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Highly Sensitive Ammonium Tetraazidoaurates(III)

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The preparation and characterization of selected ammonium and methylammonium tetraazidoaurates(III) are reported. All ammonium salts were shown to be highly explosive materials. The first crystal structure of such an ammonium salt, that of $[Me_4N][Au(N_3)_4]$, features polymeric units of the anion, which are linked by weak Au···Au interactions.

In the very recent past, there has been considerable interest in the chemistry of binary main-group and transition-metal azides.[1,2] Gold azide species, in particular, exist in the anionic form in the oxidation states I+, $[Au(N_3)_2]^-$, and III+, $[Au(N_3)_4]^-$, whereas the neutral azides AuN_3 and $Au(N_3)_3$ are unknown to our knowledge.[3] The tetraazidoaurate(III) anion can be stabilized using relatively large counterions, such as $[Ph_4As]^+$, $[Et_4N]^+$, $[n\text{-}Bu_4N]^+$, or $[Me_3(cetyl)N]^+$.[4,5] In contrast, alkali-metal tetraazidoaurates(III) are reported to be extremely explosive materials.[4–6] Our interest in high-nitrogen-containing element azides prompted us to carry out a study on ammonium tetraazidoaurates(III), where only sparse information, with respect to the above-mentioned examples, exists. According to previous reports, a decrease in the size of the ammonium cation should likely cause an increase of the sensitivity of the salts.

The preparation of tetramethylammonium tetraazidoaurate(III) (**1**) is identical with the procedure described for those with other larger cations[4b,5a] (eq 1).

$$H[AuCl_4] \xrightarrow[H_2O/EtOH]{(1)\ \text{excess}\ NaN_3/(2)\ [Me_4N]Br} \underset{\mathbf{1}}{[Me_4N][Au(N_3)_4]} \qquad (1)$$

The synthesis of the ammonium salts with lower methyl content is slightly different (eq 2).

$$[R_2NH_2][AuCl_4] \xrightarrow[MeOH]{\text{excess}\ AgN_3} \begin{array}{l}[R_2NH_2][Au(N_3)_4] \\ R = Me\ (\mathbf{2}),\ H\ (\mathbf{3})\end{array} \qquad (2)$$

The hitherto not described dimethylammonium tetrachloroaurate(III) was prepared in a fashion similar to that described for $[NH_4][AuCl_4]$.[7] Crystals of $[Me_2NH_2][AuCl_4]$ suitable for X-ray diffraction decomposed repeatedly upon contact with the X-ray beam depositing gold. A similar behavior was observed during the crystal structure determination of $[NH_4][AuCl_4]$.[8]

Explicit Safety Hazard! Ammonium tetraazidoaurate(III), $[NH_4][Au(N_3)_4]$ (**3**), exploded on various occasions and is an extremely dangerous material.[9] The dimethyl- and tetramethylammonium salts **1** and **2** explode violently upon contact with a flame.

The salts **1**,[10] **2**,[11] and **3**[11] display red-orange crystalline solids and exhibit, as to be expected, an increased sensitivity with less carbon content. Initial studies show that the carbon-free ammonium tetraazidoaurate (**3**) is a promising candidate

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† Crystal structure determination.

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(9) General considerations: *All manipulations were carried out under light exclusion in plastic beakers and on a small scale with extreme care. Appropriate shielding is essential; for a detailed description of the equipment, please see ref 1b.* (a) A solution of $[NH_4][Au(N_3)_4]$ in methanol exploded upon attempts of solvent removal with a rotary evaporator, leaving no residues of the glass flask except powdered glass! (b) A solution of $[NH_4][Au(N_3)_4]$ in acetone exploded under light exclusion upon slow evaporation of the solvent in a polypropylene beaker surrounded by a wire netting located in a safety cabinet, resulting in a completely destroyed beaker! The originally intended preparation of the full methylammonium series including the $[MeNH_3]$ and $[Me_3NH]$ tetraazidoaurate(III) salts was refrained from because of the observed hazards.

