

# The Unprecedented $[S_4N_2O_{10}]^{2-}$ Anion in the Molecular Gold Complexes $[Au_2Br_2(S_4N_2O_{10})_2]$ and $[Au_2Cl_2(S_4N_2O_{10})_2](S_2O_5Cl_2)$

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**Abstract:** The reaction of hexachlorophosphazene,  $P_3N_3Cl_6$ , with  $SO_3$  and the gold halides  $AuCl_3$  and  $AuBr_3$ , respectively, leads to the new cyclic anionic tetramer,  $[S_4N_2O_{10}]^{2-}$ , which is coordinated to  $Au^{3+}$  in the dimeric complexes

$[Au_2X_2(S_4N_2O_{10})_2]$  ( $X=Cl, Br$ ). The  $[S_4N_2O_{10}]^{2-}$  anion can be seen as the condensation product of two sulfate anions,  $[SO_4]^{2-}$ , and two amidosulfate anions,  $[NH_2SO_3]^-$ .

## Introduction

Amidosulfuric acid,  $NH_2SO_3H$ , also known as sulfamic acid, is the most simple nitrogen derivative of sulfuric acid. It can be seen either as the amide of sulfuric acid or as a sulfonic acid derivative of ammonia,  $NH_3$ . In this case, a  $[HSO_3]$  group replaces one hydrogen atom of  $NH_3$ . Also the remaining hydrogen atoms can be substituted, leading to imido-*bis*-sulfuric acid,  $NH(SO_3H)_2$ , and nitrido-*tris*-sulfuric acid,  $N(SO_3H)_3$ . While  $NH_2SO_3H$  and its salts are well studied and frequently used,  $NH(SO_3H)_2$  and  $N(SO_3H)_3$  are not known as neat acids, and also the knowledge on their salts is very limited.<sup>[1–5]</sup> The nature of the S–N bond still leaves a plenty of scope for novel SN compounds which was recently demonstrated by the synthesis of the tetraimido sulfuric acid,  $H_2S(NtBu)_4$  and the sulfur nitride oxide,  $S_6N_2O_{15}$ .<sup>[6–7]</sup> With  $S_6N_2O_{15}$  we shed some more light on the higher sulfonic acids of ammonia, because this cage-type molecule is the anhydride of  $N(SO_3H)_3$ .<sup>[7]</sup> It shows the two nitrogen atoms connected by three  $[S_2O_5]$  bridges according to  $N\{S(O)_2O(O)_2S\}_3N$ .  $S_6N_2O_{15}$  forms in the reaction of hexachlorophosphazene,  $P_3N_3Cl_6$ , and  $SO_3$ . The ability of  $P_3N_3Cl_6$  to act as a Lewis base in the reaction with  $SO_3$  under formation of  $P_3N_3Cl_6 \cdot 3SO_3$  has already been described in 1954.<sup>[8]</sup> It is reasonable to assume that this compound is the first step of the reaction that leads to  $S_6N_2O_{15}$ . It is not understood, how the decomposition of  $P_3N_3Cl_6 \cdot 3SO_3$  occurs and thus, scrutiny of the reaction appears to be reasonable. In course of our investigations, we also explored the presence of various metals in the reaction mixture. It turned out that the reaction of  $P_3N_3Cl_6$  with

$SO_3$  leads to the formation of the previously unknown anion  $[S_4N_2O_{10}]^{2-}$  when  $AuCl_3$  and  $AuBr_3$ , respectively, are added to the reaction mixture. The reaction sequence is not clear up to now. However, we assume that the formation of the adduct  $P_3N_3Cl_6 \cdot 3SO_3$  will also be the step in this reaction. If  $S_6N_2O_{15}$  is an intermediate of the reaction or if the  $Au^{3+}$  ions interact directly in the decomposition of  $P_3N_3Cl_6 \cdot 3SO_3$  is currently under investigation. Therefore, we started to perform especially NMR investigations and in situ Raman measurements. However, this is challenging due to the unconventional  $SO_3$  solvent.

