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The Unique *bis*-(Disulfato)-aurate Anion $[Au(S_2O_7)_2]^-$: Synthesis and Characterization of $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$

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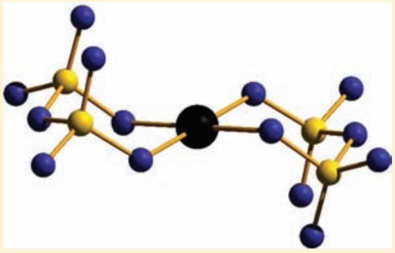
Supporting Information

ABSTRACT: The reaction of $Au(OH)_3$ and oleum (65% SO_3) in the presence of M_2SO_4 (M = Li, Na) afforded yellow single crystals of $Li[Au(S_2O_7)_2]$ (triclinic, $P\bar{1}$, $Z = 1$, $a = 532.20(3)$, $b = 649.69(4)$, $c = 836.72(5)$ pm, $\alpha = 107.982(2)°$, $\beta = 90.171(2)°$, $\gamma = 102.583(2)°$, $V = 267.80(3)$ Å^3) and $Na[Au(S_2O_7)_2]$ (monoclinic, $P2_1/n$, $Z = 2$, $a = 533.31(3)$, $b = 1193.38(7)$, $c = 907.67(5)$ pm, $\beta = 98.548(3)°$, $V = 571.26(6)$ Å^3). Both compounds exhibit the unprecedented $[Au(S_2O_7)_2]^-$ anion in which a square planar coordination of the central gold atom is achieved by the chelating attachment of two disulfate groups. The disulfates were characterized by means of IR spectroscopy and DTA/TG measurements. For both compounds, the decomposition occurs via several steps and is finished at about 450 °C at the stage of elemental gold and the sulfates M_2SO_4 (M = Li, Na), as revealed by X-ray powder diffraction of the residues.



1. INTRODUCTION

The first systematic investigations of gold compounds containing complex oxoanions can be traced back to 1827 when Mitscherlich reported that elemental gold dissolves in concentrated selenic acid.[1] Later on, this reaction was studied further by Lenher,[2] and finally Caldwell and Eddy claimed that the product of the reaction can be used for glass coloring purposes.[3] However, it was only in the early 1980s when the first structure elucidations revealed the nature of the reaction products,[4] which turned out to be gold oxoselenates(IV). A similar story can be told for sulfates of gold, which were also investigated a long time ago by Schottländer,[5] but which lacked characterization even until 2001, when we were able to prepare the binary gold(II)-sulfate $Au_2(SO_4)_2$ that shows a metal−metal bonded $[Au_2]^{4+}$ dumbbell, which is coordinated by two chelating and two mondentate sulfate groups.[6] In the course of these investigations, also a number of ternary gold(III)-sulfates showing ${}^1_\infty[Au(SO_4)_{4/2}]$ anionic chains connected via alkaline metal ions could be gained,[7] but binary $Au_2(SO_4)_3$ is still elusive. Thus, besides the above-mentioned $Au_2(SO_4)_2$, the fluorosulfate $Au(SO_3F)_3$,[8] which forms $[Au(SO_3F)_3]_2$ dimers, and the phosphate $AuPO_4$[9] are the only binary gold compounds with complex oxoanions known so far. Also, for other common oxoanions, only polynary compounds were described until now, e.g., the unprecedented perchlorate $(ClO_2)[Au(ClO_4)_4]$,[10] various nitrates containing the $[Au(NO_3)_4]^-$ anion,[11] and the iodate(V) $K[Au(IO_3)_4]$.[12] These compounds exhibit discrete anionic complexes with the gold atoms in square planar coordination of four monodentate oxoanions which are linked by the respective counter cations.