10.1021/ic051543i CCC: $30.25

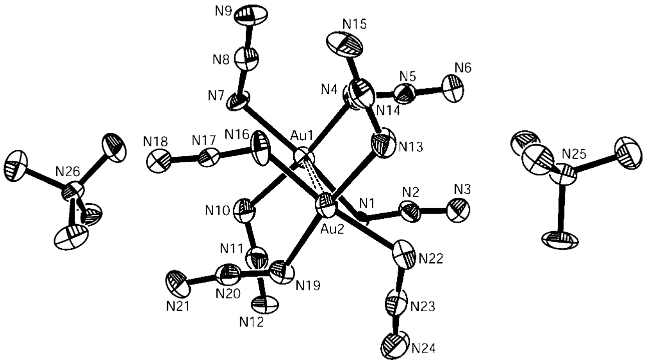

Figure 1. Molecular structure of **1** in the crystal (displayed is a “dimeric” unit). Ellipsoids are shown with 40% probability. Bond lengths (Å) and angles (deg) of the anions: Au1−N1 2.015(6), Au1−N4 1.996(9), Au1−N7 2.071(7), Au1−N10 2.04(1), Au2−N13 2.04(1), Au2−N16 1.95(1), Au2−N19 2.02(1), Au2−N22 2.06(1), N1/4/7/10−N2/5/8/11 1.19(1)−1.21(1), N2/5/8/11−N3/6/9/12 1.15(1)−1.16(1), N13/16/19/22−N14/17/20/23 1.19(1)−1.24(1), N14/17/20/23−N15/18/21/24 1.13(1)−1.16(1), Au1···Au2 3.507(3); N1−Au1−N4 99.7(3), N1−Au1−N7 173.3(3), N1−Au1−N10 88.6(3), N10−Au1−N4 171.6(4), Au1−N1/4/7/10−N2/5/8/11 116.6(7)−124.3(7), N1/4/7/10−N2/5/8/11−N3/6/9/12 172(1)−176(1); corresponding angles of the Au2 anion are similar.

for the deposition of gold on surfaces, which can serve as a hydrogenation catalyst.[12]

The product from the decomposition is always colloidal gold. The formation of dinitrogen is detected after short periods by ^{14}N NMR spectroscopy as evidence of slow decomposition in solution (pressure formed) aside from gold deposition. In addition to the friction and impact sensitivity of these salts, light sensitivity is observed, similar to that of the tetrachloroaurates(III).

Various attempts were required to determine the crystal structure of **1** because of the additional sensitivity to X-ray exposure [as observed already for tetrachloroaurate(III) salts], shown in Figure 1.[13]

