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Synthesis and Structural Characterization of a Halide-Free Rhombohedral Silver-Alkynyl Cage Complex $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$

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The novel cationic complex $[Ag_{14}(C_2tBu)_{12}]^{2+}$ has been synthesized by four reactions: reaction of $[Ag(C_2tBu)]_n$ and $AgBF_4$ in acetone in a 6:1 mole ratio, that of $HC{\equiv}CtBu$ and $AgBF_4$ in water in the absence of a base, treatment of $[AgC_2tBu]_n$ with HBF_4 in acetone or that of $\{[Ag_3(C_2tBu)_2][BF_4]\}_n$ with $[Ag(C_2tBu)]_n$ in a 1:4 mole ratio. Single-crystal X-ray studies showed it to be a hexacapped cube of silver(I) atoms, with twelve η^1, μ^3-C_2tBu ligands.

Introduction

Since the pioneering work of Nast[1] on acetylide complexes, dramatic developments in the field, parallel to the advances in organometallic chemistry, have been accomplished. The versatile mode of bonding of the alkynyl ligand resulted in numerous polynuclear alkynyl complexes.[2,3] Different aspects of the subject have been reviewed extensively.[2,4] Luminescence properties, particularly of mixed-metal platinum(II)-copper(I) and -silver(I) alkynyl complexes have been studied widely.[5] In the field of pure coinage metal alkynyls, new aspects of organometallic chemistry emerged when bis(phenylethynyl) metallates $[M(C_2Ph)_2]^-$ (M = Cu, Ag, Au) were treated with metal phenylacetylide polymers $[M(C_2Ph)]_n$ (M = Cu, Ag, Au). Consecutive steps of ethynylation and condensation of the formed anionic and cationic moieties resulted in the formation of homonuclear $[Ag_5(C_2Ph)_6]^-$ and heteronuclear $[Au_2Cu(C_2Ph)_4]^-$, $[Au_3M_2(C_2Ph)_6]^-$ (M = Cu, Ag), $[Ag_6Cu_7(C_2Ph)_{14}]^-$ and $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ complexes.[6] Extension of ethynylation reactions to neutral complexes resulted in the complexes $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$, $[Ag_2Cu_2(C_2Ph)_4(PPh_3)_4]$, $[AuAg(C_2Ph)_2]_n$, $[AuCu(C_2Ph)_2]_n$ and $[AgCu(C_2Ph)_2]_n$.[6i,7] Silver cages of various structures encapsulating the dianion C_2^{2-}, which is isoelectronic with CN^-, have been reported.[8] Recently anion-templated, rhombohedral silver-alkynyl cages $[Ag_{14}(C_2tBu)_{12}X]^+$ (X = F, Cl, Br) were synthesized and structurally identified.[9] Earlier we reported the synthesis and structure of the novel cationic silver alkynyl polymer $[Ag_3(C_2tBu)_2]_n[BF_4]_n$.[10] We now report new aspects of the chemistry resulting from the synthesis of halide-free rhombohedral silver alkynyl complex $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$ and its structure.

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Results and Discussion

The addition of $AgBF_4$ to $[Ag(C_2tBu)]_n$ in a 1:6 mole ratio in acetone gave a clear solution. Normal workup resulted in the slow precipitation of colourless crystals of $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$. Elemental analysis agrees very well with this formulation. The infrared spectrum has a strong $\nu(C{\equiv}C)$ signal at 2036 cm^{-1}. This frequency is dramatically lower than that of the linear complex $[Ag(C_2Ph)_2]^-$[6i] (by ca. 50 cm^{-1}), which indicates a bridging mode of bonding. A very strong band at 1077 cm^{-1} was assigned to BF_4^-.

Single-crystal X-ray structure determination showed that the fourteen silver atoms are arranged in a hexacapped cube of silver atoms (rhombohedral dodecahedron) with twelve η^1, μ^3-alkynyl ligands, each pair of alkynyl groups are almost linearly bonded to each capping silver atom, and every ligand bridges two nearby silver atoms on each edge of the cube (Figure 1).

