

Dynamic disorder in the high-temperature polymorph of bis[diamminesilver(I)] sulfate - reasons and consequences of simultaneous ammonia release from two different polymorphs

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Dynamic disorder in the high temperature polymorph of bis[diamminesilver(I)] sulfate - reasons and consequences of simultaneous ammonia release from two different polymorphs

High-temperature tetragonal polymorph of diamminesilver(I) sulfate ($a=8.6004(4)$, $c=6.2123(6)$) (compound **1-HT**) has been prepared and characterized. The phase transformation of the low-temperature polymorph of diamminesilver(I) sulfate (compound **1-LT**) into the high-temperature polymorph (compound **1-HT**) partly coincides with the initial stage of the thermal decomposition of compound **1-LT**. Selecting appropriate conditions, the two processes have been separated and the standard heat of formation of the LT polymorph ($\Delta H^{298} = -1208.92$ kJ/mol) and the enthalpy of polymorphic transformation ($\Delta H_{LT \rightarrow HT} = 13.18$ kJ/mol) have been determined. The high-temperature XRD results showed that the lattice constants of LT polymorph (**1-LT**) extend in the direction of a , b , and compresses in the direction of c in the **1-HT** polymorph. According to high temperature SXRD data, the Ag-Ag distance (in the direction of c) shortens from 3.20 (**1-LT**) to 3.11 Å (**1-HT**), while the extension in the a, b direction weakens/disrupts the N-H...O-S hydrogen bonds and the coordinative Ag...O-S interactions. The IR and Raman spectroscopic data confirm the weakening/breaking of N-H...O-S hydrogen bonds. A vacuum-assisted thermal deammoniation experiment in the preparation of monoamminesilver(I) sulfate complex showed that the product is the mixture of silver(I) sulfate and the starting diamminesilver(I) sulfate complex.

Keywords: sulphate; thermal decomposition; phase transition; DSC; evolved gas analysis; diamminesilver(I)

Introduction

Continuing our research concerning the redox interactions among counter ions of compounds containing redox-active cationic/anionic parts [1–8], we have started studies on the synthesis and characterization of $[\text{Ag}(\text{NH}_3)_n]_z(\text{XO}_m)$ type amminesilver complexes where n and z may be varied between 1-3 and $m=1-4$, respectively (X =elements of the 5th-7th group of the periodic system) [9]. In this work, we focus on the sulfate salts of amminesilver(I) complexes. There are five amminesilver(I) sulfate compounds described in the literature. The most stable and studied compound among them is the bis(diamminesilver(I)) sulfate, $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$, discovered and studied first by the Mitscherlich brothers [10, 11]. It has numerous applications including as a catalyst in the ultramicro determination of nitroglycerine in explosives [12], as reducing agent/precursor in the preparation of ultrafine metal powders [13, 14], and as heat and saline water resistant disinfectant [15], [16]. Bis(diamminesilver(I)) sulfate exists in two polymorphic forms, namely as a low-temperature tetragonal (compound **1-LT**) and a high-temperature tetragonal polymorph (compound **1-HT**) [17, 18]. The structure of compound **1-LT** was studied in detail [17–19], however, the nature of the phase transition observed around its decomposition point and the properties of the high-temperature modification (**1-HT**) are incompletely characterized [20–22].

There is uncertain information about the existence of a monoammine complex, $[\text{Ag}(\text{NH}_3)]_2\text{SO}_4$ (compound **2**), [23] [24]. The analogous monoamminesilver(I) nitrate and was found to be the solid solution of AgNO_3 and $[\text{Ag}(\text{NH}_3)]\text{NO}_3$, and the monoamminesilver(I) nitrite was proved to be $[\text{Ag}(\text{NH}_3)]_2[\text{Ag}(\text{NO}_2)_2]$ [25]. Thus, the existence of the monoamminesilver(I) sulphate is questionable.

Numerous triamminesilver(I) salts with various oxygen-containing anions were prepared in the reaction of the appropriate solid silver(I) salt with gaseous ammonia. [23, 26–28]. However, reaction of silver sulfate with ammonia have resulted in only the bis(diamminesilver(I)) sulfate complex (compound **1-LT**). Compound **1-LT** did not absorb additional ammonia even at long reaction times or at low temperatures. Heat treatment of compound **1-LT** at 85-87 °C for 30 min, however, resulted in the formation of highly reactive high-temperature polymorph (compound **1-HT**), which can easily absorb additional two molecules of ammonia and result in $[\text{Ag}(\text{NH}_3)_3]_2\text{SO}_4$ (compound **3**) [21]. Reychler reported the preparation of compound **1-LT** in the reaction of silver(I) sulfate and ammonia gas [27]. The cryoscopic and the electrolytic conductivity measurements showed that one of his samples contained one diamminesilver and one triamminesilver(I) cation, $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{NH}_3)_3]\text{SO}_4$ (compound **4**), however, its detailed preparation conditions and its properties were not given [27]. It is unknown whether compound **4** is a single-phase material or a mixture of bis(diamminesilver(I)) and bis(triamminesilver(I)) sulfates formed accidentally from the high-temperature modification of compound **1-LT**. To study this issue, the preparation of bis(triamminesilver(I)) sulfate (compound **3**) - and its precursor, compound **1-HT**, are demanding.

In order to do the first step of these studies, here we report the preparation and properties of the high-temperature modification of compound **1-LT** (compound **1-HT**) and investigate the thermal stability and deammoniation of both compounds **1-LT** and **1-HT** in the temperature range of phase transition are presented.

Experimental part

In the synthesis experiments, the chemical grade silver sulfate, 25 % aq. ammonia, sodium hydroxide, nitric acid, sodium chloride, barium nitrate, hexachloroplatinic acid and methyl red indicator were supplied by Deuton-X Ltd. For chemical analysis of compound **1-LT** was dissolved in a known amount of 0.2 M nitric acid. The nitric acid remaining back after neutralizing the ammonia content of the complex **1-LT** was titrated with 0.1 M NaOH in the presence of methyl red indicator [29] and with gravimetry using H_2PtCl_6 [30]. The solution left back after the titration rendered to be slightly acidic, with the addition of a few drops of diluted nitric acid. The silver and barium contents were measured as AgCl and BaSO_4 gravimetrically [30]. The complex identity was studied with X-ray powder diffraction (XRD) analysis and infrared spectroscopy (IR spectroscopy) following the methods given previously [20, 31–35].

The Raman spectroscopic measurements were performed on a Horiba Jobin-Yvon LabRAM- microspectrometer coupled with a 785 nm diode laser source (~50 mW power) and an Olympus BX-40 optical microscope. No optical density filter was applied to decrease the laser intensity. The laser beam was focused by an objective (20X, NA=0.4). The confocal hole of 1000 μm and 950 groove mm^{-1} grating monochromator was used in a confocal system and light dispersion. The measured spectral range was between 100 and 2000 cm^{-1} with 5 cm^{-1} resolution and the exposure time of the sample was 10 s. A Linkam THMS600 microscope stage was used for temperature control.

