

THERMAL AND STRUCTURAL STUDIES ON $\text{Zn}(\text{NH}_3)_4\text{S}_2\text{O}_6$

G. Liptay¹, C. Varhelyi², L. Hiltunen³ and M. Leskelä⁴

¹Department of Chemistry, Budapest Technical University, H-1521 Budapest, Hungary

²Department of Chemistry, Babes-Bolyai University, R-3400 Napoca-Cluj, Romania

³Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo, Finland

⁴Department of Chemistry and Biochemistry, University of Turku, SF-2500 Turku, Finland

SUMMARY

Studies on preparation and thermal behaviour of tetraammine zinc(II) dithionate have been carried out. In the thermal decomposition between 100 and 350 °C the releasing order of gaseous products is NH_3 , $\text{SO}_2 + \text{NH}_3$ and 2 NH_3 and the final product above 350 °C is ZnSO_4 . Tentative structural studies have been made by means of single crystal X-ray diffraction method. The compound crystallizes in orthorhombic structure (space group $\text{Pmm}2_1$) with $a = 6.937$, $b = 6.365$, and $c = 12.285 \text{ \AA}$ and $Z = 2$.

INTRODUCTION

The chemistry and structures of dithionato complexes have been sparsely studied. This is probably due to the decomposition tendency of the $\text{S}_2\text{O}_6^{2-}$ ion. Only the structures of alkali dithionates and some $\text{MS}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ compounds ($M = \text{Mg}, \text{Ba}, \text{Ni}, \text{Zn}$) are known (refs. 1-5). In structure chemistry of metal complexes the dithionate ion has been used as counter anion (refs. 1,6). The only amminedithionate structure known so far is that of $\text{Cu}(\text{NH}_3)_4\text{S}_2\text{O}_6$ (ref. 1).

The synthesis of ZnS_2O_6 has been published already 80 years ago (ref. 7). The coordination of NH_3 ligands to zinc in ZnS_2O_6 is possible and the ammine complex has also been synthesized at the beginning of this century (ref. 7). Thermal stability of dithionates is limited because the dithionate ion decomposes to sulfate already above 150 °C. Earlier thermoanalytical measurements have shown that dithionato complexes containing also other ligands than $\text{S}_2\text{O}_6^{2-}$ are more stable than bare dithionato complexes (ref. 8).

In the present paper the thermal behaviour and tentative results from structural studies of $\text{Zn}(\text{NH}_3)_4\text{S}_2\text{O}_6$ are reported.

EXPERIMENTAL

Synthesis

$\text{Zn}(\text{NH}_3)_4\text{S}_2\text{O}_6$ powder was prepared by mixing ZnSO_4 and BaS_2O_6 solutions together in 1:1 molar ratio. The BaSO_4 precipitation formed was filtered off. The clear solution was treated by an excess of NH_3 solution. The microcrystalline precipitation formed was separated and washed by small amount of NH_3 solution.

In single crystal growth the clear ZnS_2O_6 solution obtained after separation of BaSO_4 was not directly treated with ammonia but covered together with a NH_3 solution (2-3 %) under a glass bell jar. The crystals were grown in 2-3 weeks.

Thermal analysis

The thermoanalytical investigations were carried out with a MOM-OD2 derivatograph simultaneously recording the TG, DTG and DTA curves. Typical sample weight was 200 mg and the heating rate was 5 °C/min. The measurements were carried out both in air and N_2 atmosphere. Platinum crucibles were used and in DTA measurements alumina was the reference material.

Some measurements were also carried out with a Netzsch 429 instrument equipped with a quadrupole mass spectrometer. These experiments were made in alumina crucibles. The intermediate and end products were also characterized by IR spectroscopy.

X-ray diffraction

The X-ray diffraction studies were made with a Syntex P2₁ automatic four-circle diffractometer employing graphite monochromatized $\text{MoK}\alpha$ -radiation. The unit cell parameters were calculated by least-squares refinement of 25 reflections. The intensities of 965 reflections were collected and the 815 reflections with $I > 3 \sigma(I)$ were considered significant and used in structure determination. The systematic absences in the original intensity data indicated the space group $\text{Pmn}2_1$ (No. 31). The positions of Zn and S atoms were obtained by direct methods. The structure solving and refinements were carried out with SHELX-76 program package (ref. 9). The structure was refined to an R-value of 6.5 % by using unisotropic temperature factors for Zn and S atoms and isotropic factors for N and O atoms. Hydrogen atoms could not be found in the difference Fourier map.

The details of the structure determination will be given elsewhere as soon as better results will be obtained. Obviously because of the poor quality of

the crystals some disorder in oxygen positions was observed.

RESULTS AND DISCUSSION

Thermal analysis

Figure 1 shows the TG, DTG and DTA curves of the crystalline tetra-amminezinc(II) dithionate. The thermal decomposition begins above 100 °C. The small weight-decrease before 100 °C means loss of adsorbed water molecules. This weight loss fails if the sample is carefully dried.

The decomposition process contains four separated stages. The first stage occurs between 100 °C and 180 °C and according to the weight loss it corresponds the loss of one NH₃ molecule. In the second decomposition step which occurs between 180 °C and 250 °C the material loses both one NH₃ and one SO₂ molecule. The TG curve does not contain any clear plateau of Zn(NH₃)₂SO₄ but gradual decomposition continues. The third decomposition step between 250 °C and 300 °C represents again the loss of one ammonia molecule. The last decomposition process above 300 °C is complex (several peaks in the DTG curve) but the weight change corresponds roughly to one NH₃ molecule.

