Structural Investigations and Thermal Behaviour of Mercury(II) Sulfito Complexes

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Abstract. The crystal structures of $(NH_4)[HgSO_3Cl]$ (1) and of $(NH_4)_2[Hg(SO_3)_2]$ (2) were determined from single crystal diffractometer data sets. 1: 22 °C, *Pnma*, Z = 4, a = 15.430(3), b = 5.525(1), c = 6.679(1) Å, R(F) = 0.0256, $R_w(F^2) = 0.0642$ (all 1056 unique reflections). 2: -108 °C, $P2_12_12_1$, Z = 4, a = 6.2240(4), b = 9.3908(6), c = 13.6110(8) Å, R(F) = 0.0179, $R_w(F^2) = 0.0493$ (all 2699 unique reflections). The structure of 1 contains bent Cl-Hg-SO₃ entities (site symmetry *m*; d(Hg-Cl) = 2.3403(13) Å, d(Hg-S) = 2.3636(12) Å, $\angle(Cl-Hg-S) = 164.51(5)^\circ$, $d(S-O) 2\times 1.458(3)$ Å, 1.468(4) Å, $\bar{d}(S-O) = 1.461$ Å) linked to undulated ribbons parallel to the *b*-axis by intermolecular secondary bonds SO…Hg ($d(O \dots Hg) = 2 \times 2.595(3)$ Å). These ribbons in turn aggregate to layers around the *bc*-plane. The layers are stacked along the *a*-axis with interlayer distances of a/2. The structure of 2 is made

up of O₃S-Hg-SO₃ moieties (d(Hg-S) = 2.3935(7), 2.3935(8) Å; \angle (Hg-S-Hg) = 174.41(3)°; \bar{d} (S-O) = 1.474 Å), that are linked to ribbons parallel to the *a* axis by coordination of Hg to three remote O atoms (2.801(4) < d(Hg-O) < 2.844(3) Å). Adjacent ribbons are joined together by an additional Hg-O contact of 2.733(3) Å, leading to a three-dimensional anionic framework. Both crystal structures are stabilised by disordered NH₄⁺ cations, placed between the anionic layers or in the vacancies of the framework, *via* moderate hydrogen bonding interactions N-H···O with donoracceptor distances ranging from 2.8 to 3.2 Å. 1 and 2 were further characterised by thermal analysis (TG, DSC). They start to decompose at temperatures above 130 °C.

Keywords: Mercury; Sulfito ligands; Structure elucidation

Introduction

In connection with structural and spectroscopic studies of sulfito complexes of the platinum group metals [1, 2], we turned our attention again to sulfito complexes of mercury(II). Although several compounds within the systems M-Hg^{II}-SO₂-H₂O (*M* is ammonium or an alkali metal) have been reported over hundred years ago [3, and references therein], only one inorganic mercury(II) sulfito complex is structurally well-characterised, viz. Na₂[Hg(SO₃)₂]·H₂O [4]. Its crystal structure comprises [O₃S-Hg-SO₃] moieties with Hg-S bond lengths of ca. 2.40 Å that are comparable with the Hg-S bond length of 2.377 Å observed for trigonal α -HgS (cinnabar) [5]. From previous infrared spectroscopic measurements of (NH₄)[HgSO₃Cl] and (NH₄)₂[Hg(SO₃)₂] [6] it was derived that their structures likewise contain mercury atoms with S-coordinated ligands, but a full structure analysis has not been given in the original communication or in the meantime. Therefore we started single crystal growth experiments for (NH₄)[HgSO₃Cl] (1) and $(NH_4)_2[Hg(SO_3)_2]$ (2) and report here the crystal structures

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Institute of Chemical Technologies und Analytics Division of Structural Chemistry Vienna University of Technology Getreidemarkt 9 / 164-SC A-1060 Vienna / Austria E-mail: mweil@mail.zserv.tuwien.ac.at and the thermal behaviour of these compounds. A detailed interpretation of the vibrational spectra of **1** and **2** on the basis of the present structural data is given elsewhere [7].

Experimental Section

Synthesis

Single crystal growth of both compounds was accomplished by following a slightly modified procedure given by *Barth* [8] and *Spacu and Drăgulescu* [9], respectively.