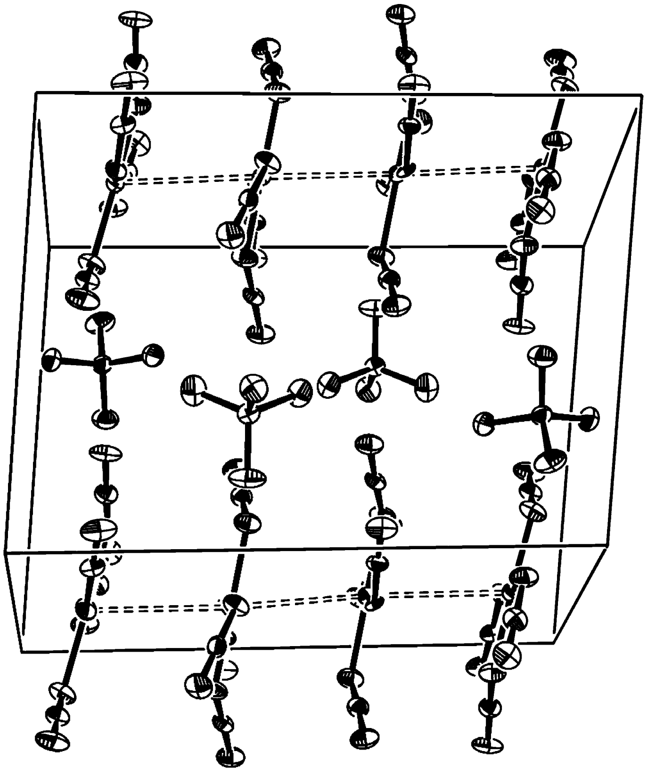

Figure 2. Packing diagram of **1** with a view along the *a* axis, showing the stacking of the anions. Dashed lines represent alternating Au···Au contacts of 3.507(3) and 3.584(3) Å.

The gold atoms are surrounded by azide groups in the expected square-planar fashion with bond lengths and angles in the expected ranges, similar to those observed for $[Ph_4As][Au(N_3)_4]$.[3] A striking difference in this structure is the presence of polymeric stacking of the anion, consisting of weak Au···Au interactions of 3.507(3) and 3.584(3) Å.[14] These distances are slightly below the sum of the van der Waals radii (3.6 Å).[15] There is clearly no inversion center between the gold atoms, although it appears as such.

Figure 2 shows a plot of the packing diagram of **1**, featuring a stacking of monomeric anions in parallel layers with the $[Me_4N]^+$ units located in between.

To find out whether there exist intrinsic Au···Au contacts between individual $[Au(N_3)_4]^-$ anions, hybrid density functional theory calculations on a possible $[Au(N_3)_4]_2^{2-}$ dimer were performed starting with an Au···Au distance of 2.0 Å.[16]

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(10) Into a solution of 0.100 g (0.25 mmol) of $H[AuCl_4]\cdot 3H_2O$ in 10 mL of water in a beaker is added 0.7 g (10.0 mmol) of NaN_3. The color changes from yellow to red. Into this mixture is added, with stirring, a solution of 1.5 g (10.0 mmol) of $[Me_4N]Br$ in 10 mL of water/ethanol. Upon cooling with ice, the salt $[Me_4N][Au(N_3)_4]$ (**1**) precipitates as red-orange needles (0.065 g, 59%). ^{1}H NMR (acetone-d_6): δ 3.43 (Me, s). ^{13}C NMR (acetone-d_6): δ 55.9 (Me, t, $^1J_{C-14N} =$ 4.0 Hz). ^{14}N NMR (acetone-d_6): δ −132.8 (N_β), −178 (N_γ), −279 (N_α), −338.6 (Me_4N). IR (KBr): 3034 w (ν_{CH}), 2044/2037/2013 vs (ν_{as,N_3}), 1482 m, 1447 w, 1414 w, 1380 w, 1264 m (ν_{s,N_3}), 949 m, 581 vw, 566 vw, 424 m cm^{-1}. Raman (100 mW): 3036 (10)/2978 (11)/2953 (9)/2920 (10) (ν_{CH}), 2062 (33)/2035 (21)/2011 (15) (ν_{as,N_3}), 1449 (18) (δ_{CH}), 1284 (14) (ν_{s,N_3}), 1020 (12), 999 (13), 950 (12), 755 (14), 690 (13), 674 (13), 403 (100) (ν_{AuN}), 391 (32), 235 (33), 212 (30), 160 (15) cm^{-1}. Anal. Calcd for $C_4H_{12}N_{13}Au$: C, 10.9; H, 2.8; N, 41.5. Found: C, 11.3; H, 2.9; N, 41.3.

