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Formation and Characterization of Bisthiourea Zinc Formate

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Formation of a new complex in the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system at 25 °C was established by the solubility method. Its composition was determined to be $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$. The bisthiourea zinc formate (BTZF) is an incongruently soluble salt at 25 °C. It has been characterized by X-ray powder diffraction, IR spectroscopy and thermal analysis. The infrared spectra reveal that thiourea forms a zinc-sulfur bond. Thermal decomposition at a temperature of 400 °C yields ZnS.

INTRODUCTION

A number of studies on metal coordination compounds of thiourea with inorganic salts have been reported recently. The great interest in these compounds is due to their non-linear optical properties.[1–5] However, papers dealing with the thiourea complexes of metal formates are comparatively scarce. The existence of a complex salt, $Zn(HCOO)_2 \cdot CS(NH_2)_2$ (1:1), has been reported by Gyoryova *et al.*[6] It was obtained by a preparative method at high temperature. The complex salt $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ (1:2) is also known, its crystal structure being determined by Nardelli *et al.*[7,8] The latter complex salt was found in the $Cd(HCOO)_2$-$CS(NH_2)_2$-CH_3OH system as well.[9] It was of interest to study the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system, since a thorough investigation would give more information on the solid phases formed in this system at an appropriate temperature.

The present paper aims to study the solubility diagram of the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system at 25 °C and to characterize the new solid phase obtained using X-ray powder diffraction, IR spectroscopy and thermal analysis. There are no literature data on solubility in the system.

EXPERIMENTAL

Materials

The zinc formate was prepared by neutralizing dilute formic acid (1:1) with zinc hydroxy carbonate at 70–80 °C. The solution was filtered and concentrated. The crystals were obtained after cooling the solutions to room temperature, then recrystallized from distilled water and dried in air. Chemical and X-ray powder analyses showed that $Zn(HCOO)_2 \cdot 2H_2O$[10] was obtained. The thiourea and other reagents used were of analytical grade.

Solubility Method

The solubility in the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system was studied by the Khlopin method of isothermal decrease of supersaturation;[11] aqueous solutions containing both salts

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TABLE I. Solubility in the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system at 25 °C

Liquid phase, *w* / %		Wet solid phase, *w* / %		Solid phase
$Zn(HCOO)_2$	$CS(NH_2)_2$	$Zn(HCOO)_2$	$CS(NH_2)_2$	
5.38	–	–	–	$Zn(HCOO)_2 \cdot 2H_2O$
8.23	9.85	60.92	2.83	$Zn(HCOO)_2 \cdot 2H_2O$
12.01	19.07	65.07	4.74	$Zn(HCOO)_2 \cdot 2H_2O$
15.32	25.45	63.12	7.11	$Zn(HCOO)_2 \cdot 2H_2O$
15.90	25.55	51.93	24.45	eutonics
15.82	25.92	38.95	42.25	$Zn(HCOO)_2 \cdot 2CS(NH_2)_2$
16.07	30.18	37.03	41.78	$Zn(HCOO)_2 \cdot 2CS(NH_2)_2$
17.09	33.22	39.87	44.79	$Zn(HCOO)_2 \cdot 2CS(NH_2)_2$
18.51	36.00	38.01	44.62	$Zn(HCOO)_2 \cdot 2CS(NH_2)_2$
18.32	36.08	23.27	66.93	eutonics
18.07	35.82	6.15	78.53	$CS(NH_2)_2$
15.09	32.12	5.24	76.20	$CS(NH_2)_2$
10.93	28.00	4.75	71.32	$CS(NH_2)_2$
5.29	20.67	2.63	67.05	$CS(NH_2)_2$
–	13.39	–	–	$CS(NH_2)_2$

taken, in different ratios, were prepared at 60–70 °C, then they were cooled in a thermostat at 25 °C and stirred until constant concentration of the saturated solution, *i.e.*, equilibrium, was achieved. Preliminary experiments showed that the equilibrium in the system was attained in about 15–20 h. The suspension was then filtered and the liquid and wet solid phases were analyzed. The concentration of zinc ions in both phases were determined complexometrically at pH = 10 using Eriochrome Black T as indicator.[12] The amount of thiourea was evaluated after oxidation with hydrogen peroxide to sulfate ions and determination of the latter by the standard gravimetric analysis.[13] The solid phase composition was determined by the graphic method of Schreinemakers for wet residues.[14]

