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ON THE NATURE OF ISOMERISM IN OXALATECOPPER(II) DIAMMINE

THERMAL DECOMPOSITION OF α-, β-, AND γ-$Cu(C_2O_4)(NH_3)_2$

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ABSTRACT

The mechanisms of the thermal decompositions of various isomers of $Cu(C_2O_4)(NH_3)_2$ were studied in this work. Data were obtained by the DSC technique and Derivatograph as well as infrared spectra and chemical analysis. The destruction of the complexes was found to take place in three steps—the first two of them being endothermic, and the third one exothermic. The values of ΔH_1, apparent activation energy and stoichiometry of the first step of destruction suggest that certain differences in bonding of the oxalate groups in each isomer lead to quite significant differences in their thermal decomposition.

INTRODUCTION

As part of a general study[1–3] of isomerism of Cu(II) complex compounds, in this paper we study the conditions of preparation and structures of α-, β-, and γ-$Cu(C_2O_4)(NH_3)_2$. (Two of them have been studied before[4].) We have established that differences between modifications resulted from a different type of bonding of the oxalate group to the central atom, and also from different distortions of the coordination polyhedron around Cu(II). While α-$Cu(C_2O_4)(NH_3)_2$ is Cu(II) surrounded with ligands in the form of a prolongated tetragonal bipyramid[1] β-$Cu(C_2O_4)(NH_3)_2$ probably takes the form of a compressed one[2]. There is no detailed information on the structure of the γ modification, although its infrared spectrum shows a more symmetric coordination of the oxalate group[3] as is the case for the α modification.

This work was directed towards obtaining information on the course of reactions taking place during thermal decomposition of the modifications of $Cu(C_2O_4)(NH_3)_2$, and to find out to which extent these processes are influenced by structural differences. The problem of energetic differences between the prolongated and the compressed tetragonal bipyramids as well as their different reactivity in substitution reactions was theoretically solved by Bersuker[5] for the complexes with a homogeneous coordination sphere. However, the complexes under study have a heterogeneous coordination sphere, and the reaction mechanism is also complicated due to the polymeric structure of $Cu(C_2O_4)(NH_3)_2$. That is the reason why we did not try to solve the "intimate" mechanism[6] of reactions taking place during thermal decomposition of the $Cu(C_2O_4)(NH_3)_2$ modifications.

EXPERIMENTAL

The studied complexes have been prepared by methods previously described[2–4]. The composition of complexes and intermediates of thermal decomposition (Table I) has been analytically controlled using complexometric (Cu(II)), magnetic (C_2O_4) and distillation (NH_3) methods.

TABLE I

ANALYTICAL DATA FOR α-, β- AND γ-$Cu(C_2O_4)(NH_3)_2$

Compound	*% Cu*		*% C_2O_4*		*% NH_3*	
	found	*calc.*	*found*	*calc.*	*found*	*calc.*
α-$Cu(C_2O_4)(NH_3)_2$	34.22	34.24	47.55	47.42	18.18	18.35
β-$Cu(C_2O_4)(NH_3)_2$	34.13	34.24	47.17	47.42	18.05	18.35
γ-$Cu(C_2O_4)(NH_3)_2$	34.20	34.24	47.42	47.42	18.25	18.35
Intermediate of thermal decomposition of						
α-$Cu(C_2O_4)(NH_3)_2$	37.10	37.69[a]	51.05	52.22[a]	11.05	10.09[a]
β-$Cu(C_2O_4)(NH_3)_2$	37.33	37.69	50.30	52.22	11.70	10.09
γ-$Cu(C_2O_4)(NH_3)_2$	36.47	37.69	45.79	52.22	14.38	10.09
Final product of thermal decomposition of						
α-$Cu(C_2O_4)(NH_3)_2$	77.5	79.88[b]	—	—	—	—
β-$Cu(C_2O_4)(NH_3)_2$	77.5	79.88				
γ-$Cu(C_2O_4)(NH_3)_2$	73.83	79.88				

[a] Calculated for $Cu(C_2O_4)(NH_3)$.
[b] Calculated for CuO.

The type of bonding between the oxalate groups and ammonia molecules to the central atom has been studied by infrared spectra, using a nujol-suspension technique in a Perkin–Elmer 137 spectrophotometer.

