

A review on fulminating gold (Knallgold)

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Abstract

Expensive and explosive! The reaction of ammonia and gold(III) compounds leads to explosive products known as “fulminating gold”. Gold scientists should be aware of the potential hazards involved in the reaction of these starting materials. Herein, a historic and scientific review on this fascinating substance is presented. Fulminating gold has been known since medieval times, but cannot be fully characterized due to its polymeric and heterogeneous character. Magnetic measurements confirm previous EXAFS analyses that the gold atoms have a square planar coordination environment (AuN₄-moieties that are partly connected and form a 3-dimensional network). The explosive properties and resulting safety instructions are discussed in detail as well.

Keywords: aurum fulminans, explosives, gold-nitrogen bond, safety, alchemists



N this paper, we review the history (as far as significant), the chemistry and hazards of fulminating gold. “Fulminating gold” generally terms the explosive reaction products of gold(III) compounds (such as halogenides, oxides and hydroxides) with ammonia. In this paper we focus on fulminating gold produced from gold(III) chloride or hydrogen tetrachloroaurate(III). This type of fulminating gold is also termed “Chloridknallgold” in literature. The expression “fulminating” might be confusing and should not be mistaken for the energetic fulminate anion (CNO⁻).

The History of the first high explosive

The early work


Since fulminating gold is synthesized by using readily available chemicals – gold(III) chloride and ammonia – and leads to an unexpectedly explosive substance, it is no surprise that it has been known to alchemists since medieval times (alchemist symbol ). The German alchemist Sebald Schwaeztzer first mentions fulminating gold (*aurum fulminans*) in literature in his *Chrysopoeia Schwaeztzeriana* in 1585. A reprint of this monograph dates back to 1718 [1] (Translated: *Manuscripts on the True Preparation of the Philosopher's Stone*). It is still available in some German libraries (see Figure 1).

Figure 1

Chrystopoeia Schwärtzeriana.
Das ist:
SEBALDI SCHWÄRTZERS,
ehemahligen berühmten Churfürst.
Sächsischen Artisten und würck-
lichen Adepti,
Manuscripta,
Von der
Wahrhafften Bereitung
des
Philosophischen Steins/
Wie selbige vor diesem mit seiner eigenen Hand
entworfen/ und bey dem Churfürstl. Sächsischen
Hause in Originali verwahrlich aufbehalten
worden/
Nebst dem rechten
zu solchen Manuscriptis gehörigen
Schlüssel;
Auch unterschiedlichen Abrißten der darzu
dienlichen Ofen/
Aus einer unverfälschten durch viele Mühe und
Unkosten erlangten Copia nunmehr jederman vor
Augen gelegt/ und mit einigen nützlichen Anhängen
von verschiedenen curiösen Processen
vermehret.
HAMBURG,
Bey Samuel Heil/ in S. Johannis Kirche. 1718.

(85)

Antim. gehört vor die Sudler/ man findet auch da-
bey einen mercklichen Abgang am O/ kostet auch drey
mahl so viel Mühe/ hierbey werden Sie schwerlich
1 Mechen verlihren/ und ist die Arbeit in einem Tag
verrichtet/ jedoch daß das Aquafort vorher in selb-
gem Tag 1 mahl rectificiret sey/ denn wann Sie es
fällen/ vereinbahrt sich die Solution Y mit dem O/
das doch darvon soll gereinigt werden/ hinwiederum;
wiewol wann es nicht anders seyn kan/ so schadet das
gefällte eben nicht viel/ massen der Salmiac solches meh-
stens wieder präcipitiret. Dieses ist nun die wahre
Philosophische Reinigung; Wann dieses nun ge-
trocknet/ so solviren Sie es mit reinem Aquafort und
Salmiac/ diesen O Ralck wiederum in aller masse/ wie
schon gelehret. NB. Nun muß unmaßgeblich das
Aquafort rectificiret seyn.

Nun belieben Sie das Aquafort bis auf die Trock-
ne in der Asche abzugießen/ und zu dieser Arbeit wer-
den Sie einen halben Tag gebrauchen.

Wiederum belieben Sie frisches Wasser aufzugie-
ßen/ und solviren es zum andern mahl/ ziehen es auch
wiederum bis auf die Trockene ab/ alsdann solviren
Sie es zum dritten mahl also. Sie müssen aber acht
geben/ daß Sie es nicht ganz sondern nur halb abzie-
hen/ so wird die Materia Delicht seyn/ dann nehmen
Sie es vom Feuer/ und lassen es erkalten.

Dann präcipitiren Sie das O mit Ol. Tartar./
welches folgender gestalt gemacht wird/ Sie nehmen
§ 3 Sal

(84)

chen; Nim denn von der Tinctur 1 Gran, lege sol-
ches auf ein glühendes Silber-Blech/ schmilzet es
sonder Rauschen/ hast du gewonnen/ und die Arbeit
glücklich geendet/ probire es denn auf P oder Y &
videbitur ejus toni. Soli Deo Gloria.

Philosophice das Aurum Fulminans zu prepariren
und wie man selbiges zur höchsten Rei-
nigung bringet.

Sie belieben in einer Phiole zu thun 8 Loth O zu
16 Loth Aquafort, das seine gehörige Stärke hat/
gießen selbiges darauff/ und lassen es in Asche oder
Sand saulich warm werden/ alsdann nehmen Sie
ohngefähr 8 Loth Salmiac, werffen denselben allmäh-
lich hinein/ und das so offt/ bis Sie sehen/ daß das
Wasser nicht mehr angreiffen wil/ denn hat die Na-
tur ihr rechtes Pondus.

Wann nun nichts mehr solviret/ gießen Sie die
Solution, so fern noch was rückständig/ ab/ und
procediren mit dem Residuo gleichergestalt/ bis alles
solviret ist.

Nun nehmen Sie vor 3 oder 6 Pfening Cypri-
schen Vitr., solviren solches in Aqua comm., filtri-
ren es/ also/ daß es lauter und nicht trübe sey/ hiermit
präcipitiren Sie das O/ und edulcoriren den Ralck
mit warm Wasser/ so werden Sie das O viel schö-
ner/ als wenn es 3 mahl durch die Spheram Saturni
gangen wäre/ vor Sich finden/ (Diese Arbeit mit dem
Antim.


(86)

Sal Tartar., solviren solches so viel als es wil/ lassen
es in einer Abrauch-Schale evaporiren/ legen denn
das Sal im Keller/ so schmilzet es per se balde/ die-
ses ist das so genante Lixivium Tartari, hiervon müs-
sen Sie ein fein Glas voll bey der Hand haben/ und
dieses können Sie wegen obiger Arbeit zugleich mit
verfertigen/ so gewinnt man an der Zeit viel.

Wenn Sie nun hiermit das O präcipitiren/ müs-
sen Sie behutsam verfahren/ sonst fängt es an zu
schlagen/ oder läuft von dem Drausen über.

Wenn nun alles verbrauset und das O präcipiti-
ret ist/ müssen Sie es wohl edulcoriren/ damit das
Sal darvon komme/ wann dieses geschehen/ werden
Sie ein schönes Purpur-farbenes Aurum Fulminans
vor Sich finden.

Diese Arbeit kan in 4 Tagen verrichtet werden/ so
daß man zu der gangen Arbeit nicht über 5 Tage zu-
bringer/ alsdann ist die Philosophische Präparation
des Auri Fulmin. geschehen. Sat dictum.



CLA-

Reprint of the original manuscript of Sebald Schwartzer's recipe for the synthesis of fulminating gold

Unprofessionally translated, Schwaertzer writes:

The philosophy of preparing the Aurum Fulminans and how to bring it to highest purity.

You may wish to put 8 Lots [approx. 8x16 g!] of ☉ [gold] into a vial and to add 16 Lots of Aquafort [concentrated nitric acid], which has a considerable concentration / and gently warm it in [a bath of] ashes or sand / then take approximately 8 Lots of Salmiac [ammonium chloride] and slowly throw it into the beaker / do that / until you can see / that the water does not want to etch any further / then nature has its right Pondus.