## Results and Discussion

The  $[S_4N_2O_{10}]^{2-}$  anion can be traced back to the aforementioned imido-*bis*-sulfuric acid  $NH(SO_3H)_2$ . The anhydride of this acid would be the cyclic dimer  $NH\{S(O)_2O(O)_2S\}_2NH$ . The hydrogen atoms of the  $[NH]$  groups are still acidic and the gold complexes with the anion  $[S_4N_2O_{10}]^{2-}$  are, thus, the first representative of a salt of this new acid.

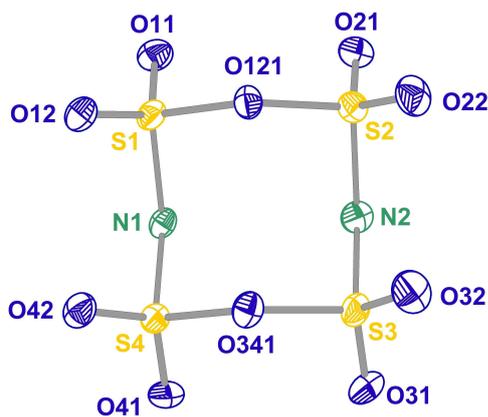
The  $[S_4N_2O_{10}]^{2-}$  anion is a ring consisting of four vertex-connected tetrahedra (Figure 1). The backbone of the ring consists of two S–N–S and two S–O–S bridges with bonding angles around  $123^\circ$  in both cases. The distances within these bridges are slightly, but significantly, different displaying mean values S–N of 166.4(6) pm and S–O of 163.4(6) pm (see caption of Figure 1 and supporting information). The S–O distances are in line with reported values for disulfates,<sup>[9–11]</sup> while the values for the S–N bonds are larger than found for the potassium nitrido-*bis*-sulfate,  $K_3[N(SO_3)_2] \cdot H_2O$ , which show values of 160 pm.<sup>[1,12]</sup>

This difference can be attributed to the strong bonding of the  $[S_4N_2O_{10}]^{2-}$  anion to the  $Au^{3+}$  ions in the presented molecules  $[Au_2X_2(S_4N_2O_{10})_2]$  ( $X=Cl, Br$ ). In these complexes two gold atoms are connected to dimers which are terminated by two  $[S_4N_2O_{10}]^{2-}$  anions (Figure 2 and Figure 3). The latter act as chelating ligands and the distances Au–N range from 201.8(4) to 203.9(3) pm ( $X=Cl$ ) and 203.6(7) to 205.1(7) pm ( $X=Br$ ). The distances to the bridging halide anions are about 232.5(1) pm ( $X=Cl$ ) and 243.3(1) pm ( $X=Br$ ) and are in accordance with the observations for the trihalides  $AuX_3$ , which show also dimeric

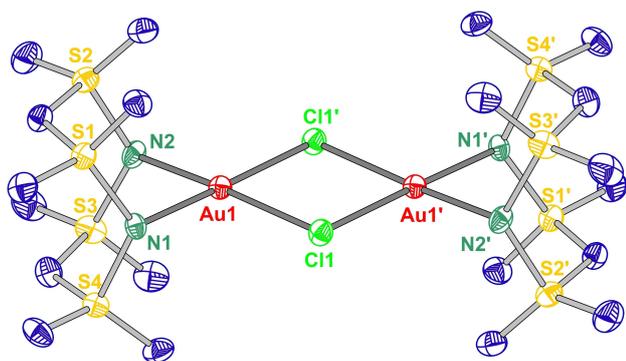
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**Figure 1.** Structure and labelling of the  $[S_4N_2O_{10}]^{2-}$  as observed in the dimeric  $[Au_2Cl_2(S_4N_2O_{10})_2]$  molecule. Selected distances (in pm) and angles (in  $^\circ$ ) compared to theoretical values (in *italics*): S(1–4)–O<sub>terminal</sub> (O11, O12; O21, O22; O31, O32; O41, O42) 139.7(3)/141.1(3)/142.2, S1–O121 164.0(3)/164.83, S2–O121 162.1(3)/164.81, S3–O341 163.8(3)/164.82, S4–O341 162.7(3)/164.85, N1–S1 166.9(4)/168.29; N1–S4 166.0(4)/168.32, N2–S2 166.6(4)/168.29, N2–S3 166.5(4)/168.33; S1–O121–S2 123.4(2)/123.6; S3–O341–S4 123.0(2)/123.5; S1–N1–S4 122.6(2)/123.5; S2–N2–S3 123.1(2)/123.54. The thermal ellipsoids are set to a 70% probability level.