 (NH_4) [HgSO₃Cl] (1): Under constant stirring 2.7 g (10 mmol) solid HgCl₂ (Merck, p.A.) was added to a solution of 3.0 g $(NH_4)_2SO_3\cdot H_2O$ (22 mmol; Aldrich, 92 %) in 30 ml water. After complete dissolution of the mercury component (*ca.* 10 min), the clear solution was filtered and allowed to stand in the dark. Colourless crystals of 1 with an edge length up to 3 mm and a plate-like habit were obtained after five days. The crystals were separated by filtering, washed with mother liquor, ethanol and diethylether and dried over CaCl₂ in a desiccator. Unlike stated in [6], the crystals are stable under atmospheric conditions for several months.

 $(NH_4)_2[Hg(SO_3)_2]$ (2): 432 mg solid HgO (2 mmol), freshly prepared by precipitation from a HgCl₂ (Merck, p.A.) solution with diluted NaOH solution (Merck, p.A.), was dissolved under constant stirring in 15 ml (NH₄)₂SO₃ solution (Aldrich, 92 %; 1.76 g, 13 mmol). The solution became clear within several hours, was filtered and then allowed to stand in the dark. Colourless crystals of **2**, mostly with a prismatic habit and an edge length up to 5 mm,



grew within five days. The crystals were then filtered, washed with mother liquor, acetone and diethyl ether, and were dried over $CaCl_2$ in a desiccator. Within one week the crystals (both in the mother solution or when dried) start to decompose under blackening and a noticeable smell of SO₂. When covered with a thin film of mother liquor and embedded in "magic oil" (low viscous perfluoropoly-ether 216, Riedel de Haën), the crystals were sufficiently stable for X-ray data collection at low temperatures.

Single-crystal diffraction

The optical quality of selected crystals was checked under a polarising microscope. X-ray diffraction intensities of the single crystals

 Table 1
 Details of data collection and structure refinement

Compound Crystal dimensions / mm Crystal color Crystal shape Crystal system Space group, no. Formula units Z	NH ₄ [HgSO ₃ Cl] 1 0.06 ⁻ 0.24 ⁻ 0.24 colourless plate orthorhombic <i>Pnma</i> , #62 4	$(NH_4)_2[Hg(SO_3)_2]$ 2 0.18·0.30·0.42 colourless prism orthorhombic $P2_12_12_1$, #19 4
a / \dot{A}	15.430(3)	6.2240(4) 9.3908(6)
c / Å $V / Å^3$	6.6790(12) 569.4(2)	13.6110(8)
Formula weight / $g \cdot mol^{-1}$ μ / mm^{-1}	334.14 27.769	396.79 19.862
X-ray density / g·cm β Range $\theta_{\min} - \theta_{\max}$ Range h	3.898 2.64 - 31.94 $-22 \rightarrow 22$	$\begin{array}{r} 3.313\\ 2.64 - 31.95\\ -9 \rightarrow 9 \end{array}$
k l	$\begin{array}{c} -8 \rightarrow 8 \\ -9 \rightarrow 9 \end{array}$	$\begin{array}{c} -13 \rightarrow 12 \\ -20 \rightarrow 20 \end{array}$
Measured reflections Independent reflections	6573 1056	8571 2699
Obs. reflections $[I > 2\sigma(I)]$ R_i Trans. coef. T_{\min} ; T_{\max} Number of normetator	960 0.0418 0.0575; 0.2866	2650 0.0371 0.0439; 0.1244
Number of parameters Ext. coef. (SHELXL97) Diff. elec. dens. max; min / $e^{} Å^{-3}$ (dist. / Å, atom) $R[F^2 > 2\sigma(F^2)]$ $wR2(F^2$ all) Goof	41 0.0038(4) 2.97 (0.76, Hg); -1.45 (0.62, Hg) 0.0228 0.0642 1.167	101 0.00320(19) 1.57 (0.83, Hg); -1.02 (0.71, Hg) 0.0179 0.0493 1.078
CSD number	410860	410859

Table 2 Atomic coordinates and equivalent isotropic displacement parameters $/ \mathring{A}^2$

