DOI: 10.1002/anie.201202195

Cluster Compounds

High-Nuclearity Silver Ethynide Clusters Assembled with Phosphonate and Metavanadate Precursors**

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Dedicated to Prof. James Trotter on the occasion of his 80th birthday

Self-assembly through the reversible association of a few simple molecular building blocks into a variety of multicomponent species is a powerful means of obtaining structurally complex cluster and host–guest compounds.[1] Much work has been done in the exploration and understanding of the self-assembly of intricate polyoxometalates (POMs).[2] The building-block principles that have been established are beginning to yield fruitful results in the designed construction of POMs with desired properties.[3] On the other hand, selective chemical species have been successfully employed as internal or external templates to induce the formation of POMs in solution, and assembly control has been achieved by targeting specific templates that shift the equilibrium toward the realization of a predetermined structure.[4]

The multinuclear $\mathrm{R{-}C{\equiv}C{\supset}Ag}_n$ ($n = 3$, 4, 5; R = alkyl, aryl, heteroaryl) metal-ligand supramolecular synthon[5] is a versatile building block for the anion-templated synthesis of high-nuclearity silver(I) ethynide clusters.[6] Recently, we reported a high-nuclearity mixed-metal anionic silver(I) ethynide cluster, $[(\mathrm{V_2O_7})_2@\mathrm{Ag_{44}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{14}@(\mathrm{V_{32}O_{96}})]^{10-}$, which was synthesized by condensation and cyclic oligomerization of $[\mathrm{VO_3}]^-$ units in an organic medium in which a globular $(\mathrm{V_2O_7})_2@\mathrm{Ag_{44}}$ cluster serves as a cationic template to induce the assembly of a "cluster within a cluster", with its outer shell composed of a polyoxovanadium(V) macrocycle $\{\mathrm{V_{32}O_{96}}\}$.[6h] We have now isolated three unprecedented mixed-metal giant clusters with the silver(I) *tert*-butylethynide moiety and various phosphonate-functionalized oxovanadate building blocks as their surface components, as well as different numbers and kinds of anionic species as their encapsulated templates: $\{\mathrm{Cl_2}@\mathrm{Ag_{21}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_9[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]_2[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}](\mathrm{MeOH})_2(\mathrm{H_2O})_2\}\cdot 2\,\mathrm{MeOH}\cdot 2\,\mathrm{H_2O}$ (**1**), $[(\mathrm{Et})_4\mathrm{N}^+]_3\{[(\mathrm{O_2})\mathrm{V_2O_6}]_2@\mathrm{Ag_{36}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{12}[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(t\mathrm{BuPO_3})_2(\mathrm{NO_3})_7(2\text{-ClPy})(\mathrm{DMF})\}$ (**2**), and $[(\mathrm{Et})_4\mathrm{N}^+]_2\{[(\mathrm{O_2})\mathrm{V_2O_6}]_2\mathrm{Cl}@\mathrm{Ag_{36}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{11}[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2[(t\mathrm{BuPO_3})_2(\mathrm{VO_2})](t\mathrm{BuPO_3})_2(t\mathrm{BuPO_3H})(\mathrm{DMF})(\mathrm{NO_3})_2(\mathrm{Et_2O})(\mathrm{H_2O})_3\}\cdot 2\,\mathrm{DMF}\cdot 2\,\mathrm{Et_2O}\cdot 4\,\mathrm{H_2O}$ (**3**).

The reaction of $(\mathrm{Et_4N})\mathrm{VO_3}$ in methanol with $t\mathrm{BuPO_3H_2}$, $\mathrm{AgC{\equiv}C}t\mathrm{Bu}$, $\mathrm{AgBF_4}$ and a small amount of $(\mathrm{BzEt_3N})\mathrm{Cl}$ as a chloride source yielded $\{\mathrm{Cl_2}@\mathrm{Ag_{21}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_9[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]_2[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}](\mathrm{MeOH})_2(\mathrm{H_2O})_2\}\cdot 2\,\mathrm{MeOH}\cdot 2\,\mathrm{H_2O}$ (**1**). Single-crystal X-ray analysis[7] revealed that complex **1** is a solvated, neutral mirror-symmetric, cashewnut-shaped $\mathrm{Ag_{21}}$ cluster encapsulating a pair of template chloride ions (Figure 1), with argentophilic Ag···Ag bond distances in the range 2.811(2)–3.188(2) Å. Each chloride coordinates to six silver atoms with Ag···Cl distances varying from 2.581(6) to 3.028(6) Å, which are shorter than those found in $[\mathrm{Ag_{19}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{11}(\mathrm{CF_3CO_2})_7\mathrm{Cl}]$ (2.940–3.847 Å) and