In recent years, we have considerably extended our investigations on the preparative potential of highly concentrated acids toward various metals, with special emphasis on refractory and noble metals. While for the refractory metals, especially reactions with fuming sulfuric acid (25−65% SO_3) turned out to be very useful;[13] the preparation of platinum sulfates worked especially well with concentrated sulfuric acid.[14] Also, selenic acid has been used successfully, e.g., for the preparation of $Au_2(SeO_3)_2(SeO_4)$,[15] which exhibits puckered layers according to ${}^2_\infty[Au(SeO_3)_{3/3}(SeO_4)_{1/2}]$ and the palladium compounds $Pd(SeO_4)$, $Pd(SeO_3)$, and $Pd(Se_2O_5)$.[16] The latter two have been obtained independently also by Albrecht-Schmitt and Ling.[17] As part of our investigations, we took also closer look at the system of gold/oleum, with the gold usually applied in the form of its hydroxide. Interestingly, the reaction of $Au(OH)_3$ with SO_3-rich oleum led again to $Au_2(SO_4)_2$.[6] However, if additionally alkaline metal ions are present, the formation of *bis*-(disulfato)-aurate anions is observed, which are described here for the first time. It is worthwhile to mention that this type of compound is not only of academic interest but has gained severe attention since the catalytic abilities of gold and gold compounds have contributed significantly to the observed renaissance of gold chemistry.[18]

2. EXPERIMENTAL SECTION

2.1. Synthesis. $Au(OH)_3$ was prepared starting from elemental gold according to a literature procedure.[19] A total of 50 mg (0.2 mmol) of $Au(OH)_3$, 1 mL of oleum (65% SO_3), 22 mg (0.2 mmol) of Li_2SO_4, and 28 mg (0.2 mmol) of Na_2SO_4, respectively, were filled in glass tubes ($d = 16$ mm; $l = 300$ mm). The tubes were torch-sealed under a vacuum, placed in a resistance furnace, and heated up to 250 °C. The temperature was maintained for 24 h. Upon slow cooling (1.8 °C/h), a large number of yellow colored and extremely moisture sensitive single crystals were

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obtained. They were collected by decantation of the mother liquor under inert conditions. The yield was approximately 80% with respect to the initial gold hydroxide.

It seems to be worthwhile to mention that the application of gold hydroxide is mandatory for the reaction. Analogous reactions starting with tetrachloroauric acid or its salts failed.

The single crystals of $M[Au(S_2O_7)_2]$ (M = Li, Na) are extremely hygroscopic and have to be handled under strict exclusion of moisture. Hydrolysis leads to a brownish residue, most probably $Au(OH)_3$. Treatment with organic solvents like absolute THF or ethyl acetate for the removal of adhering fuming sulfuric acid resulted in decomposition of the compounds under the formation of elemental gold. Thus, removal of the acid is best done mechanically.

Caution! *During the reaction and even after cooling down to room temperature, the glass tubes might be under pressure. The tubes have to be protected with an explosion shield during reaction and should be cooled with liquid nitrogen before they are opened.*

2.2. X-Ray Crystallography. Several single crystals of $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$ were selected under protecting oil with the help of a polarization microscope and directly transferred into the cool nitrogen stream (153 K) of a single-crystal diffractometer (BRUKER APEX II and Stoe IPDS I, respectively). For the lithium compound, a triclinic unit cell could be determined, while the sodium compound exhibits monoclinic symmetry. The intensities of the respective best specimens were collected.

$Li[Au(S_2O_7)_2]$. Assuming the space group $P\bar{1}$ for $Li[Au(S_2O_7)_2]$ application of the direct methods as provided by SHELXS-97[20] revealed the position of the gold and sulfur atoms, as well as those of some oxygen atoms. Further oxygen atoms and the sodium atom could be successively located in the course of difference Fourier syntheses during the refinement with SHELXL-97.[21] A numerical absorption correction was applied to the data using the programs X-RED 1.22[22] and XSHAPE 1.06,[23] and all atoms were refined anisotropically. Finally, the structure model refined to $R_1 = 0.0206$ and $wR_2 = 0.0475$ for all data.

$Na[Au(S_2O_7)_2]$. The observed systematic absences led unambiguously to the space group $P2_1/n$. The structure solution in that space group was successful using the direct methods of SHELXS-97[20] and gave the positions of the gold and sulfur atoms. Further oxygen atoms could be successively located in the course of difference Fourier syntheses during the refinement with SHELXL-97.[21] Anisotropic temperature factors were introduced for all atoms after a numerical absorption correction was applied to the data using the programs X-RED 1.22[22] and X-SHAPE 1.06.[23] The structure model converged at residuals of $R_1 = 0.0140$ and $wR_2 = 0.0291$ for all data.

