

Synthesis and characterization of $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$: a novel layer-type structure with the acetylide dianion functioning in a $\mu_6\text{-}\eta^1, \eta^1 : \eta^2, \eta^2 : \eta^2, \eta^2$ bonding mode inside an octahedral silver cage

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In the novel double salt $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$, the C_2^{2-} dianion [bond length 1.217(7) Å] is encapsulated inside an octahedral Ag_6 cage, and the resulting cationic $[\text{C}_2@\text{Ag}_6]$ units share corners to generate metallic layers between which the perchlorate anions and aqua ligands are accommodated.

The literature contains scant information on the ligand behaviour of C_2^{2-} (acetylide dianion), in contrast to the rich coordination chemistry of its isoelectronic analogues N_2 (dinitrogen) and CN^- (acting in either cyanide or isocyanide mode). The salt-like alkali and alkaline-earth metal acetylides are readily decomposed by water, the best known example being calcium carbide, CaC_2 , which exists in at least four different crystalline modifications.¹ Of the group 11 metal acetylides, silver acetylide (Ag_2C_2 , also known as silver carbide) was first prepared as an impure yellowish powder by Berthelot in 1866.² A linear polymeric structure for silver acetylide has been inferred from its chemical properties, which are consistent with those of a molecular compound; for example, it does not react with water and is highly explosive and sensitive to shock when completely dried.³ However, the existence of the 'naked' acetylide dianion, C_2^{2-} , as a fully encapsulated species within rhombohedral Ag_8 and mono-capped square-antiprismatic Ag_9 cages in the double salts $\text{Ag}_2\text{C}_2 \cdot 6\text{AgNO}_3$ ^{4,5} and $\text{Ag}_2\text{C}_2 \cdot 8\text{AgF}$,⁶ respectively, suggests that the coordination mode of the C_2^{2-} entity in silver acetylide is much more complex than hitherto imagined.

Recently we have initiated a research project to synthesize and elucidate the X-ray crystal structures of novel compounds containing silver acetylide as a component, so as to shed some light on the nature of the interaction between the acetylide dianion and silver(I) ions. We report here the synthesis and crystal structure of a new double salt of silver acetylide with silver perchlorate, in which the acetylide dianion acts in a $\mu_6\text{-}\eta^1, \eta^1 : \eta^2, \eta^2 : \eta^2, \eta^2$ bonding mode that binds the silver cations into an unprecedented two-dimensional planar array.†

In the crystal structure of $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$, the atoms C(1), C(2), Ag(2) and Ag(3) all lie on the same crystallographic mirror plane. The measured C(1)–C(2) bond distance of 1.212(7) Å is comparable to that found in acetylene (1.205 Å), showing that the acetylide dianion retains its triple bond character inherited from the parent silver acetylide, as confirmed by its laser Raman stretching frequency. The C_2^{2-} dianion is σ -bonded to atoms Ag(2) and Ag(2^{iv}) in the *c* direction, and π -bonded to Ag(3) and Ag(3ⁱⁱ) in the *a* direction and to Ag(1) and Ag(1ⁱⁱⁱ) in the *b* direction (Fig. 1). Thus this dumbbell-like species is encapsulated inside an Ag_6 cage, and the resulting $[\text{C}_2@\text{Ag}_6]$ octahedra share vertices along the *a* and *c* directions to generate a layer structure. The distances of bridging atom Ag(2) to the C(1) and C(2^{iv}) atoms of its adjacent acetylide dianions are 2.087(3) and 2.108(6) Å, respectively, which are comparable to those (average 2.057 Å) of Ag atoms σ -bonded to the $\text{C}\equiv\text{CR}$ groups in the alkynyl complexes $[\text{Ph}_3\text{PAgC}\equiv\text{CPh}]_4 \cdot 3.5\text{thf}$ and $[\text{Me}_3\text{PAgC}\equiv\text{CSiMe}_3]_\infty$.⁷ The C(2)–C(1)–Ag(2) and C(1)–Ag(2)–C(2^{iv}) bond angles are

179.9(3) and 178.5(2)°, respectively. Therefore the coordination mode of the acetylide dianion to two metal atoms of type Ag(2) can be regarded as typical linear σ -bonding, as found in the discrete complexes $[\{\text{Ru}(\text{CO})_2(\text{Cp})\}_2(\mu\text{-C}\equiv\text{C})]$,⁸ $[\{\text{Re}(\text{CO})_5\}_2(\mu\text{-C}\equiv\text{C})]$ ⁹ and $[\text{Cu}_4(\mu\text{-dppm})_4(\text{C}\equiv\text{C})][\text{BF}_4]_2$.¹⁰ However, to our knowledge the infinite linear chain resulting from an alternate arrangement of σ -bonded acetylide dianions and type Ag(2) silver atoms in the present compound is unprecedented.