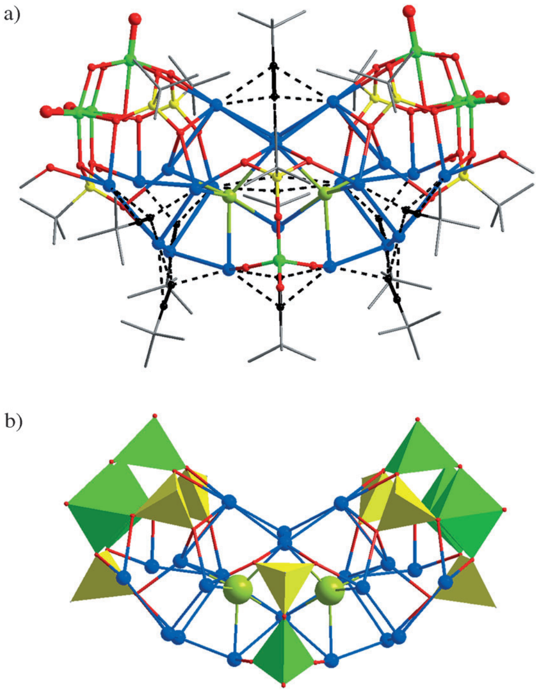

Figure 1. a) Perspective view of the neutral $\{\mathrm{Cl_2}@\mathrm{Ag_{21}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_9[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]_2[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}](\mathrm{MeOH})_2(\mathrm{H_2O})_2\}$ cluster that exhibits σ_h symmetry in complex **1**. H atoms are omitted for clarity. The ethynide groups are represented as thick black rods. The carbon atoms of the ethynide group are represented as small black spheres, and their bonds to silver atoms are indicated by broken lines. The oxygen atoms of the V=O groups are represented as larger red spheres. b) Core skeleton of the $\mathrm{Ag_{21}}$ cluster molecule with two encapsulated chloride ions. The $[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}]^{2-}$ and $[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]^{4-}$ building units are illustrated as polyhedral models. The enclosed chloride ions are represented by large lime-colored spheres. Ag blue, O red, P yellow, V green, Cl lime green.

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[**] This work was supported by the Hong Kong Research Grants Council (GRF Ref. CUHK 402710) and the Wei Lun Foundation. We thank The Chinese University of Hong Kong for the award of a Postdoctoral Research Fellowship to Y.-P.X.

$[Ag_{14}(C{\equiv}CtBu)_{12}Cl]BF_4$ (3.116–3.297 Å).[8] The cluster can be described as consisting of one $[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}]^{2-}$ and two $[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]^{4-}$ building units linked together through the $Cl_2@Ag_{21}$ core. In the $[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]^{4-}$ unit (Figure 2d), the cap-shaped trinuclear $[\mathrm{V_3O_6(OH)}]^{2+}$ subunit is composed of three V=O groups alternately bridged by three *syn* μ_2-oxo ligands and an anti μ_3-OH ligand. Each vanadium(V) atom of the trinuclear unit is further bound by two μ_2-O atoms of different phosphonates to achieve sixfold coordination; the observed V–O bond lengths are 1.804(6)–2.224(5) Å, and the V=O bond lengths are 1.586(6)–1.593(6) Å. On the other hand, the $[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}]^{2-}$ unit consists of a $\mathrm{VO_2(OH)}$ group coordinated by a μ_2-O atom from a *tert*-butylphosphonate ligand (Figure 2b), the four oxygen atoms of which coordinate to five silver atom. Of the nine peripheral tBuC≡C ligands, seven adopt a μ_3 and two a μ_4 bridging mode to coordinate to silver atoms. Additionally, two methanol molecules and two water molecules function as terminal ligands each coordinating to one silver atom, and the crystal structure also contains two solvated methanol and two water molecules in the unit cell.

