

THERMOCHEMICAL ANALYSIS OF SOLVATE COMPLEXES OF  
SILVER DIMESYLAMINIDE\*

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SUMMARY

Two new solvate complexes of silver dimesylaminide with water and acetonitrile were analyzed using several thermoanalytic and calorimetric methods (thermogravimetry, differential scanning calorimetry, thermooptical analysis, solution calorimetry). The hydrate  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$  loses its crystal water above 120 °C. The dehydration is overlapped by a phase transition which occurs at 174 °C. The acetonitrile complex  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 2 \text{CH}_3\text{CN}$  decomposes between -15 and 95 °C. The existence of the hydrate complex is remarkable, because silver salts usually do not form hydrates. For this salt, the coordination of the water molecules to silver ions has been proved by X-ray structure determination.

INTRODUCTION

According to PEARSON's HSAB concept, the coordinative interaction between the "soft" Ag(I) ion and "hard" oxygen donor centres is expected to be rather weak. Actually this is corroborated by  $^1\text{H}$ -NMR evidence on aqueous Ag(I) solutions (ref. 1) and by the well-known scarcity of stable crystalline silver salt hydrates (ref. 2). During synthetic work using  $\text{AgN}(\text{SO}_2\text{CH}_3)_2$  as a reagent, we observed the intriguing fact that this compound, on crystallization from aqueous solutions, firmly includes "traces" of water which are thermally removed only at temperatures well above 100 °C. By X-ray crystallography, the stoichiometry of the supposed hydrate was established to be  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$ . In the solid structure the water molecules are simultaneously linked by O-Ag interactions to silver ions and, via hydrogen bonds, to oxygen atoms of the anions

\* Polysulfonylamines. XVI. - For part XV see  
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(ref. 3). From acetonitrile solutions of the hydrate or the water-free compound, a solvate of composition  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 2 \text{CH}_3\text{CN}$  is obtained, whose stoichiometry is notable, since silver(I) usually prefers coordination with four molecules of acetonitrile. It may be surmised that here the anions interact with the silver ions, occupying two coordination sites. (The X-ray crystallographic investigation of this compound is presently in progress.) The acetonitrile complex is easily and completely desolvated at moderate temperatures, providing a convenient source for finely divided, reactive  $\text{AgN}(\text{SO}_2\text{CH}_3)_2$ . By atmospheric water vapour, the acetonitrile complex is slowly trans-solvated, yielding quantitatively the more stable hydrate.

These findings prompted a detailed thermoanalytical investigation of the two solvates, on which we report hereafter.

## EXPERIMENTAL

### Chemicals

$\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$  was prepared by reacting an aqueous solution of  $\text{HN}(\text{SO}_2\text{CH}_3)_2$  with freshly precipitated and thoroughly water-washed silver(I) oxide (refs. 4, 5). The hydrate was obtained by crystallization from deionized water.

$\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 2 \text{CH}_3\text{CN}$  was prepared as needle-shaped crystals by slowly cooling a saturated solution of  $\text{AgN}(\text{SO}_2\text{CH}_3)_2$  in refluxing  $\text{CH}_3\text{CN}$  to room temperature.  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ ):  $\delta = 3.1$  (s, 6 H,  $\text{CH}_3\text{SO}_2$ ); 2.1 ppm (s, 6 H,  $\text{CH}_3\text{CN}$ ).  $\text{C}_6\text{H}_{12}\text{AgN}_3\text{O}_4\text{S}_2$  (362.19 g mol $^{-1}$ ), found: C 19.50, H 3.45, Ag 29.79%; calculated: C 19.90, H 3.34, Ag 29.78%. The acetonitrile is easily removed under the influence of moist air or temperatures above  $-15^\circ\text{C}$ , so particular care was necessary on investigating this compound.

Both compounds are sensitive to light. Prolonged exposure leads to some darkening of the surface of the crystals. When freshly prepared, both compounds are colourless.

The purity of the two substances was determined by  $^1\text{H-NMR}$  as well as with thermoanalytical purity determination according to VAN'T HOFF (e.g. ref. 6). All examined samples exceeded a purity of 99.5 mol%.