Thermogravimetry mass spectrometry (TG-MS) data in air and Ar atmosphere were collected using a TA Instruments SDT Q600 thermal analyzer coupled to a Hiden Analytical HPR-20/QIC mass spectrometer. The decomposition was followed starting from room temperature to 800 °C (heating rate: 10 K min^{-1} , carrier gas flow rate = 50 $\text{cm}^3 \text{min}^{-1}$). The sample holder (and reference) was an empty alumina crucible. Sample weights used at once were 2 –3 mg. The selected ions between $m/z = 1-100$ were monitored (Multiple Ion Detection Mode, MID).

The non-isothermal differential scanning calorimetry (DSC) measurements were performed between -130 and 300 °C using a Perkin Elmer DSC 7 type apparatus. Sample weights varied between 3 and 5 mg. The measurements were done with 10 °C/min heating rate under continuous N_2 flow of 2 cm^3/min using unsealed aluminum crucibles.

XRD measurements were performed on a Philips PW-1050 type Bragg-Brentano para-focusing goniometer using Cu K_α radiation with secondary beam graphite monochromator and proportional counter. The scans were recorded in step mode (0.04 °/s) in the range of 10- 70° 2 θ . The diffraction pattern evaluation was

characterized with full profile fitting techniques. High-temperature XRD (HT-XRD) investigation was also applied for compound **1** using a at HTK-1200 Anton–Paar chamber in inert atmosphere in the range of 15–65° 2 θ . The phase composition was investigated at 25, 50, 70, 80 °C as well as on cooling at 70 and 25 °C, respectively.

Single crystal X-ray diffraction (SXR) experiments were performed on a needle-like single crystal of compound **1-HT** made with heating of a single crystal of **1-LT**. The SXR measurement was performed at 83 °C (just above the temperature of the polymorphic phase transition). The crystal was glued to a plastic loop and covered by nail polish which hermetically sealed the crystal to push back thermal decomposition and ammonia emission.

Cell parameters were determined by least-squares fittings using 1805 ($7.242 \leq \theta \leq 74.79^\circ$) reflections. Intensity data were collected on a Rigaku XTA Lab Synergy-R diffractometer (Cu-K-alpha radiation $\lambda = 1.54184 \text{ \AA}$) at 356(1) K in the range $7.2828 \leq \theta \leq 74.8909^\circ$. The resolution range was restricted by diffractometer geometry to 0.8 \AA . CrysAlisPro v.1.171.40.68a was used as data collection and data reduction software.

A total of 3532 reflections were collected from which 162 were unique [$R(\text{int}) = 0.0856$, $R(s) = 0.0155$] and the intensities of 157 reflections were greater than $2s(I)$. The completeness to q was 1.000. A tetragonal lattice with $I4/mmm$ space group symmetry was determined. A multi-scan absorption correction was applied to the data (the minimum and maximum transmission factors were 0.425 and 1.000). Numerical absorption correction was applied.

We deposited the crystallographic data for compound **1-HT** under the name CCDC-2074845 in the Cambridge Crystallographic Data Centre (CCDC) (available via www.ccdc.cam.ac.uk/data_request/cif.)

Hydrogens could not be generated on the ammonia nitrogen because of its disorder. The hydrogens could not be found either in difference maps due to the presence of the silver cations and presumably due to their disorder. The measurement has been performed using copper radiation and therefore the data/parameter ratio is poor, 7.71. -3.00 e \AA^{-3} electron density remained in the structure which is acceptable in inorganic crystals. Thermal ellipsoids of the disordered oxygens are quite prolate but cannot be split into two positions. The disorder of the sulfate anions at high temperature just above the thermal decomposition temperature is dynamic, the sulfate oxygens have a long-range motion and no well-defined disordered positions exist for them. The atom site occupancies of the oxygen and nitrogen were constrained at 0.25 and 0.5 respectively for symmetry considerations.

We placed the crystallographic data for compound **1-HT** under the name CCDC-2064722 in the Cambridge Crystallographic Data Centre (CCDC) (available via www.ccdc.cam.ac.uk/data_request/cif.)

Diffuse reflectance spectra of compound **1-LT** in the UV and Vis regions (200–340 and 340–800 nm) were measured at room temperature using a Jasco V-670 UV–Vis spectrophotometer and a NV-470 type integrating sphere (BaSO₄ standard was used as a reference).

Fourier-transform Infrared (FT-IR) spectra of samples were recorded in the attenuated total reflection mode (Bruker Alpha FT-IR spectrometer, resolution: 2 cm^{-1}) between 4000 and 400 cm^{-1} . The high-temperature IR spectrum was recorded by a Bruker Tensor 37 FTIR spectrometer in the range of 4000 - 600 cm^{-1} with 32 scans and 4 cm^{-1} resolution using a DTGS detector. The measurements were conducted with ATR accessory with KRS-5 lenses (Specac Golden Gate). The sample was placed onto the ATR crystal and the sample holder was heated up to $80\text{ }^{\circ}\text{C}$ with a 300°C/h temperature ramp. The cold IR measurements were performed in the same range and resolution (Bruker IFS 66v FT-IR spectrometer, KBr pellets) in a liq. N_2 cooled flow-through cryostat.

Results and Discussions

Preparation of mono- and diamminsilver(I) sulfates (compounds 1-LT, 1-HT and 2)

Compound **1-LT** was prepared according to the method used first described by Mitscherlich [10] via dissolution of silver sulfate in aq. ammonia. The salt crystallized out easily and could be kept for a long time in a dark place, it could even be exposed to the air, without decomposition. However, on exposure to the light, the crystals became dark soon. Its chemical and phase composition were determined by chemical analysis and XRD (ESI Fig. 1). Compound **1-LT** is well soluble in water [11, 23] and can be crystallized out as colorless, 4-5 cm long, thin needles. We also prepared compound **1-LT** using the interaction of gaseous ammonia with solid silver(I) sulfate [23, 26]. Solid silver sulfate can take gaseous ammonia very slowly [23], and in contrast to other silver salts which can form triamminesilver complexes [26, 37], for this case only the diammine complex (**1-LT**) can be isolated [21, 26, 38]. The same method was given by Rose [23] and Racousine [24] to prepare compound **2** (monoammine complex), however, the reaction time was too short to complete the ammonia uptake which resulted in only a mixture of the unreacted silver sulfate and compound **1-LT**. Longer reaction time resulted in only compound **1-LT** and the subsequent removal of ammonia in vacuum resulted in silver(I) sulfate (reversible ammonia uptake). The intermediate deammoniation product of compound **1-LT** at $\text{NH}_3/\text{Ag}=1:1$ molar ratio (prepared in high vacuum at $\sim 40\text{ }^{\circ}\text{C}$ in 20 h, ESI Fig.2) was proved to be the mixture of silver sulfate and compound **1-LT**.