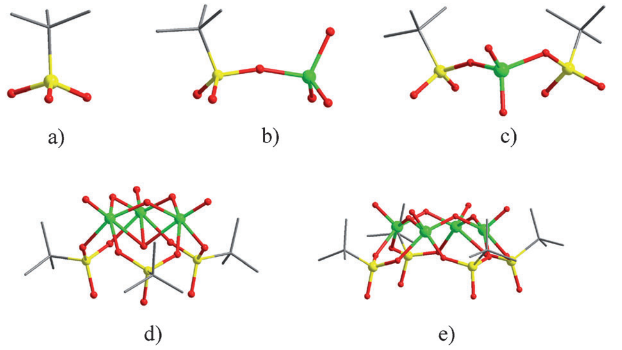
a) b) c) d) e)

Figure 2. Structure building units. a) The *tert*-butylphosphonate ligand in **1**–**3**. b) $[(t\mathrm{BuPO_3})\mathrm{VO_2(OH)}]^{2-}$ in **1**. c) $[(t\mathrm{BuPO_3})_2(\mathrm{VO_2})]^{3-}$ in **3**. d) $[(t\mathrm{BuPO_3})_3\mathrm{V_3O_6(OH)}]^{4-}$ in **1**. e) $[(t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ in **2** and **3**. H atoms are omitted for clarity. C gray, O red, V green, P yellow.

A solution of AgC≡CtBu and $AgBF_4$ in DMF was treated with a mixture of $t\mathrm{BuPO_3H_2}$, $(\mathrm{Et_4N})\mathrm{VO_3}$, 2-chloropyridine, and a small amount of aqueous hydrogen peroxide in DMF, yielding an orange-red solution from which orange prismatic crystals of $[(\mathrm{Et})_4\mathrm{N}^+]_3\{[(\mathrm{O_2})\mathrm{V_2O_6}]_2@\mathrm{Ag_{36}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{12}[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(t\mathrm{BuPO_3})_2(\mathrm{NO_3})_7(2\text{-ClPy})(\mathrm{DMF})\}$ (**2**) were deposited. Complex **2** possesses an anionic ellipsoidal cluster shell composed of thirty-six silver(I) ions consolidated by two $[(t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ capping units on opposite sides, two *tert*-butylphosphonate ligands, seven nitrate anions, a 2-chloropyridine, a DMF, and twelve peripheral $t\mathrm{BuC{\equiv}C^-}$ ligands, which encapsulates a pair of template $[(\mathrm{O_2})\mathrm{V_2O_6}]^{4-}$ anions (Figure 3). In the $[(\mathrm{O_2})\mathrm{V_2O_6}]^{4-}$ moiety, the peroxo group is connected to a $[(t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ surface unit with peroxo O_{po}–O_{po} bond lengths in the range of 1.316(4) to 1.479(2) Å, whereas the other six oxygen atoms are bound to silver atoms by μ_1, μ_2-η^1,η^1 or μ_3-η^1,η^1,η^1 ligation modes. The boat-shaped cyclic $[\mathrm{V_4O_8}]^{4+}$ fragment in each $[(t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ capping unit is composed of four V=O groups held together by four μ_2-oxo ligands each binding two adjacent vanadium(V) atoms, with each *tert*-butylphosphonate ligand adopting a μ_6 bridging mode to coordinate to two vanadium and four silver atoms (Figure 2e). Two *tert*-butylphosphonate ligands, each adopting the μ_6 bridging mode to bind six silver atoms, consolidate the mixed-metal cluster shell with Ag–O_P (O_P = oxygen atom of the *tert*-butylphosphonate ligand) bond lengths ranging from 2.123(2) to 2.400(2) Å. Seven nitrate anions adopt μ_1, μ_2, μ_3, or μ_4 ligation modes to coordinate to silver atoms with Ag–O_n (O_n = oxygen atom of the nitrate ligand) distances varying from 2.272(6) to 2.806(6) Å. Overall charge balance against the giant silver–vanadium anionic cluster is provided by three $\mathrm{Et_4N^+}$ counter cations in the crystal structure.