### Apparatus

The thermogravimetric studies were carried out with a Stanton-Redcroft STA 780 simultaneous thermal analyzer. As sample holders we used quartz or inconel crucibles in a combined TG/DTA hangdown.

The atmosphere was a constant flow of dry nitrogen (44 ml/min). The applied heating rates were in the range of 1 to 4 K/min.

For the differential scanning calorimetry we used the calibrated heat flux calorimeters Heraeus DTA 500 and Mettler FP 80/84 (ref. 7). Sealed aluminium pans served as sample holders. If not especially mentioned, they were pierced with a thin needle before starting the experiment to allow the evolved vapour to escape. The temperature interval studied was -100 to 260 °C. The heating rate was 2 to 5 K/min. The thermooptical measurements were carried out using the Mettler FP 80/84 instrument, which allows simultaneous DSC and TOA monitoring.

Solution calorimetry was executed by I. Steppuhn with an isoperibol solution calorimeter LKB 8700-1.

## RESULTS AND DISCUSSION

### $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$

A typical DSC-experiment using a sample of powdered salt is shown in Fig. 1. The vapour evolution starts at 120 °C and passes into the sharp peak of the phase transition, occurring at an onset temperature of  $174.4 \pm 0.3$  °C. Due to the superposition of both processes, only the sum of the enthalpies is directly measurable. The sum of dehydration enthalpy and phase transition enthalpy was determined by integration of the DSC-peak between 120 and 190 °C as  $18.42 \pm 0.49$  kJ mol<sup>-1</sup>. Several different attempts to separate the two enthalpies failed.

In a pierced capsule (i.e. when the water vapour is allowed to escape) the phase transition is irreversible. During cooling to 80 °C and repeated heating no deviation from the base line could be detected. On the contrary, in a closed capsule (see Fig. 2) during cooling a sharp exothermic peak at  $151.5 \pm 0.6$  °C is observed. The dehydration peak measured during the second heating is different from the dehydration peak of the first heating. The onset temperatures vary between 143 and 158 °C. As the capsules are not quite tight under the arising high pressures (ca. 8 bar), so that the water vapour can partly escape, no conclusions can be drawn from the obtained enthalpy values. It seems that the water is not completely rebuilt into the crystal.

A DSC-scan under reduced pressure (ca. 40 mbar) resulted in a curve which was only slightly different from the curves measured at standard pressure. Shape and temperature ranges of dehydration were nearly identical. This demonstrates the strongly bonded

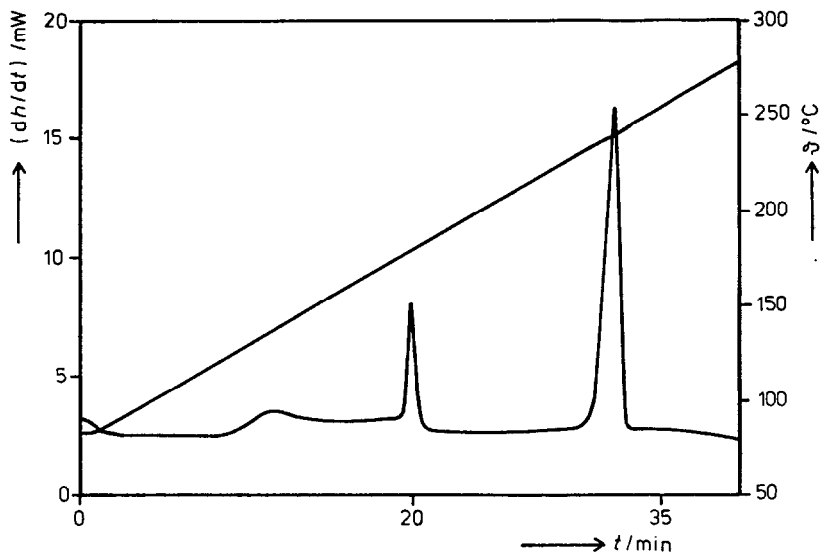


Fig. 1. DSC-scan of  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$  in a pierced aluminium capsule, showing dehydration, phase transition and melting.

crystal water.