This metal cage is similar to the cage of $[Ag_{14}(C_2tBu)_{12}X][BF_4]$ (X = F, Cl, Br), in which the X^- anion is located at the centre of the cage.[9] We found, however, that halide ions are not a prerequisite to the formation and stability of the cage as claimed by other workers.[9] Unlike the case in complexes $[Ag_{14}(C_2tBu)_{12}X][BF_4]$,[9a,9b] the BF_4^- anions are unambiguously located here. There is a weak Ag···F interaction [2.499(4) Å]. The ^{19}F NMR spectrum showed two reso-

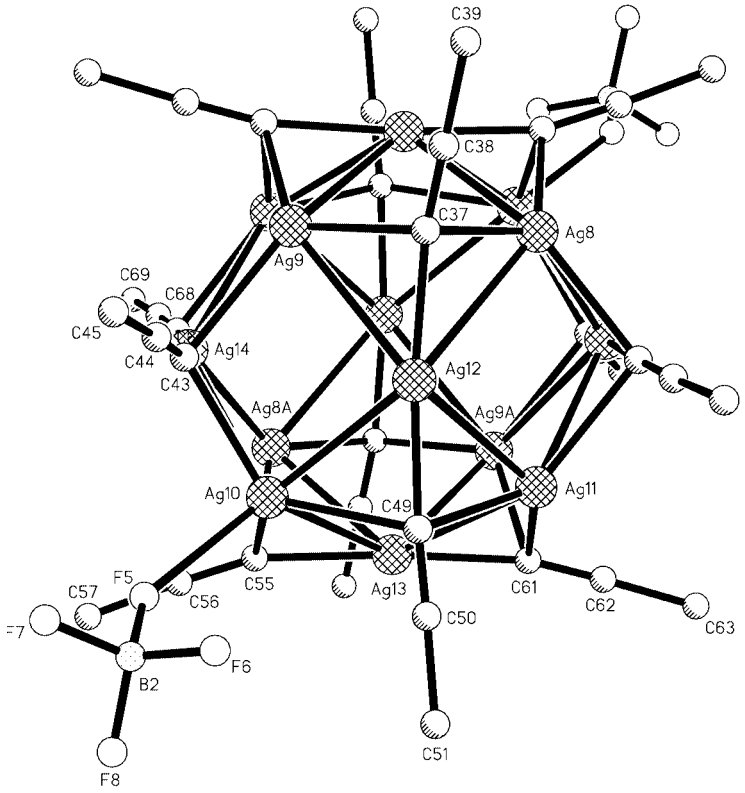

Figure 1. Structure of $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$. Methyl groups of tertiary butyl groups have been omitted for clarity.

nances characteristic for BF_4^- at –151.62 and –151.57 ppm.[9a,9b]

The most interesting finding that emerges from the comparison of the encapsulated halide-anion Ag_{14} cages[9a,9b] with the present anion-free Ag_{14} cage is that the encapsulated fluoride anion shrinks the Ag_{14} cage, while the bromide ion expands it. The mean Ag–Ag bond length in the anion-free cage is 2.9747(7) Å, which is almost equal to the corresponding value in the chloride-encapsulated cage [2.971(2) Å], but is 0.015 Å shorter and 0.064 Å longer than the corresponding bond lengths in the bromide- and fluoride-encapsulated cages, respectively.

This cationic cluster represents the highest homoleptic finite polynuclear monosubstituted alkynyl complex to be synthesized and structurally identified. Although neutral ligands and anions[11,12] are known to depolymerize monosubstituted alkynyl coinage metal polymers $[M(C_2R)]_n$ (M = Cu, Ag, Au), this reaction represents the first cationic depolymerization reaction for these polymers.