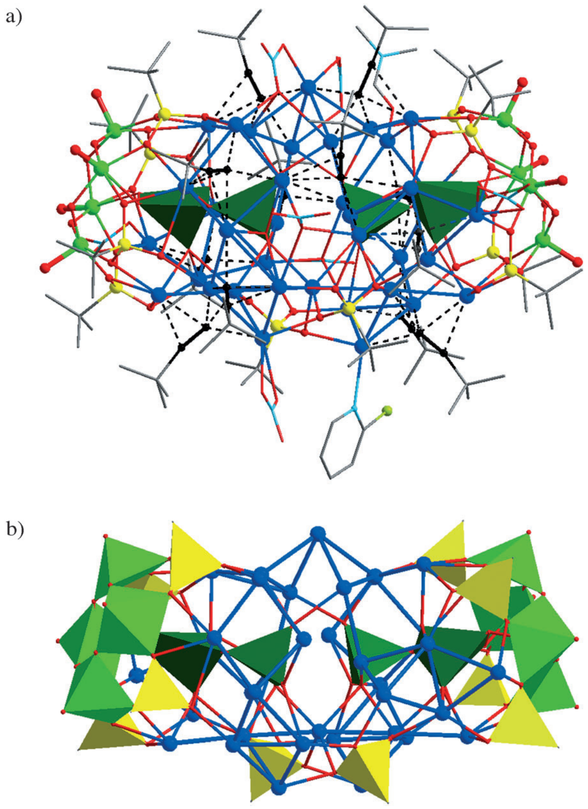

Figure 3. a) Perspective view of the anionic $\{[(\mathrm{O_2})\mathrm{V_2O_6}]_2@\mathrm{Ag_{36}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{12}[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(t\mathrm{BuPO_3})_2(\mathrm{NO_3})_7(2\text{-ClPy})(\mathrm{DMF})\}^{3-}$ cluster with two encapsulated $[(\mathrm{O_2})(\mathrm{V_2O_6})]^{4-}$ templates in complex **2**. H atoms are omitted for clarity. b) Core skeleton of the Ag_{36} cluster. The $[(t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ building units and the $[(\mathrm{O_2})(\mathrm{V_2O_6})]^{4-}$ templates are illustrated as polyhedral models. See Figure 1 for atom labeling; Ag blue, N sky blue, V green (peripheral), dark green (template).

The $[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]^{4-}$ unit also exists in two previously reported high-nuclearity silver(I) phenylethynide clusters, $\{(\mathrm{NO_3})_2@\mathrm{Ag_{16}}(\mathrm{C{\equiv}CPh})_4[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(\mathrm{DMF})_6(\mathrm{NO_3})_2\}$ and $\{[(\mathrm{O_2})\mathrm{V_2O_6}]_3@\mathrm{Ag_{43}}(\mathrm{C{\equiv}CPh})_{19}[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_3(\mathrm{DMF})_6\}$.[6g] Notably, three $[(\mathrm{O_2})\mathrm{V_2O_6}]^{4-}$ template ions are accommodated within the neutral Ag_{43} cluster in the latter complex, as compared to only two inside the anionic Ag_{36} cluster of **2**.

The synthetic procedure used to obtain $[(\mathrm{Et})_4\mathrm{N}^+]_2\{[(\mathrm{O_2})\mathrm{V_2O_6}]_2$ $\mathrm{Cl}@\mathrm{Ag_{36}}(\mathrm{C{\equiv}C}t\mathrm{Bu})_{11}[(t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2[(t\mathrm{BuPO_3})_2(\mathrm{VO_2})](t\mathrm{BuPO_3})_2(t\mathrm{BuPO_3H})(\mathrm{DMF})(\mathrm{NO_3})_2(\mathrm{Et_2O})$-