Thermal decompositions of the $Cu(C_2O_4)(NH_3)_2$ modifications have been studied on the Derivatograph OD 120 (MOM Budapest). The measurements were carried out in a platinum crucible with Pt–Pt,Rh thermocouples in an air atmosphere. The sample weight was 100 mg, the temperature increase 3 deg min^{-1} and the galvanometer's sensitivity: DTA 1/10, DTG 1/10. For measuring the heats of decomposition a Perkin–Elmer differential scanning calorimeter, Model DSC-1B, calibrated by melting point of pure indium (429 °K), was used. Samples weighing about 5 mg (accuracy ±0.02 mg) have been placed in aluminium sample pans with pierced covers to permit gaseous decomposition products to escape. The temperature range over which most reactions were studied was 157 to 287 °C, usually scanned at 8 deg min^{-1}. All of the measurements were carried out under a dry nitrogen atmosphere. From the obtained DSC curves, using the method[7] the values E_A (apparent activation energy) and n (reaction order) have been determined as well. The values of decomposition heat (ΔH), apparent activation energies (E_A) as well as reaction orders (n) are shown in Table II. The uncertainties are expressed as the standard deviation of the mean.

RESULTS AND DISCUSSION

As the data obtained from the Derivatograph show, the thermal decompositions of α-, β- and γ-$Cu(C_2O_4)(NH_3)_2$ start at about 200 °C (Fig. 1). The thermogravimetric curves indicate for all three modifications a one-step reaction leading to CuO formation. However, the DTG and DTA curves do not imply a one-step reaction. On the contrary, they indicate that the reaction is divided into three steps, different for each modification. To establish differences in thermal decomposition of the complexes, we decided to use a differential scanning calorimeter. As can be seen on Figs. 2–4 the destruction of all three modifications proceeds in two endothermic reactions immediately following each other, followed by an exothermic reaction (not shown in Figs. 2–4). The obtained values of ΔH for both endothermic reactions (ΔH_1 and ΔH_2 respectively) as well as the total ΔH value (ΔH_t) are given in Table II together with temperature parameters T_i (at which the pen first deviates from the baseline) and T_M (at which the enthalpy change is at maximum).

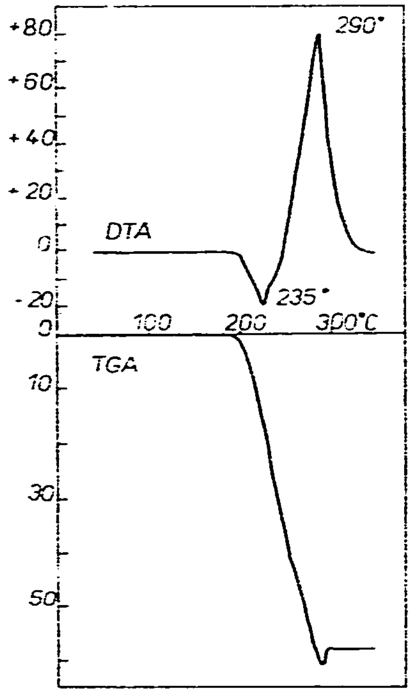

Fig. 1. Derivatogram of $Cu(C_2O_4)(NH_3)_2$.

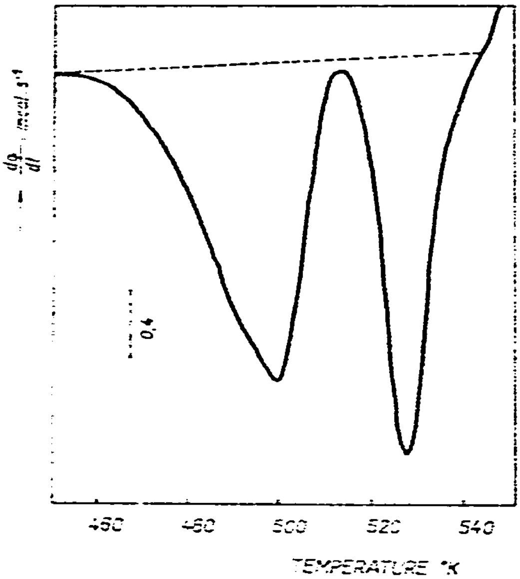

Fig. 2. DSC thermogram of α-$Cu(C_2O_4)(NH_3)_2$.