With solution calorimetry we determined the enthalpy difference between the fresh and the fully dehydrated sample. This difference is equal to the sum of dehydration enthalpy and phase transition enthalpy. To obtain this value we dissolved one fresh and one dehydrated sample in water at 25  $^{\circ}\text{C}$ , respectively. The difference between the integral values of solution to the same final concentration resulted to  $7.56 \pm 0.16 \text{ kJ mol}^{-1}$ . This value is much smaller than the fore-mentioned value measured with DSC on account of the different measuring temperatures. The distinction is due to the different heat capacities and to the heat of evaporation of water, which is not included in the value obtained at 25  $^{\circ}\text{C}$ . If this is taken into account, the value from solution calorimetry agrees within 1.5% with the value from DSC.

The melting point in an open capsule, i.e. the melting point under standard pressure, was determined as  $237.7 \pm 0.3 \text{ }^{\circ}\text{C}$ , the enthalpy of fusion was  $26.48 \pm 0.69 \text{ kJ mol}^{-1}$ . The melting peak measured in a closed capsule (Fig. 2) obviously differs in shape, position and size from the melting peak shown in Fig. 1. In a closed capsule the water vapour readily dissolves in the liquid phase of the molten salt. There it acts as an impurity in the

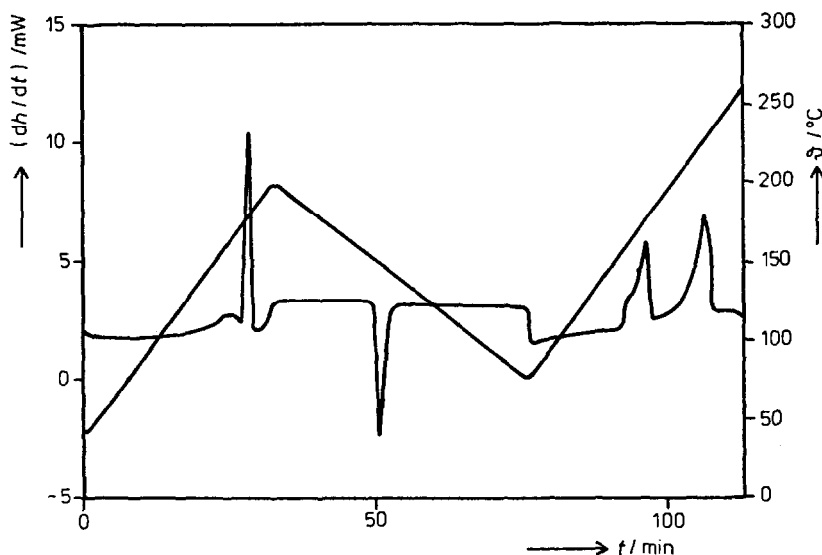
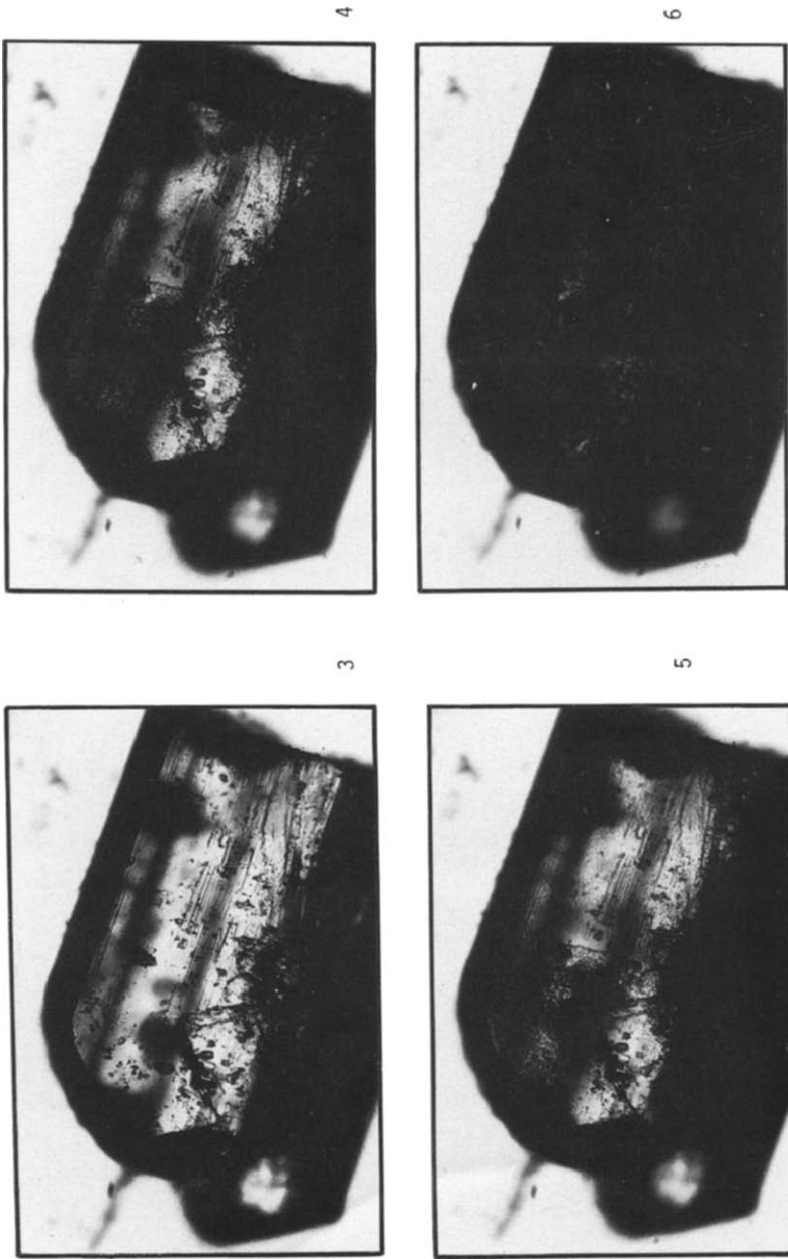