$(H_2O)_3\}\cdot 2DMF\cdot 2Et_2O\cdot 4H_2O$ (**3**) is similar to that of **2**, except that $(BzEt_3N)Cl$ as a chloride source was added to the reaction mixture. Complex **3** exhibits an anionic Ag_{36} cage encapsulating a chloride and two $[(O_2)V_2O_6]^{4-}$ anions (Figure 4). The core skeleton can be taken as arising from fusion of $Cl@Ag_{13}$ and $[(O_2)V_2O_6]_2@Ag_{30}$ cages by sharing seven Ag vertices. The Ag⋯Cl distances fall in the range from 2.411(5) to 2.985(3) Å. The structure of the $[(O_2)V_2O_6]$ moiety is identical to that found in **2**, with the peroxo group connecting to the $[(tBuPO_3)_4(V_4O_8)]^{4-}$ surface unit, and with six oxygen atoms bounding to silver atoms. The high-nuclearity Ag_{36} cluster skeleton is stabilized by one $[(tBuPO_3)_2(VO_2)]^{3-}$, two $[(tBuPO_3)_4(V_4O_8)]^{4-}$, one $tBuPO_3H^-$, and two $tBuPO_3^{2-}$ building units. The structure of the $[(tBuPO_3)_4(V_4O_8)]^{4-}$ moiety is also identical to that found in **2**, with each *tert*-butylphosphonate ligand adopting a μ_6 bridging mode to coordinate to two vanadium and four silver atoms. The $[(tBuPO_3)_2(VO_2)]^{3-}$ unit (Figure 2c) consists of the central VO_2 group and two *tert*-butylphosphonate ligands in which one oxygen atom serves as the common vertex of $\{VO_4\}$ tetrahedra, while the remaining oxygen atoms are bound to silver atoms in μ_2-η^1, η^1 or μ_3-η^1,η^1, η^1 ligation modes with Ag−O bond distances from 2.207(1) to 2.688(1) Å. Each $tBuPO_3^{2-}$ unit adopts the μ_6 bridging mode to coordinate to six silver atoms. However, in the $tBuPO_3H^-$ unit, two oxygen atoms coordinate to four silver atoms, and its third protonated oxygen atom is not involved. Each $tBuC{\equiv}C$ ligand adopts μ_3- or μ_4- bridging modes to link a planar or butterfly silver(I) tetragon, and a total of eleven ethynide ligands are peripherally coordinated to silver atoms in order to hold the cluster together. Additionally, a DMF, an ether, three water molecules, and two nitrate anions each coordinate to one silver atom, and the crystal structure also contains two DMF, two ether, and four water solvate molecules in the unit cell. Overall charge balance against the mixed-metal anionic cluster is provided by two Et_4N^+ counter cations in the crystal structure.

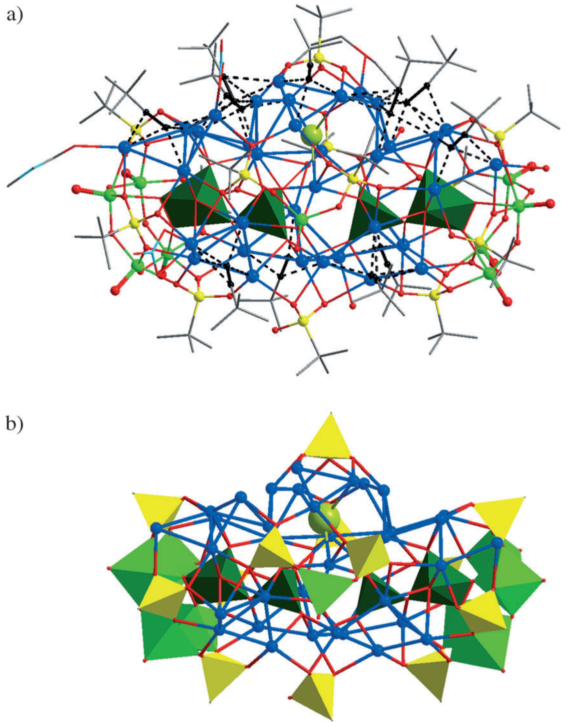

Figure 4. a) Perspective view of the $\{[(O_2)V_2O_6]_2Cl@Ag_{36}(C{\equiv}CtBu)_{11}[(tBuPO_3)_4V_4O_8]_2[(tBuPO_3)_2(VO_2)](tBuPO_3)_2(tBuPO_3H)(DMF)(NO_3)_2(Et_2O)(H_2O)_3\}^{2-}$ cluster that encapsulates a chloride and two $[(O_2)(V_2O_6)]^{4-}$ template ions in complex **3**. H atoms are omitted for clarity. b) Core skeleton of the Ag_{36} cluster anion. The $[tBuPO_3H]^-$, $[tBuPO_3]^{2-}$, $[(tBuPO_3)_4(V_4O_8)]^{4-}$ and $[(tBuPO_3)_2(VO_2)]^{3-}$ building units and the $[(O_2)(V_2O_6)]^{4-}$ templates are illustrated as polyhedral models. See Figure 1 for atom labeling; Ag blue, N sky blue, V green (peripheral), dark green (template).

The syntheses and structural characterization of **1**–**3** showed that large silver(I) ethynide clusters can be built up by an assembly process in solution. Metavanadates of monovalent cations generally contain infinite chains of corner-sharing VO_4 tetrahedra. It is remarkable tha, in the presence of $tBuPO_3H_2$, the precursor $(Et_4N)VO_3$ undergoes transformation to yield various oxovanadium(V) phosphonate building blocks, namely $[(tBuPO_3)VO_2(OH)]^{2-}$, $[(tBuPO_3)_2(VO_2)]^{3-}$, $[(tBuPO_3)_3V_3O_6(OH)]^{4-}$ and $[(tBuPO_3)_4(V_4O_8)]^{4-}$, which induce the formation of silver(I) ethynide cluster shells by Ag−O bonding interactions.

