

The synthesis, identification, and X-ray structure of a novel cationic alkynyl silver cluster polymer $[\text{Ag}_3(\text{C}_2\text{Bu}')_2]^+_n$

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Abstract

The reaction between AgBF_4 and $[\text{Ag}(\text{C}_2\text{Bu}')_n]$ in 1:2 mol ratio affords the novel cationic polymer $[\text{Ag}_3(\text{C}_2\text{Bu}')_2]^+_n$. The crystal structure has been determined by single-crystal X-ray diffraction study. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Coordination polymer; Alkynyl cluster; Silver cluster; Group 11; X-ray diffraction

1. Introduction

New aspects of chemistry for Group 11 metals have emerged from the reactions of the linear anionic complexes $[\text{M}(\text{C}_2\text{Ph})_2]^-$ with $[\text{M}(\text{C}_2\text{Ph})_n]$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$). The reactions did not stop at depolymerization, but gave novel anionic homo- and heteronuclear alkynyl-containing clusters of coinage metals [1]. The chemistry was extended to give neutral clusters and heteronuclear polymers of the same metals [2].

We now report the synthesis, identification, and single-crystal X-ray structure of a novel cationic polymer $[\text{Ag}_3(\text{C}_2\text{Bu}')_2]^+_n$, which represents a new class of alkynyl-containing clusters of coinage metals. The new complex is the first example of a cationic coinage metal compound complexed with only substituted alkynyl ligands to be reported and structurally characterized. Although the neutral silver alkynyl complexes $[\text{Ag}(\text{C}_2\text{R})\text{PMe}_3]_n$ ($\text{R} = \text{Ph}, \text{SiMe}_3$) are of polymeric nature [3,4], their structures markedly differ from this complex. A number of trinuclear copper(I) and silver(I) $\mu^3\text{-}\eta^1$ -cationic alkynyl complexes have been recently reported, but all contain the diphosphine ligand

$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ [5]. Also, a number of complexes having C_2^{2-} ligand, which is *iso*-electronic with N_2 and CN^- , encapsulated inside silver cages of different nuclearity have been reported [6]. For example, the dianion C_2^{2-} in the double salt $\text{Ag}_2\text{C}_2 \cdot 2\text{AgClO}_4 \cdot 2\text{H}_2\text{O}$ is encapsulated inside an octahedral Ag_6 cage. The cationic Ag_6 units generate metallic layers through sharing corners. The perchlorate anions and aqua ligands are situated between the layers [6b].

2. Results and discussion

The addition of $[\text{Ag}(\text{C}_2\text{Bu}')_n]$ to a solution of AgBF_4 in acetone in 2:1 mol ratio immediately gave a clear solution. Addition of hexane afforded colourless crystals of the trinuclear cationic cluster polymer complex $\{[\text{Ag}_3(\text{C}_2\text{Bu}')_2][\text{BF}_4] \cdot 0.6\text{H}_2\text{O}\}_n$. The IR spectrum showed a sharp band at 2007 cm^{-1} assigned to $\nu(\text{C}\equiv\text{C})$. This frequency is lower than the corresponding $\nu(\text{C}\equiv\text{C})$ in $[\text{Ag}(\text{C}_2\text{Bu}')_n]$ and in the linear $[\text{Ag}(\text{C}_2\text{R})_2]^-$ by ca. 45 and 80 cm^{-1} , respectively. This dramatic lowering in $\nu(\text{C}\equiv\text{C})$, compared to that found in $[\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-$ and $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph})_4(\text{PPh}_3)_2]$ [1b,2], can be attributed to the presence of η^2, η^2 -coordinated alkyne ligand as well as to relatively strong π -interaction in this complex.