Then take Cypric Vitriol [probably a mixture of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$] as much as you can get for 3 or 6 Pfennig, dissolve it in common water, filter it off / so that / it is clear and no longer turbid / herewith precipitate the ☉ / and edulcorate the lime [precipitate?] with warm water / so you will get the ☉ in much nicer form / than when it had been going through Spheram Saturni [lead spheres] [...] you will notice a significant loss of ☉ / it also takes threefold efforts [...] This is the true philosophic purification; When it is dried / dissolve it in Aquafort and Salmiac, this ☉ lime, as stated above.

You may wish to evaporate the Aquafort to dryness in ashes / and it will take you half a day to do this work.

Then pour fresh water onto it / and dissolve it another time / evaporate it to dryness / then dissolve it a third time. You must pay attention / that you do not evaporate it completely but only half of it / so the Materia will be oily / then take it from the fireplace / and let it cool down.

Then precipitate the ☉ with Ol. Tartar. [Oil of Tartar, concentrated potassium carbonate solution] [...] You have to be careful / when precipitating ☉ with that [Oil of Tartar] / otherwise it might start to strike [explode] / or it might cause heavy foaming and overflow.

As soon as everything is no longer effervescent and the ☉ is precipitated / you need to edulcorate it / to let the salt escape / when this is finished / you will find a beautiful purple-colored Aurum Fulminans.

This work can be finished within 4 days / so that the complete work does not take longer than 5 days / then the philosophic preparation Auri Fulmin. is done.

Sat dictum.

It was Johann Kunckel von Löwenstern (1630-1703) who found the correct explanation for the formation of fulminating gold upon the addition of potassium carbonate to the gold(III) solution according to the original recipe: Since Schwaertzer used ammonium chloride for the production of aqua regia, the solution of hydrogen tetrachloroaurate(III) still contained a significant amount of ammonium ions, which readily set ammonia free when treated with a base like concentrated potassium carbonate solution.

However, fulminating gold is not only one of the first known “compounds” of gold, but it is the first high-explosive known to mankind, and even older than famous historic explosives like mercury(II) fulminate (Knallquecksilber) [2].

Interestingly, the alchemists of the 16th and 17th century believed that the shock wave of exploding fulminating gold aims downwards only [3]. This myth was “busted” by Thomas Willis [4] in a simple experiment. He heated a small amount of fulminating gold on a spoon and covered it with a coin. Upon explosion the coin flew to the rafters. Robert Hooke performed similar experiments and reformulated the ancient ideas of combustion on account of his observations.

Johann Rudolf Glauber (1604-1670) observed the purple fumes of exploding fulminating gold and used incredible amounts of this substance for the gold-plating of objects. Much later, two (less hazardous) technical applications are documented in patent literature: Photography on the basis of fulminating gold and silver compounds as the light-sensitive substances [5] and therapeutic uses of gold succinimide, which can be prepared from succinimide and gold compounds such as fulminating gold [6].

Probably almost every chemist of the 19th century once worked on fulminating gold, since its constitution was still unknown. In the course of these investigations, probably many explosions occurred. One severe incident of Jöns Jakob Berzelius in 1809 is documented [7]. He was injured by an explosion in the course of handling more than 10 grams (!) of fulminating gold. Some glass shards of the beaker perforated his left hand and injured his eyes. As a consequence of his injuries he had to stay for months in a darkened room until he could finally see again, although a certain opacity of his right eye remained for years. His wounded hand healed, too, leaving purple-colored scars.

The work of Scheele, Lavoisier and Dumas

Until the 19th century, many scientists still believed that fulminating gold can be produced by the reaction of milk of lime and gold(III) chloride or other chemical reactions. By analyzing fulminating gold, Carl Wilhelm Scheele found the evidence that ammonia is the only responsible reagent for its formation. He also proved that the gas that is generated upon its explosion, is (mostly) dinitrogen [8]. In a first attempt to define a chemical “formula” for fulminating gold, Antoine Lavoisier concluded from Scheele’s work that it was an “oxide d’or ammoniacal” [9].

Jean Baptiste Dumas applied systematic chemical analysis to gain further insight into the fulminating gold [10]. He found that it consists not only of gold and nitrogen but also hydrogen and chlorine. He ground the substance with copper(II) oxide so that it could be heated and decomposed without explosion. From the decomposition products he calculated the elemental ratios. He concluded that fulminating gold was a salt with ammonium as the cation and a gold-nitrogen compound (“azoture d’or”) as the anion.

The work of Raschig

Friedrich Raschig found that fulminating gold was not one homogeneous compound but a mixture of more than one compound [11]. Despite the fact, that fulminating gold contains a certain amount of oxygen, he suggested a mixture of $\text{HN}=\text{Au}-\text{NH}_2$ and $\text{HN}=\text{Au}-\text{Cl}$ and concluded that the gold-nitrogen bonds of those amido and imido ligands are responsible for the explosive character. Although such gold-nitrogen bonds often can be found in explosive gold compounds, e.g. the extremely explosive tetraazidoaurates(III) like $\text{NH}_4[\text{Au}(\text{N}_3)_4]$ [12], numerous examples of non-explosive compounds containing Au–N-bonds are known, e.g. the amide $[(\text{CH}_3)_2\text{AuNH}_2]_4$ and $[(\text{CH}_3)_2\text{AuN}(\text{CH}_3)_2]_2$ [13], $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ [14], $[\text{AuCl}_3\text{NH}_3]$ [15], $[\text{AuBr}_2(\text{NH}_3)_2]^+$ [16]. Raschig's assumption was therefore too general but a good basis for further studies.

However, some hundred years later, Hans-Norbert Adams [17] found that $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ leads to the formation of a very explosive compound, when treated with sodium amide in liquid ammonia under water-free conditions. In a Guinier powder diffractogram, he could identify ammonium nitrate as a by-product of this reaction [18]. Adams concludes that this indicates the primary formation of amido ligands. From this observation it is likely that some gold(III) amides are explosives, too. However, fulminating gold definitely does not consist of isolated amide/imide compounds according to Raschig's suggestion.

The work of Weitz

Ernst Weitz [19] investigated the constitution of fulminating gold in one of the most comprehensive studies ever performed on this topic. He used all analytical methods that

were state of the art at that time and gained more scientific information about this extraordinary explosive substance. Some of his results were of fundamental character for all further studies. Nevertheless, he finally erroneously concluded that fulminating gold was a mixture (ratio of $\text{Au}:\text{N}=1:1.5$) of “diamido-imido-aurichloride” $\text{Cl}(\text{NH}_2)\text{Au}-\text{NH}-\text{Au}(\text{NH}_2)\text{Cl}$ and $\text{Au}_2\text{O}_3 \cdot 3\text{NH}_3$ (or $2\text{Au}(\text{OH})_3 \cdot 3\text{NH}_3$, respectively). He ignored the very poor solubility of fulminating gold in most solvents; from a chemist's point of view, one would expect a certain solubility at least for the isolated $\text{Cl}(\text{NH}_2)\text{Au}-\text{NH}-\text{Au}(\text{NH}_2)\text{Cl}$ molecule. However, he was correct that fulminating gold has an extremely high tendency of formation in the aqueous system gold(III) – ammonia – chlorine.

The latest works

Several decades later, Professor Joachim Strähle (University of Tübingen, Germany) and his co-workers Hans-Norbert Adams, Ulrich Gräßle and Joannis Psilitelis (in collaboration with Prof. Helmut Bertagnolli, Stuttgart), made – to the authors' knowledge – the last major attempts to solve the problem of the constitution of fulminating gold [18, 20, 21]. Their results will be discussed extensively in the following sections.

