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The di(thiourea)gold(I) complex $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{SO}_3\text{Me}]$ as a precursor for the convenient preparation of gold nanoparticles

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Abstract: The synthesis of $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{SO}_3\text{Me}]$ (**1**) (a) by the anodic oxidation of gold metal in an anolyte of thiourea and methansulfonic acid and (b) by the reaction of $\text{Au}(\text{OH})_3$ with an aqueous solution of methanesulfonic acid in the presence of thiourea is reported. The structure of **1** in the solid state has been determined by single-crystal X-ray diffraction showing a linear S–Au–S unit with the thiourea ligands in a leaflet structure folded by $113.2(3)^\circ$. The cation of complex **1** is a dimer, based on short S...C interactions between two adjacent mononuclear cations. The thermal decomposition behavior of **1** was studied by TG and TG-MS confirming that it decomposes under inert gas or oxygen atmosphere in four steps in the temperature range of 200–650°C. Initial decomposition starts with the release and fragmentation of one of the thiourea ligands, followed by the anion degradation. Powder X-ray diffraction studies specified the formation of gold metal. Based on this observation, complex **1** was used as precursor for the formation of gold nanoparticles (Au NPs) in 1-hexadecylamine ($c=4.0 \text{ mol L}^{-1}$) at $T=330^\circ\text{C}$ without any

addition of reducing agents. TEM, electron diffraction, and UV/Vis spectroscopy studies were carried out. Au NPs of size $15 \pm 4 \text{ nm}$ were formed, showing the characteristic surface plasmon resonance at 528 nm.

Keywords: bis(thiourea) gold complex; electrolysis; nanoparticles; solid-state structure; thermal behavior.

1 Introduction

Diverse techniques exist for applying very thin gold coatings to solid surfaces, mainly on metals, most often on copper, silver and nickel [1–4]. Most commonly, chemical and electrochemical gold plating is used commercially, i.e. in electronics industry, to provide a corrosion resistant conductive film [5]. Examples include electrical connectors, printed circuit boards etc. In gold plating chemistry, soluble gold chloride and gold cyanide complexes are commonly used [6]. The most important gold plating chemical is $\text{K}[\text{Au}(\text{CN})_2]$ [6]. However, gold cyanide complexes are toxic [7] and hence it is desirable to develop and use environment friendly precursors.

Recently, great efforts have been made to prepare group 11 metal layers based on predefined nanoparticles (=NPs), as they have discrete particle sizes between 1 and 100 nm diameter [8]. Nanoparticles have unique physico-chemical properties, which are affected by the particle size, shape, size distribution and particle-to-particle interaction [9–16]. For example, group 11 metal NPs allow the design of smart materials including nano-devices [17–23], owing to their unique optical [24–36], electrical [37–45], magnetic [46–51], catalytic [52–63], or biological [64–71] properties. Two synthetic methodologies for metal colloid generation are predominantly used, which are the *top-down* and *bottom-up* approach [72]. The latter procedure enables the straightforward synthesis of defined gold nanoparticles (Au NPs) by, for example, chemical reduction of a gold source [73], decomposition of metal-organic compounds [74–77] or applying electrochemical [78] as well as photochemical [79] methods. Turkevich and coworkers prepared gold colloids in aqueous media

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by the reduction of chloroauric acid with sodium citrate [80], whilst the Brust-Schiffrin method reduces chloroauric acid by sodium borohydride in the presence of an alkanethiol [81]. Furthermore, the Möller group prepared Au NPs using sodium borohydride or hydrazine as reducing agent in micelles [82]. These methodologies need the use of reducing agents and the presence of stabilizing surfactants [80–82].

Herein we report on the efficient synthesis of the gold(I) coordination complex $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{SO}_3\text{Me}]$ by using either electrolysis or a wet chemical process. Its chemical and physical properties are described and its use as a precursor for Au NPs is discussed.

2 Results and discussion

The title complex $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{SO}_3\text{Me}]$ (**1**) could be prepared by either electrolysis or by the reaction of $\text{Au}(\text{OH})_3$ with thiourea in aqueous solution in the presence of methanesulfonic acid at ambient temperature, whereby thiourea reduces Au(III) to Au(I) and is itself oxidized to formamidine disulfide [83, 84] (Scheme 1).

Electrolysis was performed in a cell where the half chambers were separated by an ion-selective membrane, containing as anolyte an aqueous solution of methanesulfonic acid and thiourea. The oxidation of the gold anode occurs by applying a potential of smaller than 7.0 V.