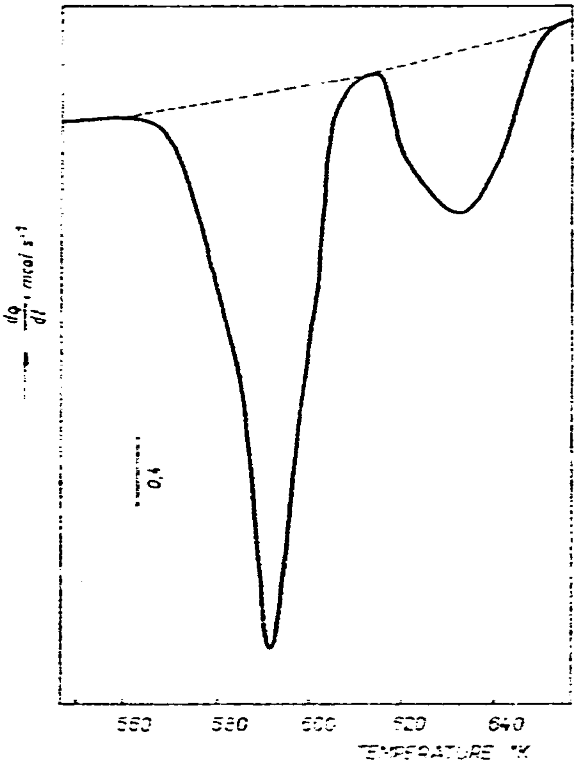

Fig. 3. DSC thermogram of β-$Cu(C_2O_4)(NH_3)_2$.

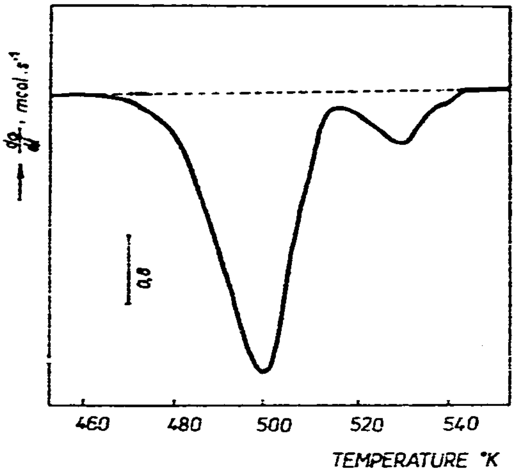

Fig. 4. DSC thermogram of γ-$Cu(C_2O_4)(NH_3)_2$.

TABLE II

HEATS OF DECOMPOSITION, APPARENT ACTIVATION ENERGIES AND REACTION ORDERS DETERMINED FROM DSC CURVES FOR α-, β- AND γ-$Cu(C_2O_4)(NH_3)_2$

Complex	α-$Cu(C_2O_4)(NH_3)_2$	β-$Cu(C_2O_4)(NH_3)_2$	γ-$Cu(C_2O_4)(NH_3)_2$
1. Endothermic reaction			
T_i [°K]	455	460	465
T_M [°K]	499	491	502
ΔH_1 [kcal mole^{-1}]	10.5±0.2	13.9±0.3	18.8±0.4
E_{A1} [kcal mole^{-1}]	59	68	61
n	0.7	1	0.7
2. Endothermic reaction			
T_i [°K]	516	512	518
T_M [°K]	530	532	530, 540
ΔH_2	6.95±0.15	5.45±0.15	2.3±0.20
ΔH_s	17.5	18.4	21.1

Results of analytical control of products formed during the first endothermic reaction (Table I) show that, in the case of the α and β modifications, the destruction process initially loses one mole of ammonia, while the bonding of the oxalate group undergoes no essential changes. This fact is supported by comparison of infrared spectra of α and β modifications[3] with those of intermediates (Table III). Hence, the first part of thermal decomposition of α and β modifications can be characterized by a stoichiometric equation as follows:

$$Cu(C_2O_4)(NH_3)_2\ (s) \rightarrow Cu(C_2O_4)(NH_3)_2\ (s) + NH_3\ (g)$$

The situation is quite different for γ-$Cu(C_2O_4)(NH_3)_2$ as can be seen from the intermediate composition data in Table I. The first step of the thermal decomposition of

