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Polyoxometalates Made of Gold: The Polyoxoaurate $[Au^{III}_4As^{V}_4O_{20}]^{8-}$**

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Polyoxometalates (POMs, discrete nanosized metal oxo anions) are an increasingly fascinating object of study owing to their enormous structural diversity and unique combination of properties, such as thermal and oxidative stability, tunability of acidity and redox activity, and ability to activate easily accessible "green" oxidants (O_2 and H_2O_2), thus making them attractive for applications in many different areas, for example, in catalysis, magnetism, nanotechnology, and medicine.[1] Although this class of compounds was discovered as far back as 1826,[2] until recently POMs were known predominantly for Group 5 and 6 addenda metals in high oxidation states (e.g. W^{6+}, V^{5+}).

In 2008 we reported the synthesis, structure, and preliminary catalytic studies of $[Pd^{II}_{13}As_8{}^{V}O_{34}(OH)_6]^{8-}$ (**$Pd_{13}As_8$**), the first member of a novel subclass of polyoxoanions built exclusively of d^8 Pd^{II} addenda metal ions.[3] All Pd^{II} ions in **$Pd_{13}As_8$** retain square-planar coordination geometry, in sharp contrast to all other known discrete POMs, which generally contain metal centers in octahedral environments. Even more recently we have shown the possibility of preparing other hetero-13-palladate derivatives, in which the $\{AsO_4\}^{3-}$ capping fragments in **$Pd_{13}As_8$** are replaced by lone-pair-containing $\{Se^{IV}O_3\}^{2-}$ and organic-functionalized $\{PhAs^{V}O_3\}^{2-}$ groups.[4a] We also demonstrated the existence of another structural type of polyoxopalladate, $[Pd_{15}P_{10}O_{50}]^{20-}$ (**$Pd_{15}P_{10}$**), which comprises 15 Pd^{II} addenda ions and adopts the shape of a star pentagon.[4b] We also discovered that the **$Pd_{12}L_8$** heteropolypalladate shell in the above species can stabilize unusual coordination numbers and geometries for the encapsulated Pd^{II} ion, including unprecedented eight-fold cubic coordination.[4a] Wickleder et al. reported the solid-state d^7 metal cluster anion $[Pt^{III}_{12}O_8(SO_4)_{12}]^{4-}$, which is composed of six dumbbell-shaped $[Pt_2]^{6+}$ ions linked by oxo and sulfate bridges.[4c,d]

There is great interest in soluble late-transition-metal oxo complexes as potential models of so-called MO_x "suboxide clusters", which have been proposed to be crucial intermediates in noble-metal-based heterogeneous catalytic oxidation systems.[5,6] Furthermore, noble-metal-based materials are important as catalysts in numerous industrially relevant processes and devices, including low-temperature and environmentally benign O_2-based oxidations, reforming, automobile converters, and fuel cells.[7] This background warrants an extension of our polypalladate(II) work to other d^8 metal ions (e.g. platinum(II), gold(III)).

The Au–O bond is known to be weak and unstable, as seen with gold(III) oxide Au_2O_3, which decomposes at about 160 °C.[8] Discrete gold(III) oxo complexes have been synthesized only recently, and all of them are stabilized by chelating organic nitrogen-donor ligands.[9] Hill et al. have reported two Au^{III}-containing heteropolytungstates, in which the gold(III) ion is octahedrally coordinated and also has a terminal Au^{III} oxo bond.[10a] Very recent relativistic DFT computational studies performed by Bagno and Bini indicate that such a species is expected to be very unstable and should possess extremely unusual ^{183}W and ^{17}O NMR characteristics.[10b] The weakness and hence the high reactivity of the Au^{III}–O bond provide much potential for gold oxo compounds as oxygen donors in oxidation reactions, such as the epoxidation of olefins.[11]

Herein we report the first example of a fully inorganic discrete heteropolyaurate $[Au^{III}_4As^{V}_4O_{20}]^{8-}$ (**Au_4As_4**, Figure 1 a), which was synthesized in aqueous medium at room temperature and isolated as the hydrated sodium salt $Na_{13}[(H_2O)_4(NO_3)_2Na_5\{Au^{III}_4As^{V}_4O_{20}\}_2]\cdot 39\,H_2O$ (**1**). The polyanion **Au_4As_4** was prepared by alkaline hydrolysis of hydrogen tetrachloroaurate $H[AuCl_4]$ followed by condensation of the obtained tetrahydroxogold(III) complex $[Au(OH)_4]^-$ in the presence of arsenate ions by decreasing the pH value of the reaction mixture from 11.5 to 7.8. It is well known that acidification of $[Au(OH)_4]^-$ solutions leads to the formation of insoluble $Au(OH)_3$, which further undergoes aging processes including the release of water molecules and polymerization, thus resulting in the formation of colloidal particles with dimensions of 80 nm and larger.[12] Apparently in our case, the arsenic ions act as protecting groups preventing condensation of the tetrameric **Au_4As_4** polyanions to colloidal species, although a small amount of gold(III) hydroxide is

