

Note

THERMAL DECOMPOSITION OF AN UNUSUAL COMPLEX OF COPPER SULFATE WITH ACETAMIDE

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Most complexes of acetamide with first row transition metals involve compounds containing singly charged anions, and complexes of metals near the end of the period are rare. Recently, the first complex of acetamide with copper sulfate was described [1]. The complex was formulated as the 2 : 1 complex, $\text{CuSO}_4 \cdot 2 \text{CH}_3\text{CONH}_2$. Although X-ray and spectral data were presented, no thermal studies were described. It was reported that complexes of cobalt, nickel, and zinc could not be obtained by the same synthetic method used to prepare the copper complex. There was no indication as to the reason for the instability of these complexes. Accordingly, we have prepared a complex of acetamide with copper sulfate, and this report describes synthetic and thermal studies on that complex.

EXPERIMENTAL

Barvinok and Mashkov [1] reported that $\text{CuSO}_4 \cdot 2 \text{CH}_3\text{CONH}_2$ was obtained by heating finely ground copper sulfate pentahydrate and acetamide in a mole ratio of 1 : 10 at 90°C for 2 h with periodic mixing. This method of preparation was used in this work. However, as will be described later, the light green product appeared not to contain 2 moles of acetamide per mole of CuSO_4 . It appears that the product is instead $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$ and that it retains approximately one molecule of water per molecule of complex.

In an alternate method, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ was dehydrated by heating at 150°C until a constant weight was obtained. The complex with acetamide was prepared by a method similar to that previously described [2]. Anhydrous CuSO_4 was refluxed with a methanol solution of acetamide so that the ratio of acetamide to copper sulfate was 10 : 1. After refluxing for 2 h, the mixture was cooled and the light blue product was separated. It was washed several times with hot dichloroethane and acetone to remove the excess acetamide. TG studies showed that the product was anhydrous and contained no volatile solvent. Sulfate was determined gravimetrically as BaSO_4 [3]: calcd. for $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$, 37.6%; found, 38.7%. The amount of ligand present was established by TG: calcd., 35.7%, found, 34.7%.

Thermogravimetric analysis was carried out using a Perkin-Elmer thermogravimetric system Model TGS-2. Procedures employed were similar to those previously described [4]. Data were analyzed according to the Coats and Redfern method [5] using the equations

$$\ln \ln \frac{1}{1-\alpha} - 2 \ln T = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (1)$$

when $n = 1$ and, when $n \neq 1$

$$\ln \left[\frac{1 - (1-\alpha)^{1-n}}{(1-n) T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (2)$$

Computations were carried out for $n = 0, 1/3, 2/3, 1$ and 2 using a Texas Instruments TI-59 programmable calculator with a program previously described [6].

RESULTS AND DISCUSSION

TG curves obtained for the CuSO_4 complex with acetamide prepared by the method of Barvinok and Mashkov showed a gradual loss of mass amounting to about 5% in the range $70\text{--}150^\circ\text{C}$. Assuming that the starting complex is actually $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2 \cdot \text{H}_2\text{O}$, the loss of H_2O would correspond to a loss of 6.7%. Two separate preparations behaved identically. Therefore, it appears that the product that we obtained by the method of Barvinok and Mashkov [1] was not the expected $\text{CuSO}_4 \cdot 2 \text{CH}_3\text{CONH}_2$ but rather $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2 \cdot \text{H}_2\text{O}$, and it was light green in color rather than the reported light blue. By starting with anhydrous CuSO_4 and a solution of acetamide in methanol, refluxing the mixture produced an anhydrous, unsolvated product that was light blue. However, it too contains only 1.5 moles of ligand per mole of CuSO_4 . It thus appears that neither method used in this work exactly replicates the preparation described by Barvinok and Mashkov [1].

After the dehydration of the product obtained by the method of Barvinok and Mashkov, the decomposition was virtually identical to that of the light

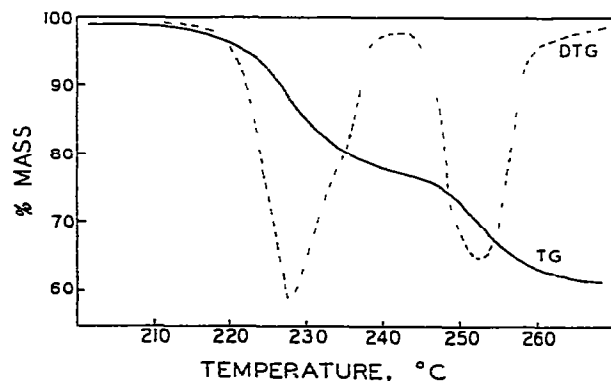
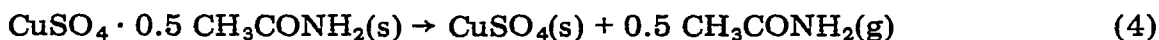
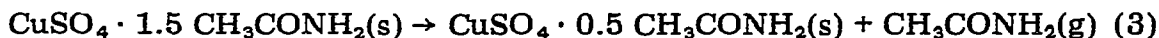


Fig. 1. TG and DTG curves for the decomposition of $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$.

blue $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$ prepared by the method of Farran and House [2]. TG and DTG curves for the decomposition of $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$ are shown in Fig. 1. The decomposition is a two-step process occurring as follows



These processes occur in the ranges 210–240°C and 245–260°C, respectively. The calculated mass losses for these processes are 23.8 and 11.9% while the mean values observed are 21.6 and 12.1%, respectively. It is interesting that a temperature which is approximately the same as the boiling point of acetamide must be reached before significant decomposition occurs. This may indicate that the complexes are not really stable at a temperature of greater than 200°C but that there is simply no way for acetamide to be evolved at lower temperatures.

Table 1 shows data for the reactions represented by eqns. (3) and (4). In all runs, both reactions gave the highest correlation coefficients when the data were fit to the second-order Coats and Redfern equation. Activation energies for both steps of the decomposition are higher than the expected metal–ligand bond energies unless chelation occurs. It is likely that the structure of $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$ involves one acetamide chelated on each copper center and one acetamide bridging between two copper centers. Sulfate coordination could then complete the coordination sphere of each copper ion. The sulfate groups can function as monodentate or bidentate ligands as required [7]. Therefore, the two-step process could represent the loss of terminal acetamide (one molecule per copper ion) as the first reaction and the loss of the bridging acetamide (one molecule for each two copper ions) as the second reaction. This difference could reflect the much higher activation energy for the latter process.

Barvinok and Mashkov [1] reported that the acetamide complexes of nickel, cobalt, and zinc could not be obtained using their method of synthesis. We are currently exploring the synthesis of acetamide complexes of these metals using our previously described method [2]. The thermal studies carried out in this work reveal no unusual stability characteristics of the

TABLE 1

Reaction parameters for the decomposition of $\text{CuSO}_4 \cdot 1.5 \text{CH}_3\text{CONH}_2$

Reaction	Temp. range (°C)	Mass loss		Correlation coefficient ^{a,b}	E_a^a (kJ mole ⁻¹)
		Calcd.	Found ^a		
(1)	210–240	23.8	21.6 ± 0.4	0.9986 ± 0.0012	410 ± 4
(2)	245–260	11.9	12.1 ± 0.2	0.9976 ± 0.0013	734 ± 15

^a Shown as mean value ± standard deviation.

^b For fitting data to the second-order Coats and Redfern equation.

acetamide complex of copper studied here that would indicate any reason why the complexes with other metals would be so unstable as to be impossible to prepare by other methods.

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