2.3. Thermal Analysis. The investigation of the thermal behavior of both compounds was performed using the thermoanalyzers TGA/SDTA851^e and TGA/DSC1 (both Mettler-Toledo GmbH, Schwerzenbach, Switzerland) for $Na[Au(S_2O_7)_2]$ and $Li[Au(S_2O_7)_2]$, respectively. In a flow of dry nitrogen, about 11 mg of each compound was placed in a corundum crucible and heated at a rate of 10 K/min up to 1050 °C. The collected data were processed using the software of the analyzers (Mettler-Toledo STARe V9.3).[24]

2.4. X-Ray Powder Diffraction. The residues of the thermal decomposition of $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$ have been characterized by means of X-ray powder diffraction with a STADI P powder diffractometer (Stoe + Cie, Darmstadt, Germany) using Cu $K\alpha$ radiation and a flat sample holder. The intermediate phase observed during the decomposition of $Na[Au(S_2O_7)_2]$ at 280 °C was measured with the same diffractometer, but the sample was prepared in a glass capillary. The diffraction data were processed with the WinXPow 2007 program package (Stoe, V. 2.20).[25]

2.5. IR Spectroscopy. IR spectra data were collected with a Bruker Tensor 27 Spectrometer using the ATR method (attenuated total reflection). Spectra were collected within a range of 6500 to 550 cm^{-1}. The IR data were processed with the OPUS 2.0.5 program.[26] We also attempted to gain Raman spectra of $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$ (spectrometer FRA106, Bruker, Karlsruhe, Germany, excitation: 1064 nm radiation of a Nd:YAG laser), but in both cases the compounds changed color upon irradiation, probably due to decomposition in the laser beam.

Table 1. Crystallographic Data for $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$

chemical formula	$Li[Au(S_2O_7)_2]$	$Na[Au(S_2O_7)_2]$
crystal size	0.24 × 0.30 × 0.39 mm	0.08 × 0.10 × 0.82 mm
molar mass	556.15 g/mol	572.20 g/mol
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
lattice parameters	$a = 532.20(3)$ pm	$a = 533.31(3)$ pm
	$b = 649.69(4)$ pm	$b = 1193.38(7)$ pm
	$c = 836.72(5)$ pm	$c = 907.67(5)$ pm
	$\alpha = 107.982(2)°$	
	$\beta = 90.171(2)°$	$\beta = 98.548(3)°$
	$\gamma = 102.583(2)$	
cell volume	$V = 267.80(2)$ Å^3	$V = 571.26(6)$ Å^3
no. of formula units	1	2
temperature	153 K	153 K
radiation	Mo−K_α, $\lambda = 71.07$ pm	Mo−K_α, $\lambda = 71.07$ pm
μ	14.595 mm^{-1}	13.724 mm^{-1}
extinction coeff	0.095(3)	0.0083(3)
measured reflns	16679	9067
unique reflns	3377	1406
with $I_o > 2\sigma(I)$	3377	1296
R_{int}	0.0818	0.0240
R_σ[a]	0.0389	0.0140
R_1;[b] wR_2[c] ($I_o > 2\sigma(I)$)	0.0202; 0.0487	0.0123; 0.0280
R_1;[b] wR_2[c] (all data)	0.0202; 0.0487	0.0140; 0.0291
data/parameter	3377/95	1406/95

[a] R_σ is defined as $\Sigma[\sigma(F_o^2)]/\Sigma[F_o^2]$. [b] R_1 is defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] wR_2 is defined as $\{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

3. RESULTS AND DISCUSSION

3.1. Crystal Structures. Although $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$ crystallize with different symmetries, their crystal structures are very similar. Both contain the $[Au(S_2O_7)_2]^-$ anion, showing the gold atom situated at crystallographic sites bearing inversion symmetry ($Li[Au(S_2O_7)_2]$, 1*h* of space group $P\bar{1}$; $Na[Au(S_2O_7)_2]$, 2*a* of space group $P2_1/n$; Table 1). In accordance with their trivalent oxidation state, the coordination of the gold atoms is square planar. If Au−O distances above 300 pm are taken into account, the observed Au−O contacts (327 pm for the lithium and 310 pm for the sodium compound) would lead to a *pseudo*-octahedral coordination sphere of the central gold atom. However, a rationalization of the coordination contributions of these oxygen atoms, e.g., with the help of the ECoN concept (effective coordination number) as implemented in the program MAPLE,[27] shows that only very weak interactions can be assumed.

