Cluster Compounds

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$\{[Ag_{42}(CO_3)(C{\equiv}CtBu)_{27}(CH_3CN)_2][CoW_{12}O_{40}]_2\}[BF_4]$: An Intercluster Sandwich Compound

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The primary motivation for our research on intercluster compounds (ICCs) that consist of different, charged building blocks with sizes exceeding 1 nm in diameter is to provide well-defined materials, at least with respect to structural order, that allow the study of particle-size-dependent (nanoscopic) properties without inhomogeneous signal broadening effects. Using polyoxometalates[1,2] or C_{60} fullerides[3] as anions, and gold[1,3] or silver clusters[2] as cations, a number of intercluster compounds have been prepared as coarse crystalline materials. From these examples, some insight in the factors that determine the crystalline structure has already been gained. Besides the trivial effects that result from the sizes of the building units and the cation/anion ratio, the short-range and long-range (Coulomb) interactions are of comparable strength, thus enabling anions to have direct mutual contact.[2] Until now, we have employed particularly stable prefabricated building units. For advancing this field, we are pursuing two further objectives. The first is to utilize the notorious diverseness of polyoxometalates[4] and metal clusters,[5] and to include larger cluster units that are either pre-synthesized or formed in situ from dissolved feedstocks in establishing homogeneous equilibria, with crystallization as the selection process. The second objective is the removal of the ligands that separate the cationic and anionic building blocks in order to make the materials more responsive to external electric or magnetic stimuli. Herein, we present the title compound, which represents the first intercluster sandwich displaying ligand-free interfaces, and also a new Ag_{42} cluster that was formed in situ during the synthesis, to show the principle attainability of these two objectives.

As a source of the silver clusters, we recently started using silver alkynyl clusters as the cationic building blocks. The chemistry of alkynyl compounds was pioneered by Nast and Schindel,[6] and the subject has since been reviewed extensively.[7] Mak and Zhao conducted systematic studies on various pure silver alkynyl complexes; they reported that $\{Ag(C{\equiv}C\text{-}R)\}_n$ can serve as a supramolecular synthon for the synthesis of discrete molecules as well as of one-, two-, and three-dimensional coordination networks.[8] One of the first large discrete clusters, $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]OH$, was obtained by Rais et al.[9] Following this result, Q.-M. Wang and coworkers recently succeeded in synthesizing several large silver alkynyl clusters.[10] The silver clusters $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][BF_4]$ and its halogen-free variant $[Ag_{14}(C{\equiv}CtBu)_{12}][BF_4]_2$ have been shown to be suitable building blocks for our purpose, as they are stable in solution and soluble in various solvents. Our first intercluster compounds, for example, $[Ag_{14}(C{\equiv}CtBu)_{12}(CH_3CN)_2][W_6O_{19}]$,[2] contain the same Ag_{14} cluster. In two incidences this Ag_{14} cluster was generated in situ from the polymeric $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$ during crystallization.

In this work we report the first intercluster sandwich compound, $\{[Ag_{42}(CO_3)(C{\equiv}CtBu)_{27}(CH_3CN)_2][CoW_{12}O_{40}]_2\}^+$ (**Ag-42**; Figure 1),[11] which was obtained from silver alkynyl clusters and $\alpha\text{-}(nBu_4N)_5[HCoW_{12}O_{40}]$ in a one-pot reaction. The self-assembly of **Ag-42** is sensitive to the Keggin anion and the solvent chosen, yet is rather robust with respect to the silver source, and both $[Ag_{14}(C{\equiv}CtBu)_{12}][BF_4]_2$ and $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$, are suitable starting compounds. The turquoise crystals of **Ag-42** are stable in solution and become brittle when exposed to air. According to DTA measurements, **Ag-42** decomposes at 300 °C, with the recorded mass-loss corresponding to complete removal of the ligand sphere.

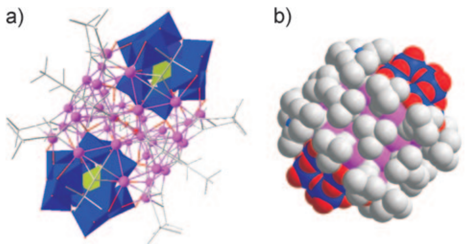

Figure 1. a) Polyhedral/ball-and-stick representation of $\{[Ag_{42}(CO_3)(C{\equiv}CtBu)_{27}(CH_3CN)_2][CoW_{12}O_{40}]_2\}^+$ (**Ag-42**). b) Space-filling view of **Ag-42**. Ag pink, O red, W blue, C grey.