A possible method for the preparation of compound **2** is the partial deammoniation of compound **1-LT** by heating at $80\text{ }^{\circ}\text{C}$ and ambient pressure. However, the HT-XRD experiments showed a mixture of Ag_2SO_4 as a primary reaction product and a phase, which was assigned to compound **1-HT** at $80\text{ }^{\circ}\text{C}$ (ESI Fig.3, Fig. 1).

Figure 1 summarizes the known preparation methods of silver(I) sulfate ammine complexes.

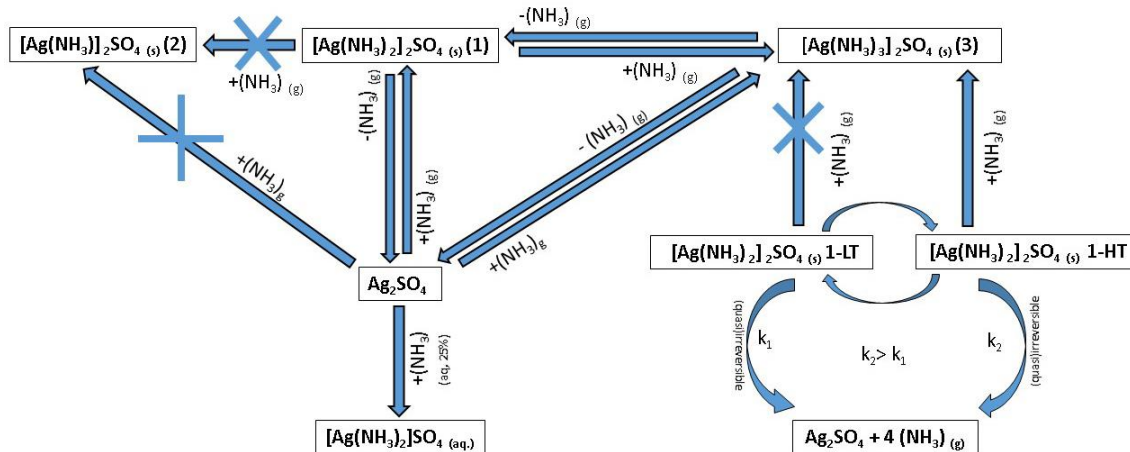


Figure 1 The preparation possibilities of ammine complexes of silver(I) sulfate.

The decomposition reaction rate constants of compounds **1-LT** and **1-HT** were determined by Torgonskaya [21] between 60 and 100 °C. Calculating the effect of temperature on the k value (decomposition reaction rate constant) between 64 and 70 °C then from 83 to 93 °C, 0.192/°C (**1-LT**) and 0.188/°C (**1-HT**) values were found, respectively, which are almost equal. However, considering the range 70 to 80 °C (the range for the phase transition), the increase was 0.343/°C, twice higher increase than the expected from the temperature effect. This increasing may partly be attributed to the effect of phase transition (weakening of the lattice forces). It means that the decomposition rate of **1-HT** modification was faster than that of **1-LT** modification.

The lattice energy of compound **1-HT** should be lower than compound **1-LT**, due to the weakening/breaking of secondary bonding effects (hydrogen bonds, coordination bonds). Accordingly, the deammoniation rate of compound **1-HT** was faster (a shoulder relating to the decomposition of **1-LT** can be detected on the DTG) (ESI Fig. 4) than that of compound **1-LT**. The increased reactivity of compound **1-HT** towards ammonia (under pressure of course) is the consequence of that the lattice of **1-HT** is broken easier than that of **1-LT**. [21] The difference between the lattice energies for **1-LT** and **1-HT** is large enough to result in a negative Gibbs energy for the reaction between **1-HT** and ammonia and the ammonia uptake becomes spontaneous.

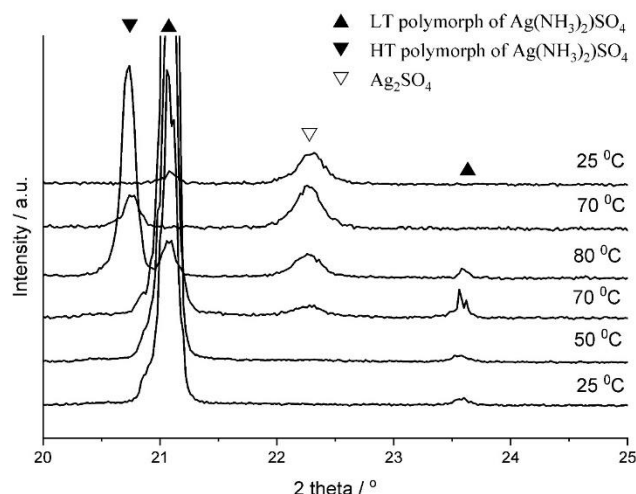


Figure 2 XRD patterns of compound **1-LT** between 25 and 70 °C and compound **1-HT** at 80 °C

Phase transition and properties of the high-temperature polymorph of diamminesilver(I) sulfate (compound 1-HT)

The existence of the high-temperature polymorph of $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$ (compound **1-HT**) has been detected by XRD [17], DSC, [20] NMR [22] and electrical resistivity [21] methods, however, its exact structure and the crystallographic parameters were unknown up to now (Fig.2). According to our results, compound **1-HT** showed tetragonal crystal structure with $a=b=8.588$, $c=6.220$ Å and $V=456.8$ Å³ cell parameters. Comparing the cell volumes of compound **1-LT** (455.4 Å³) and compound **1-HT**, we found only ~0.3% volume increase. Table 1 shows the expected high temperature lattice constants of compound **1-LT** (marked with *), which were calculated from room temperature lattice constants considering the heat expansion coefficients [38]. Our experimental powder XRD measurements confirmed that the volume increase between 25 and 80 °C is negligible (Table 1), however, at 80 °C the lattice constants a and c sharply changed (c decreases whereas a increases).

During cooling from 80 to 70 °C, compound **1-HT** transforms back into compound **1-LT** (Fig.2), which means that the polymorphic **1-LT** to **1-HT** phase transition is reversible. The decomposition of compound **1-LT** into Ag_2SO_4 can also be observed at the phase transition temperature range, thus peak intensity of **1-LT** strongly decreases, and peaks belong to Ag_2SO_4 appear, thus the phase-transition more rather quasi-reversible. The phase transition temperature (LT ↔ HT, Fig. 2) coincided at ~80 °C at the beginning of the thermal decomposition temperature of compound **1-LT** and **1-HT** as well [20, 21].

Table 1. Experimental lattice constants of $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$ polymorphs (compounds **1-LT** and **1-HT**) at various temperatures

Compound	t, °C	a=b, Å	c, Å	Ref./method
Compound 1-LT	19	8.442	6.399	[17], SXRD
	23.5+/-1.5	8.4375	6.3936	[20], SXRD
	Room temp.	8.43	6.35	[18], SXRD
	25-80	8.436	6.399	Our, PXRD
Compound 1-HT	80	8.437*	6.400*	Our, PXRD
	80	8.588	6.220	Our, PXRD
	80	xx	xx	Our, SXR

*Calculated values from the lattice constants found at 25 °C and the values of heat expansion coefficients [38].