The $[AuO_4]$ squares are nearly undistorted and show O−Au−O angles close to 90° and Au−O distances in the range from 196.7(2) to 198.3(2) pm. These observations match pretty well the findings for gold(III) compounds with oxoanions up to now.[4,6−12] However, the new feature of the compounds under

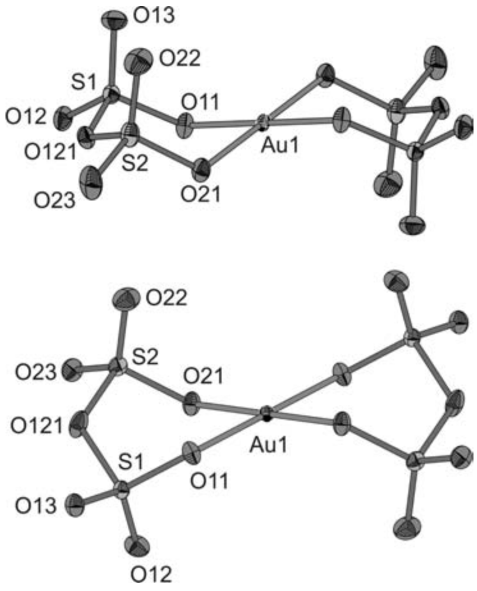

Figure 1. The C_i symmetric *bis*-(disulfato)-aurate anions in the crystal structures of Na[Au(S_2O_7)$_2$] (on top) and Li[Au(S_2O_7)$_2$] (at bottom). In the sodium compound, the $S_2O_7^{2-}$ groups exhibit nearly C_{2v} symmetry with respect to the alignment of the two [SO_3] moieties. The latter are twisted with respect to each other in Li[Au(S_2O_7)$_2$], leading to nearly C_s symmetry. The thermal ellipsoids are drawn at a 50% probability level; the labeling scheme is in accordance with Table 2.

discussion is the coordination of the gold atoms by two *chelating* inorganic ligands (Figure 1). Up to now, this motif has only been realized with organic ligands.[28] With respect to the observed distances and angles within the disulfate groups, this anion seems to be particularly suitable for such a type of coordination. Especially the angles within the bridge S−O−S (124.7(1)° for M = Li and 122.7(1)° for M = Na, respectively) exhibit no significant deviations from the (unfortunately few) values reported so far.[29] The distances S−O can be divided into three groups: The terminal oxygen atoms that are only coordinated to M^+ cations show short bond lengths around 142 pm. Those distances of oxygen atoms bonded to the gold atoms are about 10 pm larger, and the S−O values within the S−O−S bridge are found between 161 and 164 pm (Table 2). According to these bond length variations, the disulfate groups have only C_1 symmetry in both compounds. Neglecting these alterations, C_{2v} symmetry would be found for the $S_2O_7^{2-}$ ions in Na[Au(S_2O_7)$_2$] and C_s symmetry for those in Li[Au(S_2O_7)$_2$]. The difference arises from the orientation of both [SO_3] moieties in the anions with respect to each other. If viewed along the S−S direction, they are ecliptic in the sodium compound with a O13−S1−S2−O22 torsion angle of only 3.8° and twisted with an O22−S2−S1−O12 angle of 161.5° in the lithium compound (Figure 1). Charge compensation for the [Au(S_2O_7)$_2$]$^-$ anions is achieved by Li^+ and Na^+ ions, respectively. They are also located on special sites with C_i symmetry and have an octahedral surrounding of six monodentate disulfate groups (Figure 2). Within the [NaO_6] octahedron, the Na−O distances fall in a narrow range between 232.3(2) and 235.6(2) pm, while for [LiO_6], Li−O bond lengths from 205.4(2) up to 219.8(2) pm are found. On the other hand, with respect to the O−M−O angles, the [NaO_6] octahedra are more strongly distorted (83.24(7)−96.76(7)°) than the lithium analogues (89.38(6)−90.62(6)°).