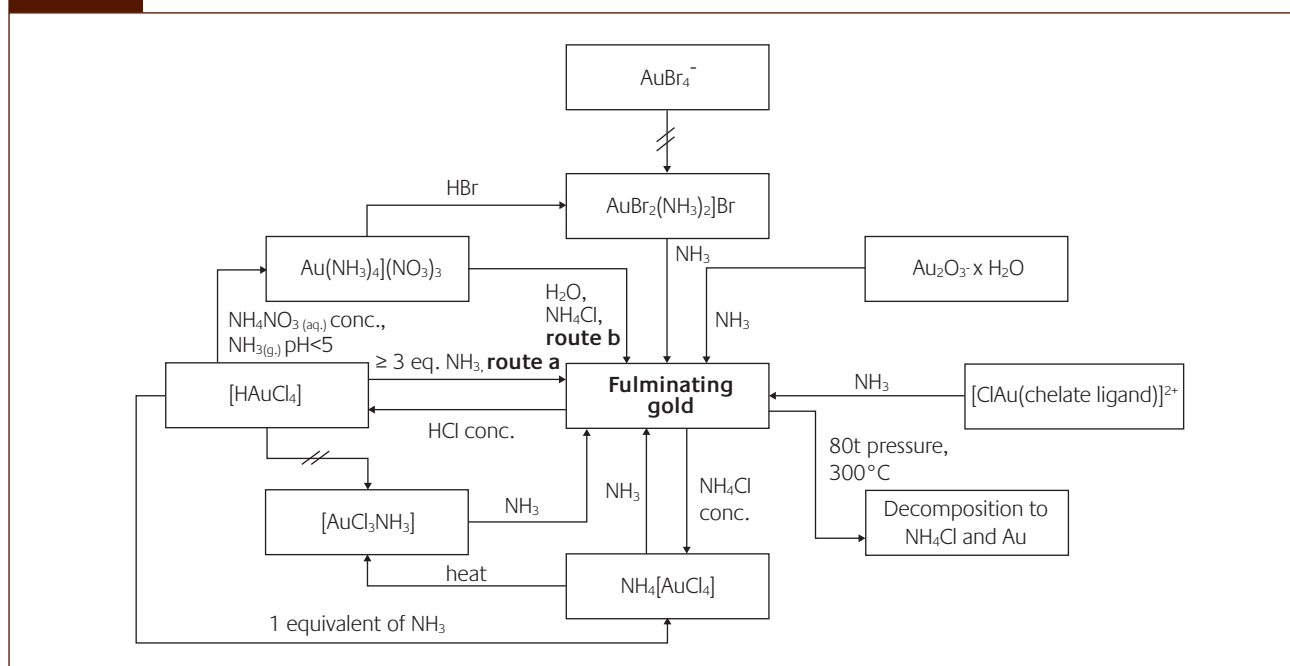
The Chemistry of fulminating gold

General aspects

Some reactions in the system gold – ammonia are summarized in Scheme 1 (below).

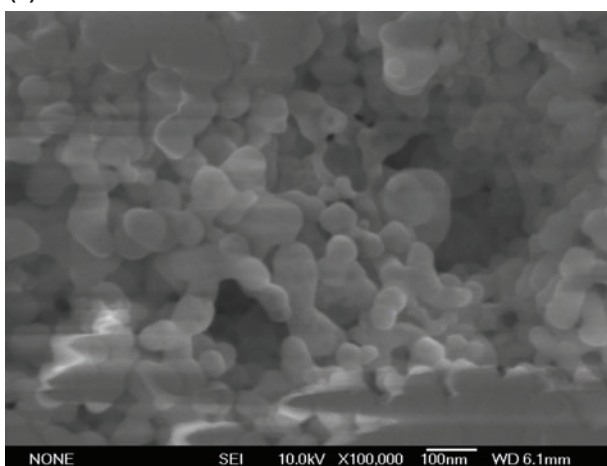
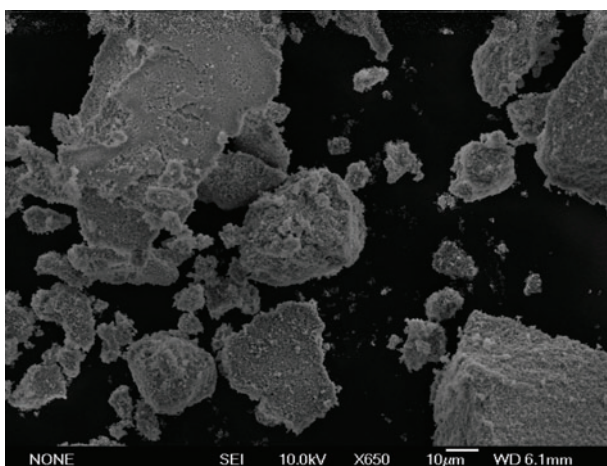
Tetraamminegold(III) nitrate, $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$, is the only exception, where, due to the excess of NH_4^+ and NO_3^- ions, a reaction of ammonia and hydrogen tetrachloroaurate(III)

Scheme 1



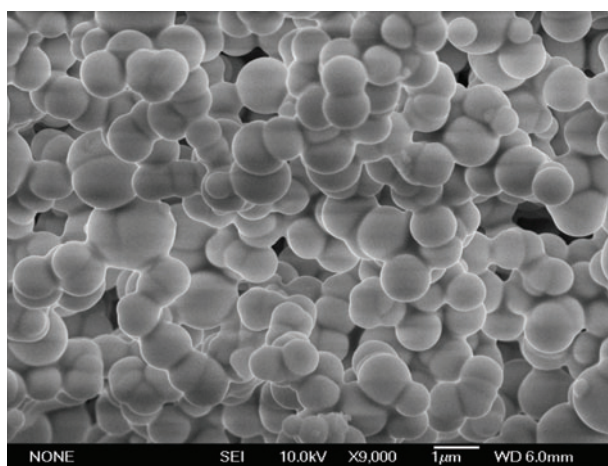
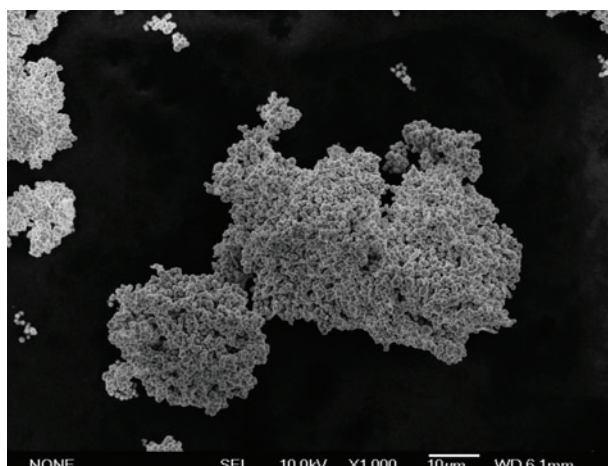
Overview of some reactions in the system gold – ammonia, partly after [18, 19]

Figure 2

Fulminating gold produced via route **a**

EDX analysis (mass -%)

Au 86, N 5, Cl 9, O not detected

Fulminating gold produced via route **b**

EDX analysis (mass -%)

Au 73, N 12, Cl 12, O 3

SEM pictures of fulminating gold

does not yield fulminating gold [14]. The tetraamminegold(III) ion has been intense object of investigation with respect to stability and acid dissociation [22], vibrational spectroscopical properties [23] and its comproportionation with gold to the corresponding diamminegold(I) complex [24]. Weitz observed that the hydrolysis of $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ with the mild Lewis base Cl^- (route **b**) leads to a seemingly homogeneous species of fulminating gold. He therefore – erroneously – concluded that this product was a “quite pure” $\text{Cl}(\text{NH}_2)\text{Au}-\text{NH}-\text{Au}(\text{NH}_2)\text{Cl}$. Indeed, route **b** is the method of choice if a homogeneous (with respect to color, grain size and macroscopic morphology) and hardly explosive product is desired. The morphologic differences in fulminating gold, whether produced via route **a** or **b** are shown in the electron microscope pictures in Figure 2. Energy Dispersive X-Ray (EDX) analytical data should be regarded rather as qualitative than as quantitative information.

Route **b** fulminating gold appears as partly welded globules with a size of approximately 1 μm in diameter, whereas the same substance synthesized via route **a** consists of much smaller particles (50 nm) of different shapes and

morphologies. In both pictures, crystalline structures are completely missing. We also applied powder X-ray powder diffraction to several batches of fulminating gold and found that it was amorphous only (only one broad glass-peak appeared in the diffractograms).