According to the DTA curve the first three processes are exothermic as can be expected. Surprisingly the fourth decomposition stage shows exothermic peaks in air. In nitrogen this stage is neither complex nor exothermic but simply an endothermic step. Similar observations have been observed by us earlier (ref. 10,11). If the measurements are carried out in platinum crucible in static air and the decomposition produces NH₃ above 300 °C the Pt walls of the crucible catalyze the oxidation reaction of NH₃. This oxidation reaction is exothermic and the degradation is proved only as an apparent side reaction.

The reaction mechanisms presented above were also confirmed by IR spectroscopy and mass spectroscopy. The isolation of intermediate products for IR measurements was made by lifting the furnace at right temperature and allowing the sample to cool rapidly. After the first reaction step the IR spectrum showed a change only in the range characteristic for S₂O₆²⁻. The bands shifted to lower energies and the band at 1000 cm⁻¹ splitted to a doublet. This indicates changes in the structure and that the bonds become looser. After the second decomposition step the bands of S₂O₆²⁻ were very weak and the bands characteristic for sulfate ion dominated. The spectra after the third and fourth steps both showed the presence of SO₄²⁻. The difference between these spectra was in the absence of NH₃ absorptions after the fourth step.

The results obtained from the studies of gaseous products by a TG/MS equipment were consistent with the TG and IR measurements. The mass spectra

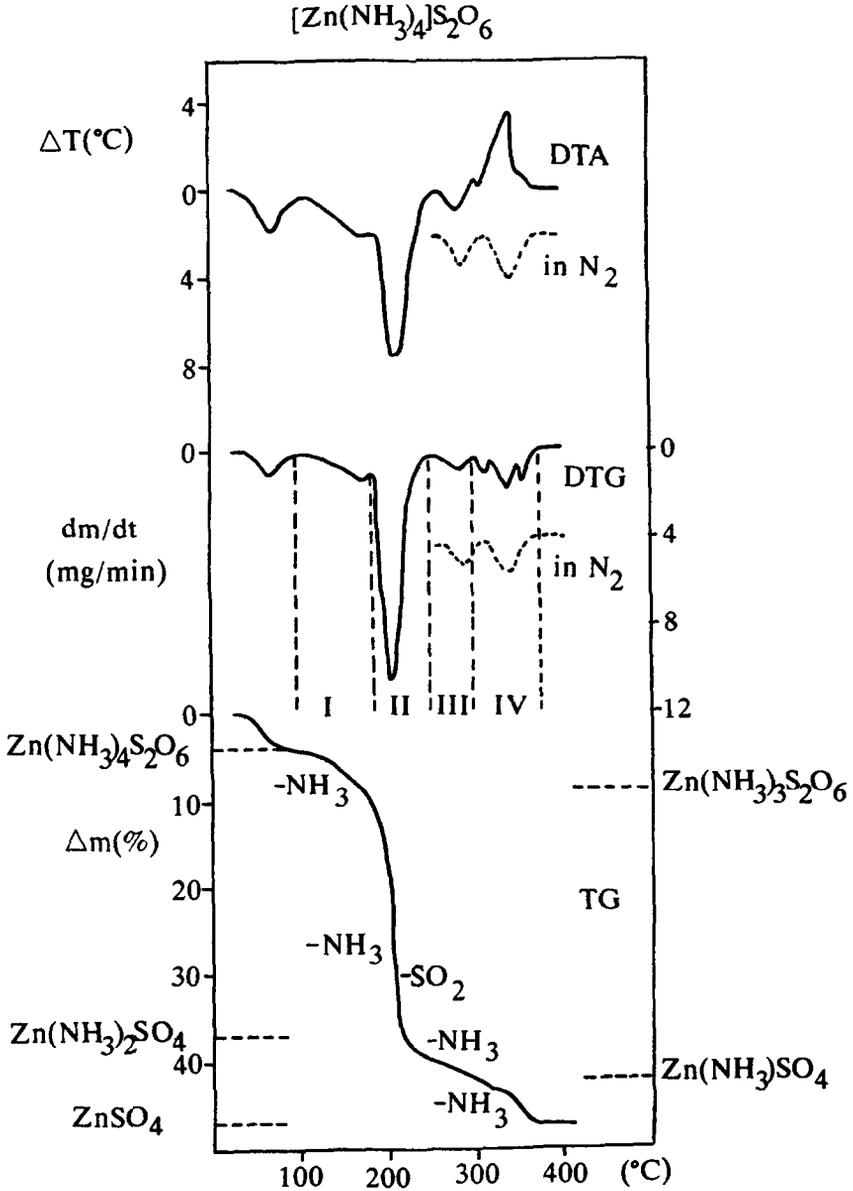


Fig. 1 The TG, DTG, and DTA curves of $\text{Zn}(\text{NH}_3)_4\text{S}_2\text{O}_6$ in static air (solid line) and in nitrogen (dotted line) atmosphere.

showed that in the first, third and fourth decomposition step NH_3 was the main gaseous product. In the second step both NH_3 and SO_2 were liberated.

X-ray diffraction

The structural studies showed that both the zinc and sulfur atoms lie in special positions. The coordinates for Zn atoms are $x = 0$, $y = 0.1423$, $z = 0$, for S(1) atom $x = 0.5$, $y = 0.3426$, $z = 0.8112$ and for S(2) atom $x = 0$, $y = 0.3308$, $z = 0.3479$. The nitrogen atoms locate tetrahedrally around the zinc ion and the Zn-N distances vary between 2.02-2.07 Å. The dithionate ion is not coordinated to the zinc atom. The situation is similar as found for example in zinc tetraammine halides (ref. 12).

The S-S distance in the dithionate ion is 2.127 Å. Sulfur-oxygen distances vary between 1.405 - 1.435 Å but there exists some disorder in the positions of the oxygen atoms. The detailed description of the structure will be published elsewhere as soon as better crystal and data are available.

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