Whilst the Keggin anion $[CoW_{12}O_{40}]^{6-}$ entered the intercluster compound with virtually no change in its composition and structure, a new silver alkynyl cluster with 42 silver ions was formed. This cationic unit is coordinated by 27 *tert*-butylethynyl ligands and two acetonitrile ligands, and has a CO_3^{2-} anion at its center. The silver cage has a quite uncommon toroidal shape with direct contacts to two polyoxometalate anions that close its open ends. The anion counterion to the sandwich compound is BF_4^-, which was identified by IR measurements.

The resulting cationic supramolecular units are packed to approximate a body-centered-cubic structure. The carbon atom of the carbonate anion is located at the Wyckoff position 2a with site symmetry *mm2* in space group *Pmmn*. From

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Figure 2 it is clear that the carbonate/silver cluster has a close to D_{3d} point symmetry.

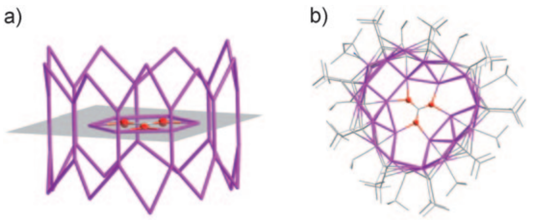

Figure 2. a) Representation of the $[Ag_{42}(CO_3)]$ cluster, and b) a top-down view including ligands.

The silver cage consists of a ring of nine six-membered rings of silver ions that are joined by their *trans* edges. The geometry of the rings is not regular; in particular, the hexagons are bent towards a boat conformation. The Ag–Ag bond lengths are in the range 2.8590(15)–3.2072(14) Å. Such distances are clearly indicative of the presence of d^{10}–d^{10} interactions.[12] At the midpoint height of the cylinder, there are six additional silver ions that link the central carbonate group to the surface silver atoms. The C–O bond lengths range from 1.25(1)–6(3) Å, which is in good agreement with the distances found in other carbonates. Each of the oxygen atoms coordinates to two silver ions at distances of 2.038(14)–2.111(13) Å, and each silver ion in the inner ring is in contact with four silver ions in the outer cage. The whole silver cage is stabilized by a ligand sphere of *tert*-butylethynyl and two additional acetonitrile molecules. The ligands are arranged in three rows around the cluster, overcapping triangles (μ^3) and squares (μ^4) of silver atoms. The two additional acetonitrile molecules coordinate to only one silver atom each.

The naked silver cage has a diameter of about 1.1 nm, 2 nm including the ligand sphere. The polyoxometalates are situated above and below the silver toroid, each with the first layer of three linked $[WO_6]$ octahedra that are completely surrounded by the silver cage (Figure 1 a).

The distances between the silver atoms of the cluster and the oxygen atoms of the polyoxometalates range from 2.517(1) to 2.778(9) Å, and thus are comparable to the Ag–O distances as found in, for example, Ag_2SO_4,[13] $AgVO_3$,[14a] and $AgMnO_4$.[14b]

The constitution of **Ag-42** is additionally supported by IR spectroscopy data. An IR vibration band at 1073 cm^{-1} confirmed the presence of BF_4^-, the counteranion of the supramolecular unit. A band at 2028 cm^{-1} confirmed the presence of the C≡C group, and the bands at 946, 880, and 769 cm^{-1} are assigned to the Keggin anion. The vibration band of the carbonate group appeared at 1626 cm^{-1}. Originally, the carbonate anion was not added intentionally. We assume that the small amount present has entered the reaction vessels from air in the same way as described by Wang and co-workers in their synthesis of $[Ag_{17}(C{\equiv}CtBu)_{14}(CO_3)]OTf$ and $[Ag_{19}(C{\equiv}CtBu)_{16}(CO_3)]BF_4{\cdot}MeOH$.[10c] Owing to the size of the building blocks, there is a significant interstitial space of 11.4 % (calculated using PLATON[15]) accommodating the counteranion and the additional solvent molecules in a disordered fashion. The presence of paramagnetic Co^{2+} in high magnetic dilution is confirmed by magnetic susceptibility measurements (Curie behavior, $\mu_{eff} = 3.84\ \mu_b$; see the Supporting Information).