Atom	Wyckoff position	x	у	Ζ	$U_{\rm eq}$ ^{a)}
NH ₄ [H	IgSO ₃ Cl] (1)				
Hg	4 c	0.495603(12)	1/4	0.26561(3)	0.02217(11)
s	4 c	0.61409(7)	1/4	0.04132(17)	0.0181(2)
Cl	4 c	0.40821(9)	1/4	0.5520(2)	0.0311(3)
O1	4 c	0.6927(2)	1/4	0.1653(6)	0.0295(8)
O2	8 <i>d</i>	0.61277(19)	0.0332(6)	-0.0829(6)	0.0461(8)
N	4 c	0.2684(3)	³ / ₄	0.4225(7)	0.0269(9)
(NH ₄) ₂	2[Hg(SO ₃) ₂] (2)				
Hg	4 a	0.99208(2)	0.233618(14)	0.628401(8)	0.00628(5)
Sĩ	4 a	1.0023(2)	0.33519(9)	0.78962(5)	0.0065(2)
S2	4 a	0.9660(2)	0.15324(10)	0.46195(6)	0.0061(2)
O1	4 a	1.1638(5)	0.0753(4)	0.4327(2)	0.0134(7)
O2	4 a	0.8766(5)	0.2464(3)	0.8599(2)	0.0126(6)
O3	4 a	0.7742(5)	0.0628(4)	0.4489(2)	0.0125(7)
O4	4 a	0.9431(5)	0.2847(3)	0.4025(2)	0.0146(6)
O5	4 a	1.2306(5)	0.3380(4)	0.8200(2)	0.0150(7)
O6	4 a	0.9119(6)	0.4796(3)	0.7840(3)	0.0178(7)
N1	4 a	0.4532(6)	-0.1032(4)	0.5302(2)	0.0146(8)
N2	4 <i>a</i>	1.0384(6)	0.4265(4)	0.2280(2)	0.0123(7)

were collected at 22(1) °C for 1, and at -108(3) °C for 2 in a cold stream of nitrogen. ω -scans with 0.3° rotation width and 30 s exposure time per frame were recorded on a SMART APEX three-circle diffractometer equipped with a CCD camera (Bruker AXS; Mo $K_{\bar{\alpha}}$ radiation, $\lambda = 0.71073$ Å). Three independent sets of 600 frames were measured thus scanning the whole reciprocal sphere with high redundancy. The measured intensities were corrected for Lorentz and polarisation effects, and an absorption correction was applied using the multi-scan approach with SADABS [10]. The crystal structures were solved by direct methods and refined with the SHELXTL program package [11]. In the final least-squares cycles the thermal displacement parameters of all atoms were refined anisotropically. For both structures the hydrogen atoms of the ammonium cations could not be located from difference Fourier maps, and thus were not included in the refinement (see also discussion of a potential orientational disorder due to the hydrogen bonding

Table 3 Selected distances / Å and angles /°

NH	4[HgSO3	Cl] 1				
Hg Hg Hg Hg Hg Hg	Cl S O2 #1 O2 #2 Cl #4 Cl #5	2.3403(13) 2.3636(12) 2.595(3) 2.595(3) 3.3643(10) 3.3643(10)	N N N N N N N	O1 #5 O1 #6 O1 #7 O2 #8 O2 #7 O2 #9 O2 #1	2.818(6) 3.056(3) 3.056(3) 3.060(5) 3.060(5) 3.153(6) 3.153(6)	
S S	O2 O2 #3	1.458(3) 1.458(3) 1.468(4)	Cl O2 O2 #3	Hg S S	S O2 #3 O1	164.51(5) 110.6(4) 109.43(16)
3	01	1.400(4)	O2 #3 O2 #3 O2 O1	S S S	Hg Hg Hg	110.49(13) $110.49(13)$ $106.34(16)$

Symmetry operators to generate equivalent atoms: #1: 1–x, –y, –z; #2: 1–x, $^{1/2}$ +y, –z; #3: x, $^{1/2}$ -y, z; #4: 1–x, 1–y, 1–z; #5: 1–x, –y, 1–z; #6: x– $^{1/2}$, y– $^{1/2}$, $^{1/2}$ -z; #7: x– $^{1/2}$, y, $^{1/2}$ -z; #8: x– $^{1/2}$, $^{-1/2}$ -y, $^{1/2}$ -z; #9: 1–x, y– $^{1/2}$, –z.