Crystal structure features of 1-LT and 1-HT-modifications

SXRD measurement of compound **1-HT** above 80 °C was first planned in a capillary under ammonia atmosphere. However, the high reactivity of compound **1-HT** compared to compound **1-LT** and the formation of compound **3** disclosed this option [21]. Therefore, we decided to cover the crystal in nail polish to hermetically seal it, preventing decomposition during the measurement. Numerous experiments had to be carried out with precise temperature setting since the majority of the crystals decomposed within the first few minutes of the measurement.

The space group symmetry of **1-HT** ($I4/mmm$) is higher as compared to **1-LT** ($P-42_1c$) which becomes possible by the disordered arrangement of both the complex cation and the sulfate anions (Figure 3)

SYMMETRY RELATION OF THE POLYMORPHS

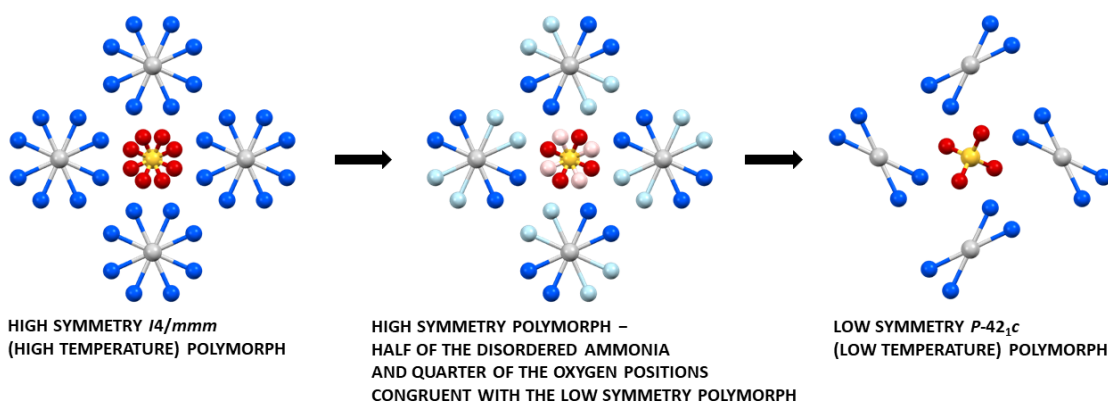


Figure 3 Overlap of **1-HT** disordered structure with **1-LT** viewed from the c crystallographic direction.

In the structure of **1-HT** (similarly to **1-LT**) polymeric chains are formed among the $\text{Ag}(\text{NH}_3)_2$ units, which are linked by Ag-Ag argentophilic interactions (Fig. 4). The

Ag-Ag chains are running parallel in the direction of the c axis [18, 19]. The interatomic distances, angles and lattice parameters are given in ESI Table 2-8.

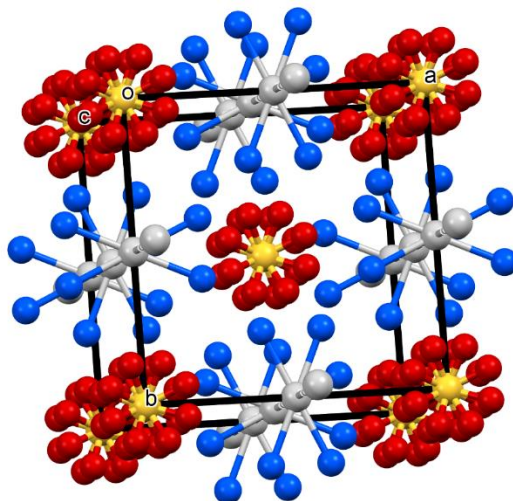


Figure 4 Crystal packing of **1-HT** showing the Ag-Ag chains running along with the c axis and the disorder of the ammonia ligands and sulfate anions.

The temperature dependence of spin-lattice relaxation time showed the existence of a structural transformation around 330 K, which could not be recognized by wide-line NMR measurements. Rapid reorientation of NH_3 groups around a threefold axis was found and the freezing of this rotation was found only below 250 K [22]. The appearance of E modes of coordinated ammonia in the Raman spectrum of a linear diamminesilver(I) complex showed that it is freely rotated (D_{3h} symmetry) [31]. In spite of this, some of the IR bands show the presence of hydrogen bonds [33, 34]. The high thermal motion of the atoms is expressed in weakening of the $l=0$ reflections of hkl values (when $l=0$, the planes are parallel with c axis, when $l \neq 0$, there are angles of planes relating to the c axis) confirms the relative free rotation of the coordinated ammonia molecules.

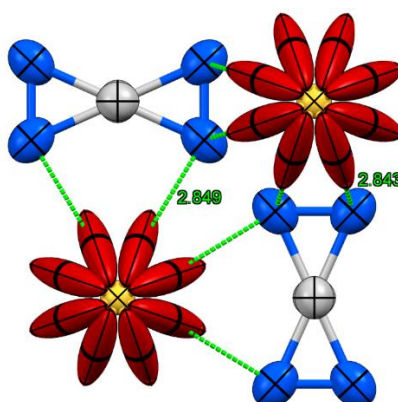


Figure 5 Short contacts (less than the sum of van der Waals radii, green dashed lines) between disordered ammonia molecules and sulfate-ions in compound **1-HT**.

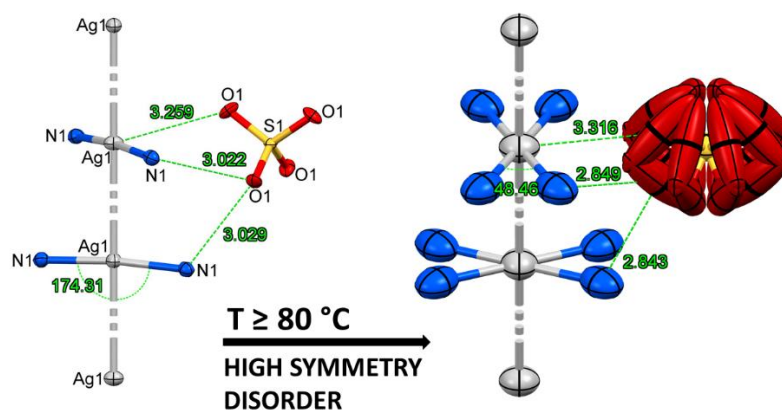


Figure 6 Comparison of main geometric data of compound **1-LT** [18] and **1-HT**.

The detailed study of high temperature (80 °C) powder XRD of compound **1-LT** (compound **1-HT**) (Fig. 2), in agreement with the SXRD measurements, showed that the *c* cell parameter was compressed during the phase transition. The Ag-Ag chains were parallel to the *c* axis and the Ag ions could be found at $z=0.0$, $z=0.5$ or $z=1.0$ coordinates. The Ag-Ag distance was always the half of the *c* axis length, which indicated the original Ag-Ag distance ($c/2=3.20$ Å) decreased to 3.11 Å and the Ag-Ag interaction became stronger. The elongation of the unit cell in the *a* and *b* directions (from 8.442 Å to 8.568 Å) could be explained by the weakening of the secondary interactions between the Ag-Ag chains and the anions, and the dynamically disordered sulfate anions (Fig. 3 and 6) fill larger space than the regular isolated ones. Two disordered ammonia molecules were coordinated to each silver ion. The disordered sulfate anions were placed at the corners and in the center of the unit cell, sulfate ions were disordered over four different positions.