Fig. 2. DSC-scan of  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$  in a closed aluminium capsule (heating to 200 °C with 5 K/min, cooling to 70 °C with -3 K/min and renewed heating to 260 °C with 5 K/min), showing the reversibility of phase transition and dehydration.

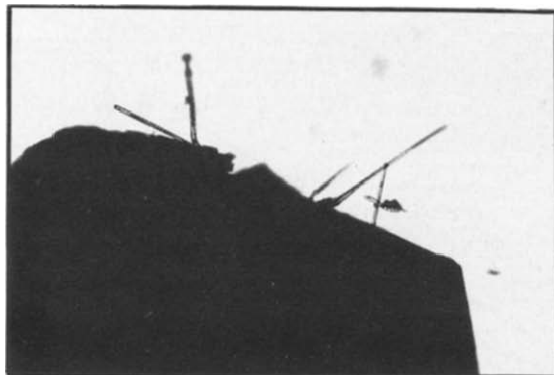
sense of VAN'T HOFFS law and consequently decreases the melting point. The enthalpy of fusion is decreased on account of the heat of condensation of the water vapour evolved during dissolution.

Thermooptical analysis of a single crystal (Figs. 3-6) shows the progress of the very fast phase transition. The photographs are taken at intervals of a few seconds. After the phase transition the crystal is yellowish and opaque. It is fragmented into many very small crystals although the external shape is preserved. This leads to a loss of transparency, so that the crystal appears dark under the microscope. During the phase transition long whiskers grow out of the sides of the crystal (Figs. 7-8).