Table 2. Selected Bond Length and Angles for Li[Au(S_2O_7)$_2$] and Na[Au(S_2O_7)$_2$]

	M = Li	M = Na
	bond lengths/pm	
Au1−O11 (2×)	196.7(2)	197.7(2)
Au1−O21 (2×)	197.9(1)	198.3(2)
S1−O12	141.1(2)	141.9(2)
S1−O13	141.8(2)	141.8(2)
S1−O11	151.9(2)	152.4(2)
S1−O121	160.7(2)	161.0(2)
S2−O22	141.2(2)	141.2(2)
S2−O23	141.9(2)	141.3(2)
S2−O21	152.4(2)	152.4(2)
S2−O121	163.7(2)	164.1(2)
M1-O12 (2×)	207.1(2)	235.6(2)
M1-O13 (2×)	219.8(2)	233.6(2)
M1-O23 (2×)	205.4(2)	232.3(2)
	bond angles/deg	
O11−Au1−O21 (2×)	88.99(6)	89.29(7)
O11−Au1−O21 (2×)	91.01(6)	90.71(7)
O12−S1−O13	119.9(1)	120.0(1)
O12−S1−O11	112.3(1)	107.5(1)
O13−S1−O11	107.73(9)	112.8(1)
O12−S1−O121	107.9(1)	103.19(9)
O13−S1−O121	103.63(9)	108.3(1)
O11−S1−O121	104.0(1)	103.49(9)
O22−S2−O23	121.2(1)	121.7(1)
O22−S2−O21	113.3(1)	112.7(1)
O23−S2−O21	107.8(1)	107.7(1)
O22−S2−O121	105.5(1)	108.2(1)
O23−S2−O121	103.9(1)	102.3(1)
O21−S2−O121	103.29(9)	102.01(9)
S1−O121−S2	124.7(1)	122.7(1)

In the crystal structures of Li[Au(S_2O_7)$_2$] and Na[Au(S_2O_7)$_2$], the [Au(S_2O_7)$_2$]$^-$ anions and the [MO_6] octahedra are arranged on chains running along the *a* axis of the unit cells, which is almost identical for both compounds (M = Li, 532.20(3) pm; M = Na, 533.31(3) pm; Figure 3).

3.2. IR Spectroscopy. The $S_2O_7^{2-}$ group may adopt different symmetries depending on the orientation of the [SO_3] moieties with respect to each other, and on the nature (symmetric or asymmetric) of the S−O−S bridge. In most cases, C_{2v} symmetry is observed with ecliptic arranged [SO_3] fragments. If the fragments are in opposite orientation with respect to each other, the anion exhibits C_s symmetry. In the first case, 21 normal modes are expected representing the symmetry classes A_1 (7×), A_2 (4×), B_1 (6×), and B_2 (4×), of which 17 are IR-active. The normal modes considering C_s symmetry with the classes A′ (11×) and A″ (10×) are all IR-active. However, with respect to the crystal structures discussed above in both compounds, the disulfate groups display C_i symmetry, and 21 vibrations should be observable on IR excitation, if further factor group splitting is neglected. Indeed, both spectra show numerous bands which are, however, not completely resolved (Figure 4). An assignment of the observed frequencies was done based on literature data

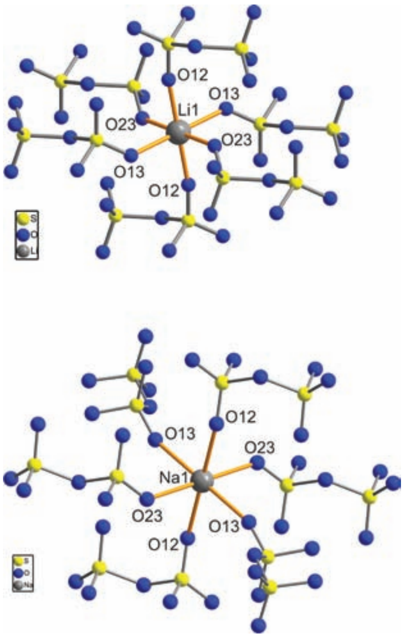

Figure 2. Coordination of the alkaline cations in Li[Au(S_2O_7)$_2$] (on top) and Na[Au(S_2O_7)$_2$] (at bottom). Both cations are located on crystallographic sites with inversion symmetry and show quite regular coordination. The labeling is according to the entries in Table 2.