After appropriate work-up, complex **1** could be isolated as a colorless air stable solid in a yield of 85% (electrolysis) or 98% (wet synthetic procedure). Complex **1** is soluble in common polar organic solvents and water.

The gold(I) complex **1** has been characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopy, high resolution ESI-TOF mass spectrometry, elemental analysis and single-crystal X-ray diffraction. The thermal behavior of **1** was studied by TG (thermogravimetry), TG-MS (TG-coupled mass spectrometry) and DSC (Differential Scanning Calorimetry).

The ^1H NMR spectrum of **1** shows for the NH_2 units two signals at $\delta = 8.18$ and 8.47 ppm, which are shifted downfield by 1.3 ppm if compared to the free thiourea ligand. The de-shielding is caused by the coordination of the thione unit to Au^+ resulting in an increase of the

π -electron density in the C–N bond [85–87]. The Me group of the counter ion is observed as a singlet at $\delta = 2.41$ ppm.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum a characteristic resonance signal at $\delta = 175.3$ ppm is observed for the C=S carbon atom, shifted up-field by 8.5 ppm as compared to non-complexed thiourea [86]. Complexation endorses the decrease of the C=S bond order, resulting in the formation of a partial CN double bond character [85, 86].

IR spectroscopy was used to investigate the nature of the ligand-to-metal coordination of **1**. Therein, the presence of a non-coordinated mesylate anion was evidenced by the appearance of two bands at 1193 cm^{-1} ($\nu_{\text{as}}(\text{SO}_3)$) and 1058 cm^{-1} ($\nu_{\text{as}}(\text{SO}_3)$) [88]. The $\nu(\text{NH})$ absorptions of the thiourea ligands at $3100\text{--}3400\text{ cm}^{-1}$ and the $\delta(\text{NH}_2)$ vibrations at 1600 cm^{-1} are representative for this family of complexes [89]. The respective asymmetric $\nu(\text{CN})$ mode at 1469 cm^{-1} is shifted to higher frequencies by 26 cm^{-1} as compared to non-coordinated thiourea. The $\nu(\text{C}=\text{S})$ vibration of **1** is shifted from 725 to 710 cm^{-1} upon coordination, confirming the dative binding of the thiourea ligands to gold(I) [90]. Further proof of thiourea coordination is provided by the appearance of the asymmetric $\nu(\text{C}=\text{S})$ bands at 1432 and 1385 cm^{-1} [89, 90].

2.1 Solid-state structure

The molecular structure of **1** in the solid state has been determined by single-crystal X-ray diffraction (Fig. 1). Selected bond distances (Å) and angles (deg) are summarized in the caption of Fig. 1. Suitable single crystals were obtained by slow cooling of a concentrated ethanol solution from 60°C to ambient temperature.

Complex **1** crystallizes in the monoclinic space group $C2/c$ with one formula unit in the asymmetric unit. The gold(I) ion is coordinated by two thiourea ligands (Au1-S1 $2.2774(14)\text{ Å}$ and Au1-S2 $2.2727(14)\text{ Å}$) in a linear fashion (S1-Au1-S2 $179.50(5)^\circ$), similar to other bis(thiourea) gold complexes, e.g. $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{Br}]$ and $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{Cl}]$ [91, 92].

The C=S entity is rotated by $106.17(18) / 107.31(19)^\circ$ (Au1-S1/2-C1/2) towards the linear S1-Au1-S2 unit ($179.50(5)^\circ$), which also agrees with previous findings (see above) [91, 92]. The coordination of the C=S moiety increases the C=S bond length from, e.g. 1.688 Å [93] for

Scheme 1: Synthesis of complex **1**. (i) HCl-HNO_3 (3:1, v/v). (ii) NaOH . (iii) MeSO_3H , $\text{S}=\text{C}(\text{NH}_2)_2$.