These results are reminiscent of the very recent findings by Q.-M. Wang and co-workers,[16] who have managed to wrap polyoxometalates in silver ions, with the aggregates obtained fully covered with alkynyl ligands. The topology of **Ag-42** is different in that a silver cluster of 42 atoms is sandwiched between two polyoxometalates. The polyoxometalates above and below the toroidal structure do not have any attached ligands, and thus offer the opportunity to grow extended aggregates, at least in one dimension. Moreover, we regard this result of general importance in the context of our long term goal of synthesizing extended solid structures consisting of nanometer-sized anionic and cationic building blocks that have ligand-free interfaces because it demonstrates the principle feasibility of such an objective.

Experimental Section

All crystallization experiments were performed under ambient conditions and under dry argon in a glovebox. Acetonitrile was purchased form Fluka and used as received. For the experiments under argon, the solvent was dried and distilled prior to use. $[Ag_{14}(C{\equiv}CtBu)_{12}Cl][OH]$,[17] $[Ag_{14}C{\equiv}CtBu)_{12}][BF_4]_2$,[8] $\{[Ag_3\ (C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$,[18] and α-$(nBu_4N)_5[HCoW_{12}O_{40}]$[19] were prepared according to their literature procedures. For the crystallization, 3 $mmol\,mL^{-1}$ $[Ag_{14}(C{\equiv}CtBu)_{12}][BF_4]_2$ and 2 $mmol\,mL^{-1}$ α-$(nBu_4N)_5[HCoW_{12}O_{40}]$ were dissolved in acetonitrile and the solution was filled in glass tubes of diameter < 2 cm. For the syntheses using $\{[Ag_3(C{\equiv}CtBu)_2][BF_4]{\cdot}0.6\,H_2O\}_n$, the molar ratio was 7:1. After a few days, turquoise crystals of **Ag-42** were formed at the walls of the tubes. The yield ranges from 40 to 60 % of the amount of silver employed. For single crystal analyses, a crystal was picked from a solution with a droplet of inert oil, transferred rapidly to the diffractometer, and measured at 100 K. The material was ground for IR spectroscopy. IR (KBr disks): $\tilde{\nu} = 2008$ (s, C≡C); $CoW_{12}O_{40}^{6-}$: 931(s), 860(s), 768(s). Quantitative analysis (ICP-OES) resulted in the ratio Ag/Co/W/C/B: 35.8(expected 35.6):0.88(0.9):34.12(34.6):18.5(15.7):0.1(0.08), thus confirming the results of the single crystal structure analyses.

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[11] Crystal data and structure refinement of **Ag-42**: turquoise rhombic crystals ($0.15\times0.05\times0.05\,\text{mm}^3$), orthorhombic, space group *Pmmn*, $a=21.3892(11)$, $b=30.4371(16)$, $c=20.7845(11)$ Å, $\alpha=\beta=\gamma=90°$, $V=13\,521.2(12)$ Å^3, $\rho_{\text{calcd}}=3.068\,\text{g}\,\text{cm}^{-3}$, $Z=2$, $\mu(\text{Mo}_{\text{K}\alpha})=7.56\,\text{mm}^{-1}$, $\lambda=71.073$ pm, Bruker AXS Smart APEX diffractometer, graphite monochromator, ω scans, semiempirical absorption correction (G. M. Sheldrick, *SADABS*—Bruker AXS area detector scaling and absorption, version 2008/1, University of Göttingen, Germany **2008**); structure solution and refinement with SHELXTL (“”A short history of *SHELX*“: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122), $T=100$ K, 123 609 measured reflections, 14 751 symmetry-independent reflections ($2\theta_{\max}=53.10°$), 577 refined parameters, $R_1=0.0473$ ($F^2>2\sigma(F^2)$), $R_1=0.0473$, $wR_2=0.1564$ (all data). Apart from C and N, all atoms were refined with anisotropic displacement parameters. H atoms are not included in the crystallographic data. CCDC 774418 (**Ag-42**) 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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