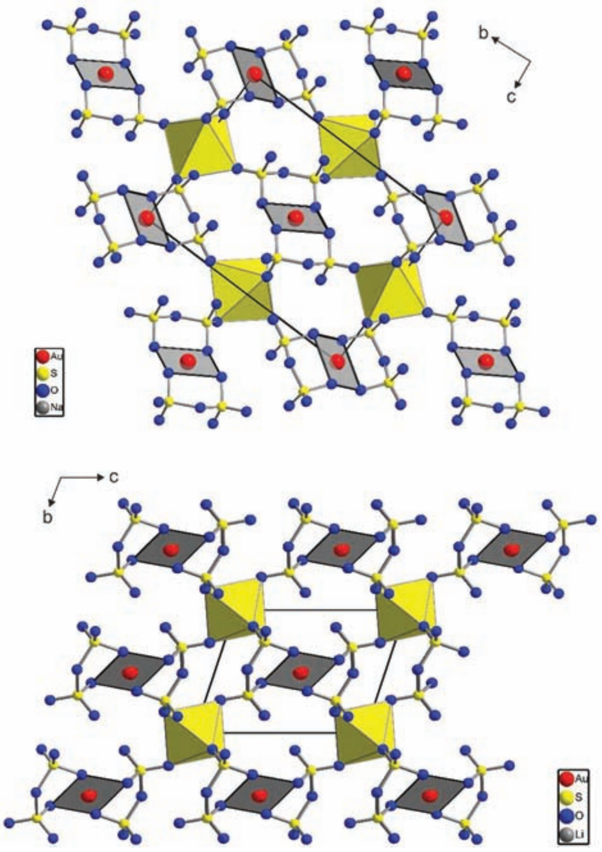

Figure 3. Crystal structures of Na[Au(S_2O_7)$_2$] (on top) and Li[Au(S_2O_7)$_2$] (at bottom) shown as a projection on the respective (100) planes. Both the square planar [AuO_4] units as well as the [MO_6] octahedra (drawn in yellow) are aligned in the [100] direction.

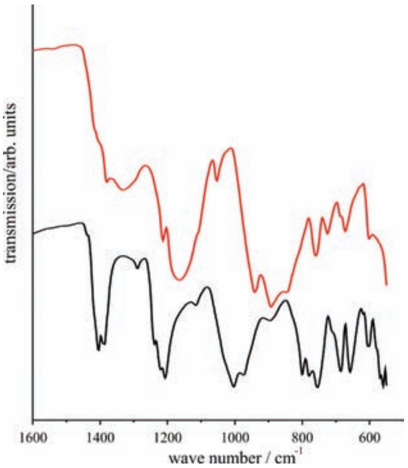

Figure 4. IR spectra of Li[Au(S_2O_7)$_2$] (red) and Na[Au(S_2O_7)$_2$] (black).

Table 3. IR Spectra of Li[Au(S_2O_7)$_2$] and Na[Au(S_2O_7)$_2$]^a

Li[Au(S_2O_7)$_2$]		Na[Au(S_2O_7)$_2$]		
energy/cm^{-1}		energy/cm^{-1}		assignment[27]
		560	s	$\delta_s SO_3$
601	w	603	m	
		658	s	δ_{as} SO_3
672	w	686	s	
725	w	755	s	ν_{as}SOS
760	m	780	s	ν_sSOS
		800	s	
893	s	895	w	
941	s	974	m	
1054	m	1003	s	
1164	s	1116	w	ν_s SO_3
1213	w	1207	s	
		1220	w	
		1239	w	
1334	m	1289	w	ν_{as} SO_3
1380	w	1387	s	

[a] s = strong; m = medium; w = weak.

(Table 3).[30] The latter were obtained for $K_2S_2O_7$ and $Na_2S_2O_7$. Compared to these data, severe splitting of bands is observed especially for the stretching vibrations ν(S—O), in accordance with the different S—O distances within the $S_2O_7^{2-}$ ions. It seems that a reliable assignment can only be done on detailed quantum mechanical calculations, favorably taking into account the entire [Au(S_2O_7)$_2$]$^-$ anion.