The structure contains numerous hydrogen bonding interactions between ammonia donors and sulfate acceptors (Figure 5) [18]. The N...O distances in the N...O-S linkages are 3.022 Å and 2.849 Å in the **1-LT** and **1-HT** modification, respectively (Figure 6). In the **1-HT** modification, the sulfate ions have a highly disordered “ball like” shape which refers to a dynamic disorder and high mobility resulting in breaking up/weakening the hydrogen bonds in the structure of compound **1-HT** and lowering lattice energy toward that in compound **1-LT**.

In the structure of the Ag_2SO_4 decomposition product, the Ag-Ag chains are retained but distorted (the Ag-Ag bond length is 3.073 Å and the Ag-Ag-Ag angle 136.10°). The coordination sphere around the silver ion is six-fold and it consists of two argentophilic bonds and four coordinative bonds of sulfate oxygens. As a result, a 3-dimensional polymeric structure is formed (Fig. 7) [43].

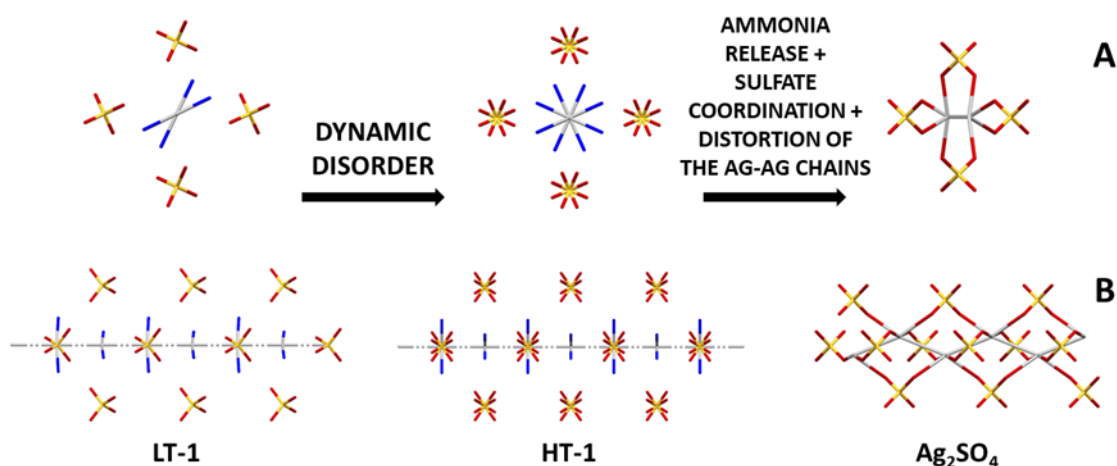


Figure 7. Structural changes during the phase transition and decomposition steps (A: view in the direction of the Ag-Ag chains, B: view along the Ag-Ag chains)

Spectroscopic studies on compounds 1-LT and 1-HT

The room temperature and low temperature infrared and Raman studies on compound **1-LT** and its deuterated form, including correlation analysis, have already been performed [33]. The role of hydrogen bonds and their disruption are expected to play a significant role in the decomposition of the **1-HT** a modification, thus the IR and Raman studies are also performed at 80 °C either.

The linear $[\text{Ag}(\text{NH}_3)_2]^+$ ions at the C_2 symmetry sites resulting in the removal of E degeneracy and enable the IR inactive modes of the isolated $[\text{Ag}(\text{NH}_3)_2]^+$ ion change to be IR active. For the sulfate ions at sites of S_4 , the E and F_2 components are split. Correlation analysis on the high-temperature modification (compound **1-HT**) has been performed (Fig. 7 and ESI Fig. 5). The complex cation modes were evaluated as the translational modes of silver ion and separate ammonia molecules.

Silver-ion has two hindered translational modes in D_{4h} , the A_{2u} (T_z) and E_u (R_{xy}) modes. According to these modes, two bands are expected in the far-IR region (ESI Fig.5).

Due to the disorder of the ammonia molecules, it is not possible to extend the correlation to the factor group. The site occupancy of each of the 4 sites is only 0.25, which means that interactions of identical oscillators (the latter is at the origin of the correlation field splitting) are severely hindered. One could expect splitting of the normal NH_3 modes (ESI Fig.5), with some degree of broadening (due to overlap of bands). Ideally, each mode should give rise to a quartet of bands (a consequence of 4 different sites).

The primitive cell of compound **1-HT** ($[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$, $Z = 1$) is one half of the unit cell. However, due to the disordered species, the sulfate anions are located at sites with impossible symmetry (impossible in the sense that their site group is not a subgroup of T_d). Therefore, in order to perform the f-g analysis [40], we applied the least common supergroup (O_h) of both the molecular point group and the site group. The results are

presented on Fig. 8 and ESI Fig. 6). In this way, we could expect 1-1 IR and Raman bands of ν_s (B_{1u} and A_{1g}), and 2-2 bands for ν_{as} (A_{2u} , E_u and B_{2g} , E_g), δ_s (A_{1u} , B_{1u} and A_{1g} , B_{1g}) and δ_{as} (A_{2u} , E_u and B_{2g} , E_g) modes, respectively.

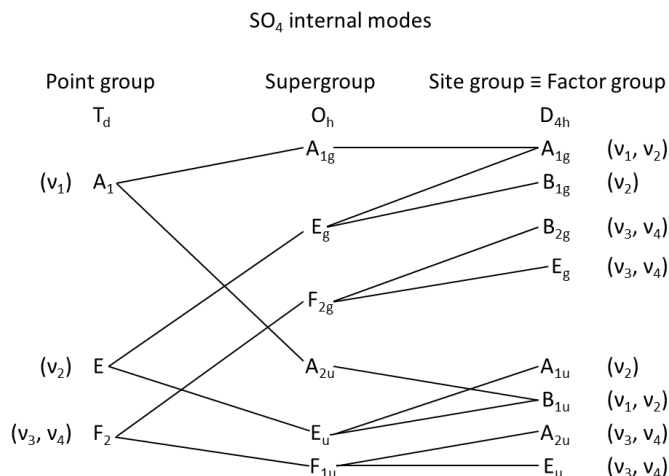


Figure 8. Correlation analysis of sulfate ion in compound **1-HT**.

IR spectral characteristics of compounds **1-LT** and **1-HT**

The IR spectra of compound **1-LT** were studied between 87 and 301 K (ESI Fig. 7). In a heated sample holder, the spectrum of compound **1-HT** could also be recorded. (ESI Fig. 8). The low-temperature (-186 °C) and room temperature (28 °C) IR data of compound **1-LT** and the **1-HT** polymorph (at 80 °C) are compared in Table 2 and ESI Figs. 8-9.