Fig. 1: ORTEP plot (displacement ellipsoids at the 50% probability level; hydrogen atoms as spheres with arbitrary radii) of the molecular structure of **1** with atom numbering scheme. Selected bond lengths (Å), angles and torsion angles (deg): Au1–S1 2.2774(14), Au1–S2 2.2727(14), C1=S1 1.726(6), C2=S2 1.728(5), C1–N1 1.314(7), C1–N2 1.308(6), C2–N3 1.302(7), C2–N4 1.314(7); S1–Au1–S2 179.50(5), C1–S1–Au1 106.17(18), C2–S2–Au1 107.31(19), N1–C1–N2 119.3(5), N3–C2–N4 119.7(5), S1–C1–N1 117.8(4), S1–C1–N2 123.0(4), S2–C2–N3 118.0(4), S2–C2–N4 122.3(4); C1–S1–S2–C2 113.2(3).

non-coordinated thiourea to herein 1.726(6) / 1.728 (5) Å, which corresponds to data of similar complexes of this type [94]. The C–N distances of 1.302(7)–1.314(7) Å are not affected by the coordination [93], lying in the range between C=N double (1.279 Å) and N–C_{sp3} single bonds (1.469 Å), revealing a significant amount of delocalization [95].

The planar thiourea entities (rmsd = 0.0055/0.0056 Å) [96] show a leaflet structure with a C1–S1–S2–C2 torsion angle of 113.2(3)°. A CSD database survey (see Fig. S4, Supporting Information available online) shows that this leaflet angle can range from 0 to 180°, which is rather unspecific and predominantly affected by the hydrogen bond network and the allocation of the counter ions.

Although aurophilic interactions are not observed in the crystals, short intermolecular contacts smaller than the sum of their van der Waals radii consolidate the packing of the ions. S...C(NH₂)₂ interactions between S2 and C1 of adjacent cations result in a dimer $[\mathbf{1}_2]^{2+}$ with a chair conformation (Fig. 2). Further interactions are based on hydrogen bonds that exclusively occur between the nitrogen atoms of the cationic fragment and the oxygen atoms of the mesylate anions (Table 1). Thereby, N1, N3 and N4 act as hydrogen bond donors towards two oxygen

Fig. 2: ORTEP plot (50% probability level) of $[\mathbf{1}_2]^{2+}$ formed by intermolecular S...C interactions (orange). Anions are omitted for clarity. Geometric interaction properties: S2...C1 = 3.400(5) Å (van der Waals radii: $\Sigma_{C,S} = 3.50$ Å), Au1–S2...C1A = 85.4°, S2...C1A–S1A = 101.1°; symmetry code: (A) $1/2 - x, 1/2 - y, -z$.

Table 1: Geometric details (Å, deg) of the hydrogen bond interactions in **1**.

D–H...A	D...A (Å)	D–H...A (deg)	Symmetry code
N1–H1A...O1	2.879(6)	101	$1/2 - x, 3/2 - y, -z$
N1–H1A...O2	3.063(6)	142	$1/2 - x, 1/2 - y, -z$
N1–H1B...O1	2.879(6)	103	$1/2 - x, 3/2 - y, -z$
N2–H2A...O2	2.905(6)	151	$1/2 - x, 1/2 - y, -z$
N3–H3D...O3	2.874(6)	139	$1 - x, -y, -z$
N3–H2E...O2	3.016(6)	158	$x, -1 + y, z$
N4–H4A...O3	2.893(6)	149	$x, -y, 1/2 + z$
N4–H4B...O1	2.863(6)	148	$x, 1 - y, 1/2 + z$

atoms of different anions, except for N2, where only one interaction is observed. Each cation is thus connected to 6 anions (Fig. 3) and the dication in total interacts with 10 mesylate anions. Consequently, each mesylate accepts hydrogen bonds from 6 cations, whereby O1 and O3 interact with two and O2 with three nitrogen atoms (Fig. 4). The

Fig. 3: Ball-and-stick model of **1** showing the cation and its hydrogen bond interactions (blue) towards the mesylate anions. Geometric details and symmetry operations are summarized in Table 1.

Fig. 4: Ball-and-stick model of **1** showing the mesylate anion and its hydrogen bond interactions (blue) towards the cation. Geometric details and symmetry operations are summarized in Table 1.

combination of all these interactions results in a three-dimensional network, involving all ionic components.

2.2 Thermal behavior

The thermal behavior of **1** was studied by TG, TG-MS and DSC methods to gain information on the thermal decomposition mechanism of the complex.

TG measurements were performed in atmospheres of nitrogen (gas flow of 20 mL min^{-1}) and oxygen (gas flow of 20 mL min^{-1}) in the temperature range of $40\text{--}800^\circ\text{C}$ with a heating rate of 10 K min^{-1} . Additionally, a continuous nitrogen carrier gas flow of 40 mL min^{-1} was used. The decomposition of **1** occurs in four steps with an over-all weight loss of 56.3% in the range of $T=200\text{--}650^\circ\text{C}$ (Fig. 5).