The orthogonal pair of filled π orbitals of the acetylide dianion interact unsymmetrically with Ag(1) and Ag(3) and their symmetry equivalents, such that silver atoms of type Ag(3) serve as bridges to link adjacent infinite chains to form a metallic layer (Fig. 1). The distances of atom Ag(3) to C(1) and C(2) are 2.554(4) and 2.382(6) Å, and the C(1)–C(2)–Ag(3) and C(2)–C(1)–Ag(3) angles are 83.9(3) and 68.0(3)°, respectively. Thus the coordination mode of the acetylide dianion to silver atoms of type Ag(3) can be regarded as unsymmetrical π -bridging, which differs from the symmetrical acetylide–copper interaction observed in $[\text{Cu}_4(\mu\text{-dppm})_4(\text{C}\equiv\text{C})][\text{BF}_4]_2$.¹⁰ Similar unsymmetrical π -bonding also occurs between the acetylide dianion and silver atoms of type Ag(1), which are

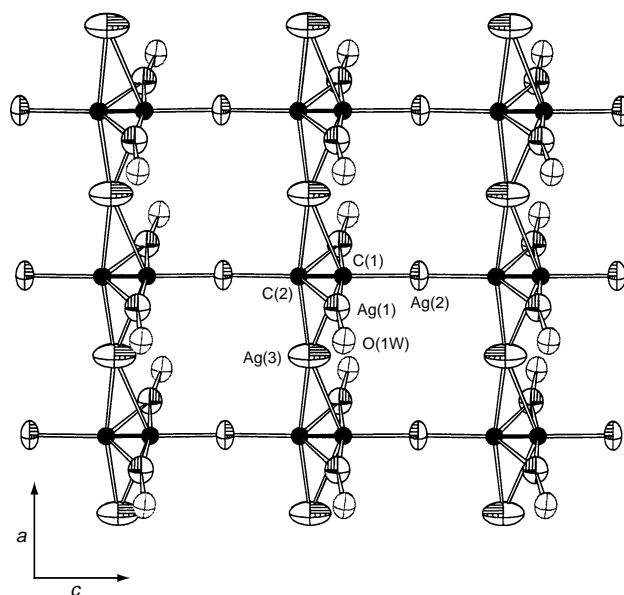


Fig. 1 Cationic layer composed of C_2^{2-} and Ag^+ ions in the crystal structure of $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$ viewed along the *b* axis. The thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.212(7), Ag(1)–C(1) 2.3448(4), Ag(1)–C(2) 2.579(2), Ag(2)–C(1) 2.087(3), Ag(2)–C(2^{iv}) 2.108(6), Ag(3)–C(1) 2.554(1), Ag(3)–C(2) 2.382(6), Ag(3ⁱⁱ)–C(1) 2.596(4), Ag(3ⁱⁱ)–C(2) 2.448(6), Ag(1)–O(1W) 2.304(2); Ag(1)–C(1)–Ag(1ⁱⁱⁱ) 173.5(2), C(1)–Ag(1)–O(1W) 171.4(1), C(2)–C(1)–Ag(2) 179.9(3), C(1)–Ag(2)–C(2^{iv}) 178.5(2), C(2)–Ag(3)–C(2^{iv}) 166.8(3), C(1)–C(2)–Ag(3) 83.0(3), C(2)–C(1)–Ag(3) 69.4(3). Symmetry codes: i, *x*, *y*, $-1 + z$, ii, $1 + x$, *y*, *z*, iii, $x, \frac{1}{2} - y, z$, iv, *x*, *y*, $1 + z$, v, $-1 + x, y, z$.