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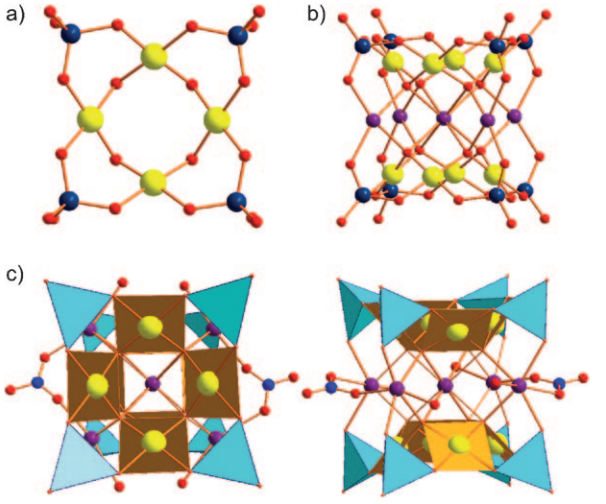

Figure 1. Ball-and-stick representation of a) **Au$_4$As$_4$** and b) the **Na$_5$Au$_8$As$_8$** fragment. c) Combined ball-and-stick/polyhedral representation of the $[(H_2O)_4(NO_3)_2Na_5Au_8As_8O_{40}]^{13-}$ dimeric assembly: top (left) and side (right) views. Au yellow, As dark blue, O red, Na purple, N blue; {AuO$_4$} dark yellow squares, {AsO$_4$} turquoise tetrahedra.

always present as a side product in the formation of the title polyoxoaurate.

A combination of synthetic parameters such as high concentrations of Au^{III} and AsO_4^{3-} ions (0.1–0.2 M), careful acidification, and control of the final pH value are crucial for the formation of **Au$_4$As$_4$**. Thus, too fast acidification of the reaction mixture or heating the **Au$_4$As$_4$** synthesis solution to more than 50 °C leads to insoluble Au(OH)$_3$. The purity of the initial reagent H[AuCl$_4$] also plays an important role: for example, using H[AuCl$_4$] with Au content of less than 50 % leads to the precipitation of large amounts of Au(OH)$_3$ and to a very low yield of the polyoxoaurate salt **1**. The synthesis of **Au$_4$As$_4$** can also be performed in pure water, but in this case crystallization is very difficult owing to the extremely high solubility of the polyaurate. Besides **1**, we were also able to synthesize two other salts of **Au$_4$As$_4$** by reaction of H[AuCl$_4$] in distilled water, namely $Na_{10}[Cl_4Na_5\{Au^{III}{}_4As^{V}{}_4O_{20}H_{2.5}\}_2]\cdot\sim 39\,H_2O$ (**2**) and $Na_{10}[(NO_3)_4Na_5\{Au^{III}{}_4As^{V}{}_4O_{20}H_{2.5}\}_2]\cdot\sim 25\,H_2O$ (**3**; see Supporting Information for details of synthesis).

Single-crystal X-ray analysis[13] demonstrated that the polyanion **Au$_4$As$_4$** possesses a tetrameric structure with four square-planar coordinated Au^{III} ions linked by four oxo and arsenate μ$_2$-bridging ligands (Figure 1 a). The Au^{III}–O bond lengths are in the range of 1.954(7)–1.970(7) Å for the oxo ligands and 1.991(7)–2.013(6) Å for the oxygen atoms of the arsenate fragments. Bond valence sum calculations[14] showed no protonation for any oxygen atoms. Indeed, the average Au^{III}–O bond length in **Au$_4$As$_4$** ((1.980 ± 0.023) Å) is comparable to that in other known gold(III) oxo complexes (e.g. 1.967(7) Å in [Au(6-methyl-2,2′-bipyridine)(k^2-O,C-2-oxynorbornyl)](PF$_6$),[11a] or (1.979 ± 0.008) Å in SrAu$_2$-(CH$_3$COO)$_8$[15]) and quite a bit shorter than the Au–O distance in organometallic dimethylgold(III) hydroxide ((2.154 ± 0.148) Å), which is also known to possess a tetrameric structure in the solid state.[16] The average Au–Au distance in **1** ((3.246 ± 0.024) Å) is also significantly shorter than in dimethylgold(III) hydroxide ((3.558 ± 0.052) Å). The four capping arsenic(V) ions exhibit tetrahedral geometry, with As^{V}–O bond lengths between 1.638(7) and 1.735(9) Å.