For the formation of phosphonate-functionalized oxovanadates, the choice of the solvent employed plays an important role. This is demonstrated by the reactions giving $[(tBuPO_3)VO_2(OH)]^{2-}$ and $[(tBuPO_3)_3V_3O_6(OH)]^{4-}$ in methanol, and $[(tBuPO_3)_2(VO_2)]^{3-}$ and $[(tBuPO_3)_4(V_4O_8)]^{4-}$ in DMF. On the other hand, in the synthesis of **1**, attempts to use $PhPO_3H_2$ for $tBuPO_3H_2$ only afforded $[Bz(Et)_3N^+]_8[(Et)_4N^+]_2[(V_2O_7)_2@Ag_{44}(C{\equiv}CtBu)_{14}@(V_{32}O_{96})]$.[6h]

The synthesis of **2** and **3** involving dropwise addition of aqueous hydrogen peroxide could provide a general procedure for incorporating peroxo groups into oxovanadates, yielding enlarged silver(I) polyoxovanadate clusters. Furthermore, in **1** the Ag_{21} cluster cavity accommodates two template chloride ions, and in **2** the Ag_{36} cluster cavity encloses two $[(O_2)V_2O_6]^{4-}$ template anions, whereas in **3** the Ag_{36} cluster cavity encapsulates a chloride and two $[(O_2)V_2O_6]^{4-}$ anions as templates.

In summary, we have synthesized and structurally characterized a neutral and two anionic high-nuclearity silver(I) ethynide clusters based on oxovanadium(V) phosphonate building blocks. Whereas $[(tBuPO_3)_4(V_4O_8)]^{4-}$ is a robust component for building multinuclear silver(I) ethynide cluster shells,[6g] analogous building units $[(tBuPO_3)_3V_3O_6(OH)]^{4-}$ and $[(tBuPO_3)VO_2(OH)]^{2-}$ are found in **1**, and $[(tBuPO_3)_2(VO_2)]^{3-}$ in **3**, for the first time. Compound **1** represents the first well-characterized neutral silver(I) polyoxovanadate cluster bearing two encapsulated chloride ions. Complex **2** provides a precedent of a giant silver(I) ethynide cluster that encapsulates two $[(O_2)(V_2O_6)]^{4-}$ templates. Complex **3** has the same nuclearity as **2** but betters it by accommodating an additional chloride ion; it also provides the first example of a cluster that has both $tBuPO_3^{2-}$ and $tBuPO_3H^-$ ligands bound to silver(I) centers.

The present study opens the way to synthetic studies of novel silver ethynide clusters employing potential precursors exemplified by arsonic acids and oxomolybdates.

Experimental Section

All chemicals were purchased from commercial sources and used as supplied. $(Et_4N)VO_3$ was synthesized by the literature method.[9]

1: tBuC≡CAg (0.095 g, 0.500 mmol) and $AgBF_4$ (0.098 g, 0.500 mmol) were dissolved in methanol (6 mL), and then $(BzEt_3N)Cl$ (0.011 g, 0.050 mmol) was added. After adding a 5 mL methanol solution of $(Et_4N)VO_3$ (0.117 g, 0.500 mmol) and tBuPO$_3$H$_2$ (0.069 g, 0.500 mmol), the resulting solution was kept under stirring for 15 min, and after 30 min a clear orange-red solution was obtained. Slow evaporation of the clear solution afforded orange prismatic crystals of **1**. Yield: ca. 18 % (based on V). Elemental analysis (%) calcd for $C_{86}H_{171}P_7Cl_2V_7Ag_{21}O_{46}$: C 21.29, H 3.55; found: C 21.37, H 3.41. Selected IR data (KBr): $\tilde{\nu} = 2003$ (C≡C), 960, 957, 945, 897, 875, 754, 725, 669, 585, 579 cm^{-1} ($[(PO_3)_3V_3O_6(OH)]_2$-$[(PO_3)VO_2(OH)]$).