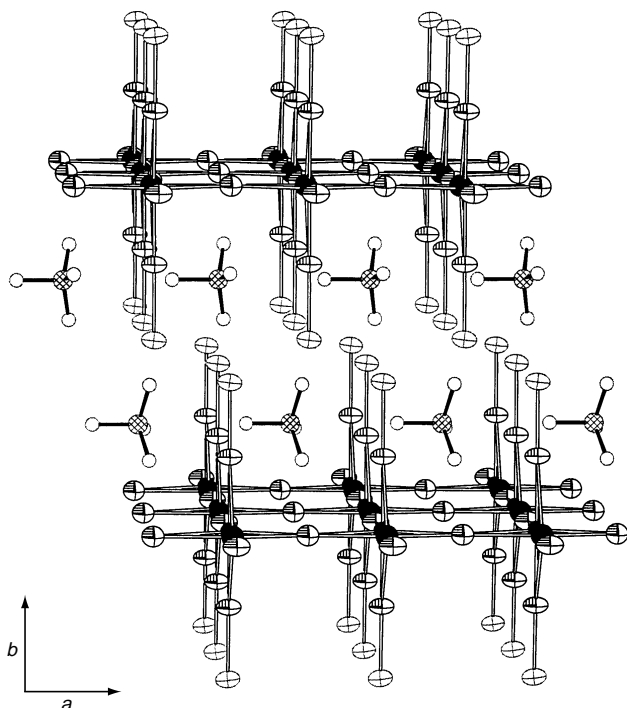


Fig. 2 Crystal structure of $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$ viewed along the c axis. For clarity the disordered perchlorate ion is shown in only one of its two orientations, and the hydrogen bonds between the aqua ligands and the perchlorate ions have been omitted.

linked to C(1), C(2) and terminal aqua ligand O(1W) at distances of 2.3448(4), 2.579(2) and 2.304(2) Å, respectively. The dihedral angle between the planes defined by C(1)–C(2)–Ag(3) and C(1)–C(2)–Ag(1) is 90.7°.

The ClO_4^- ion exhibits twofold disorder with two equally populated, opposite orientations that share a common set of three basal oxygen atoms. The terminal aqua ligands that are coordinated to type Ag(1) silver atoms form donor hydrogen bonds to the ClO_4^- ions, thereby contributing to the stability of the structure. Fig. 2 shows that the cationic layers are completely separated by ClO_4^- anions, so that the crystal structure of the present compound may be considered as a stack of alternate conducting and insulating layers. This potential anisotropic conducting property of the metallic layer will be further studied.

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Notes and References

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† *Synthesis of $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$* : aqueous silver nitrate solution was stirred and a slow stream of acetylene gas was bubbled into it until saturation was reached at ambient temperature. The white precipitate of Ag_2C_2 was isolated by filtration, washed several times with deionized water, and stored in the dark in wet form. **CAUTION**: Ag_2C_2 in the dry state detonates easily by mechanical shock, and only a small quantity should be prepared for immediate use in any chemical reaction. Moist Ag_2C_2 is added to 2 ml of a concentrated aqueous solution of AgClO_4 with stirring until saturation is reached. The excess amount of Ag_2C_2 was filtered off, and the solution was placed in a desiccator charged with P_2O_5 . After several days a good crop of colorless crystals of $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$ was obtained. The Raman spectrum (Renishaw Raman Image Microscope System 2000) of this product exhibits absorption peaks at 2103.9 and 2167.1 cm^{-1} in the $\Delta\nu(\text{C}\equiv\text{C})$ region, which originate from Fermi resonance between the stretching frequency of C_2^{2-} with the first overtone of the irradiating laser line at 1123.5 cm^{-1} .

§ *Crystal data*: $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$, $\text{C}_2\text{H}_4\text{Ag}_3\text{Cl}_2\text{O}_{10}$, $M = 690.43$, monoclinic, space group $P2_1/m$ (no. 11), $a = 4.798(1)$, $b = 21.341(2)$, $c = 5.406(1)$ Å, $\beta = 90.01(1)^\circ$, $U = 553.5(1)$ Å³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 74.96$ mm^{-1} ; 767 observed data [$|F_o| > 4\sigma(F_o)$] out of 845 unique reflections converged to $R1 \equiv \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.053$ and $wR2 \equiv [1/\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma wF_o^4]^{1/2} = 0.157$. CCDC reference 182/721.

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