Crystallization of fulminating gold

The most reliable way of characterizing a compound is crystal structure analysis by X-ray diffraction. Many methods are known for the growing of single crystals or crystalline powder, partly after [18]:

1. Crystal growth from the gas phase
 - a) by chemical reactions
 - b) by transport reactions
 - c) by sublimation
2. Crystal growth in a molten materials
3. Crystal growth in solid phase
 - a) by recrystallization
 - b) by polyphase-diffusion
4. Crystal growth in solutions
 - a) by recrystallization

- b) by diffusion and chemical reactions
5. Crystal growth under hydrothermal conditions
 6. Crystallization of amorphous substances under high pressure and/or high temperatures.

Adams concluded that due to its physical and chemical properties, crystallization of fulminating gold cannot be achieved by methods 1), 2), 3) and 4a). In general, we agree with this hypothesis. Fulminating gold decomposes at approximately 210°C (sometimes with explosion) without melting. Sublimation leads to decomposition or explosion of fulminating gold. Ammonium chloride could be identified by X-ray diffraction as one subliming decomposition product. One tiny greenish-yellow crystal could be isolated from a Mark-tube, in which we tried to temper and/or sublime fulminating gold (1 week at 200°C). With a size of only a few microns, it was too small to determine the crystal structure. However, we believe that the crystal contains gold and light atoms only, but no chlorine. The crystallographical cell could be vaguely determined (see Table 1).

Adams stated that fulminating gold is insoluble and cannot be crystallized from solutions. However, in this study, several solvents were applied to investigate the solubility of fulminating gold: carbon tetrachloride, nitrobenzene, hexamethylphosphoric triamide, acetonitrile, dimethylsulfoxide and dimethylformamide. To our surprise, we found that, after almost two months, small amounts of fulminating gold (route **a**) dissolved in acetonitrile and dimethylformamide. This fact could be observed by the

yellowish-green color of the solution. The other solvents remained colorless. Recrystallization from the solution by slow evaporation or by influencing the solvent's polarity in an ether chamber, however, failed as well. Evaporation of the solvent forms a small amount of amorphous material again, which readily dissolves in the same solvent again.

A couple of experiments aiming at the crystallization of fulminating gold in gels have been performed previously and in this study. In general, the slow diffusion velocity in gels drastically decreases the formation of seed crystals, and allows the crystallization of large crystals of compounds that usually form fine precipitates like silver chloride or calcium carbonate – just like fulminating gold. Adams attempted the crystallization of fulminating gold in sodium silicate-derived silica gels under different conditions, by varying the gel's density, the concentrations of the starting materials, the gel's pH value or by application of homogeneous and heterogeneous formation of seed crystals (AuOCl crystals), by different geometries of the experimental apparatus or by application of liquid ammonia under high pressure. He always obtained amorphous precipitates or metallic gold (at high pH values). Our experiments in gels prepared from aqueous tetramethoxysilane suspensions failed as well and only yielded amorphous brownish-yellow precipitates.

Like Adams, we found that crystallization of fulminating gold by applying gaseous ammonia to solutions of hydrogen tetrachloroaurate(III) fails.

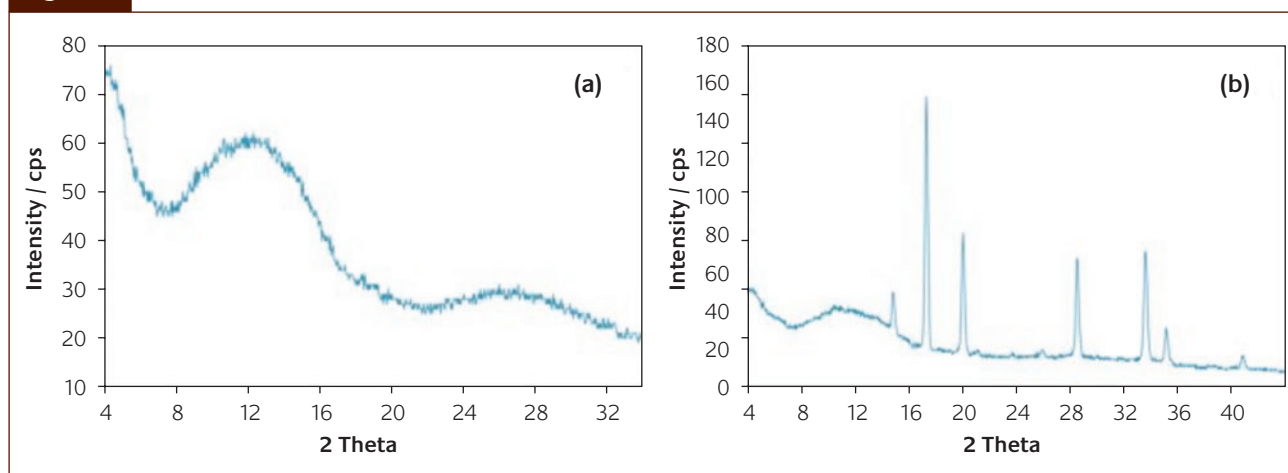
In this study, crystallization at high pressures and elevated

Table 1

Crystallographical cell of a sublimation/tempering product of fulminating gold: (single crystal diffractometry, 233 reflections used for cell determination)

a /Å	b /Å	c /Å	α /°	β /°	γ /°	V /Å ³	Crystal system	Lattice
7.641	7.853	7.855	75.63	81.76	75.03	439.5	triclinic	P-lattice

Figure 3



Two diffractograms of fulminating gold pressed at 80 tons (40 kbar) and 190°C (a) and 230°C (b), respectively. In (a), only the broad glass peak can be observed, whereas in (b) the same glass peak as well as the peaks of the decomposition products (Au⁰ and NH₄Cl) are shown

temperatures was attempted. For this purpose, amounts of approx. 35 mg of fulminating gold were filled in boron nitride crucibles and pressed in a belt-apparatus at 80 tons [25]. Three experiments with different temperatures were conducted; 190, 230 and 300°C. After one hour, the gold compound was filled in a Mark-tube and measured with the Guinier X-ray powder diffractometer. In case of 190°C, the substance was still amorphous. At higher temperatures, characteristic peaks of ammonium chloride and crystalline metallic gold appeared in the diffractogram (see Fig. 3). Therefore, fulminating gold decomposes even at high pressure and elevated temperature without prior crystallization. This method, by the way, could be an effective method for the production of highly X-ray diffracting crystalline gold powder.

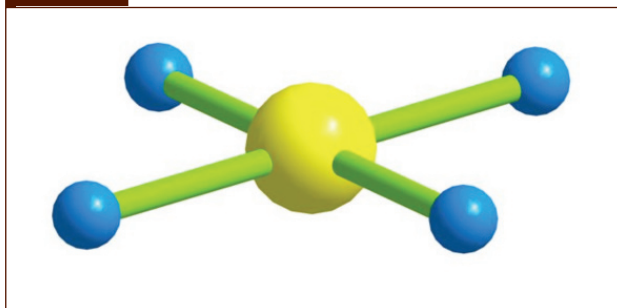
From all these facts discussed above, it can be concluded that fulminating gold is an amorphous mixture of probably polymeric compounds – a condensation product of $[\text{Au}(\text{NH}_3)_4]^{3+}$ on the way to $\text{Au}\equiv\text{N}$. The gold atoms are linked via $\mu\text{-NH}_2$ and $\mu_3\text{-NH}$ bridges, as indicated by vibrational spectroscopy by [18]. Adams suggests that fulminating gold is the product of hydrolysis of $[\text{Au}_2(\mu\text{-NH}_2)(\mu_3\text{-NH})_2]\text{Cl}$.

EXAFS analyses

In his PhD thesis, Joannis Psilitelis applied EXAFS (Extended X-Ray Absorption Fine Structure) measurements to gain insight to the structural constitution of fulminating gold [21]. This method can be used within various types of substances, even in amorphous and heterogeneous materials and liquids. He found that even in fulminating gold precipitated with only a slight excess of ammonia, a gold atom is no longer coordinated by chlorine atoms but exclusively by nitrogen atoms in its first coordination sphere (see Fig. 4).