**Figure 2.** Structure and labelling of the molecular dimer  $[Au_2Cl_2(S_4N_2O_{10})_2]$  in the crystal structure of  $[Au_2Cl_2(S_4N_2O_{10})_2](S_2O_5Cl_2)_2$ . Selected distances (in pm) and angles (in  $^\circ$ ) within the  $\{N_2AuCl_2AuN_2\}$  moiety compared to theoretical values (in *italics*): Au1–Cl1 232.6(1)/234.72, Au1–Cl1' 232.4(1)/234.67; Au1–N1 203.9(3)/201.87, Au1–N2 201.8(4)/201.83; N1–Au1–N2 86.3(2)/86.23; Cl1–Au1–Cl1' 87.0(4)/85.53; N1–Au1–Cl1 94.5(1)/94.16, N2–Au1–Cl1' 92.2(1)/94.08 (data for the respective bromide are given in the supplement). The thermal ellipsoids are set to 70% probability level.

structures according to  $Au_2X_6$ .<sup>[13–14]</sup> The distances and angles within the complexes  $[Au_2X_2(S_4N_2O_{10})_2]$  ( $X=Cl, Br$ ) are well reflected by quantum mechanical calculations (see captions of Figures 2 and 3, and Supporting Information). As expected, the calculations result in  $D_{2h}$  symmetry for the molecules, while in the solid state they exhibit only  $C_i$  ( $X=Cl$ , space group  $C2/c$ ) or even  $C_1$  symmetry ( $X=Br$ , space group  $P1$ ).

While the bromide  $[Au_2Br_2(S_4N_2O_{10})_2]$  crystallises as a pure compound, the chloride contains additional  $S_2O_5Cl_2$  molecules in the crystal structure. Interestingly, this molecule, even if long known, has been characterised thoroughly only very recently.<sup>[15]</sup> According to these investigations, different possible conformers of the molecule are stable and the solid state structures reveal

strong polymorphism. The disulfuryl dichloride molecule in  $[Au_2Cl_2(S_4N_2O_{10})_2](S_2O_5Cl_2)_2$  appears as the so-called *anti*-conformer and the observed bond and angle parameters match very well the reported findings for the pure compound.<sup>[15]</sup>

The new  $[S_4N_2O_{10}]^{2-}$  anion is the first example of a cyclic anion consisting of condensed  $[SO_4]^{2-}$  and  $[NH_2SO_3]^-$  tetrahedra, because the above mentioned imido-*bis*- and nitrido-*tris*-sulfate are monomeric species. The condensation of only  $[NH_2SO_3]^-$  ions is known in form of the cyclic trimer  $[S_3N_3O_6]^{3-}$  and tetramer  $[S_4N_4O_8]^{4-}$ .<sup>[16–17]</sup> It is worthwhile to mention that there are other anions in the system S/N/O.<sup>[18]</sup> However, these anions are usually not composed of linked tetrahedra. The anions  $[S_3N_3O_6]^{3-}$  and  $[S_4N_4O_8]^{4-}$  are usually prepared by heating sulfamide,  $SO_2(NH_2)_2$ , to a temperature between 180 and 210  $^\circ C$ . However, because the synthesis is not straightforward, the number of these anions is very limited. On the other hand, the condensation of  $[SO_4]^{2-}$  tetrahedra can only lead to linear polysulfates  $[S_nO_{3n+1}]^{2-}$  ( $n=2–6$ ).<sup>[19–23]</sup> Cyclization would result in neutral molecules and with  $S_3O_9$ , the so-called ice-type  $SO_3$  (or  $\gamma$ - $SO_3$ ), there is one known example.<sup>[24,25]</sup> The combination of the different  $[SO_4]^{2-}$  and  $[NH_2SO_3]^-$  tetrahedral, respectively, is not known up to now, probably because no suitable preparative pathway is known. According to our findings the route using  $P_3N_3Cl_6$  as a Lewis base and  $SO_3$  as a Lewis acid is very promising in this respect. In principle, numerous variations in the condensation of  $[SO_4]^{2-}$  and  $[NH_2SO_3]^-$  tetrahedra are thinkable, bearing the potential of a large number of new anions. However, even if the systematic approach seems to be sound, the synthesis of defined products turns out to be not that simple. Concerning the new  $[S_4N_2O_{10}]^{2-}$  anion it is of importance to obtain further compounds. We are especially interested in the salts with simple monovalent cations that would allow studying the anion without complexation.