The same complex was also prepared by the reaction of HC_2tBu and $AgBF_4$ in water by using different mole ratios in the absence of a base. The reactions in aqueous NH_3, which afford $[Ag(C_2R)]_n$, are well known for the identification of monosubstituted alkynes; nevertheless, no report has been documented for the reaction in the absence of a base. If the above reaction is carried out in ether, the cationic polymer $[Ag_3(C_2tBu)_2]_n[BF_4]_n$[10] is obtained. On the other hand, using $AgNO_3$ with HC_2tBu in water results in the formation of the neutral polymer $[Ag_3(C_2tBu)_2NO_3]_n$, which was reported recently.[9b] The other product of the above reactions is HBF_4 [Equation (1), Equation (2)]:

$$7\ AgBF_4 + 6\ HC{\equiv}C\text{–}tBu \rightarrow \frac{1}{2}\{[Ag_{14}(C_2tBu)_{12}][BF_4]_2\} + 6\ HBF_4 \quad (1)$$

$$3\ AgBF_4 + 2\ HC{\equiv}C\text{–}tBu \rightarrow \frac{1}{n}\{[Ag_3(C_2tBu)_2][BF_4]\}_n + 2\ HBF_4 \quad (2)$$

The acid was determined by titration and by measuring the pH of the solution. This implies that these complexes are stable in strongly acidic media.

A third procedure for the synthesis of the same complex is the reaction of HBF_4 with $[Ag(C_2tBu)]_n$ in acetone. The product was identified by usual methods and by comparison with an authentic sample. If excess acid is used, $\{[Ag_3(C_2tBu)_2][BF_4]\}_n$ is obtained [Equation (3), Equation (4)]:

$$HBF_4 + \frac{7}{n}[Ag(C_2tBu)]_n \rightarrow \frac{1}{2}\{[Ag_{14}(C_2tBu)_{12}][BF_4]_2\} + HC_2tBu \quad (3)$$

$$HBF_4 + \frac{3}{n}[Ag(C_2tBu)]_n \rightarrow \frac{1}{n}\{[Ag_3(C_2tBu)_2][BF_4]\}_n + HC_2tBu \quad (4)$$

A fourth route for the same complex involves the reaction of $\{[Ag_3(C_2tBu)_2][BF_4]\}_n$ and $[Ag(C_2tBu)]_n$ in acetone in a 1:4 mole ratio [Equation (5)]:

$$\frac{1}{n}\{[Ag_3(C_2tBu)_2][BF_4]\}_n + \frac{4}{n}[Ag(C_2tBu)]_n \rightarrow \frac{1}{2}\{[Ag_{14}(C_2tBu)_{12}][BF_4]_2\} \quad (5)$$

The cage structure of the complex indicates without doubt that a halide template is not necessary for the formation and stability of such cages. The different reactions described for the synthesis of the complex might be of general use in the synthesis of homo- and heteronuclear group 11 metal-alkynyl cluster complexes.

Experimental Section

Synthesis of $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$

Method 1: Silver tetrafluoroborate, $AgBF_4$ (98 mg, 0.5 mmol), was added to a suspension of $[Ag(C_2tBu)]_n$ (567 mg, 3.0 mmol) in acetone(20 mL). The reaction mixture was stirred for 24 h and then filtered. The solution was concentrated to a small volume and was left for crystallization. Colourless crystals of $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$ (540 mg, 81%) were obtained in two crops; m.p. 187–190 °C. IR (KBr disc):$\tilde{\nu}$ = 2036 (vs) cm^{-1} (C≡C). ^1H NMR (400 MHz, [D$_6$]-acetone, TMS): δ = 1.46 ppm. $C_{72}H_{108}Ag_{14}B_2F_8$ (2657.41): calcd. C 32.68, H 4.12; found C 32.58, H 4.04.