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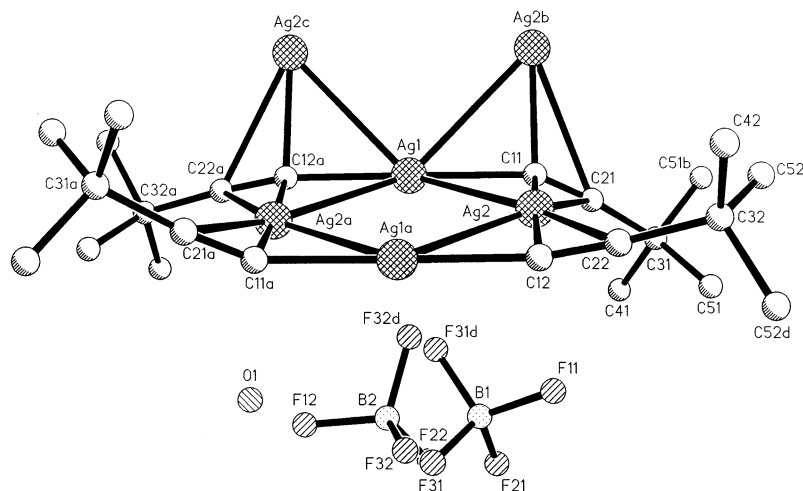


Fig. 1. Structure of $[\text{Ag}_3(\text{C}_2\text{Bu}')_2][\text{BF}_4] \cdot 0.6\text{H}_2\text{O}$. The methyl groups with the other possible orientation and the hydrogen atoms have been omitted for clarity.

The single-crystal X-ray analysis reveals the presence of two types of Ag atoms in the complex (Fig. 1). The first type, Ag1, is anionic end-on σ -bonded to two ethynyl groups Ag1–C11 2.113(14) Å and Ag1–C12a 2.086(13) Å. The second type, Ag2, is cationic side-on asymmetrically π -bonded to two ethynyl ligands Ag2–C11 2.162(8), Ag2–C21 2.753(5) Å and Ag2–C12 2.185(7), Ag2–C22 2.636(6) Å. The Ag2–C11 and Ag2–C12 distances are much shorter than the corresponding distances of 2.552(14) Å found in $[\text{Ag}(\text{C}_2\text{Ph})\text{PMe}_3]_n$ [3], 2.274(4)–2.362(4) Å found in $[\text{Ag}_5(\text{C}_2\text{Ph})_6]^-$ [1i], or 2.450(7)–2.521(7) Å found in $[\text{Ag}(\text{C}_2\text{SiMe}_3)\text{PMe}_3]_n$ [4], and indicate a stronger silver–acetylene π -interaction. Each two of $\text{Ag}(\text{C}_2\text{Bu}')_2$ moieties are glued parallel to each other by two Ag^+ ions (Ag2 and Ag2a). The Ag1, Ag2, Ag1a and Ag2a atoms are planar and approximately forming a square Ag1–Ag2 3.002(1) Å and Ag1–Ag2a 2.979(1) Å; Ag2–Ag1–Ag2a 87.41(3)° and Ag1–Ag2–Ag1a 92.59(3)°; Ag1...Ag1a 4.324(1) Å and Ag2...Ag2a 4.133(1) Å. The Ag1–Ag2 and Ag1–Ag2a distances fall within the range (2.76–3.05 Å) where significant Ag–Ag bonding has been considered to occur [1i,3,4,7]. With each other, the Ag planes form zigzag pattern with a dihedral angle of 118.78(5)° (Fig. 2). This arrangement gives Ag1 and Ag2 6 and 4 coordination numbers, respectively. The Ag atoms arrangement in the pattern can also be viewed as sets of edge-sharing tetragonal pyramids (the base atoms are Ag2, Ag2a, Ag2c and Ag2b, and the apical atom is Ag1) (Figs. 1 and 2). The polyhedron bases, which are formed of only cationic Ag atoms (Ag2), are infinitely extended in one direction (Fig. 2). The apical Ag atoms (Ag1), which are anionic and almost linearly bonded to two $\text{C}_2\text{Bu}'$ moieties C11–Ag1–C12a 178.9(6)° are alternately arranged on the opposite sides of the base plane.

3. Experimental details of $\{[\text{Ag}_3(\text{C}_2\text{Bu}')_2][\text{BF}_4] \cdot 0.6\text{H}_2\text{O}\}_n$

3.1. Synthesis, analytical and spectra

A solution of AgBF_4 (0.195 g, 1.0 mmol) in acetone was treated with $[\text{Ag}(\text{C}_2\text{Bu}')_n]$ (0.378 g, 2.0 mmol). Immediate clear colourless solution was obtained. Addition of hexane gave colourless crystals of the complex (0.460 g, 79%). m.p. 225 °C (decomp.) Found: C, 24.35, H, 3.06, Ag, 55.20. $\text{C}_{12}\text{H}_{19.2}\text{Ag}_3\text{BF}_4\text{O}_{0.6}$ requires C, 24.73, H, 3.32, Ag, 55.58, $\nu(\text{C}\equiv\text{C})$ (KBr disc), 2007 cm^{-1} , $\nu(\text{O}-\text{H})$ 3595, 3513 and 1613 cm^{-1} , $^1\text{H-NMR}$ (acetone- d_6) δ 1.48 (s).