All four Au^{III} ions in **Au$_4$As$_4$** are in the same plane and form a slightly distorted square. The oxo ligands bridging the gold centers are situated on one side of this {Au$_4$} plane, while all O-As-O bridges are on the opposite side. This arrangement results in a bowl-shaped structure of the title polyanion with idealized C_{4v} point-group symmetry.

Such geometry of **Au$_4$As$_4$** is enforced by the bidentate arsenate ligands, which bridge adjacent gold centers. The situation is very different for the above-mentioned tetrameric dimethylgold(III) hydroxide complex, which has S_4 symmetry, as in that case the Au^{III} ions are linked exclusively by four μ$_2$-OH bridges (two above and two below the nonplanar {Au$_4$} ring), with the remaining two coordination sites per gold center occupied by monodentate, terminal methyl ligands.

In the crystal structure, two **Au$_4$As$_4$** tetramers are linked through a belt composed of five sodium cations, resulting in the cuboid polyanion assembly $[(H_2O)_4(NO_3)_2Na_5Au_8As_8O_{40}]^{13-}$ (**Na$_5$Au$_8$As$_8$**). One of the sodium cations is located in the center of the **Na$_5$Au$_8$As$_8$** structure and is coordinated by eight oxo ligands of two tetrameric **Au$_4$As$_4$** species (Na–O 2.458(7)–2.540(7) Å). The four "outer" Na$^+$ ions are situated at the vertices of a distorted square, surrounding the central Na$^+$ ion and separating the two **Au$_4$As$_4$** units by a "pentasodium plane" (Figure 1 b), and they are coordinated to a μ$_2$-oxo ligand and a terminal arsenate oxygen atom of each of the two capping **Au$_4$As$_4$** fragments (Na–O 2.287(9)–2.382(9) Å). Octahedral coordination is achieved by two bridging nitrate and four terminal aqua ligands (Figure 1 c). In the two other structures, **2** and **3**, these ligands are replaced by four μ$_2$-bridging chloride or nitrate ions.

The two **Au$_4$As$_4$** polyanions in the dimer **Na$_5$Au$_8$As$_8$** are located exactly on top of each other, with an average intertetramer Au···Au distance of (5.229 ± 0.085) Å. Interestingly, the structure of the **Na$_5$Au$_8$As$_8$** assembly is identical with that in our **Pd$_{13}$L$_8$** derivatives (where L is As or Se),[3,4a] but the five noble-metal addenda positions in the central belt of the **M$_{13}$L$_8$** assembly are occupied by Na$^+$ ions in **Na$_5$Au$_8$As$_8$**. This observation indicates the importance of the **M$_{13}$L$_8$** structural type in the chemistry of noble-metal-based POMs and indicates that most likely other metal centers besides sodium can also be incorporated into these sites.

The structure and stability of the title polyanion **Au$_4$As$_4$** and its dimeric assembly **Na$_5$Au$_8$As$_8$** have been confirmed computationally (see the Supporting Information for details).

The interesting question is which species is actually present in an aqueous solution of the salts **1**–**3**. For dimethylgold(III) hydroxide it was shown that the tetrameric structure (present in the solid state) remains intact in a benzene solution, while in aqueous solution the complex dissociates to the dimeric species [Au$_2$(OH)$_2$(CH$_3$)$_4$].[16c] Our polyanions are expected to be more stable owing to the stronger gold oxo bonds (compared to the hydroxide complex) and additional stabilization of the tetramer by μ$_2$-bridging arsenate fragments. Indeed, the salts **1**–**3** can be repeatedly and successfully recrystallized from either water or

NaOAc solution, although with time recrystallization always resulted in a small amount of $Au(OH)_3$ impurity. Therefore, we expect $\mathbf{Au_4As_4}$ to be the dominant species in aqueous solution, although unequivocal experimental evidence is still needed. Considering the results of our computational studies, it is unlikely that $\mathbf{Na_5Au_8As_8}$ can be stable in aqueous medium, although the formation of such an assembly leads to the $\mathbf{M_{13}L_8}$ structural type known from our polyoxopalladates.[3,4a]