Fig. 5: TG traces of **1** under nitrogen (solid) and oxygen (dashed), (gas flow 20 mL min^{-1} (each), heating rate 10 K min^{-1}).

The thermal behavior of **1** under an atmosphere of nitrogen and oxygen is virtually identical, the last decomposition step under oxygen being finished at slightly lower temperature (N_2 : 650°C ; O_2 : 616°C). The residues at $T=800^\circ\text{C}$ of both measurements are with 43.8% close to the calculated value for elemental gold (44.3%). The formation of gold was proven by powder X-ray diffraction (PXRD) studies [ICDD 03-065-2870] (Fig. 6).

The first decomposition step of **1** shows an onset of $T=207^\circ\text{C}$ and a weight loss of 19.2%. Within this step multiple overlaying processes occur, which are associated with the release of one of the two thiourea ligands (calculated: 17.1%) and the start of the anion decomposition. The 2nd step observed at an onset of 311°C and the 3rd one at 391°C show a mass loss of 27.6% and 3.5%, respectively, indicating the further decomposition of the thiourea ligand as well as of the counter anion. The as-formed residue of 49.7% suggests the formation of Au_2S , which gradually decomposes to elemental gold in the final step (weight loss 5.9%, $T=450\text{--}650^\circ\text{C}$).

DSC studies under an atmosphere of nitrogen and oxygen show the melting point of **1** as an endothermic peak at 164°C (Fig. 7). Under inert conditions each decomposition step shows an endothermic peak ($E_2=-140.6 \text{ J g}^{-1}$, $E_3=-245.2 \text{ J g}^{-1}$), whereas under oxidative atmosphere the 1st and 2nd step are both split into an endothermic and exothermic peak (1st step: $E_2=-74.6 \text{ J g}^{-1}$, $E_3=19.2 \text{ J g}^{-1}$, 2nd step: $E_4=29.9 \text{ J g}^{-1}$, $E_5=-107.3 \text{ J g}^{-1}$), due to the oxidation of gaseous decomposition products. The final step under oxygen shows an exothermic peak ($E_7=80.7 \text{ J g}^{-1}$), which

Fig. 6: PXRD pattern (black) of the TG residue of **1** and the characteristic reflections of crystalline Au (red) [ICDD 03-065-2870].

Fig. 7: TG (solid) and DSC (dashed) traces of **1** under nitrogen (left) and oxygen (right), (gas flow 20 mL min^{-1} , heating rate 10 K min^{-1}).

fits well with the decomposition of Au_2S by the release and oxidation of sulfur to SO_2 under formation of elemental gold [97].

To confirm the thermal decomposition behavior of **1**, TG-MS coupling experiments were performed under argon

(gas flow 20 mL min^{-1} , heating rate 5 K min^{-1}). In Fig. 8 the TG traces and their first derivative as well as their respective mass-to-charge ratio (m/z) are depicted.

TG-MS coupling experiments show that the first mass decay starting at $T=200^\circ\text{C}$ is caused by the release and

Fig. 8: TG-MS traces and their 1st derivative (top) of **1** (argon, gas flow 20 mL min^{-1} , heating rate 5 K min^{-1}). Ion current (bottom) of $m/z=15$ [CH_3] $^+$, 16 [NH_2] $^+$, 32 [N_2H_4] $^+$, 44 [CS] $^+$, 48 [SO] $^+$, 64 [SO_2] $^+$ and 76 [CS_2] $^+$.

decomposition of one of the two thiourea ligands as evidenced by the appearance of fragments with $m/z=16$ $[\text{NH}_2]^+$, 32 $[\text{N}_2\text{H}_4]^+$, 44 $[\text{CS}]^+$ and 76 $[\text{CS}_2]^+$. Fragments of $m/z=15$ $[\text{CH}_3]^+$, 48 $[\text{SO}]^+$ and 64 $[\text{SO}_2]^+$ further indicate that the process is overlaid by the degradation of the anion. In the next step the decomposition of the 2nd thiourea ligand can be observed by typical fragments such as $m/z=16$, 32 and 44, as well as the anion fragmentation ($m/z=48$, 64). The last two steps are characterized by the decomposition of the remaining organics and the as-formed Au_2S by detection of fragments such as $m/z=16$, 44, 48 and 64.