Table 2. IR spectra of compound **1-LT** between -186 °C and room temperature and compound **1-HT** at 80 °C

Assignations/T, °C	Compound 1-LT			Compound 1-HT
	-186 °C	25 °C	25 °C [31]	80 °C
<i>Anion modes</i>				
$\nu_s(SO)$ (A_1)			-	
$\nu_{as}(SO)$ (F_2)	1107	10,771,066	1098, 1078	1073, 1043
$\delta_s(SO)$ (E)			-	
$\delta_{as}(SO)$ (F_2)	676, 647, 631, 615, 604	616, 602	619, 605	
<i>Cation modes</i>				
$\nu_{as}(NH)$ (A_1)	3353, 3300, 3291	3312, 3317	3320, 3230	3306
$2\delta_{as}(NH)$	3233, 3187	3247, 3229	-	3215
$\nu_s(NH)$ (A_2)	3154	3150	3150	3135
$\delta_{as}(NH)$ (E)	1647, 1605, 1592, 1580	1634, 16,411,624	1642, 1626	1614
$\delta_s(NH)$ (A_2)	1227, 1174	1192, 1234	1236	1235
$\rho(NH_3)$ (E)	746, 717, 705	732, 699	740, 703	737, 683

$\nu_s(\text{AgN})(A_1)$	-	-	400	
$\nu_s(\text{AgN})(A_2)$	529, 475	466	476	466

The IR spectra of compound **1-LT** and **1-HT** shows the weakening of the Ag-N bonds with the increasing of N-H stretching frequencies of **1-LT** compared with those of **1-HT**. It means that compound **1** has stronger Ag-N interaction than compound **1-HT**. The high thermal motion of ammonia molecules and sulfate ions in compound **1-HT** results in singlet bands at 80 °C. For compound **1-LT**, the cooling of samples results in band-rich spectra (ESI Fig. 9), with much more components than we could expect from the factor group analysis (ESI Fig. 5). The appearing of these bands could be attributed to the change in the crystal structure but between -150 and +80 °C we could not confirm the existence of any phase transition (ESI Fig.10). Furthermore, the same split band system was found at -123 °C, whereas at -73 °C the spectral features were almost identical with those found at room temperature (ESI Fig. 9). In the lack of phase transition between -73 and -123 °C, we can suppose that the strongly split band structure can be attributed to the freezing of ammonia molecules in this temperature range into various N-H...O-S hydrogen-bonded states. The bonding parameter (ϵ) characterizes the relative strength of ammonia coordination (uncoordinated free ammonia is $\epsilon=0$, the range is between 0 and 1) shows medium-strength coordination of ammonia to silver ($\epsilon=0.61$) [39].

Raman spectroscopic features of compounds 1-LT and 1-HT

Raman studies on the sample at 25 and 70 °C showed that the temperature increasing did not result in significant change in the shape of the Raman bands (Fig. 9, ESI Fig. 11). However, at 80 °C, the bands of the antisymmetric deformation mode of sulfate ion collapsed into one wide band. The split components was observed for the ammonia ligand disappeared and one wide band appeared. These collapses indicated that the secondary interactions between the $\text{Ag}(\text{NH}_3)_2^+$ and SO_4^{2-} ions (Ag...O-S and N-H...O-S interactions) have been changed in remarkably and these could not be attributed to the temperature effect solely.

Table 3. Assignment of Raman bands in compounds **1-LT** and **1-HT**, at 25 or 70, and 80 °C, respectively

Mode/Temperature, °C	25	70	80
Sulfate modes			
$\nu_s(\text{SO})(A_1)$	995	975	978
$\nu_{as}(\text{SO})(F_2)$	1107, 1078	1106, 1082	1116, 1085
$\delta_s(\text{SO})(E)$	447	447	445
$\delta_{as}(\text{SO})(F_2)$	621, 612	621, 613	611
Cation modes			
$\nu_s(\text{AgN})(A_1)$	402	400	398
$\nu_{as}(\text{AgN})(A_2)$	476	-	-
$\delta(\text{NAgN})(E)$	187, 163	160, 124	154

$\rho(NH)(E)$	727, 692	726, 689	708
$\rho_s(NH) (A_2)$	1217	1215	1209
$\delta_{as}(NH)(E)$	1665, 1643	1661, 1643	1647

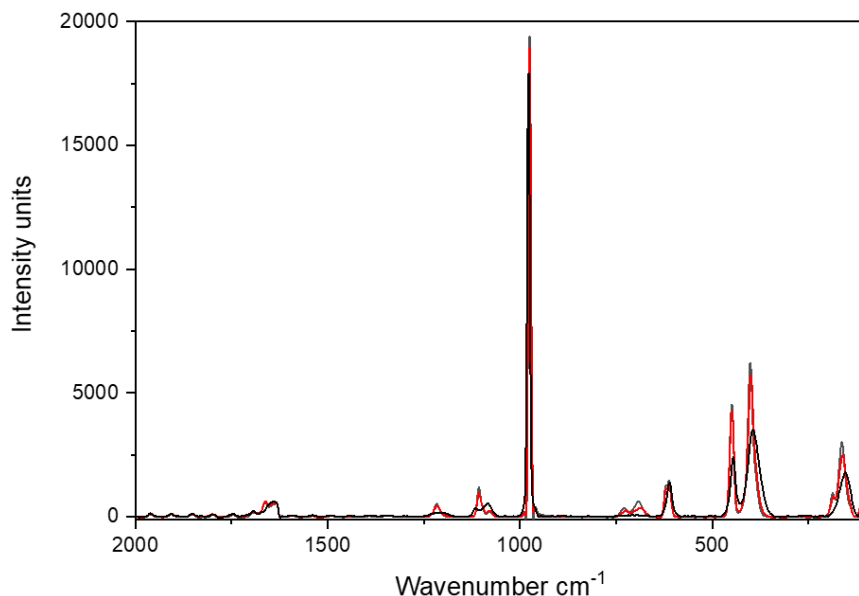


Figure 9. Raman spectra of compound **1-LT** and **1-HT** at 25/70 and 80 °C

UV spectroscopic results on compound 1

UV studies on solid compound **1-LT** showed two absorption bands at 253 and 383 nm, which might be attributed to the silver(I) 4d-5s metal-centered and a N_p-Ag_{5s} LMCT (ligand-to-metal charge transfer) transitions (ESI Fig. 12 and 13), respectively [44].