2: $(Et_4N)VO_3$ (0.117 g, 0.500 mmol), tBuPO$_3$H$_2$ (0.011 g, 0.080 mmol), and 0.1 mL aqueous H_2O_2 (30 %) were dissolved in DMF (4 mL), and then tBuC≡CAg (0.095 g, 0.500 mmol) and $AgBF_4$ (0.098 g, 0.500 mmol) were added under stirring. After 15 min, 2-chloropyridine (0.010 g, 0.088 mmol) was added. An orange-red solution was collected by filtration. The orange-red crystals were obtained by diffusion of Et_2O into the reaction mixture. Yield: ca. 11 % (based on V). Elemental analysis (%) calcd for $C_{144}H_{269}N_{12}P_{10}ClV_{12}Ag_{36}O_{84}$: C 20.71, H 3.25, N 2.01; found: C 20.84, H 3.18, N 1.87; Selected IR data (KBr): $\tilde{\nu} = 2007$ (C≡C), 1059, 955, 885, 866, 787, 755, 623, 602, 543, 506 cm^{-1} ($[(V_4O_8)(V_2O_6)(O_2)$-$(PO_3)_4]$).

3: $(Et_4N)VO_3$ (0.117 g, 0.500 mmol), tBuPO$_3$H$_2$ (0.011 g, 0.080 mmol), and 0.1 mL aqueous H_2O_2 (30 %) were dissolved in DMF (4 mL), and then tBuC≡CAg (0.095 g, 0.500 mmol), $AgBF_4$ (0.098 g, 0.500 mmol), and $(BzEt_3N)Cl$ (0.011 g, 0.050 mmol) were added under stirring. After 15 min, 2-chloropyridine (0.010 g, 0.088 mmol) was added. An orange-red solution was collected by filtration. The orange-red crystals were obtained by diffusion of Et_2O into the reaction mixture. Yield: ca. 12 % (based on V). Elemental analysis (%) calcd for $C_{155}H_{322}N_7P_{13}ClV_{13}Ag_{36}O_{92}$: C 21.30, H 3.71, N 1.12; found: C 21.41, H 3.55, N 1.27; Selected IR data (KBr): $\tilde{\nu} =$ 2006 (C≡C), 1055, 958, 918, 882, 867, 765, 629, 608, 551, 515 cm^{-1} ($[(V_4O_8)(V_2O_6)(O_2)(PO_3)_4][(PO_3)_2(VO_2)]$).

Received: March 20, 2012

Keywords: clusters · ethynide · oxovanadates · phosphonates · silver

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[7] Crystallographic data: **1**: orthorhombic, $a = 26.504(3)$, $b = 35.718(4)$, $c = 15.074(2)$ Å, $V = 14270(3)$ Å^3, $T = 173$ K, space group $Pnma$, $Z = 8$, $\lambda = 0.71073$ Å, $\rho = 2.258$ cm^{-3}, $\mu(Mo_{K\alpha}) = 3.425$ mm^{-1}, $R_1 = 0.0588$, $wR_2 = 0.1137$ for $I > 2\sigma(I)$, GOF = 1.166. **2**: triclinic, $a = 21.617(4)$, $b = 25.383(5)$, $c = 30.016(6)$ Å, $\alpha = 90.0$, $\beta = 108.95(3)$, $\gamma = 117.75(3)$, $V = 13559(5)$ Å^3, $T = 173$ K, space group $P\bar{1}$, $Z = 2$, $\lambda = 0.71073$ Å, $\rho = 2.046$ cm^{-3}, $\mu(Mo_{K\alpha}) = 3.058$ mm^{-1}, $R_1 = 0.1477$, $wR_2 = 0.2854$ for $I > 2\sigma(I)$, GOF = 1.103. **3**: triclinic, $a = 23.741(2)$, $b = 24.399(2)$, $c = 26.387(3)$ Å, $\alpha = 96.403(2)$, $\beta = 97.415(2)$, $\gamma = 108.922(2)$, $V = 14146(2)$ Å^3, $T = 173$ K, space group $P\bar{1}$, $Z = 2$, $\lambda = 0.71073$ Å, $\rho = 2.052$ cm^{-3}, $\mu(Mo_{K\alpha}) = 2.984$ mm^{-1}, $R_1 = 0.0843$, $wR_2 = 0.2040$ for $I > 2\sigma(I)$, GOF = 1.057. CCDC 871840 (**1**), CCDC 871841 (**2**), and CCDC 871842 (**3**) 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.

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