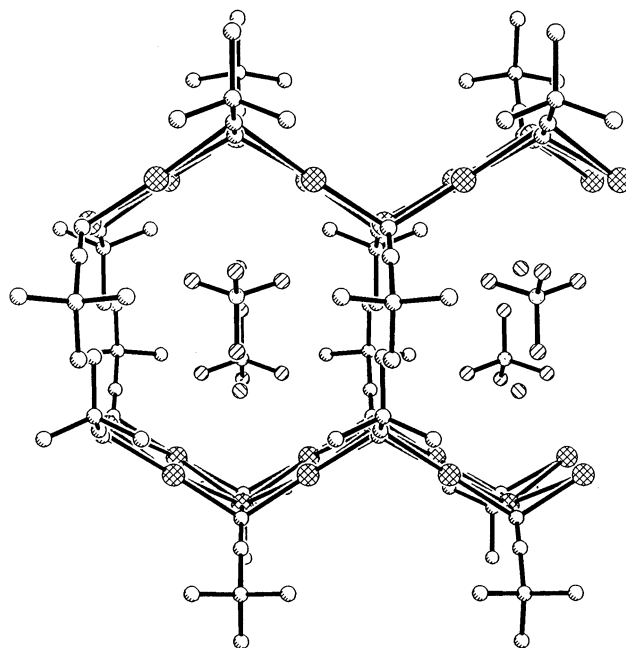


Fig. 2. Packing diagram of $\{[\text{Ag}_3(\text{C}_2\text{Bu}')_2][\text{BF}_4] \cdot 0.6\text{H}_2\text{O}\}_n$ showing the zigzag pattern of the Ag planes.

Table 1
Crystal data, intensity data collection parameters and structure refinement results

Crystal data	
Chemical formula	Ag ₅ C ₁₂ H _{19.2} BF ₄ O _{0.6}
Formula weight	583.5
Colour of crystal	Colourless
Size of specimen (mm)	0.40 × 0.20 × 0.10
Crystal system	Monoclinic
Space group, E ² I	C2/m, 0.944
Lattice constants (from 28 reflections; 2θ = 22.05–29.55°)	
a (Å)	19.610(3)
b (Å)	7.439(1)
c (Å)	12.956(2)
β (°)	106.29(1)
V (Å ³)	1814.0(5)
Z	4
D _{calc.} (g cm ⁻³)	2.132
μ(Mo–K _α) (mm ⁻¹)	3.233
F(000)	1107
Data collection	
Diffractionmeter	Siemens P4
Radiation, λ (Å)	Mo–K _α , 0.71073
Monochromator	Graphite
Scan method	ω
Range of h, k, l	–1 ≤ h ≤ 23, –1 ≤ k ≤ 8, –15 ≤ l ≤ 14
No. of independent reflections	1654
R _{int}	0.0199
No. of observed reflections	1244
Cut-off criteria	F _o > 4σ(F _o)
Absorption corrections	Empirical Ψ-scan method
Transmission coefficients	0.364–0.824
Structure refinement	
Refinement on	F ²
R [F > 4σ(F)]	0.057
wR (F ²)	0.177
w	1/[σ ² (F _o ²) + (0.0942P) ² + 14.11P] where P = (F _o ² + 2F _c ²)/3
S	1.041
No. of independent reflections used for calculation	1648
No. of parameters refined	103
Δρ (e Å ⁻³)	0.986, –0.788