Thermal decomposition of compound 1-LT and 1-HT

Thermal decomposition of compounds **1-LT** and **1-HT** was studied by Torgonskaya and Pavlyuchenko in vacuum, inert atmosphere and under ammonia at various pressures [21]. Their kinetic studies showed that the decomposition rate constant was higher for the high-temperature polymorph (compound **1-HT**) than for the low-temperature polymorph (compound **1-LT**). The reaction was assigned as simple deammoniation with the formation of silver(I) sulfate [21]. It was not mentioned that the evolved ammonia could react with silver sulfate, although Hodgkinson and Trench found water and ammonium sulfite as redox reaction products in the reaction of solid silver sulfate with ammonia. They could also isolate a white sublimate $NH_4OS(O)NH_2$ (ammonium thionamate), which in contact with water decomposed into ammonium sulfite [41]. The reaction of solid Ag_2SO_4 with gaseous NH_3 , evolved at 420 °C, which is much higher temperature than the ammonia evolution temperature in the

decomposition reaction of compound **1**. However, ammonium sulfite, as thermal decomposition product of diamminesilver(I) sulfate could be identified [23, 24].

The ammonia from some transition metal ammine complexes can react in solid phase with their oxygen-containing anions [2, 6–8]. Therefore, the ammonia evolution from compound **1-LT** generates a potential reducing agent of the silver sulfate residue. This reducing possibility prompted us to study the thermal decomposition of compound **1-LT** and to clarify the nature of the redox reaction between silver sulfate and ammonia with DSC and evolved gas analysis techniques.

Evolved gas analysis was performed in air and argon atmosphere up to 800 °C. We found that the decomposition reaction proceeds in the same way for both atmospheres (Fig. 10 and 11). In argon, thermal degradation of compound **1-LT** begins at 74 °C. Coinciding with this decomposition step, a phase transition of compound **1-LT** into **1-HT** observed on the DSC curve (~80 °C) (ESI Fig. 14 and 15). Similar to previous findings, the decomposition rate constant of **1-LT** was smaller than that of **1-HT** [21], therefore, a part of **1-LT** decomposes whereas another part simultaneously transformed into **1-HT**. The formed **1-HT** decomposes faster than **1-LT**, which result in a small shoulder on the DTG peak at 81 °C (ESI Fig. 4). The compound **1-LT/1-HT** in argon or air loses 18.9 and 17.9% of its mass in the first two decomposition steps (the calculated value for the complete ammonia loss is 18.9 %).

The lattice energy of compound **1-HT** should be lower than that of compound **1-LT** due to the weakening/breaking of secondary bonds (hydrogen- and coordination bonds). Therefore, the deammoniation of compound **1-HT** can be definitely faster than that of compound **1-LT**. It can also explain the increased reactivity of **1-HT** towards ammonia because easier breaking of its lattice induces to easier formation of the triammine complex (compound **3**). The difference between the lattice energies of **1-LT** and **1-HT** is large enough to reach the point when the Gibbs energy of the reaction becomes negative for compound **1-HT**, and the ammonia uptake becomes spontaneous.

The detected gaseous oxidation products (H₂O, NO_x) showed minor side reactions involving redox interactions of ammonia. An important feature of the decomposition process is the absence of SO₂ as a gaseous decomposition product. In argon atmosphere, there is no other oxygen source than the sulfate ion, thus in the lack of gaseous SO₂, some other solid sulfate reduction products should form. The ammonium sulfite detected earlier [23, 24] can decompose with the formation of elemental sulfur or sulfur-rich solids like di- or polythionates [42].

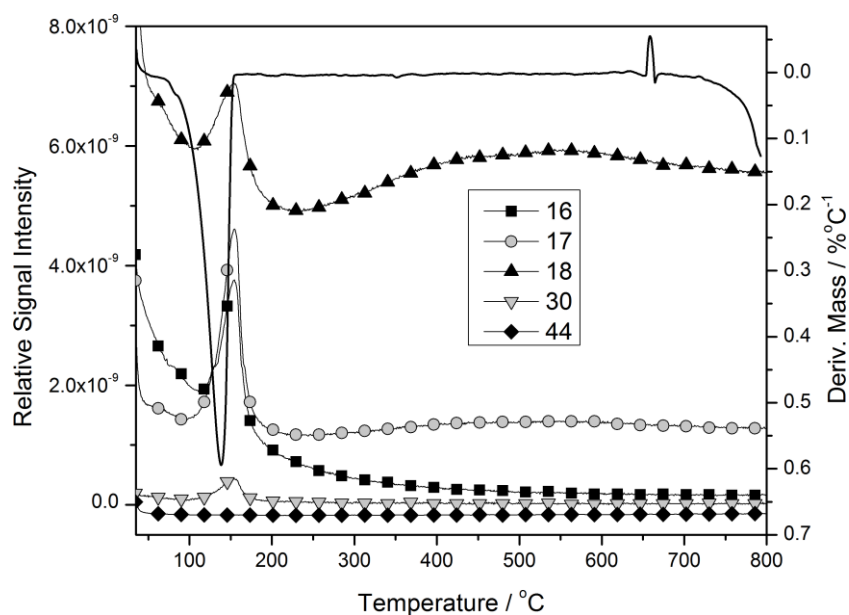


Figure 10 TG-MS of compound **1-LT (1-HT)** under argon atmosphere at $m/z=18$ (H_2O), 17 (OH and NH_3) and 16 (O and NH), 30 (NO) and 44 (N_2O).

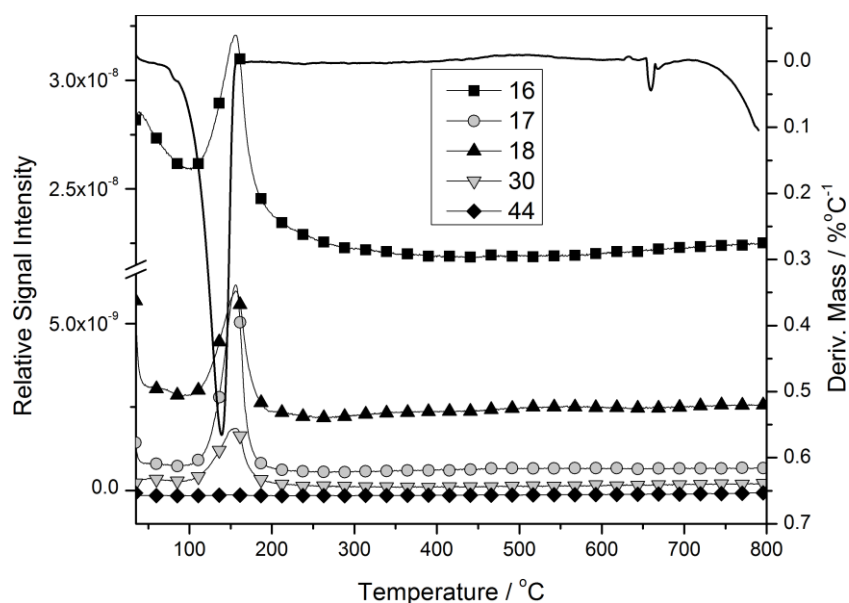


Figure 11 TG-MS of compound **1-LT (1-HT)** under air at $m/z=18$ (H_2O), 17 (OH and NH_3) and 16 (O and NH), 30 (NO) and 44 (N_2O).