(NH ₄) ₂ [Hg(SO ₃) ₂] 2						
Hg	S1	2.3935(7)	N2	O4	2.788(5)	
Hg	S2	2.3935(8)	N2	O1 #7	2.884(5)	
Hg	O6 #1	2.733(3)	N2	O2 #2	2.915(5)	
Hg	O3 #2	2.801(4)	N2	O5 #8	2.920(5)	
Нg	O1 #3	2.843(3)	N2	O3 #7	2.965(5)	
Hg	O4 #4	2.844(3)	N2	O6 #9	3.035(5)	
-			N2	O5 #3	3.204(5)	
S 1	O6	1.470(3)				
S 1	O5	1.480(3)	S1	Hg	S2	174.41(3)
S 1	O2	1.491(3)				
S2	O3	1.475(3)	O6	S1	05	111.5(2)
S2	O4	1.483(3)	O6	S1	O2	110.4(2)
S2	01	1.487(3)	O5	S1	O2	109.51(19)
			O6	S1	Hg	108.05(14)
N1	O3	2.766(5)	O5	S1	Hg	106.79(13)
N1	O1 #4	2.796(5)	O2	S1	Hg	110.57(13)
N1	O2 #5	2.881(5)				
N1	O5 #1	2.887(5)	O3	S2	O4	109.61(19)
N1	O2 #6	2.906(5)	O3	S2	01	110.76(18)
N1	O4 #3	3.129(5)	O4	S2	01	110.07(19)
			O3	S2	Hg	110.52(13)
			O4	S2	Hg	105.08(12)
			O1	S2	Hg	110.66(13)

Symmetry operators to generate equivalent atoms: #1: -x+2, $y-1/_2$, -z+3/2; #2 $x+1/_2$, $-y+1/_2$, -z+1; #3: $x-1/_2$, $-y+1/_2$, -z+1; #4: x-1, y, z; #5: -x+3/2, -y, $z-1/_2$; #6: -x+1, $y-1/_2$, -z+3/2; #7: -x+2, $y+1/_2$, $-z+1/_2$; #8: -x+5/2, -y+1, $z-1/_2$; #9: -x+3/2, -y+1, $z-1/_2$.

^{a)} U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

geometry). The final difference Fourier maps did not indicate any additional atomic sites, and the highest difference peaks were located close to the mercury positions. Analysis of the refined atomic coordinates with the program PLATON [12] did not reveal any higher symmetry. Moreover, for the structure of $\mathbf{2}$, the refined Flack parameter [13] of 0.014(8) using 1103 Friedel pairs gave a clear indication of the absence of a centre of symmetry.

Further details of data collection and structure refinement are summarised in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2, and selected interatomic distances and angles are given in Table 3. Additional crystallographic information on the two structures is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, email: crysdata@fiz-karlsruhe.de, by quoting the literature citation, the name of the authors and the depository number listed at the end of Table 1. Drawings of structural details were produced using the program ATOMS [14].

Thermal behaviour

Thermoanalytical measurements were performed in an open system under N₂ flow on a Mettler-Toledo TG-50 system (35-600 °C, heating rate 5 °C·min⁻¹, corundum crucibles) and a Mettler-Toledo DSC-25 system (35-550 °C, heating rate 5 °C·min⁻¹, aluminium pans with a pierced lid).

Results and Discussion

Description of the structures

The crystal structure of 1 is made up of Cl-Hg-SO₃ entities with site symmetry *m*. The Hg-Cl bond is slightly shorter



Fig. 1 (NH₄)[HgSO₃Cl]. The chains extending parallel to the *b*-axis with anisotropic displacement parameters drawn at the 90 % probability level. Strong bonds are given as solid lines, weak bonds as open lines.



Fig. 2 (NH_4) [HgSO₃Cl]. Perspective view along the *b*-axis of the crystal structure. Strong bonds are represented by solid lines, weaker bonds by open lines and Hg···Cl interactions by dashed lines. Hydrogen bonds N···O are omitted for clarity.