TABLE III

ABSORPTION BANDS OF OXALATE GROUPS IN THE INFRARED SPECTRA OF α-, β- AND γ-$Cu(C_2O_4)(NH_3)_2$ AND INTERMEDIATES IN THEIR THERMAL DECOMPOSITION

Band assigment	*α-$Cu(C_2O_4)(NH_3)_2$*		*β-$Cu(C_2O_4)(NH_3)_2$*		*γ-$Cu(C_2O_4)(NH_3)_2$*	
	initial	*intermediate*	*initial*	*intermediate*	*initial*	*intermediate*
ν_aO–C–O	1715	1710 sh	(1710)	1694		(2180–2130)
	1685	1680	1665	1665	1665	1663
	1630	1635		1638	1624	1625
	1615	1610	1624	1625		1601
ν_sO–C–O	1340	1350				1420
		1320	1409	1409	1417	1350
ν_sO–C–O		1263		1256		1273
	1270	1256	1263	1250	1263	1256
δO–C–O		815	781	809	790	790
	778	798	777	790	781	780

this complex cannot be described by such a simple equation as in the former cases, since the destruction of the oxalate group has already taken place in this reaction step. The infrared spectra of γ-$Cu(C_2O_4)(NH_3)_2$[3] and the intermediate during its destruction are quite different. This supports the above-mentioned mechanism of the thermal decomposition of γ-$Cu(C_2O_4)(NH_3)_2$.

The ΔH values found for individual reactions agree with the stoichiometry of the thermal decomposition for all modifications; differences between them are greater than the deviations from the mean values.

The observed trend of differences at the ΔH_1 and ΔH_s values was unexpected. We have found the lowest ΔH_1 and ΔH_s values to be α-$Cu(C_2O_4)(NH_3)_2$ prepared under optimal conditions for the preparation of the most stable form. As the studied reactions take place in the solid state, the obtained values of ΔH_1 cannot be rigorously regarded as a gauge of the bond strength. All the same it is interesting to compare our values of ΔH_1 for α-$Cu(C_2O_4)(NH_3)_2$ (elongated tetragonal bipyramid) and β-$Cu(C_2O_4)(NH_3)_2$ (most likely a compressed tetragonal bipyramid) with the theoretically predicted[5] central atom–ligand bonds energies in complex compounds of copper(II) with homogeneous coordination spheres, where the coordination polyhedron is deformed due to the Jahn–Teller effect. On the other hand, the increase of the ΔH_1 value for β-$Cu(C_2O_4)(NH_3)_2$ might be caused by the initial destruction of the oxalate group. We suppose that the high ΔH_1 value for γ-$Cu(C_2O_4)(NH_3)_2$ is due to a simultaneous decrease in concentration of the ammonia molecules and the oxalate groups.

The ΔH_2 value (the energy of the second endothermic reaction) is the highest for α- and the lowest for γ-$Cu(C_2O_4)(NH_3)_2$. This fact is in agreement with the structure, and with already determined mechanism of thermal decompositions for single modifications.

The fact that the endothermic part of the thermal decomposition for all three modifications can be partly overlapped by the exothermic part of the reaction

$$CuO + CO \rightarrow Cu + CO_2 \qquad \Delta H = 30.1 \text{ kcal mole}^{-1}$$

accompanying the copper(II) oxalates destruction[8], means that we cannot predict the relative stabilities of α-, β- and γ-$Cu(C_2O_4)(NH_3)_2$ purely from the ΔH values.

Using the method in ref. 6 we have obtained the values of apparent activation energies (E_A) and reaction orders (n) given in Table III for the first endothermic reactions. We have found the lowest activation energy for α and the highest one for the β modification; the E_A value for γ-$Cu(C_2O_4)(NH_3)_2$ is intermediate.

CONCLUSION

Regarding the thermal decomposition of complex compounds as a certain type of substitution reaction, it can be stated that the substitution reactions start at α- and β-$Cu(C_2O_4)(NH_3)_2$ on the short bond by splitting one molecule of ammonia. That course of reaction, usual at copper(II) complexes[9] is aided by the fact that anions occupying the positions on the longer bonds form bridges to the neighbouring central atoms at the same time. Hence, the reaction opening on such a place needs a greater amount of energy than the breakdown of the copper ammonia bond.

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