We also performed solution electrochemistry studies of **1** in a pH 7 medium. The main observations are described in detail in the Supporting Information. In short, cyclic voltammetry and controlled-potential electrolyses indicate one-step reduction of Au^{III} to Au^0 with accompanying nucleation. It is worth noting the large negative peak potential shift, in the range of 0.950 V, observed for the reduction of redissolved **1** compared to that of $[AuCl_4]^-$ in the same medium. Such an important reduction potential shift underscores the strong complexation of the Au^{III} centers within **1**.

In summary, we have prepared the first polyoxoaurate $\mathbf{Au_4As_4}$ as a discrete inorganic gold(III) oxo complex by using simple open-beaker, aqueous solution synthesis techniques. Thereby we have shown that our recent discovery of the fundamentally novel field of polyoxopalladate chemistry is just an entry to the hitherto unexplored, tremendously rich and aesthetic area of late-transition-metal-based POMs. Future synthesis of such compounds will most likely enrich significantly our understanding of the hydrolysis of late-transition-metal salts in aqueous solutions. Moreover, $\mathbf{Au_4As_4}$ represents a potential model for the active catalyst in heterogeneous gold-based oxidations using molecular oxygen. We plan to perform catalytic studies on the title polyanion, and in order to make compositional derivatives of $\mathbf{Au_4As_4}$ we plan to replace the arsenate capping groups by phosphate or vanadate, thus allowing NMR spectroscopic investigation of the solution chemistry of polyoxoaurates. Also organic-functionalized capping groups RXO_3 (where $X = As^V, P^V, Si^{IV}, Ge^{IV}$; R = alkyl, aryl) could be interesting and may allow for polyoxoaurates to be supported on surfaces. Another exciting possibility is to replace the Na^+ ions in $\mathbf{Na_5Au_8As_8}$ by d- and f-block metal ions. We also see the potential of noble metalates as discrete precursors for highly dispersed nanoparticles with tremendous catalytic power.

Experimental Section

Preparation of **1**: $H[AuCl_4]$ (0.210 g, 0.618 mmol) was dissolved in 2 M aqueous NaOAc (5 mL). Then the pH value of the resulting yellow solution was adjusted to 11.5 by addition of 6 M NaOH. During dropwise addition of NaOH the color of the reaction mixture changed from bright yellow to orange and then to light yellow. After 15 min $AgNO_3$ (0.425 g, 2.50 mmol) was added under vigorous stirring to remove the Cl^- ions (the pH value of the reaction mixture should be controlled by addition of NaOH solution during the addition of $AgNO_3$ and precipitation of AgCl). The obtained white precipitate of AgCl containing a small amount of brown $Ag_2O{\cdot}nH_2O$ was removed by filtration. $Na_2HAsO_4{\cdot}7H_2O$ (0.195 g, 0.625 mmol) was added to the resulting light yellow solution. After dissolution of disodium hydrogen arsenate, the pH value of the reaction mixture was carefully adjusted to 7.8 by dropwise addition of 6 M HNO_3. During the addition of acid the color of the reaction solution changed to deep yellow or even orange. The obtained solution was stirred at room temperature for 40 min and then filtered to remove a small amount of solid $Au(OH)_3$. Slow evaporation of the filtrate at room temperature in an open vial resulted in yellow block-shaped crystals within six weeks. During the evaporation process small amounts of $Au(OH)_3$ and black Au^0 have to be removed by filtration from time to time. The obtained crystals were collected by filtration and dried in air. Yield: 0.070 g (22 % based on Au). IR (2 % KBr pellet): $\tilde{\nu} = 3446$ (sh), 2220 (sh), 1649 (s), 1384 (s), 882 (s), 781 (s), 667 (m), 570 (m), 537 cm^{-1} (m). Elemental analysis (%) calcd for $Na_{13}[(H_2O)_4(NO_3)_2Na_5\{Au^{III}{}_4As^V{}_4O_{20}\}_2]\cdot 39H_2O$ (**1**): Na 10.03, Au 38.2, As 14.5, N 0.68, H 2.10; found: Na 9.84, Au 38.0, As 14.3, N 0.70, H 2.20. The thermogram (25–1200 °C) of **1** is shown in the Supporting Information.

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