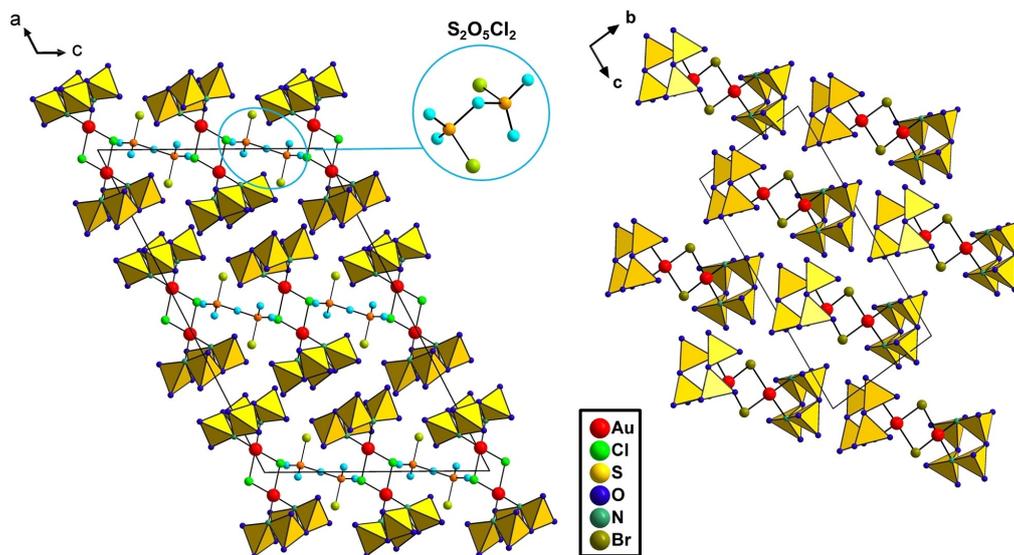
## Experimental

Full details of synthesis, characterisation and quantum chemical calculations can be found in the Supporting Information.

Deposition Number(s) 2154742 (for  $[Au_2Cl_2(S_4N_2O_{10})_2](S_2O_5Cl_2)_2$ ) and 2154741 (for  $[Au_2Br_2(S_4N_2O_{10})_2]$ ) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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**Figure 3.** Crystal structures of  $[\text{Au}_2\text{Cl}_2(\text{S}_4\text{N}_2\text{O}_{10})_2](\text{S}_2\text{O}_5\text{Cl}_2)_2$  (left) and  $[\text{Au}_2\text{Br}_2(\text{S}_4\text{N}_2\text{O}_{10})_2]$  (right). In the monoclinic chloride compound the dimers show inversion symmetry, in the triclinic bromide the complexes are located on general sites bearing no symmetry elements. The crystal structure of the chloride compound contains additional  $\text{S}_2\text{O}_5\text{Cl}_2$  molecules, as emphasized in different colours in the left part of the figure. To provide a better overview the  $[\text{SO}_3\text{N}]$  moieties are illustrated as polyhedra. (crystallographic details are given in the Supporting Information).

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** sulfur trioxide · gold · sulfuric acid · amidosulfate · solvothermal synthesis

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