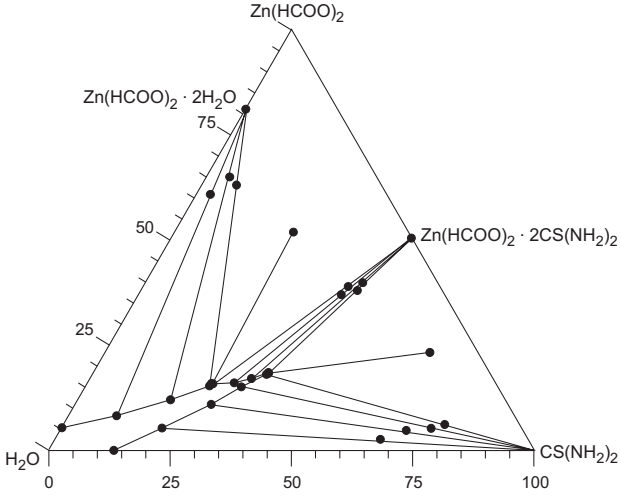

Figure 1. Solubility diagram of the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system at 25 °C (*w*/%).

Apparatus

X-Ray diffraction analysis was carried out with a DRON-3 powder diffractometer using Cu-Kα radiation with a nickel filter at a scanning speed of 1 ° min^{-1} in a 2θ diffraction interval of 10–60 °. The infrared spectra were recorded on a Bruker model IFS 25 Fourier transform interferometer (resolution < 2 cm^{-1}) using KBr discs as matrices. Ion exchange or other reactions with KBr were not observed. Thermal investigations were performed on a Paulik-Paulik Erday MOM OD-102 derivatograph. DTA and TG curves were obtained in a static air atmosphere with a sample mass of 125 mg, at a heating rate of 10 °C min^{-1} from ambient temperature to 700 °C using a standard corundum crucible. The reference substance was pure α-Al_2O_3.

RESULTS AND DISCUSSION

Solubility Diagram

Solubility data for the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system at 25 °C are listed in Table I, and the solubility phase diagram is shown in Figure 1. They are expressed in mass fraction, *w*/%. Three crystallization fields are distinguished in this diagram: wide fields of $Zn(HCOO)_2 \cdot 2H_2O$ and $CS(NH_2)_2$, and a narrow crystallization field of the complex salt $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$ (1:2). The complex compound crystallizes from solutions containing 15.90 % zinc formate and 25.55 % thiourea up to solutions containing 18.32 % zinc formate and 36.08 % thiourea. The solubility diagram data show unambiguously that at 25 °C a complex salt (composition 1:2) was obtained. The compound reported by Gyoryova *et al.* was synthesized by the reaction in water solutions at 40–80 °C using zinc formate and thiourea in stoichiometric ratios.[6]

TABLE II. X-ray diffraction data of $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$

d_{obs} /Å	*I*/*I*o	d_{obs} /Å	*I*/*I*o
6.177	100	2.239	29
6.054	84	2.172	3
5.744	60	2.131	10
5.594	90	2.083	12
4.910	19	2.060	5
4.492	60	2.044	10
4.303	10	2.008	7
4.161	15	1.967	14
3.615	90	1.948	5
3.522	11	1.907	11
3.475	15	1.883	11
3.395	45	1.845	4
3.193	7	1.802	8
3.091	84	1.748	8
3.060	57	1.718	13
3.015	75	1.709	15
2.873	33	1.686	6
2.782	60	1.672	4
2.736	7	1.645	8
2.670	17	1.622	3
2.602	10	1.591	4
2.458	14	1.597	3
2.385	5	1.565	3
2.348	13	1.543	9
2.310	9	1.525	3

The solid phases were isolated from the system by filtering, washing with alcohol and drying in air, and then identified by chemical analysis, X-ray powder diffraction, IR spectroscopy and DTA.

$Zn(HCOO)_2 \cdot 2CS(NH_2)_2$ forms colorless crystals. Chemical analysis shows 50.67 % $Zn(HCOO)_2$ and 49.68 % $CS(NH_2)_2$, (theoretical composition: 50.51 % and 49.49 %, respectively).

X-Ray and IR Spectroscopy

X-ray powder diffraction analysis confirms the results of the solubility diagram data, indicating the formation of three solid phases in the system. The diffraction pattern of BTZF differs from those of $Zn(HCOO)_2 \cdot 2H_2O$[10] and $CS(NH_2)_2$.[15] The d-spacings and relative intensities of 50 reflections are given in Table II.