2.3 Nanoparticle formation

The gold(I) complex **1** was used as a precursor for gold nanoparticle formation. With reference to the decomposition temperature of **1** (Fig. 5), 1-hexadecylamine (b. p. 330°C) was used as solvent. This amine is also expected to prevent the agglomeration of the Au NPs, due to its coordination properties [98].

The Au NPs were synthesized by heating a 1-hexadecylamine solution of **1** (4.0 mmol L⁻¹) first to 200°C, followed by heating to 330°C, to ensure complete decomposition, at a constant heating rate of 25 K min⁻¹. NP formation was observable by a typical color shift from yellow to deep red between 200 and 250°C. This observation shows that **1** decomposes in solution at about the same temperature as found for the solid state (Fig. 5; onset: 207°C). The solution was then cooled to 50°C and hexane was added to prevent solidification of 1-hexadecylamine. The Au NPs were precipitated by addition of ethanol and separated by centrifugation. After washing with ethanol, the Au NPs were re-dispersed in hexane for analysis.

The Au NPs have been characterized by transmission electron microscopy (TEM), electron diffraction and UV/Vis spectroscopy. The UV/Vis spectrum in hexane showed a broad absorption at 528 nm, due to the characteristic surface plasmon resonance (SPR) of the Au NPs (Fig. 9) [99].

TEM was used to determine the size and size distribution of the Au NPs. Mainly spherical particles with a mean diameter (d) of 14.5 nm and a standard deviation of $\sigma=3.9$ nm (size variation $c_v=27\%$) were obtained (Fig. 10). Electron diffraction studies confirmed the formation of Au NPs (see Fig. S6, Supporting Information available online).

3 Conclusion

The gold(I) complex $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{SO}_3\text{Me}]$ (**1**) was synthesized by electrolysis and a wet chemical approach.

Fig. 9: UV/Vis spectrum of Au NPs in hexane formed by thermal decomposition of **1** in 1-hexadecylamine ($c=4.0$ mmol L⁻¹) at 330°C.

Single-crystal X-ray diffraction analysis revealed a linear S–Au–S unit with the thiourea ligands in a 113.2(3)° folded leaflet structure. Short S...C interactions between the sulphur atom and the carbon atom of the coordinating thiourea ligands of adjacent cations result in the formation of a dimer. Anions and cations interact via hydrogen bonds between the NH_2 groups of the cation and the oxygen atoms of the mesylate anions, resulting in a three-dimensional network. TG investigations displayed a four-step decomposition between 200 and 650°C independent of the applied atmosphere (nitrogen, oxygen). TG-MS studies confirmed that the first step is related to the decomposition of one of the two thiourea ligands as evidenced by the detection of $[\text{NH}_2]^+$ and $[\text{N}_2\text{H}_4]^+$ fragments, followed by the anion degradation by appearance of $[\text{CH}_3]^+$, $[\text{SO}]^+$ and $[\text{SO}_2]^+$ fragments. Consecutive heating to $T=650^\circ\text{C}$ produced elemental gold, which was proven by PXRD studies of the TG residue. Heating of **1** in 1-hexadecylamine allowed for the formation and stabilization of essentially spherical Au NPs of size 14.5 ± 3.9 nm. Compared to classical methods of gold nanoparticle formation, the addition of reducing agents is not necessary.

4 Experimental section

4.1 General

Chemicals were purchased from commercial suppliers and were used without any further purification. The synthesis of Au NPs was carried out by a modified methodology published by Adner et al. [100, 101] and was performed under an atmosphere of argon using standard Schlenk techniques. All solvents used for Au NPs formation were

Fig. 10: TEM image and size distribution of Au NPs obtained by thermal decomposition of **1** ($c = 4.0 \text{ mmol L}^{-1}$, $d = 14.5 \text{ nm}$, $\sigma = 3.9 \text{ nm}$) at $T = 330^\circ\text{C}$.

degassed by sonication under vacuum using the sonication bath SONOREX RK 100 by BANDELIN electronic GmbH & Co. KG. Hexane was dried using a M. Braun SBS-800 purification system (stationary drying with molecular sieve columns $3 \text{ \AA}$). 1-Hexadecylamine (98%) was melted at 60°C and degassed in a sonication bath (5 cycles). Methanesulfonic acid (BASF SE, 5 volume-% in water) was used for the wet chemical and electrochemical synthesis of **1**. Gold (99.99% purity), as well as gold and platinum electrodes, has been produced by Saxonia Edelmetalle GmbH. A NafionTM membrane was used for the electrolysis.