3.3. Thermal Decomposition. The thermal decomposition of Li[Au(S_2O_7)$_2$] and Na[Au(S_2O_7)$_2$] occurs in three steps, of which the first two between 150 and 350 °C are not well separated (Figures 5 and 6). The last step is found at about 400 °C and leads finally to elemental gold and the respective sulfates M_2SO_4 (M = Li, Na). This could be unambiguously proved by the X-ray powder pattern of the residues (Figure 5 and 6) and is furthermore confirmed by the observed melting points of the sulfates in the DTA curve at 849 °C for Li_2SO_4 (Lit: 845 °C)

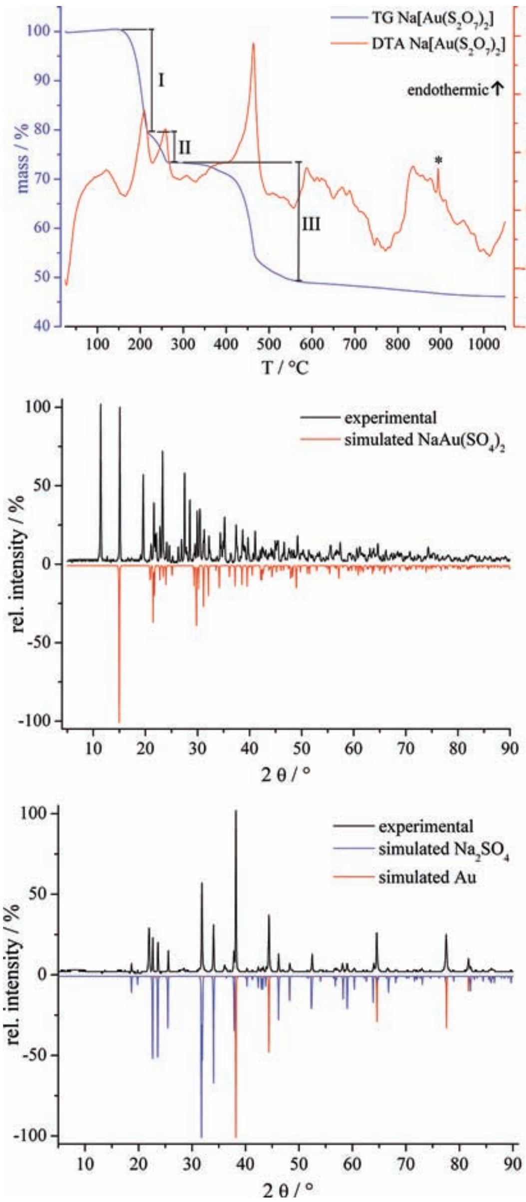

Figure 5. Thermal decomposition of $Na[Au(S_2O_7)_2]$. On top, the DTA/TG diagram is shown, which shows essentially three decomposition steps. Steps I and II are in close proximity and are attributed to the successive loss of SO_3, leading to $NaAu(SO_4)_2$ at the end of step II. The occurrence of the latter is proved by the XRD pattern gained from the 280 °C intermediate (middle diagram), which also shows a yet unidentified product. According to the XRD diffractogram of the final residue (at bottom), the third step leads to Na_2SO_4 and elemental gold. The asterisk in the upper diagram indicates the melting point of Na_2SO_4.