This is in exact agreement with the coordination mode of the square planar tetraamminegold(III) cation (Au–N bond length 202 pm) [14]. In a second coordination sphere, there are either four gold atoms or only one (in a distance of 350 pm to the centered gold atom). In one possible interpretation, the gold atoms of both spheres can be connected by an Au–N–Au bridge (angle 120°) or, alternatively,

Figure 4



The fundamental, square planar AuN_4 -moiety of fulminating gold. The atomic distances are 202 pm for all Au–N bonds, and the angles are 90° and 180°, respectively

fulminating gold is built of planar layers of AuN_4 -moieties. The existence of Au–N bonds has been evidenced by vibrational spectroscopy as well.

Magnetic measurements

Magnetic susceptibilities were determined with a SQUID magnetometer (MPMS-XL5, Quantum Design Inc.) between 4 and 400 K with magnetic flux densities up to 5 Tesla. Samples of about 15 mg of fulminating gold (type **b**) were loaded in gelatin capsules and fixed in a straw as the sample holder. The data were corrected for the sample holder and the core diamagnetism. We measured the magnetic susceptibilities in magnetic flux densities of 0.8 Tesla, 1 Tesla, 2 Tesla and 5 Tesla. The sample is diamagnetic, but shows different susceptibilities at 300 K:

$$\chi_g (0.8 \text{ T}) = -3.09 \times 10^{-7} \text{ g}^{-1} \text{ cm}^3$$

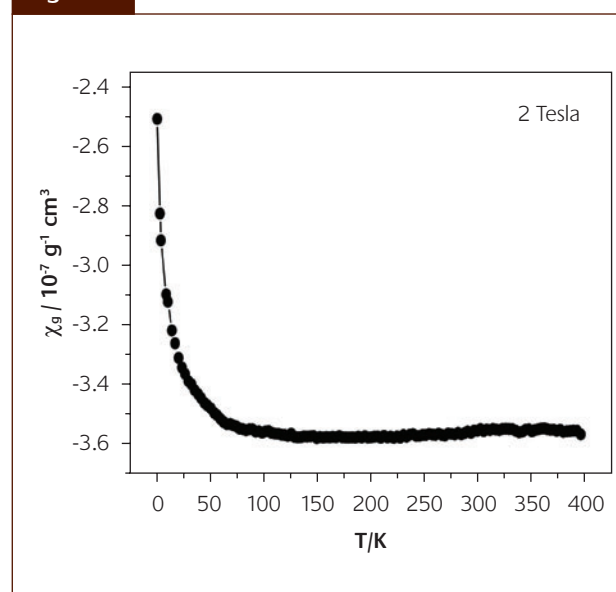
$$\chi_g (1 \text{ T}) = -3.13 \times 10^{-7} \text{ g}^{-1} \text{ cm}^3$$

$$\chi_g (2 \text{ T}) = -3.54 \times 10^{-7} \text{ g}^{-1} \text{ cm}^3$$

$$\chi_g (5 \text{ T}) = -3.35 \times 10^{-7} \text{ g}^{-1} \text{ cm}^3$$

Figure 5 shows the temperature dependency of the magnetic susceptibility in a magnetic flux density of 2 Tesla. The diamagnetic character of fulminating gold offers structural information. For ions with a d^8 electron configuration, diamagnetism occurs only in a strictly square planar coordination environment [26, 27]. A deviation from this geometry results in paramagnetism for d^8 compounds. From this fact, we can confirm the square planarity of the AuN_4 -moiety which has also been found in previous EXAFS analyses (see above and Figure 4).

Figure 5



Temperature dependency of the magnetic susceptibility of fulminating gold (magnetic flux density of 2 Tesla)

Table 2

A selection of elemental analyses (expressed as atomic ratios), after [18]

Mol NH ₃ per Au	Atomic ratio in fulminating gold, data taken from [18]				Atomic ratio in fulminating gold, data taken from [19] ²⁾			pH of solution	Explosive properties
	Au	N	Cl	O ¹⁾	Au	N	Cl		
3	1.0	0.95	1.36	0.33				slightly acidic	Deflagration upon heating
4	1.0	1.11	1.02	0.43	1.0	1.16	1.12	neutral	
4					1.0	0.99	1.07		
5	1.0	1.33	0.55	0.54	1.0	1.49	0.64	slightly basic	
6	1.0	1.35	0.44	0.84	1.0	1.47	0.59	basic	
8	1.0	1.36	0.32	0.87	1.0	1.51	0.52		
8 ³⁾	1.0	1.38	0.28	1.07	1.0	1.49	0.47		Explosion upon impact

¹⁾ The residue to 100% is assumed to be O (neglecting the content of hydrogen).

²⁾ Analysis of the solutions and conclusion to the composition of the precipitate.

³⁾ After washing several times with water.

Electrical experiments

In our attempts to measure the electrical resistivity of fulminating gold, it soon became evident, that strongly reproducible results are not easily obtained by simple four-probe-techniques at ambient pressure. However, fulminating gold is a substance with a very high electrical resistivity. This approves that ammonia does not reduce the Au³⁺ ions to metallic gold. Nevertheless, additional attempts were made to measure the electrical resistivity in the belt apparatus with only two contacts at variable pressures up to 40 kbar (using route **b** fulminating gold). Here some indications were found that the electrical resistivity of fulminating gold decreases with increasing pressure. In order to establish this effect quantitatively, it is intended to measure the resistance in a diamond anvil cell up to several hundred kilobars at ambient temperature.

Elemental analyses

In the reaction of gold(III) compounds and ammonia, fulminating gold is formed only with an ammonia excess of at least a factor of three in relation to Au³⁺. An equimolar addition of diluted ammonia solution leads to the formation of NH₄[AuCl₄] [15]. However, the fulminating gold species show different elementary analyses as a function of the precipitation conditions, primarily the amount of ammonia added. These hardly predictable differences have been observed already by Weitz and Adams (see Table 2).

Believing that Adam's results are the more reliable due to the use of modern elemental analytical facilities, extreme values of 1.4 atoms nitrogen and 0.3 atoms chlorine per atom gold are obvious from Table 2.

It is obvious that with increasing amounts of ammonia in

the course of precipitation (or washing), the content of chlorine in the product decreases, so does washing with pure water. Obviously, Cl⁻ is then substituted by OH⁻ or O²⁻. The results of an elemental analysis vary therefore from batch to batch. Reproducible syntheses of fulminating gold with identical elemental analytical values are hardly possible. In our investigations, we found that fulminating gold produced via route **a** is not even homogeneous within one batch. Two samples (a light one with light brownish-yellow color and a dark brown-colored one) of one precipitation batch were submitted to elemental analysis (H and N determined by a

Table 3

Some elemental analyses of fulminating gold (mass-%). Bold figures are from the same precipitation batch (n.d. = not determined)

Sample code	Route of production (see Scheme 1)	Au N H Cl			
		Au	N	H	Cl
29	a (Au ³⁺ :NH ₃ ≈ 1:3)	79.5	6.33	1.27	10.60
30	a	78.8	n.d.	n.d.	n.d.
45	a	81.0	n.d.	n.d.	n.d.
64a	a	84.3	5.88	1.14	15.82
(dark brown fraction)					
64b	a	90.5	7.22	1.39	9.12
(light brown fraction)					
65	b	87.8	9.81	1.75	9.19
77	b	n.d.	10.09	1.71	11.30

Fulminating gold produced via route **b** is characterized by higher homogeneity from the first sight than when synthesized via route **a**. Interestingly, despite its much higher nitrogen content, route **b** fulminating gold is less explosive than the route **a** product

vario EL elemental analyzer, Cl by a Metrohm Titroprocessor 686 analyzer) and showed two very different compositions (see Table 3, samples 64a and b). The gold content (determined by ICP-AES) varies to a large extent as well. In several samples, it is so high that the sum of the constituents would theoretically be far beyond 100%. This is also a good indication for inhomogeneties within the batch.