4.2 Instruments

NMR spectra (500.3 MHz for ^1H and 125.8 MHz for $^{13}\text{C}\{^1\text{H}\}$) were recorded using a Bruker Avance III 500 spectrometer operating at 293 K. Chemical shifts δ are reported in ppm (parts per million) downfield from tetramethylsilane in $(\text{CD}_3)_2\text{SO}$ (^1H NMR $\delta = 2.50 \text{ ppm}$; $^{13}\text{C}\{^1\text{H}\}$ NMR $\delta = 39.52 \text{ ppm}$). The infrared spectrum was recorded between 500 and 4000 cm^{-1} with a Thermo Nicolet 200 FT-IR spectrometer. Elemental analysis was performed with a Thermo FLASH EA 1112 Series instrument. The high resolution ESI-TOF mass spectrum was measured with a Bruker micrOTOF QII equipment. The melting point was determined by using a Gallenkamp MFB 595 010 M melting point apparatus. TG/DSC experiments were performed with a Mettler Toledo TGA/DSC1 1100 system with an UMx1 balance. The TG-MS experiment was performed with a Mettler Toledo TGA/DSC1 1600 system with a MX1 balance coupled with a Pfeiffer Vacuum MS Thermostar GSD 301 T2 mass spectrometer. For PXRD measurements

the STOE powder diffractometer STOE Stadi P with Ge(111) monochromator $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$, 40 kV, 40 mA) was applied. Transmission electron microscopy (TEM) was performed with a PHILIPS CM 20 FEG operated at 200 kV. Sample preparation for TEM investigations were made by drop coating of the Au NPs dispersion in hexane on a carbon-coated copper grid (CARBON FILM 300 MESH, COPPER, Electron Microscopy Sciences). UV/Vis spectra were recorded with a Genesys 6 instrument (Thermo Electron Corporation) in quartz cuvettes (Company Roth, 1.0 cm optical path length) between 400 and 700 nm (measurement interval 0.2 nm).

4.3 Synthesis of $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2][\text{SO}_3\text{Me}]$ (**1**)

The title complex was prepared by two different synthetic methodologies, which were both performed under aerobic conditions.

4.3.1 Wet chemical synthesis

Gold (10.00 g, 50.7 mmol) was dissolved by adding 66 mL of aqua regia (3:1 conc. HCl to conc. HNO_3) followed by stirring the solution at 95°C for 4 h to produce $\text{H}[\text{AuCl}_4]$ [102]. The chloroauric acid thus obtained was treated five-times with conc. HCl (5 mL each) to remove the excess of HNO_3 , NOCl and NO. After evaporation of HCl by vacuum distillation, deionized water was added to give 500 mL of a $\text{H}[\text{AuCl}_4]$ aqueous solution (0.1 mol L^{-1}). Dropwise addition of 8 mL of an aqueous solution of NaOH (50 weight-%) resulted in the precipitation of $\text{Au}(\text{OH})_3$, which was filtered

off and washed five-times with deionized water (25 mL each). Afterwards, $\text{Au}(\text{OH})_3$ was dispersed in 300 mL of methanesulfonic acid. Then thiourea (15.45 g, 203.0 mmol) was added in a single portion. After 60 min of stirring, water was evaporated and the residue was recrystallized from ethanol at 60°C. Complex **1** was obtained as a colorless solid. Yield: 22.00 g (49.5 mmol, 98% based on Au).

4.3.2 Electrochemical synthesis

To an electrolysis cell separated by an ion selective NafionTM membrane, methanesulfonic acid was added. Thiourea was dissolved in the anode half-chamber to reach concentrations in the range 35–55 g L⁻¹. The gold anode and a platinated titanium cathode were added to the cell (Scheme 2). Application of a voltage of smaller than 7.0 V led to a step-wise dissolution of the anode. The solid product appearing in the anolyte was isolated by evaporation of water. After recrystallization of the as-obtained residue from ethanol at 60°C and subsequent vacuum filtration, complex **1** could be isolated as a colorless solid. Yield: 31.00 g (69.8 mmol, 85% based on the gold losses at the anode).