(11) Into a solution of 0.2 mmol of $[Me_2NH_2][AuCl_4]$ or $[NH_4][AuCl_4]$ in 5 mL of methanol in a beaker is added 1.7 mmol of AgN_3. An immediate color change from yellow to red is observed. The mixture is stirred for 24 h and then separated carefully from insoluble silver salts. Slow evaporation in the case of the dimethylammonium salt yields pure $[Me_2NH_2][Au(N_3)_4]$ (**2**) in almost quantitative yield. In the case of $[NH_4][Au(N_3)_4]$ (**3**), attempts to isolate the pure salt mostly result in explosions, probably during the crystallization process. Spectroscopic data of **2**. ^{1}H NMR (acetone-d_6): δ 3.78 (NH_2, s), 3.01 (Me, s). ^{13}C NMR (acetone-d_6): δ 35.9 (Me, br). ^{14}N NMR (acetone-d$_6$): δ −132.8 (N_β), −178 (N_γ), −280 (N_α), −358.0 (Me_2NH_2). Spectroscopic data of **3**. ^{1}H NMR (CD_3OD): δ 4.85 (NH_4, s). ^{14}N NMR (CD_3OD): δ −133.6 (N_β), −179 (N_γ), −280 (N_α), −368.8 (NH_4). ^{14}N NMR (H_2O): δ −133.9 (N_β), −179 (N_γ), −282 (N_α), −361.5 (NH_4).

(12) Lopez-Sanchez, J. A.; Winfield, J. M.; Krumm, B.; Klapötke, T. M.; Lennon, D., manuscript in preparation.

(13) Triclinic, *P*1; $a = 9.973(2)$ Å, $b = 10.246(2)$ Å, $c = 13.625(3)$ Å; $\alpha = 94.14(3)°$, $\beta = 93.63(3)°$, $\gamma = 110.42(3)°$; $V = 1295.7(4)$ Å^3; $Z = 2$; $\rho = 2.252$ g/cm^3; $T = 213$ K; $R_{int} = 0.0253$; R1 = 0.0444, wR2 = 0.1116 (4σ data); R1 = 0.0700, wR2 = 0.1240 (all data); GOF = 0.954; largest diff peak/hole 2.582/−2.929 e/Å^3.

(14) Estimated standard deviation.

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(16) The calculations were performed with the *Gaussian03* program package[17a] at the B3LYP level of theory using a cc-pVDZ basis set for nitrogen and a small-core ECP-60-MDF relativistic pseudopotential replacing 60 core electrons at the gold atoms.[17b,c] The remaining Au valence electrons were treated with a basis set of the following contraction: (12s12p9d3f2g)/[6s6p4d3f2g].

Full geometry optimization always resulted in a dissociation of the dimer, forming two individual $[Au(N_3)_4]^-$ anions. From this, it can be concluded that, at the level of theory applied (not taking a point charge model into account),[18] the two $[Au(N_3)_4]^-$ anions are not bound in the gas phase and that there are (in the gas phase) no bonding Au···Au interactions. Therefore, it is more likely that the interactions found in the crystal structure are the result of packing effects. However, to our knowledge, this is one rare, probably the first, example found in gold(III) chemistry, while for gold(I), cluster and hypercoordinated gold compounds frequently with Au···Au interactions are found.[15]

A comparison to isoelectronic platinum(II) in the two available crystal structures of tetraazidoplatinate(II) shows no comparable Pt···Pt interactions between the anionic units (Pt···Pt distance of 11.198 Å, likely because of the large counterion $[Ph_4As]^+$ in both cases).[19] However, in the crystal structures of $[Et_4N]_2[PtBr_4]$ (3.59 Å) and $K_2[PtCl_4]$ (4.13 Å) with smaller cations, closer Pt···Pt contacts are found, leading to columnar structures of the tetrahalogenoplatinate(II) anions.[20] Those contacts are in a range comparable to the distances found in our structure.

In summary, this study has shown that salts of tetraazidoaurate(III) with ammonium counterions exist but display very sensitive materials, which should be handled with great caution. Attempts to prepare hydrazinium tetraazidoaurate(III) failed because of the strong reducing power of the hydrazinium cation. In straightforward reactions, the formation of nitrogen and gold as decomposition products is detected. Work on tetraazidoaurates(III) involving other and further suitable small cations is in progress.

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Supporting Information Available: X-ray crystallographic files for compound **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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