Frequencies, assignment and relative intensities of the bands of the formate groups and thiourea in the infrared spectra of BTZF in the region 4000–400 cm^{-1} are summarized in Table III and are shown in Figure 2. The assignments of the bands of $HCOO^-$ were done by analogy to the studies on metal formate (simple and double salts)[16–20] and those of $CS(NH_2)_2$ – to the studies on metal thiourea complexes.[1,2,21–23]

Crystal structures of a number of metal thiourea complexes have been determined by X-ray diffraction: in all the cases, only sulfur-metal bonds were found to be present.[24–30] In the crystal structure of $Cd(HCOO)_2 \cdot 2CS(NH_2)_2$ (1:2), a Cd-S bond was established as well.[8] According to literature data,[1,2,21–23] differences between the thiourea itself and all its metal complexes are confined to two bands only. Upon complex formation, the band of thiourea at 1412 cm^{-1} is split and that at 730 cm^{-1} is both split and shifted to a lower frequency. These bands corresponds to the antisymmetric and symmetric C-S stretching vibrations and they split because of the formation of a metal-sulfur bond.[22]

It can be seen from Table III and Figure 2 that the antisymmetric C-S stretching vibrations are split into two bands at 1431 and 1402 cm^{-1} and the symmetric C-S stretching vibrations are split into two bands at 715 and 707 cm^{-1} (shoulder) and shifted to lower frequencies.

TABLE III. Infrared spectral data (cm^{-1}) and band assignments for $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$

Wavenumber / cm^{-1}	Assignment
3428 s	ν_{as} N-H stretch
3360 sh	
3317 m	
3270 sh	ν_s N-H stretch
3127 s	
2925 w	ν_1 C-H stretch
2846 m	
2745 w	$2\nu_5$ $HCOO^-$
2703 sh	
1671 s	δ NH_2
1638 vs	
1620 vvs	ν_4 as COO stretch
1602 vs	
1522 m	ν_{as} C-N
1431 w	ν_{as} C-S
1402 m	
1384 m	ν_5 in-plane C-H bend
1327 s	ν_2 sym COO stretch
1115 w	ν_s C-N
1075 vw	ν_6 out of plane C-H bend
781 m	ν_3 sym O-C-O deformation
715 m	ν_s C-S
707 sh	
640 m	t NH_2
581 m	δ_{as} N-C-N def
487 m	δ_s S-C-N def
414 w	δ_s N-C-N def

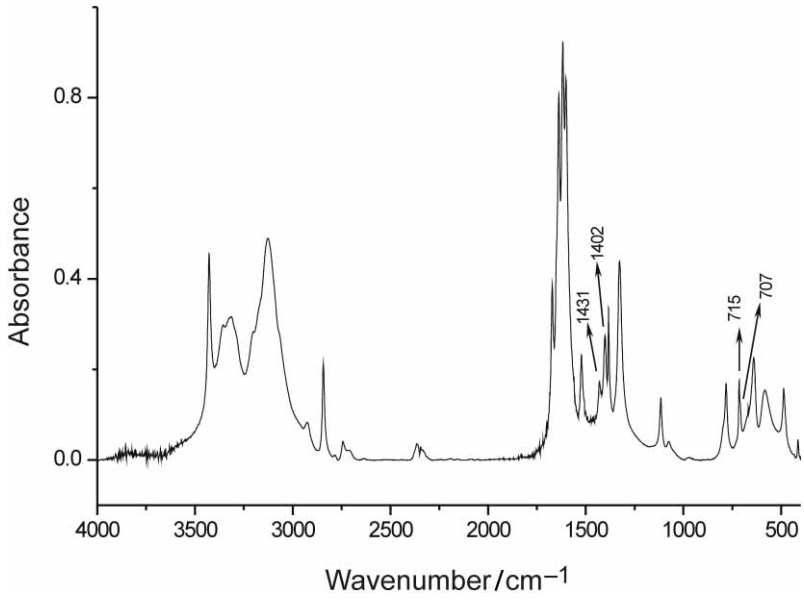

Figure 2. IR spectra of $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$ in the 4000–400cm^{-1} region.

These spectral data are an indication of the existence of the zinc-sulfur bond in bisthiourea zinc formate.

The high frequency N-H absorption bands in the region 3100–3400 cm^{-1} in the thiourea spectrum were not shifted to a lower frequency upon formation of the metal--thiourea complex, indicating that nitrogen to zinc bonds are not present and that the bonding must be between sulfur and zinc atoms.[23] The bands of BTZF in this region were not shifted to a lower frequency according to the literature data of metal thiourea complexes.[1,2,21–23]

Thermal Analysis

The thermal behavior of BTZF has been studied by TG and DTA and the derivatogram is presented in Figure 3. The results coincide with those of analogous compounds of thiourea with inorganic salts:[1,6,9,31–33] the melting takes place at the beginning, followed by complicated processes of thermal decomposition.