Derivatives of fulminating gold

Several organic amines have been applied instead of ammonia to gain insight into the chemistry of fulminating gold by reducing the possibilities of the formation of bridges via the nitrogen atoms [18]. Indeed, the product of the reaction of hydrogen tetrachloroaurate(III) and monomethylamine is a significantly less explosive light brownish amorphous precipitate. It is assumed that the methyl group blocks one possible link on the nitrogen atoms for the formation of a three-dimensional network. The explosive character of fulminating gold increases with the degree of cross-linking. When dimethylamine is used, a second hydrogen of NH_3 is substituted by a methyl group. Thus, the formation of a fulminating gold-type polymer is impossible and the reaction with $\text{H}[\text{AuCl}_4]$ yields a crystalline product – the adduct compound $\text{AuCl}_3 \cdot \text{NH}(\text{CH}_3)_2$. The use of primary amines large alkyl groups, e.g. mono-*t*-butyl-amine, hinders the formation of a three-dimensional polymer as well. The product of the corresponding reaction with $\text{H}[\text{AuCl}_4]$ is the crystalline adduct compound of the above type [18].

Adams investigated the reactions of bisethylenediamine gold(III) chloride as a model substance for fulminating gold [18]. In analogy to $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$, $[\text{Au}(\text{en})_2]\text{Cl}_3$ reacts with bases and forms $[\text{Au}(\text{en})(\text{en}_2\text{-H})]\text{Cl}_2$. It can be deprotonated further in a reaction with sodium amide, yielding $[\text{Au}(\text{en}_2\text{-2H})]\text{Cl}$. Both compounds are suitable analogs to fulminating gold and $[\text{Au}(\text{en})(\text{en}_2\text{-H})]\text{Cl}_2$ is even slightly explosive upon heating.

The above mentioned gold-nitrogen heterocycles $[(\text{CH}_3)_2\text{AuNH}_2]_4$, $[(\text{CH}_3)_2\text{AuN}(\text{CH}_3)_2]_2$ [13], $[(\text{CH}_3)_2\text{AuNH}_2]_3$ [28] and $[(\text{CH}_3)_2\text{AuNHCH}_3]_2$ [29] are mostly light sensitive but not explosive derivatives of fulminating gold. Several pyridine derivatives should be mentioned at this point as well: $\text{Hpy}[\text{AuCl}_4]$, $\text{AuCl}_3 \cdot \text{py}$, $[\text{AuCl}_2(\text{py})_2] \cdot \text{CH}_2\text{O}$ and $[\text{AuCl}_2(\text{py})_2][\text{AuCl}_2]$ [30]. In another study, $\text{AuCl} \cdot \text{py}$, $\text{AuBr} \cdot \text{py}$, $\text{AuI} \cdot \text{py}$ have been investigated [31, 32]. These compounds are light sensitive substances. The iodine compound is thermally instable and quickly decomposes above 0°C . Both compounds show interesting luminescence properties.

We investigated the reaction of anhydrous AuCl_3 and $\text{N}(\text{Si}(\text{CH}_3)_3)_3$ in absolute diethyl ether. Tris(trimethylsilyl)amine reacts much slower than ammonia or conventional organic amines. After several hours of stirring at room temperature, a small amount of a brown precipitate formed. Investigation by means of X-ray powder diffraction evidenced a partial reduction crystalline gold only. The precipitate itself was amorphous and not explosive (in the flame of a Bunsen burner).

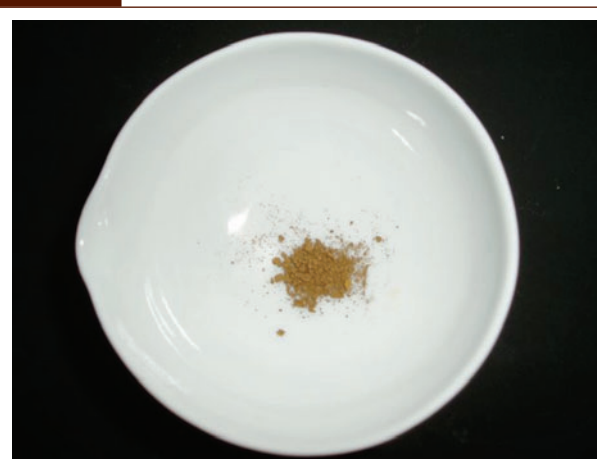
Experimental

In this study we synthesized fulminating gold via route **a** and **b**.

Route **a**-fulminating gold was synthesized primarily by the reaction of gaseous ammonia with aqueous solutions of hydrogen tetrachloroaurate(III) ($\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$ (99.9%, Sigma Aldrich). This strategy provided a continuous reaction of Au^{3+} and NH_3 avoiding a local over concentration of ammonia, which would yield a less homogeneous and more explosive and sensitive product. Generally, a beaker with aqueous hydrogen tetrachloroaurate(III) solution ($[\text{Au}^{3+}] = 10 \text{ mg/ml}$) and a beaker with aqueous ammonia (25%) were positioned in an empty desiccator. Precipitation of fulminating gold started within few minutes and generally completed after less than 30 minutes. At this point, the residual aqueous solution was colorless or slightly yellow at most. The precipitate was removed from the solution by filtration or centrifugation and washed with a minimum amount of water. Drying was performed in a desiccator over phosphorus pentoxide. Only for the determination of the explosive properties (drop hammer and friction sensitivity), route **a**-fulminating gold was precipitated in a direct reaction of aqueous $\text{H}[\text{AuCl}_4]$ and aqueous NH_3 in the molar ratio of 1:3 and 1:8, respectively. The color of route **a**-fulminating gold varies from light to dark brown, sometimes slightly yellowish, greenish or reddish, sometimes slightly purple (see Fig. 6).

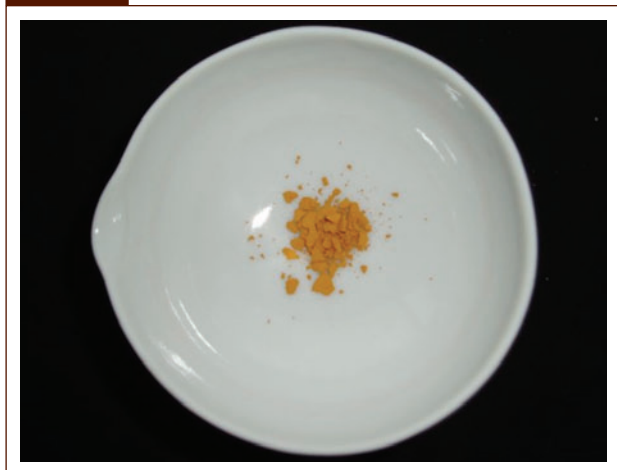
Route **b**-fulminating gold was synthesized in a two step synthesis, according to [19]. Firstly, the hydrogen tetrachloroaurate(III) solution ($[\text{Au}^{3+}] = 20 \text{ mg/ml}$) was saturated with ammonium nitrate at room temperature. Residual ammonium nitrate was removed by filtration. Ammonia gas (in the form of ammonia vapor from the bottle with a 25% solution) was bubbled through the yellow filtrate with a syringe until the solution lost its color or crystallization of white needles of the desired $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ began. After 24 hours of crystallization, the white needles were filtrated and washed with a small amount of cold water, ethanol and

Figure 6



Fulminating gold produced via route **a**

Figure 7

Fulminating gold produced via route **b**

ether. Eventually, a second fraction of $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ can be obtained from the mother liquor by bubbling ammonia vapor through the solution again. The yield after air drying was approximately 79%. In a second reaction step, the needles were dissolved in water (concentration approximately 23 mg $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ per ml H_2O). Solid ammonium chloride (20-fold molar excess compared to the tetraammine complex) was added to the clear solution. After a short time, precipitation of fulminating gold set in. Upon addition of ammonium chloride, the colorless solution first turned yellow on the bottom of the beaker, later orange or light-brown by the formation of finely dispersed fulminating gold (see Fig. 7).