Fig. 3 (NH_4) [HgSO₃Cl]. a) Arrangement of the anionic chains, and b) schematic representation of the pseudo-hexagonal rod packing in the *ac*-plane. The unit cell is outlined.



Fig. 4 $(NH_4)_2[Hg(SO_3)_2]$. The chains extending parallel to the *a*-axis with anisotropic displacement parameters drawn at the 90 % probability level. Strong bonds are given as solid lines, weak bonds as open lines.

[2.3403(13) Å] than the Hg-S bond [2.3636(12) Å] with a \angle (Cl-Hg-S) angle of 164.51(5) deviating substantially from linearity. Adjacent Cl-Hg-SO3 units are linked into undulated ribbons parallel to the *b*-axis by two intermolecular secondary donor-acceptor bonds SO---Hg with a distance of 2.595(3) Å [Fig. 1]. These ribbons in turn aggregate to layers around the *bc*-plane which are stabilised by two weak interactions Cl···Hg (d(Cl···Hg) = 3.3643(10) Å) leading to a distorted [2+2+2] octahedral coordination around mercury. The layers are stacked along the *a*-axis with an interlayer distance of a/2 = 7.715 Å [Fig. 2]. Thus, the obvious features of this structure are the one- and two-dimensional substructures, viz. ribbons and layers, which adopt the band or rod group symmetry $(b) \cdot 2_1: m - p \cdot 12_1/m \cdot 1$ and layer symmetry $(b:c)\cdot 2_1:m-p12_1/m1$, respectively [15]. The corresponding arrangement of the two-dimensional pseudo-hexagonal rod packing [16] of the chains in the ac plane is depicted in Figure 3.

The crystal structure of **2** is composed of nearly linear O₃S-Hg-SO₃ moieties [\angle (Hg-S-Hg) = 174.41(3)°]. The Hg-S bonds to the two crystallographically independent S atoms are the same within their e.s.d.'s [(d(Hg-S1) = 2.3935(7); d(Hg-S2) = 2.3935(8) Å] and are slightly longer than in **1**. This is possibly caused by the mutual trans-influence of the two sulfito ligands in **2**, and the Hg-S bonds are in the same range than those in Na₂[Hg(SO₃)₂]·H₂O [4] which likewise contains nearly linear O₃S-Hg-SO₃ moieties: [\angle (Hg-S-Hg) = 172.8(2)°; d(Hg-S1) = 2.402(6), d(Hg-S2) = 2.411(6) Å]. The O₃S-Hg-SO₃ units in **2** are linked into ribbons parallel to the *a*-axis by coordination of the mercury atom to three remote oxygen atoms (2.801(4) < d(Hg-O) < 2.844(3) Å) [Fig. 4]; an additional Hg-O con-



Fig. 5 $(NH_4)_2[Hg(SO_3)_2]$. Projection along the *a*-axis of the crystal structure packing. Strong bonds are represented by solid lines, weaker bonds by open lines. Hydrogen bonds N···O are omitted for clarity.

tact of 2.733(3) A between adjacent ribbons leads to the connection into a three-dimensional anionic framework [Fig. 5]. Again, the coordination around Hg in **2** is strongly distorted octahedral [**2**+4].

1 contains one sulfito ligand, whereas in 2 two crystallographically independent sulfito ligands are present. However, the S-O distances in the three sulfito ligands are very similar (neglecting the different data collection temperatures at -108 and $22 \,^{\circ}$ C) and range from 1.458(3) to 1.491(3) Å (Table 3). These distances are comparable with the S-O distances of the two crystallographically independent sulfito ligands in Na₂[Hg(SO₃)₂]·H₂O (*d*(S-O) range from 1.441(22) to 1.486(20) Å) and of those in other noble metal sulfito complexes, e.g. *trans*-(NH₄)₂[Ru(NH₃)₄(SO₃)₂] [17] where the sulfur atoms are bonded to the metal atoms in a similar fashion as in the title compounds.