3.2. Crystal structure determination

Crystal data, intensity collection parameters and structure refinement results are summarized in Table 1. The structure was solved by direct methods [8] and refined by full-matrix least-squares (on F²) [9]. The two independent *tert*-butyl groups (Fig. 1) are orientationally disordered, and can be split into pairs. The BF₄ (central atom B1) group is positionally disordered with BF₄ (central atom B2) group in 0.6:0.4 ratio respectively. The tetrahedral disordered groups were successfully refined as idealized rigid groups (C–C 1.520 Å and B–F 1.375 Å) with alternative partial occupancies for the related groups. The BF₄ groups and the terminal C atoms in the *tert*-butyl groups were refined

Table 2
Atomic coordinates (× 10⁴) and equivalent or isotropic displacement parameters (Å² × 10³)

Atom	x	y	z	U _{eq} ^a /U _{iso}
Ag1	2882(1)	0	4517(1)	79(1)
O1	4355(18)	5000	5608(26)	156(10)
C11	2019(8)	0	3109(11)	75(3)
C21	1842(5)	0	2176(2)	74(3)
C31	1721(1)	0	965(3)	135(8)
C41	2433(1)	0	714(9)	186(4)
C51	1298(6)	1669(4)	487(8)	186(4)
C41 ^b	927(1)	0	408(4)	186(4)
C51 ^b	2056(2)	1668(4)	638(6)	186(4)
Ag2	1632(1)	2439(1)	3656(1)	102(1)
C12	1253(7)	5000	4110(11)	74(3)
C22	678(4)	5000	3491(9)	81(4)
C32	–89(4)	5000	2799(8)	162(11)
C42	–582(6)	5000	3518(15)	186(4)
C52	–225(7)	3331(4)	2094(9)	186(4)
C42 ^b	–107(10)	5000	1619(8)	186(4)
C52 ^b	–463(4)	6668(4)	3043(13)	186(4)
B1	2995(6)	5000	2941(11)	103(10)
F11	2274(6)	5000	2467(15)	186(4)
F21	3345(9)	5000	2157(15)	186(4)
F31	3181(8)	6508(5)	3570(11)	186(4)
B2	3627(9)	5000	3925(13)	185(35)
F12	4250(11)	5000	4743(16)	186(4)
F22	3778(13)	5000	2951(14)	186(4)
F32	3239(9)	6507(5)	4003(17)	186(4)

$$^a U_{eq} = (1/3) \sum_i \sum_j a_i^* a_j^* a_i a_j$$

^b The other orientationally disordered atom.

isotropically. H atoms were included in riding mode with U_{iso} = 0.10 Å². The water molecule is also positionally disordered. Its occupancy factor was refined to 0.6. Final R = 0.057 for 1648 reflections and 103

Table 3
Selected bond lengths (Å) and bond angles (°)^a

Bond lengths			
Ag1–Ag2	3.002(1)	Ag2–C11	2.162(8)
Ag1–Ag2b	3.002(1)	Ag2–C21	2.753(5)
Ag1–Ag2a	2.979(1)	Ag2–C12	2.185(7)
Ag1–Ag2c	2.979(1)	Ag2–C22	2.636(6)
Ag1–C11	2.113(14)	C11–C21	1.159(14)
Ag1–C12a	2.086(13)	C12–C22	1.185(15)
Bond angles			
Ag1–Ag2–Ag1a	92.59(3)	C11–Ag2–C12	175.9(5)
Ag2–Ag1–Ag2a	87.41(3)	Ag2–C11–C21	108.2(6)
C11–Ag1–C12a	178.9(6)	Ag2–C12–C22	98.6(6)
Ag1–C11–Ag2	89.2(4)	Ag2–C21–C31	135.1(1)
Ag1–C12a–Ag2a	88.4(4)	Ag2–C22–C32	127.6(3)
Ag1–C11–Ag2b	89.2(4)	Ag2–C11–Ag2b	114.1(7)
Ag1–C12a–Ag2c	88.4(4)	Ag2a–C12a–Ag2c	121.4(7)
Ag1–C11–C21	146.4(12)	C11–C21–C31	171.9(11)
Ag1a–C12–C22	165.5(13)	C12–C22–C32	174.0(13)

^a Symmetry codes: (a) –x + 0.5, –y + 0.5, –z + 1; (b) x, –y, z; (c) –x + 0.5, y – 0.5, –z + 1; (d) x, –y + 1, z.

parameters. Atomic coordinates and selected bond lengths and bond angles are given in Tables 2 and 3, respectively.

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