The Hazards of fulminating gold

It appears that gold scientists are not always aware of the hazards of fulminating gold and the routes of its formation. Occasionally, warnings can be found in literature [33-34], however, reports on the preparation of gold catalysts based on the (potentially hazardous) use of hydrogen tetrachloroaurate(III) and ammonium carbonate or ammonia can be found much more regularly, see e.g. [35-40]. In this chapter, the hazards, safe treatment and disposal of fulminating gold as well as potential alternatives to the use of ammonia are shortly discussed.

Explosive properties

When initiated, fulminating gold explodes under the formation of a characteristic violet/purple plume of gold aerosols. For initiation, explosives can generally exhibit sensitivity toward impact, friction, electric discharge, thermal shock or high temperatures and other factors like changes in the chemical environment. Standardized tests for the reliable and reproducible determination of the explosive properties (such as the drop hammer or friction sensitivity), however, depend on a defined compound of high purity, because impurities can influence the sensitivity in a wide range. In case of fulminating gold, which is not a homogeneous substance, the declaration of sensitivity data must therefore be regarded as data with “informative character” only. Slight variations in the reaction conditions can influence the properties and lead to more sensitive and thus hazardous products. As stated above, the oxygen content in fulminating gold is proportional, the chloride content reciprocally proportional to the sensitivity. [18, 19] Washing the precipitate in boiling water or, even worse, alkaline solutions, increases the sensitivity in a way that the slightest touch with a sheet of paper can initiate the dry substance [41].

For the determination of sensitivity data, we applied standardized drop hammer-, friction- and spark-spraying tests. The drop hammer facility of the LMU has variable drop hammer weights (1, 5 and 10 kg) and its drop height can be adjusted in any order up to 100 cm. The sample is placed in a steel cylinder. A steel bolt is inserted into the cylinder, which is struck by the falling hammer. The friction tester uses a roughened ceramic plate and a ceramic pistil [42]. The sample is placed on the plate, then the pistil is placed on the sample by means of a lever. The force applied to the sample is varied by standardized weights that can be hung up the lever. For testing, an electric motor moves the plate forward and back. A substance is classified as friction sensitive, if the explosion or decomposition caused by friction is audible. Generally, fulminating gold is much more sensitive toward friction than to impact. This is a less common phenomenon among explosives.

We tested three samples of fulminating gold: Route **a** fulminating gold (precipitated with 3 and 8 equivalents of ammonia per Au^{3+} ion, respectively), and route **b** fulminating gold. The results of the sensitivity tests are given in Table 4. Decomposition means a significant change of color without audible or visible explosion.

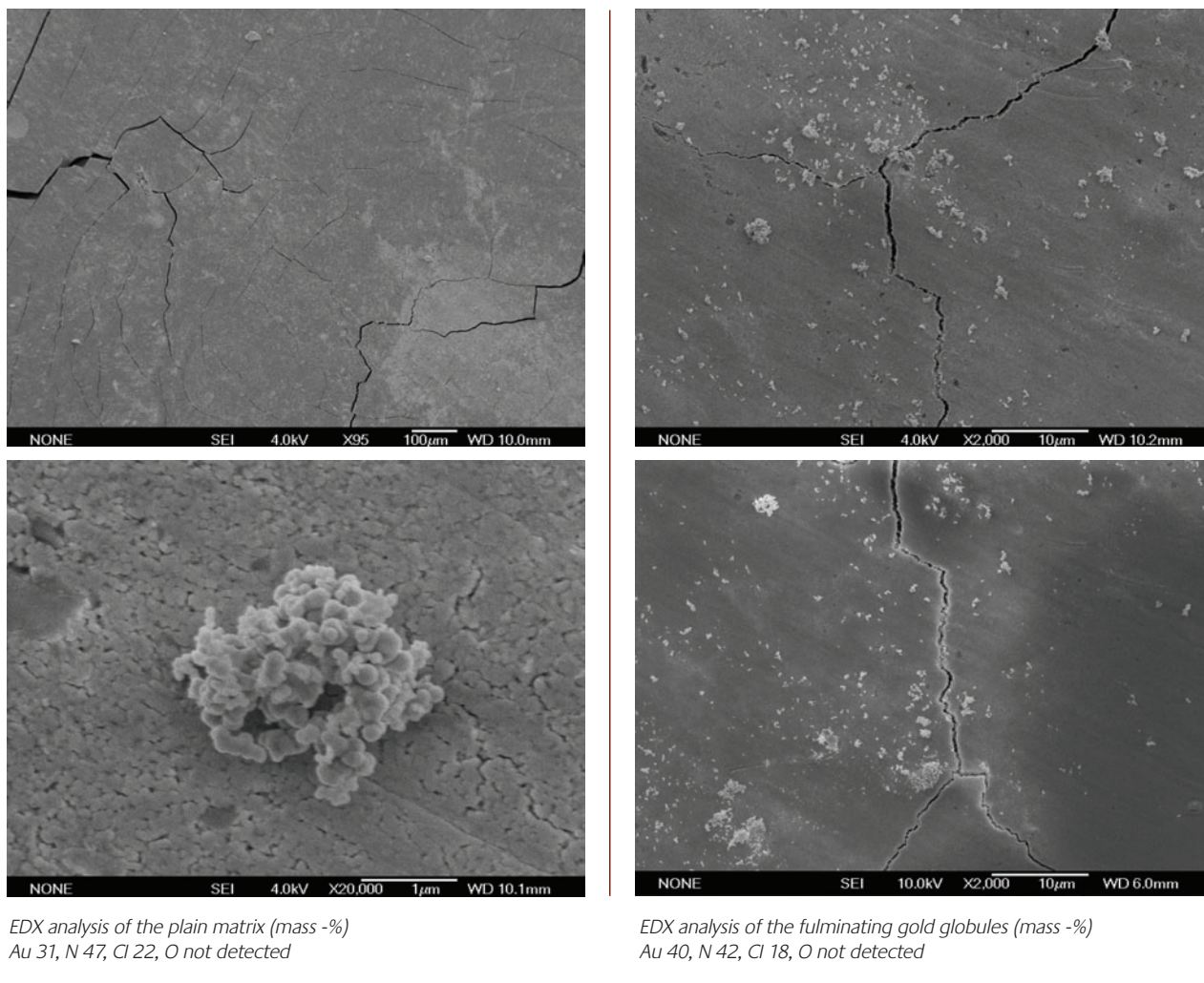
Table 4

Sensitivity data of fulminating gold

Sample	Impact (explosion)	Impact (decomposition)	Friction (explosion)	Electric discharge
Route a ($\text{NH}_3:\text{Au}=8:1$)	$\geq 11.5 \text{ J}^a$	$\geq 7.5 \text{ J}^b$	$< 5 \text{ N}^c$	explosion
Route a ($\text{NH}_3:\text{Au}=3:1$)	$> 100 \text{ J}^d$	$> 100 \text{ J}^d$	$< 5 \text{ N}^c$	decomposition
Route b	$> 100 \text{ J}^d$	$> 100 \text{ J}^d$	$> 360 \text{ N}^e$	slight decomposition

^a 5 kg drop hammer/23 cm; ^b 5 kg drop hammer/15 cm; ^c no weight on the lever; ^d 10 kg drop hammer/100cm; ^e a force of 36 kg on the sample

Figure 8



SEM picture of black, partly decomposed fulminating gold (by the impact of the drop hammer). Globules of undecomposed fulminating gold can be found on the surface

Decomposition of fulminating gold under the impact of the drop hammer yields a thin lustrous black plate. SEM images of this metal-like substance are shown in Figure 8. EDX analytical values confirm that this substance still contains gold, nitrogen and chlorine (qualitative information only).

The upper limit of the thermal stability of fulminating gold varies between 200 and 230°C. It always explodes or deflagrates in the flame of a Bunsen burner. Fulminating gold exploded violently when struck by a 600 mW laser beam in the Raman apparatus.

Safety instructions

CAUTION! Fulminating gold is an energetic material should be synthesized by fully trained personnel and in small amounts only. Proper protective measures should be taken. The following safety instructions provide a summary of all necessary safety precautions to be taken for the safe handling of fulminating gold and, for most readers even more important, instructions how to avoid the formation of this explosive.

The golden rule for your safety:

Avoid any contact of ammonia (either gaseous or in aqueous solution) to any gold(III) compound.