Compared to the metal sulfites MSO_3 or MSO_3 ·H₂O (M = Mg [18], Mn [19-21], Fe [22], Cd [23], Pb [24, 25]), where the coordination of the M atoms is accomplished by oxygen atoms, the overall mean S-O distance of the sulfito ligands is significantly shorter here (1.478 Å versus 1.533 Å). This behaviour has been discussed in the past [26] and is attributed to the metal-sulfur coordination and thus an enhanced S-O π -bonding as a consequence. All the angles around the S atoms in 1 and 2 deviate only slightly from the ideal tetrahedral geometry, with an increase of the \angle (O-S-O) angle (mean 110.1°) due to the Hg-S coordination.

The ammonium cations, located between the layers (in 1 on a mirror plane) or in the vacancies of the anionic framework (for 2), stabilise the structures by means of moderate hydrogen bonds N-H···O with donor-acceptor distances ranging from 2.8 to 3.2 Å (Fig. 6, Table 3). Although heavy scatterers are present in both structures, the localisation of H atoms in difference Fourier maps should be possible, at least on the basis of a low-temperature data set. However, for the present structure refinements it was impossible to locate the hydrogen atoms of the NH₄ groups reliably. Geometrical placement of the H atoms with subsequent refinement cycles (with or without distance and angles restraints) did not improve the reliability factors and resulted in un-





Fig. 6 Hydrogen bonding N···O with an orientational disorder of the NH₄ cations in a) (NH₄)[HgSO₃Cl] and b) in (NH₄)₂[Hg(SO₃)₂]. N···O distances are gathered in Table 3.

reasonable N-H distances and/or thermal parameters for the H atoms. This is an indication of an orientational disorder of the H atoms and is supported by the fact that the ammonium cations are surrounded by several oxygen atoms with similar donor-acceptor distances. In 1, the N atom of the ammonium group has seven oxygen neighbours (d(N-O) = 2.818(6) - 3.153(6) Å), whereas in 2, the two unique N atoms have six and seven neighbouring oxygen atoms and exhibit donor-acceptor distances of 2.766(5) to 3.129(5) Å, and of 2.788(5) to 3.204(5) Å, respectively.

Finally, it should be mentioned that in similar experiments intended to crystallize the analogous selenito complex " $(NH_4)_2[Hg(SeO_3)_2]$ ", using a $(NH_4)_2SeO_3$ solution in excess instead of $(NH_4)_2SO_3$, the solid HgO did not dissolve. However, the orange suspension became off-white during stirring for 30 hours, and X-ray powder diffraction of the obtained microcrystalline solid revealed amminemercury(II) selenite, $[Hg(NH_3)]SeO_3$ [27], as a single-phase product. In contrast to the mercury sulfito complexes 1 and 2, no coordination between the chalcogen atom and the mercury atom is realised in this compound, the structure of which contains chains of edge-sharing [HgNO_5] polyhedra and SeO_3 pyramids.

Thermal behaviour

1 is stable up to ca. 150 °C and decomposes in an internal redox-reaction under release of SO₂ into ammonium sulfate and calomel (equ. (1)) which were the only phases detected by XRPD of material heated up to 180 °C and 210 °C, respectively. This first decomposition is accompanied by a weak endothermal effect at ca. 170 °C (Fig. 7a).

$$2 \text{ (NH}_4)[\text{HgSO}_3\text{Cl}]_{, s} \rightarrow (\text{NH}_4)_2\text{SO}_{4, s} + \text{Hg}_2\text{Cl}_{2, s} + \text{SO}_{2, g}$$
(1)

Since the experimentally determined mass loss (Fig. 7a) of ca. 12.5 % is substantially higher than the theoretical mass loss of 9.6 % as calculated according to equ. 1, it appears possible that further decomposition under release of NH₃ and/or HgCl₂ has to be taken into account. This is supported by the constant mass loss of ca. 6 % between 180 °C and 250 °C. The second decomposition range is observed between 250 °C and 310 °C and features a mass loss of ca. 78 % related to the original mass, accompanied with three endothermic effects at ca. 283, 297 and 309 °C. The presence of SO_4^{2-} , Hg^{2+} and Cl^- in this molten sample was confirmed by qualitative wet-chemical methods after cooling. The corresponding XRPD measurements revealed NH₄HSO₄ (PDF-card 25-0034 [28]) and (NH₄)₃H(SO₄)₂ (PDF-card 42-1426 [28]) besides yet unknown phase(s) for material heated up to 310 °C. The occurrence of the hydrous ammonium sulfates NH₄HSO₄ and (NH₄)₃H(SO₄)₂ at this temperature is in agreement with the thermal behaviour of single phase $(NH_4)_2SO_4$ where these phases were