The thermogravimetric analysis gave a resulting weight loss of  $1.63 \pm 0.08 \%$ . This value is close to the calculated value of 1.58%. Whereas powdered samples lose their crystal water continuously from 100 to 190 °C, larger crystals (diameter ca. 2 mm) dehydrate almost exclusively during the phase transition starting at 174 °C. This suggests a diffusion-controlled contracting volume mechanism of dehydration. In the molten phase exothermic decomposition, accompanied by weight loss, begins.



Figs. 3-6. Photographs of a single crystal of  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot \frac{1}{4} \text{H}_2\text{O}$  (diameter ca. 0.2 mm), taken on the Mettler FP 80/84 instrument. The figures show the progress of the phase transition at 174 °C. The photographs are taken at intervals of a few seconds. The magnification is 1:100 in all photographs.



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Figs. 7-8. Photographs of the whiskers grown out of the edges of a single crystal of  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 1/4 \text{H}_2\text{O}$  during the phase transition. The magnifications are 1:100 and 1:250.

#### $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 2 \text{CH}_3\text{CN}$

The thermogravimetrically determined weight loss gave the calculated value of 22.7 weight%. The two acetonitrile molecules are lost successively. The individual desolvation enthalpies could be measured with DSC (Fig. 9). The first acetonitrile molecule is set free from  $-15$  to  $60$  °C with a desolvation enthalpy of  $51.5 \pm 1.7 \text{ kJ mol}^{-1}$ , the second from  $60$  to  $95$  °C with a desolvation enthalpy of  $56.6 \pm 1.8 \text{ kJ mol}^{-1}$ . The temperature ranges determined by thermogravimetry are slightly different from the values obtained by DSC due to the different environment. However,

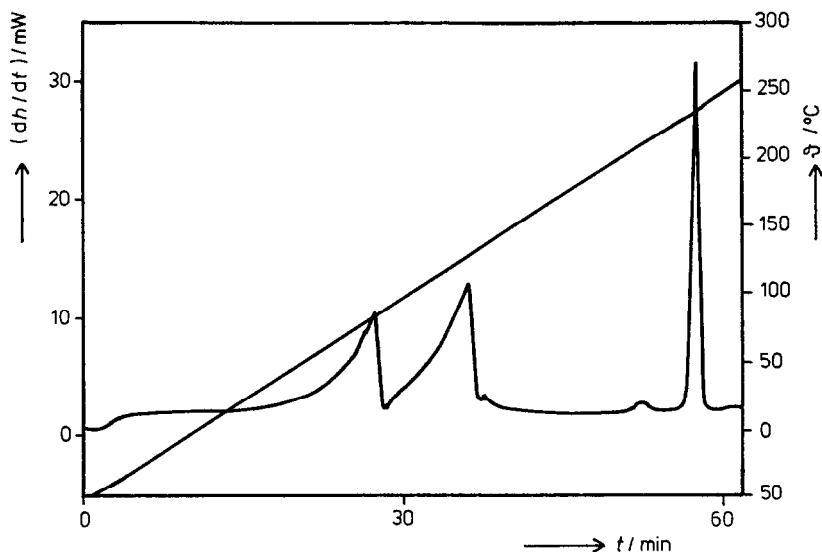


Fig. 9. DSC-scan of  $\text{AgN}(\text{SO}_2\text{CH}_3)_2 \cdot 2 \text{CH}_3\text{CN}$ , showing the successive evolution of the two acetonitrile molecules, the small endothermic peak at 190 °C (see text) and the melting process.

we consider the values obtained by thermogravimetry given above to be more relevant, because the atmosphere is better defined (approximately constant nitrogen atmosphere) and there is no obstruction for the gaseous acetonitrile to escape.

The enthalpy of fusion determined by DSC was  $25.20 \pm 0.66 \text{ kJ mol}^{-1}$ , the melting point  $230.5 \pm 0.3 \text{ °C}$ . Around 190 °C a small and broad endothermic peak appeared with enthalpy values between 0.1 and  $1.4 \text{ kJ mol}^{-1}$ . The onset temperature varied between 190 and 200 °C. A dependence of peak size and onset temperature on crystal size, desolvation grade or intruded water could not be detected. Possibly this effect results from an endothermic phase transition.

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