If, for any reason, this is not possible, follow the safety instructions listed below. Handling of explosives always involves a certain risk. The following rules will reduce the risk to a minimum.

- If possible, use secondary amines or primary amines with a large alkyl group (e.g. mono-*t*-butyl amine) instead of ammonia to avoid the formation of explosive products.
- Avoid an excess of ammonia (which increases the product's sensitivity) in the course of your reaction. Use as little as possible.
- In your reactions with gold(III) compounds, be aware that some chemicals may release ammonia, e.g. ammonium carbonate or urea at elevated temperature.
- Without a major excess of ammonia, the addition of significant amounts of sodium or potassium cyanide to

the slightly basic solution can prevent the precipitation of fulminating gold [35, 43]. Be aware of the formation of very toxic hydrogen cyanide gas from acidic solutions!

- Do not wash the precipitate, neither with water, nor (even worse) with ammonia solutions or bases. Both leads to the formation of even more sensitive and explosive products.
- If you accidentally obtain a precipitate from a reaction of gold(III) compounds and ammonia, do not dry it, but keep it moist. Only the dry product is explosive.
- Precipitation in presence of excess amounts of NH_4^+ and/or Cl^- (e.g. NH_4Cl or NH_4NO_3) leads to a less (in case of Cl^-) or not explosive (in case of NH_4^+) product.
- Do not synthesize or handle larger quantities than 500 mg of fulminating gold.
- Use safety equipment when handling fulminating gold, such as: safety goggles, face shield, leather coat, earthing (person and equipment), Kevlar™ gloves and wrist protectors and ear plugs. In general, avoid the use of glass or metal equipment (e.g. spatula) because of the possible formation of shards or shrapnels in case of an explosion. Use plastic beakers and spatula instead. Only for the drying of wet, freshly precipitated fulminating gold in the desiccator, the use of a glass beaker has turned out as practicable, because fulminating gold tends to adsorb on the bottom of a polypropylene beaker in the course of drying, from where it can be removed only by hazardous scratching.
- Avoid friction to the dry product. Remember its high friction sensitivity. Act in a concentrated way and handle the product with care and precaution.
- For safe disposal of fulminating gold, dissolve it in hydrochloric acid (concentrations > 0.2 M). Dissolution may consume some time, thus it is advisable to let the suspension stand for at least 24 hours. Thereafter, only a little residue might remain undissolved on the bottom of the beaker. It can be wiped out with a paper towel without a hazard.

Conclusions

Fulminating gold is a fascinating explosive substance of historic and scientific interest. However, it is a heterogeneous mixture of polymeric compounds with variable properties. Thus its constitution cannot be expressed by a simple formula. Adam's theory that fulminating gold is the product of partial hydrolysis of $^3[\text{Au}_2(\mu\text{-NH}_2)(\mu_3\text{-NH})_2]\text{Cl}$ is probably very close to the truth. In magnetic measurements, fulminating gold showed to be diamagnetic. Thus the gold atoms are coordinated by four nitrogen atoms in square planar low-spin complexes. This confirms previous EXAFS analyses. In any case, scientists have to be aware of the hazards involved in the reaction of gold(III) compounds and ammonia. Fulminating gold is unpredictable. *Sat dictum.*

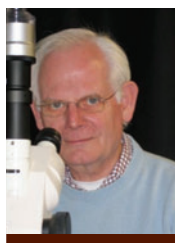
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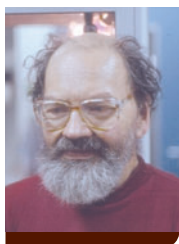
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References

- 1 S. Schwartz, *Chrysopoeia Schwartziana – Manuscripta Von der Wahrhaften Bereitung des Philosophischen Steins*. Samuel Heil, Hamburg, 1718
- 2 W. Beck, J. Evers, M. Göbel, G. Oehlinger, T.M. Klapötke, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1417
- 3 O. Croll, *Basilica Chymica*, G. Tampach, Frankfurt a. Main, 1608, p. 211
- 4 T. Willis, *Diatribe de fermentatione*, in: G. Blasius, H. Wetstein (eds.), *Opera omnia*, Amsterdam, 1682, p. 37
- 5 P.E. Schoenfelder, US 730800, 1903
- 6 W.J. Pope, GB 338506, 1929
- 7 M. Speter, *Nitrocellulose*, 1930, **1**, 128
- 8 C.W. Scheele, *Chemische Abhandlung von der Luft und dem Feuer*, Upsala-Leipzig, 1777, p.110
- 9 *Encyclopédie methodique*, Chimie, vol. 1, Paris, 1786, p. 639
- 10 J. Dumas, *Ann. Chim. Phys.*, 1830, **44**, 167
- 11 F. Raschig, *Liebigs Ann.*, 1886, **235**, 341
- 12 T.M. Klapötke, B. Krumm, J.-C. Galvez-Ruiz, *Inorg. Chem.*, 2005, **44**, 9625
- 13 H.-N. Adams, U. Grässle, W. Hiller, J. Strähle, *Z. Anorg. Allg. Chem.*, 1983, **504**, 7
- 14 M. Weishaupt, J. Strähle, *Z. Naturforsch.*, 1976, **31b**, 554
- 15 J. Strähle, J. Gelinek, M. Kölmel, *Z. Anorg. Allg. Chem.*, 1979, **456**, 241
- 16 L.H. Skibsted, *Acta Chem. Scand.*, 1979, **A33**, 113
- 17 H.-N. Adams, *Diploma thesis*, Tübingen, 1976
- 18 H.-N. Adams, *PhD thesis*, Tübingen, 1985
- 19 E. Weitz, *Justus Liebigs Ann. Chem.*, 1915, **410**, 117
- 20 U. Gräßle, *PhD thesis*, Tübingen, 1985
- 21 J. Psilitelis, *PhD thesis*, Tübingen, 1999
- 22 L.H. Skibsted, J. Bjerrum, *Acta Chem. Scand.*, 1974, **A28**, 740
- 23 M. Manfait, A.J.P. Alix, C. Kappenstein, *Inorg. Chim. Acta*, 1981, **50**, 147
- 24 L.H. Skibsted, J. Bjerrum, *Acta Chem. Scand.*, 1974, **A28**, 764
- 25 J. Evers, *Habilitation thesis*, München, 1982
- 26 K. Iglhaut, *PhD thesis*, München, 1991
- 27 C.V. Banks, R.V. Vander Haar, R.P. Vander Wal, *J. Am. Chem. Soc.*, 1955, **77**, 324
- 28 U. Grässle, J. Strähle, *Z. Anorg. Allg. Chem.*, 1985, **531**, 26
- 29 U. Grässle, W. Hiller, J. Strähle, *Z. Anorg. Allg. Chem.*, 1985, **529**, 29
- 30 H.-N. Adams, J. Strähle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 65
- 31 H.-N. Adams, W. Hiller, J. Strähle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 81
- 32 W. Conzelmann, W. Hiller, J. Strähle, G.M. Sheldrick, *Z. Anorg. Allg. Chem.*, 1984, **512**, 169
- 33 J.A. Cusumano, *Nature*, 1974, **247**, 456
- 34 J.M. Fisher, *Gold Bull.*, 2003, **36**, 155
- 35 F. Chemnitius, *Chemiker-Zeitung*, 1927, **51**, 823
- 36 M.-K. Tung, H.-Y. Lin, Y.-W. Chen, 2006, TW 263538
- 37 D. Wang, 2006, CN 1865150
- 38 D. Yin, J. Liu, C. Li, X. Tan, 2005, CN 1583257
- 39 Q. Fu, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, *Chem. Eng. J.*, 2003, **93**, 41
- 40 Q. Xu, K.C.C. Kharas, A.K. Dabtye, *Catal. Lett.*, 2003, **85**, 229
- 41 T. Bergman, *De calce auri fulminate*, in: *Opuscula physica et chymica*, vol. 2, Upsala 1780, p. 134
- 42 <http://www.bam.de>
- 43 G. Steinhäuser, *Gold Bull.*, 2008, **41**, 51