Fig. 7 Thermal behaviour of a) $(NH_4)[HgSO_3Cl]$ and b) $(NH_4)_2[Hg(SO_3)_2]$.

observed as decomposition products above 250 °C [29]. The third decomposition range between 310 °C and 420 °C shows only a small relative mass change of ca. 10 %, but a strong endothermic effect at ca. 390 °C. The corresponding diffraction pattern of the material heated up to 430 °C (hygroscopic compound with microcrystalline appearance) revealed (NH₄)₃H(SO₄)₂ as the main product besides unknown phase(s). Hg in minor amounts and SO₄²⁻ were detected by wet-chemical methods, whereas Cl⁻ could not be analysed in this material. Above 580 °C the entire material is decomposed.

The thermolysis of **2** shows similar features as that of **1**. The compound decomposes in a first step at slightly lower temperatures than **1** between 130 °C and 150 °C into $(NH_4)_2SO_4$ and elemental mercury (equ. (2)), accompanied with a very sharp DSC effect at 132 °C (Fig. 7b). The theoretical mass loss of 16.2 % corresponding to the release of one mol SO₂ is in very good agreement with the analysed mass loss of 16.3 % at 150 °C.

$$(NH_4)[Hg(SO_3)_2]_{,s} \to (NH_4)_2SO_{4,s} + Hg_{,1} + SO_{2,g}$$
 (2)

After heating a large translucent single crystal up to 150 °C, (NH₄)₂SO₄ was the only phase observed by XRPD, and small mercury droplets were clearly visible on the surface of the now grey and opaque crystal whose shape was nearly unchanged compared with the original crystal. In a second decomposition range between 150 °C and 280 °C the overall mass loss is 61 % without a clear DSC effect. The same crystal that was heated now up to 240 °C retained its shape, but mercury droplets were no longer visible and the colour of the solid was light-grey, indicating that most of the mercury was evaporated at this temperature. The corresponding XRPD revealed traces of Hg₂SO₄, and (NH₄)₂SO₄ as the main phase. For the colourless and very hygroscopic material obtained at 310 °C, no mercury was found anymore by wet-chemical analysis. The third decomposition range between 280 °C and 410 °C goes along with two broad endothermic effects at ca. 290 °C and 405 °C. For a sample heated up to 410 °C, (NH₄)₃H(SO₄)₂ was the only phase assignable by XRPD and some additional weak reflections were present in the diffraction pattern. After the next decomposition range up to 460 °C and an overall mass loss of 95 %, the material (colourless X-ray amorphous melt) is stable to 560 °C. The decomposition of 2 is complete above 590 °C.

The thermal behaviour of **1** and **2** includes several decomposition reactions. Under oxidation of S^{IV} to S^{VI} , the first reaction step comprises a reduction of Hg^{II} to Hg^{I} for **1** and to elemental Hg for **2**, respectively. For the subsequent reactions the detailed thermolysis reactions for **1** and **2** remain mostly unclear. For **1** it is not possible to reason whether new crystalline mercury phases and/or new phases in the system NH_3 - H_2O - SO_4 are formed above 300 °C. Besides reflections of Hg_2Cl_2 and of the ammonium sulfates $(NH_4)_2SO_4$, $(NH_4)HSO_4$ and $(NH_4)_3H(SO_4)_2$, additional reflections are present in the diffraction patterns that could not be assigned to any known phase. Although for **2** no mercury was observed above $310 \,^{\circ}$ C by wet-chemical methods, some unknown diffraction pattern have also been observed for the decomposition products.

Hence, for a better insight into the decomposition mechanisms of **1** and **2**, TG/DSC experiments coupled with massspectrometric and/or vibrational spectroscopic measurements are necessary, but were not possible with the present experimental set-up.

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