Accordingly, in inert atmosphere, elementary sulfur ($m/z=32$) could be detected in a minor amount. The NH_3 and H_2O and their fragment peaks ($m/z=18(\text{OH}_2)$), $m/z=17$ (NH_3 , OH) intensities are different in air and inert atmosphere (Fig. 10 and 11). The peak $m/z=18$ belongs only to H_2O^+ while to the intensity of $m/z=17$ peak either NH_3^+ or OH^+ ions contribute. Therefore, the ratio of $m/z=18$ and 17 peak intensities can give some information about the ratio of parent (NH_3^+ and H_2O^+) ions [42]. In air atmosphere, the oxidation of ammonia (increasing the amount of water and decreasing the ammonia) with air could be expected. However, the intensity of the $m/z=18$ peak (H_2O) is smaller than that of $m/z=17$

(OH⁺ + NH₃⁺), which means that the main component of m/z=17 peak is NH₃⁺. In argon, however, the m/z=18 peak intensity is closer to the intensity of m/z=17 (OH or NH₃) peak, so the contribution of ammonia to the peak of m/z=17 is less than in air. These results could be attributed to ammonium sulfite decomposition reaction in a solid phase quasi-intramolecular redox reaction with the formation of water, nitrogen oxides and elemental sulfur [42], which have influence on the water/ammonia parent ions intensity in the evolved gas analyses. A very weak m/z=44 peak observed only in air, so it can be attributed to the N₂O formation, while the peaks at m/z=14 (N), 28 (N₂), or 16 (O) in the air atmosphere experiments could not be evaluated because of the air components (N₂, O₂). The only NO_x type oxidation product formed in both atmospheres was NO. It is highly possible that the decomposition of **1-LT** polymorph is accomplished with ammonia loss and simultaneous ammonia oxidation by the sulfate ion and the formation of S(IV) species (ammonium sulfite), whereas the decomposition of **1-HT** polymorph, which has no strong hydrogen bond systems proceeds without oxidation of ammonia. Since the polymorphic transition temperature of compound **1-LT** is lower than its decomposition peak temperature, the **1-HT** polymorph can form and decompose into ammonia and silver sulfate as that was observed. Silver sulfate has an orthorhombic-hexagonal phase transition (from ordered Fddd to disordered P6₃/mmc) at 426 °C, which is followed by melting at 658 °C [21] both in an inert and aerial atmosphere.

DSC Studies on compounds 1-LT and 1-HT.

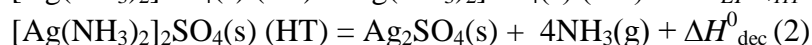
The DSC curve of compound **1-LT** measured between liq. N₂ temperature and room temperature do not show any polymorphic phase transition (ESI Suppl. 4). However, there are two endothermic peaks that indicate a phase transition and a deammoniation reaction. The differences in the reaction/polymorphic transition heat in air and inert atmosphere are small (Table 2), which confirms that oxygen does not play a role in the decomposition process. The peak temperature of deammoniation, however, is very different, and not only the atmosphere but other factors, e.g. the morphology can play a key role in it.

Table 4 Comparison of DSC results of compound **1-LT (1-HT)** found in O₂ and inert atmosphere

Parameter	In air	In N ₂	In air [20]
$T_{LT \rightarrow HT}$, °C	75	79	85
$\Delta H_{LT \rightarrow HT}$ kJ/mol	13.18	10.73	7.95
$T_{LT \rightarrow HT}$, °C	71-84	74-86	81-86<
T_{dec} (<i>peak</i>), °C	186	153.2	193
T_{dec} (<i>range</i>), °C	92-198	86-183	80(98)-193<
ΔH_{dec}^0 kJ/mol*	315.34	319.34	228.11
$\Delta H_{f,298}^0$ kJ/mol	-1208.92	-1202.47	-1120.48

*For the decomposition reaction, the $\Delta H_{f,298}^0$ values for crystalline Ag₂SO₄ (-15.88 kJ/mol) and gaseous NH₃ (-46.06 kJ/mol) were taken from ref. [20]

The weak endothermic peak in inert atmosphere could unambiguously be assigned to the phase transition found by XRD. The standard heat of formation for compound **1-LT** (Table 2) was calculated from the equations:



Supposing that the decomposition reaction heat (equation 2) is independent from the pressure and ΔC_p is negligible, ΔH_{dec} equals to ΔH^0 . The peaks of phase transition could be separated (ΔT (*lower limit of decomposition* *upper limit of phase transition* = 3 °) in air.

The small difference found between the decomposition reaction heat in air and inert atmosphere discloses the ignition of evolved ammonia with the aerial oxygen [20]. The thermal decomposition of compound **1-LT** proceeds via the formation of compound **1-HT** intermediate. Thus, the structural motifs of compound **1-HT** play a key role in the nature of the decomposition process. The lattice extension in the direction of the *a* axis weakens/breaks the N-H...O-S hydrogen bonds, thus decrease the number of redox centers (N-H...O-S) and results in a small extent of the redox reactions. The reaction between the free gaseous ammonia and the solid silver sulfate occurs at much higher temperature to complete (~420 °C) than the decomposition temperature of compound **1-LT** (<200 °C). Thus, the redox reaction takes place in the solid phase and has quasi-intramolecular character. The ammonium sulfite intermediate may also be formed in the solid phase, because no gaseous S₂ forms in the gas phase [42]. Although the silver sulfate–ammonia reaction resulted in ammonium sulfite intermediate [41], the ammonium sulfite sublimate can be formed from gaseous SO₂, NH₃ and H₂O because the ammonium sulfite decomposes at a remarkably lower temperature than what is required for the reaction between silver sulfate and ammonia.

Conclusions

High-temperature tetragonal polymorph of diamminesilver(I) sulfate ($a=8.588$, $c=6.220$) (compound **1-HT**) have been prepared and characterized. The phase transformation of low-temperature polymorphs of diamminesilver(I) sulfate (compound **1-LT**) into compound **2** coincides with the initial stage of the decomposition of compound **1-LT**. The standard heat of formation of compound **1-LT** and the enthalpy of polymorphic transformation were found to be $\Delta H_f^{298} = -1208.92$ kJ/mol and $\Delta H_{LT-HT} = 13.18$ kJ/mol, respectively. The HT-XRD results showed that the cell distances of **1-LT** polymorph elongate in the direction of a , b and compress in the direction of c in the **1-HT** polymorph. The Ag-Ag distance of **1-LT** shortens from 3.20 Å to 3.11 Å (**1-HT**), while the expansion in the a,b direction and the heat motion weaken/disrupt the N-H...O-S hydrogen bonds and the coordinative Ag...O-S interactions. A vacuum-assisted thermal deammoniation experiments during the preparation of monoamminesilver(I) sulfate complex showed that the product consists of silver(I) sulfate and the starting diamminesilver(I) sulfate complex.

The decomposition peak temperatures are very different in air and inert atmosphere (~153 and ~18 °C), which might be attributed to the same kinetic phenomena [21], especially if the oxygen can bind to the autocatalytic species, which can act only in an inert atmosphere and reach the maximal decomposition rate at a much lower temperature in an inert atmosphere (~150 °C) than in air (~190 °C).

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