure 1. (a) Atom labeling (50% thermal ellipsoids) and coordination modes of the anionic ligands in $Ag_2C_4 \cdot 6AgNO_3 \cdot 2H_2O$ **2**. Symmetry code: A $1 - x, -y, 1 - z$; B $x, 1/2 - y, -1/2 + z$; C $x, -1 + y, z$; D $x, 1 + y, z$. (b) Pseudo-hexagonal array of $[Ag_4C_4Ag_4]$ aggregates linked by independent nitrate group N(1) into a layer normal to [100]. Color scheme for atoms: Ag green, C black, O red, N blue.

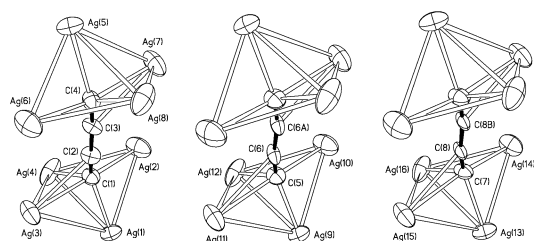


Figure 2. Perspective drawing of the three independent $[Ag_4C_4Ag_4]$ aggregates of $Ag_2C_4 \cdot 6AgNO_3 \cdot 3H_2O$ **3** (atoms are shown as 50% thermal ellipsoids). Symmetry codes: A $-x, -y, -z$; B $-x, 1 - y, -z$.

$[Ag_4C_4Ag_4]$ aggregates arranged in a pseudo-hexagonal array are connected by nitrate N(1) acting in the μ_3-O, O', O'' plus O, O' -chelating mode to form a thick layer normal to [100]. Linkage of adjacent layers by the remaining two independent nitrate groups N(2) and N(3), abetted by $O-H \cdots O$ (nitrate) hydrogen bonding involving the aqua ligand, then generates a three-dimensional network.

The crystal structure of **3**¹⁰ is similar to that of **2**, although it is more complex. There are three $[Ag_4C_4Ag_4]$ aggregates, two occupying sites of symmetry $\bar{1}$ (Figure 2), together with 12 independent nitrate groups and six aqua ligands. The $Ag-C$ bond distances between the silver caps and C_4^{2-} dianions lie in the range 2.425(8)–2.503(9) and 2.124(8)–2.419(10) Å for π and σ interactions, respectively. The lengths of the carbon-carbon triple and single bonds are in the range of 1.236(11)–1.238(11) and 1.375(12)–1.402(16) Å, respectively, being consistent with the corresponding values observed for those of complex **2**.

The $[Ag_4C_4Ag_4]$ aggregates in **3** constitute a pseudo-hexagonal array normal to [001], giving rise to a thick layer consolidated by nitrate groups N(1)–N(8) (Figure 3). This may be compared

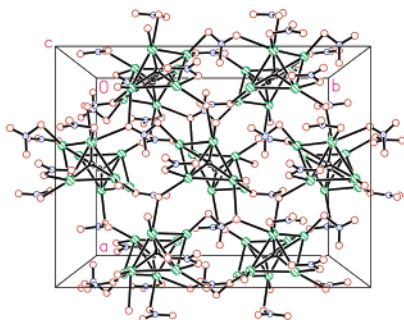


Figure 3. Layer structure of **3** generated from interconnection of a pseudohexagonal array of $[\text{Ag}_4\text{C}_4\text{Ag}_4]$ aggregates by eight independent nitrate groups. Color scheme for atoms: Ag green, C black, O red, N blue.

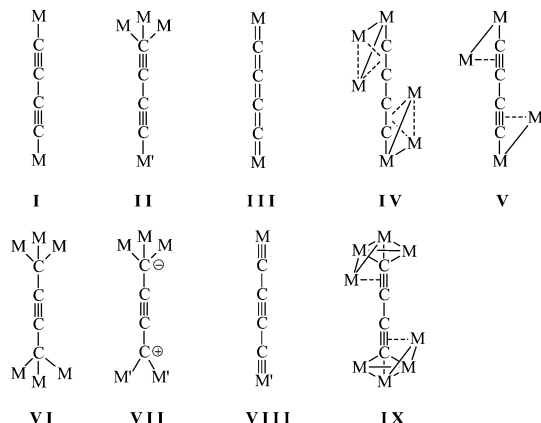


Figure 4. Coordination modes of the naked linear tetracarbon (C_4) ligand in metal complexes.

to the corresponding layer of simpler construction in **2** shown in Figure 2. The three-dimensional network of **3** consists of layers interconnected by the remaining four nitrate groups N(9)–N(12) plus six aqua ligands.

The striking disparity between the melting points of **2** (151 °C) and **3** (48 °C), despite the resemblance in their stoichiometric formulas, may be rationalized by the fact that (i) the ratio of consolidating nitrate groups in each layer to those that bind adjacent layers is 1/2 and 2, and (ii) the ratio of aqua ligands involved in interlayer O–H···O(nitrate) hydrogen bonding to $[\text{Ag}_4\text{C}_4\text{Ag}_4]$ aggregates is 2 and 3, respectively, in these two crystal structures. Intralayer binding is accordingly stronger in compound **3**, but interlayer cohesion is weaker as compared to that in compound **2**.

The known coordination modes of a naked tetracarbon chain in transitional metal complexes are illustrated in Figure 4. Mode **I** ($M = \text{Ru}$,^{5a} $M = \text{Pt}$,^{5b} $M = \text{Fe}$,^{5c} $M = \text{Au}$,^{5d} heterometallic, $M = \text{W}$, $M' = \text{Rh}$ or Ir ^{5e}), **II** (heterometallic, $M = \text{Ag}$, $M' = \text{Re}$),¹¹ and **V** ($M = \text{Fe}$)¹² occur in genuine metal complexes of 1,3-butadiyne-diene. In mode **IV** ($M = \text{Fe}$),¹³ the tetracarbon chain exhibits extensive electron delocalization, leading to bond-length averaging. Mode **III** ($M = \text{Re}$)¹⁴ shows a typical cumulenyl structure. In Mode **VI** ($M = \text{Co}$),¹⁵ **VII** (heterometallic, $M = \text{Ru}$, $M' = \text{Fe}$),¹⁶ and **VIII** (heterometallic, $M = \text{Co}$, $M' = \text{W}$),¹⁷ bond shift occurs with interconversion between single and triple bonds, and in the last instance each terminal carbon atom is triply bonded to a metal center. The new mode **IX** of C_4^{2-} in complexes **2** and **3**, exhibiting the highest ligation number¹⁸ of eight and featuring the coexistence of metal–carbon σ and π bonding, is stabilized by ionic as well as argentophilic interactions.

The ready availability of Ag_2C_4 , the second silver carbide to be authenticated, may lead to further development in the structural chemistry of C_4^{2-} , paralleling that based on C_2^{2-} , via supra-molecular assembly through a selective combination of coinage-metal ions, inorganic/organic bridging anions, and ancillary ligands.^{1c–11}

Acknowledgment. This work is supported by the Hong Kong Research Grants Council (Ref. No. CUHK 402003). We dedicate this paper to Prof. Ambrose Y. C. King on the occasion of his retirement.

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

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JA049772B