Method 2: *tert*-Butylacetylene (1.96 mL, 16.0 mmol) was added to $AgBF_4$ (389 mg, 2.0 mmol) in water (20 mL) in an ice bath. The mixture became turbid within a few minutes, and a white, floating precipitate formed. After stirring for 12 h, the white precipitate of $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$ was filtered off and dried (224 mg, 59%); m.p. 190 °C. IR (KBr disc):$\tilde{\nu}$ = 2037 (vs) cm^{-1} (C≡C). $C_{72}H_{108}Ag_{14}B_2F_8$ (2657.41): calcd.: Ag 56.62; found C 32.20, H 4.15, Ag 57.80, measured pH 1.79.

Method 3: Tetrafluoroboric acid, HBF_4 (0.103 mL, 0.46 mmol), was added to a suspension of $[Ag(C_2tBu)]_n$ (567 mg, 3.0 mmol) in acetone (25 mL) with stirring in a nitrogen atmosphere at room temperature. A clear solution was obtained within 10 min. The filtrate was concentrated to half volume. Addition of hexane (30 mL) effected the precipitation of colourless crystals of $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$ (470 mg, 77%). IR (KBr disc):$\tilde{\nu}$ = 2037 (vs) cm^{-1} (C≡C); identical in all respects to an authentic sample described above.

Method 4: Silver *tert*-butylacetylide (378 mg, 2.0 mmol) was added to solution of $\{[Ag_3(C_2tBu)_2][BF_4]\}_n$ (287 mg, 0.5 mmol) in acetone (25 mL). A clear solution was obtained within 15 min. Filtration and addition of hexane gave $[Ag_{14}(C_2tBu)_{12}][BF_4]_2$ (400 mg, 60%). IR (KBr disc): $\tilde{\nu}$ = 2037 (vs) cm^{-1} (C≡C); $C_{72}H_{108}Ag_{14}B_2F_8$ (2657.41): found C 32.56, H 4.05; identical in all respects to an authentic sample described above.

Reaction between *tert*-Butylacetylene and Silver Nitrate

tert-Butylacetylene, HC_2tBu (1.96 mL, 16.0 mmol), was added to $AgNO_3$ (340 mg, 2.0 mmol) in water (20 mL) in an ice bath. The mixture became turbid within a few minutes, and a white precipitate formed. After stirring for 12 h, the white precipitate of $[Ag_3(C_2tBu)_2(NO_3)]_n$ was filtered off, washed with water and dried (220 mg, 60%). IR (KBr disc): $\tilde{\nu}$ = 2023.5 (vs) cm^{-1} (C≡C); ref.[9b] 2022 cm^{-1}. $C_{12}H_{18}Ag_3NO_3$ (547.88): calcd. C 26.31, H 3.31, N 2.56; Ag 59.06; found C 26.00, H 3.19, N 2.69, Ag 58.80.

Crystal Data: $[C_{72}H_{108}Ag_{14}B_2F_8]$ M = 2657.38, triclinic, P$\bar{1}$, a = 13.725(1), b = 13.793(1), c = 24.466(2) Å, α = 95.16(1), β = 94.33(1), γ = 106.99(1)°, V = 4386.3(6) Å^3, Z = 2, $D_{calcd.}$ = 2.012 g cm^{-3}, μ (Mo-K_α) = 3.10 mm^{-1}, T = 120(2) K, colourless block; 52607 measured reflections, 23128 independent (R_{int} = 0.046 after semiempirical absorption correction), least-squares refinement of 924 parameters against F^2, $R(F)$ = 0.051 on 14969 independent reflections with $I>2\sigma(I)$, w$R(F^2)$ = 0.122 on all data. The structure contains two independent clusters, both at inversion centres. In one cluster, two Ag atoms are ordered, whereas twelve are disordered between two sets of positions in a 4:1 ratio (distances between alternative positions of the same atoms are 0.40 to 0.57 Å); six ethynyl ligands are disordered by a rotation around the quaternary C atom (which remains ordered), probably in concert with the disorder of the metal core. There is also rotational disorder of *t*Bu groups and monodentate BF_4 ligands. The second cluster is ordered, except for rotational disorder of two *t*Bu groups. CCDC-290250 contains 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.

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