M. p. 164°C. – ¹H NMR (500.3 MHz, (CD₃)₂SO): δ = 2.41 (s, 3 H, CH₃), 8.18 (s, 4 H, NH₂), 8.47 (s, 4 H, NH₂) ppm. – ¹³C{¹H} NMR (125.8 MHz, (CD₃)₂SO): δ = 39.8 (–CH₃), 175.3 (C(=S)) ppm. – IR (KBr): ν = 3384 (m), 3290 (m), 3198 (m), 3165 (m), 1631 (s), 1616 (s), 1495 (m), 1437 (s), 1241 (s), 1393 (s), 1193 (s), 1058 (s), 785 (m), 772 (m), 710 (m), 563 (m), 536 (m), 526 (m) cm⁻¹. – HRMS ((+)-ESI): m/z = 348.9864 (calcd. 348.9856 for $[\text{Au}\{\text{S}=\text{C}(\text{NH}_2)_2\}_2]^+$). – C₃H₁₁N₄O₃S₃Au (444.31): calcd. C 8.11, H 2.50, N 12.61; found C 8.29, H 2.38, N 12.43.

Scheme 2: Schematic illustration of an electrolysis cell for the formation of **1** (1 = platinated titanium, 2 = gold, 3 = NafionTM membrane, 4 = methanesulfonic acid, 5 = methanesulfonic acid and thiourea).

4.3.3 Synthesis of gold nanoparticles

Complex **1** (8.4 mg, 0.02 mmol) was dissolved in 5 mL of 1-hexadecylamine at 50°C. After preheating the thus obtained solution to 200°C it was further heated to 330°C at a constant heating rate of 25 K min⁻¹, which led to a color change from yellow to deep red. The temperature of the solution was kept at 330°C for 10 min. After cooling the reaction mixture to 50°C, 5 mL of hexane were added to prevent solidification of 1-hexadecylamine. Addition of 10 mL of ethanol led to precipitation of the Au NPs. Separation was carried out by centrifugation (30 min, 4000 rpm). The particles were re-dispersed in 10 mL of ethanol, isolated by centrifugation and re-dispersed in 5 mL of hexane for further analysis.

4.4 Single-crystal X-ray diffraction analysis

Data of **1** were collected with an Oxford Gemini S diffractometer at 120 K with graphite-monochromatized MoK α radiation (λ = 0.71073 Å) (Table 2). The structure was solved by Direct Methods using SHELXS-13 [103] and refined by full-matrix least-squares procedures on

Table 2: Crystallographic data for **1**.

Empiric formula	C ₃ H ₁₁ AuN ₄ O ₃ S ₃
M_r	444.31
Size, mm ³	0.4 × 0.4 × 0.4
Crystal system	Monoclinic
Space group	C2/c
a , Å	27.7054(19)
b , Å	5.0151(3)
c , Å	16.4677(11)
β , deg	104.303(6)
V , Å ³	2217.2
Z	8
D_{calcd} g cm ⁻³	2.66
μ (MoK α), mm ⁻¹	13.8
$F(000)$, e	1664.0
hkl range	–32 ≤ h ≤ 32 –5 ≤ k ≤ 5 –12 ≤ l ≤ 19
θ range, deg	3.450–24.993
Refl. total/unique	6329/1935
R_{int}	0.0361
R_1/wR_2 , ($I > 2\sigma(I)$)	0.0237/0.0570
$R(F)/wR(F)^a$ (all refl.)	0.0258/0.0579
GoF (F^2) ^b	1.123
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.70/–1.31
CCDC no.	1952839

$$^a R(F) = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}, wR(F) = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{w}, w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}, \text{ where } P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3;$$

$$^b \text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}.$$

F^2 using SHELXL-13 [104]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions and treated as riding on their parent atoms using AFIX 33 for the methyl group. The NH_2 group was treated as a terminal $=\text{CH}_2$ moiety (AFIX 93), due to its intense double bond character and in order to simplify the hydrogen network properties (*vide supra*). C–H distances were fixed at 0.96 Å (CH_3) and 0.86 Å (NH_2) with assigned temperature factors of $H_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{CH}_3)$ and $1.2U_{\text{eq}}(\text{NH}_2)$. Graphics of the molecular structure were created by using ORTEP and the SHELXTL program package [105].

CCDC 1952839 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.

5 Supporting information

Spectra, comparative crystal structure data, TEM images, and electron diffraction patterns are given as supplementary material available online (DOI: 10.1515/znb-2019-0213).

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