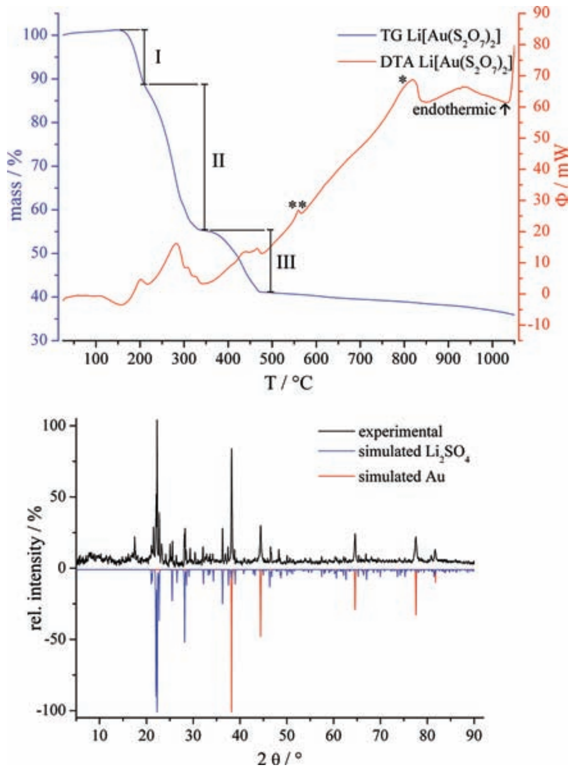

Figure 6. Thermal decomposition of $Li[Au(S_2O_7)_2]$. The DSC/TG diagram on top shows a three step decomposition similar to those of its Na congener, however, with different heights of the first two steps. In analogy to the sodium compound, the final decomposition step leads to Li_2SO_4 and elemental gold, as indicated by the XRD pattern of the residue (at bottom). The asterisk in the upper diagram indicates the melting point of Li_2SO_4, the double asterisk, its phase transition.

and 894 °C for Na_2SO_4 (Lit: 888 °C). For Li_2SO_4 also, the known phase transition from the monoclinic to the cubic modification is seen at 568 °C (Lit: 577 °C).[31] It seems to be likely that the decomposition is driven by the successive release of SO_3. In order to prove that assumption, we stopped the decomposition of $Na[Au(S_2O_7)_2]$ at $T = 280$ °C and performed an XRD powder measurement of the intermediate (Figure 5, middle). We chose the sodium compound because the crystallographic data of $NaAu(SO_4)_2$ as a possible intermediate are available for comparison, while those of the lithium phase are not.[7a] Indeed, the presence of $NaAu(SO_4)_2$ is clearly seen in the diffractogram. Additionally, several reflections occur which cannot be assigned as of now. Most likely, the decomposition of $Na[Au(S_2O_7)_2]$ to $NaAu(SO_4)_2$ is not completely finished at 280 °C, and in the XRD pattern, a SO_3 richer phase is present. The third decomposition step for both compounds is in very good accordance with the findings for the decomposition of $MAu(SO_4)_2$ (M = Li, Na) that have been reported by Donova and Siftar.[32] On the basis of our present knowledge, we propose that the decomposition of the disulfates occurs according to the following reaction sequence (compounds in italics not identified):

$$M[Au(S_2O_7)_2] \rightarrow \mathit{M[Au(S_2O_7)_{2-x}(SO_4)_x]} + x SO_3 \qquad (I)$$

$$\mathit{M[Au(S_2O_7)_{2-x}(SO_4)_x]} \rightarrow MAu(SO_4)_2 + x SO_3 \qquad (II)$$

$$MAu(SO_4)_2 \rightarrow \frac{1}{2} M_2SO_4 + Au + \frac{3}{2} SO_3 + \frac{3}{4} O_2 \qquad (III)$$

4. CONCLUSION

The present paper offers further support that reactions with and in highly concentrated mineralic acids provide efficient routes to sulfates and polysulfates. Using SO_3-rich oleum, we were able to prepare the first disulfates of gold in the form of compounds $Li[Au(S_2O_7)_2]$ and $Na[Au(S_2O_7)_2]$. Both exhibit the hitherto unknown $[Au(S_2O_7)_2]^-$ anion consisting of gold atoms in square planar coordination of two chelating disulfate groups. Upon thermal decomposition, the disulfates yield elemental gold and the respective alkaline metal sulfates. Additional investigations must show whether this complex can be stabilized also in solution so that its catalytic potential can be elucidated. Furthermore, the redox properties of the system Au/oleum need special attention. We just started to perform theoretical calculations in order to shed some light on the stability of different oxidation states of gold in oleum under various conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information files (CIF) containing the complete crystallographic data are available and can also be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247−808−666; e-mail: crysdata@FIZ-Karlsruhe.de, http://fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers 422909 ($Li[Au(S_2O_7)_2]$) and 422910 ($Na[Au(S_2O_7)_2]$), respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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