Under our experimental conditions, the BTZF is stable up to about 100 °C. Melting of the compound is observed at 120–140 °C. Melting is registered on the DTA curve with an endothermal effect at about 130 °C (there is no mass loss on the TG curve).

Thermal decomposition of the melting salt begins at about 150–160 °C. The two processes, decomposition of the complex salt and decomposition of thiourea and zinc formate, occur simultaneously. For this reason, the thermal decomposition of BTZF is complicated and produces endo- and exothermal effects.

The X-ray diffraction of the sample obtained after heating at 400 °C for several hours shows ZnS.[34] The ZnS is unstable in the air at a higher temperature and oxidized by oxygen from the air to ZnO. According to the X-ray diffraction, the sample obtained after heating at 650 °C is ZnO.[35]

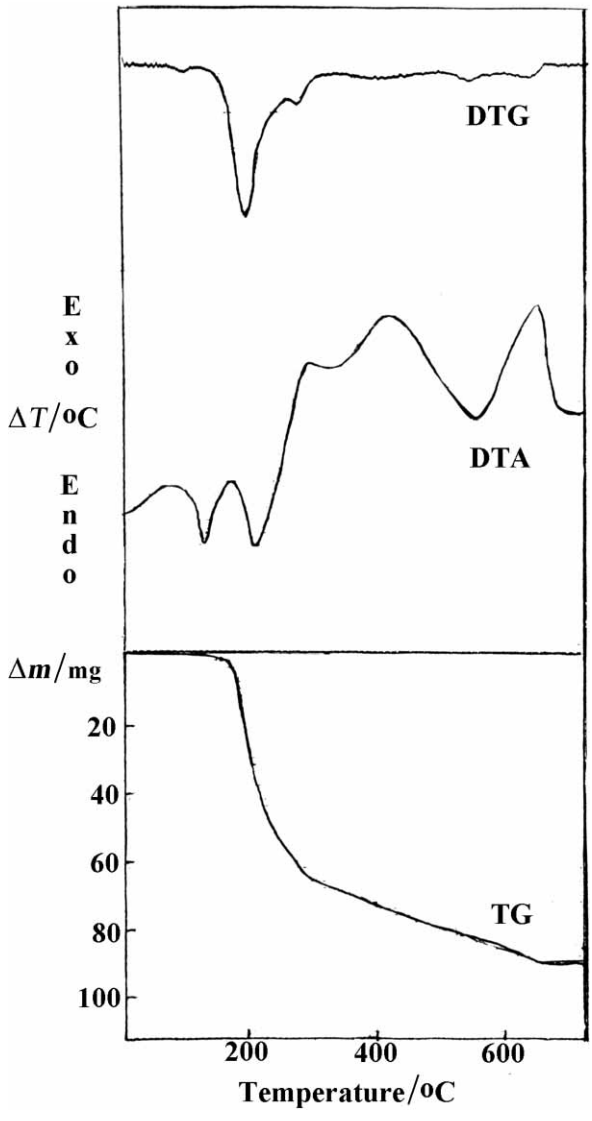

Figure 3. TG, DTA and DTG curves of $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$.

CONCLUSION

The solubility diagram of the $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O system at 25 °C has been investigated, showing the existence of a complex salt of the composition $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$, which is incongruently soluble at this temperature.

The X-ray diffraction data show that three solid phases were obtained in the system. The functional groups present in the BTZF were confirmed by IR spectral analysis. It is also evident from the IR studies that thiourea is bonded to zinc formate through sulfur. The DTA and TG data were in agreement with those of similar metal thiourea complexes, including melting and complicated processes of thermal decomposition. ZnS was obtained at a temperature of 400 °C.

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SAŽETAK

Nastajanje i karakterizacija bistiourea cinkovoga formata

Violeta Z. Vassileva i Petranka P. Petrova

Ustanovljeno je da metodom topljivosti u sustavu $Zn(HCOO)_2$-$CS(NH_2)_2$-H_2O pri 25 °C nastaje novi kompleksni spoj. Određivanje sastava pokazalo je da se radi o $Zn(HCOO)_2 \cdot 2CS(NH_2)_2$. Pri 25 °C bistiourea cinkov format (BTZF) neprimjereno je topljiva sol. Spoj je opisan rentgenskom difrakcijom na prahu, IR spektroskopijom i termičkom analizom. U infracrvenom spektru otkrivena je vrpca koja odgovara vezi cink-sumpor. Termički raspad spoja završava kod temperature 400 °C pri čemu zaostaje cinkov sulfid.