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THERMAL BEHAVIOUR OF COPPER OXALATE AND ITS MIXED LIGAND COMPLEXES WITH AMINES

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The thermal decomposition behaviour of copper oxalate hemihydrate and its complexes with different amines has been studied by TG and DTA methods in nitrogen and air atmospheres. The complexes $CuC_2O_4 \cdot 0.5\,H_2O$, $CuC_2O_4(NH_3)_2$ and $CuC_2O_4(py)$ produced Cu_2O as final residue after decomposition, whereas, another group of complexes, $CuC_2O_4(EtNH_2)_2$, $CuC_2O_4(MeNH_2)_2$, $CuC_2O_4(en)_2$ and $CuC_2O_4(An)_2$, gave a final residue of CuO. All the complexes decomposed without forming any isolable stable intermediate; an exception was $CuC_2O_4(en)_2$, which formed a binuclear intermediate complex, $[CuC_2O_4en]_2$.

A survey of the literature shows that thermal decomposition of metal oxalate complexes has been studied by numerous workers [1–6]. The decomposition of oxalate complexes is usually complicated and occurs in a series of steps. These steps involve the loss of CO and CO_2, to yield basic carbonate or oxide. Depending on the metal, reduction may also occur during the decomposition. Dollimore et al. [7] studied the decomposition of hydrated oxalate complexes of cobalt(II), nickel(II) and copper(II) and found that $K_2[Cu(C_2O_4)_2] \cdot 6\,H_2O$ first loses water, and is then converted to CuO and K_2CO_3 when heated in air, but in nitrogen atmosphere breaks down to give a mixture of $K_2C_2O_4$ and elemental copper. Wendlandt et al. [8] studied the thermal behaviour of mixed ligand complexes of zinc(II) and cadmium(II) containing ethylenediamine and oxalate. In the cadmium complex it was found that ethylenediamine was lost before rupturing of the oxalate group occurred. However, the thermal decomposition of mixed complexes of metal oxalates with amines has not been adequately studied. The present communication deals with the thermal behaviour of copper oxalate and its complexes with amines such as ammonia, pyridine, aniline, methylamine, ethylamine and ethylenediamine. The coordination behaviour and structural characteristics of these complexes have been studied extensively [9–11].

Experimental

All reagents used were of AnalaR grade.

Copper(II) oxalate hemihydrate $[Cu(C_2O_4) \cdot 0.5\,H_2O]$ was prepared by mixing solutions of copper(II) chloride tetrahydrate and oxalic acid in 1:2 molar ratio. A bluish-green complex was formed when this mixture was refluxed on a water-bath. The complex was filtered off, washed with water and ethanol, and dried in vacuum.

The amine complexes of copper(II) oxalate were prepared [9] by suspending copper(II) oxalate hemihydrate in chloroform and then adding a little more than the calculated quantity of amine. The mixture was shaken for about 3 h. The resulting complex was filtered off, washed with ethanol and dried in a vacuum. The ammonia complex of copper oxalate was prepared by dissolving $Cu(C_2O_4) \cdot 0.5\,H_2O$ in concentrated ammonia. The complex was precipitated by adding acetone.

The copper ion in the complexes was estimated by the standard method described by Vogel. Carbon, hydrogen and nitrogen were analyzed by microanalytical techniques. Detailed elemental analyses are given in Table 1.

Physical measurements

Thermal analysis:
TG: Sample weight – 10 mg
Heating rate – 10 deg/min, if not otherwise specified
Atmosphere – nitrogen
Instrument – Stanton–Redcroft TG-750 thermobalance
DTA: Heating rate – 10 deg/min
Reference material – calcined α-Al_2O_3
Atmosphere – air
Instrument – assembled unit consisting of a Gallenkamp Furnace, Omniscribe recorder and Ether Transitrol Programmer

X-ray

The X-ray diffraction patterns of the final residue after decomposition were obtained using a 11.46 cm diam. Guinier camera in conjunction with crystal reflected monochromatic CuK_α radiation.

Results and discussions

The complexes obtained, their analytical data and other physical properties are given in Table 1. The complexes are insoluble in water and common organic solvents. Their elemental composition, magnetic susceptibility, electron spin resonance and ultraviolet and visible spectral data [9, 11] show them to be of general molecular formula $CuC_2O_4L_n$ (where $L = H_2O$, NH_3, py, An, $MeNH_2$, $EtNH_2$ and en; and $n = 0.5$ for H_2O, 1 for py and 2 for other amines), and to have square-planar geometry around the copper(II) ion. Infrared spectral studies [10] reveal that the copper(II) is bonded through the oxygen of the carboxylate group of the oxalate ion and the nitrogen of the amines.

The TG and DTG curves of $CuC_2O_4 \cdot 0.5\,H_2O$ (Fig. 1) show that the complex is stable up to 220°, after which it starts to decompose without forming any stable

Table 1 *Analysis of the complexes: experimental values and theoretical values*

Complexes	Colour	Weight loss, %		Cu, %		Carbon, %		Hydrogen, %		Nitrogen, %	
		Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
$CuC_2O_4 \cdot 0.5\,H_2O$ O	Sky Blue	56.00	55.45	39.28	39.58	15.15	14.95	0.75	0.62	—	—
$CuC_2O_4(NH_3)_2$	Blue	61.50	61.45	34.40	34.25	13.21	12.93	3.15	3.23	14.95	15.09
$CuC_2O_4(C_5H_5N)$	Green	69.00	68.98	27.45	27.57	37.05	36.44	2.25	2.17	6.80	6.67
$CuC_2O_4(C_6H_5NH_2)_2$	Yellow Green	75.80	76.44	18.75	18.83	49.47	49.77	4.00	4.14	8.50	8.29
$CuC_2O_4(C_2H_5NH_2)_2$	Blue	66.50	67.00	26.50	26.31	30.15	29.81	6.00	5.79	11.65	11.59
$CuC_2O_4(CH_3NH_2)_2$	Blue	61.90	62.70	30.00	29.76	22.56	22.48	4.75	4.68	13.20	13.11
$CuC_2O_4(H_2NCH_2CH_2NH_2)_2$	Violet	70.00	70.70	23.85	23.40	26.26	26.51	5.70	5.89	19.85	20.62

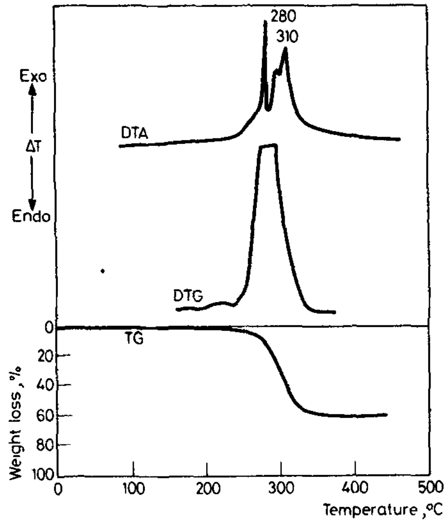


Fig. 1 TG, DTG and DTA curves of $CuC_2O_4 \cdot 0.5\ H_2O$

intermediate; the final residue is obtained at 320°. The natures of the DTG and DTA curves indicate the simultaneous liberation of H_2O and decomposition of oxalate ion. The weight loss of 56% (theoretical 55.45%) in nitrogen atmosphere show that the final residue is Cu_2O. This observation is in agreement with the thermal decomposition behaviour of copper oxalate as reported by Dual [12]. The DTA curve (Fig. 1) of the complex displays two well-defined exothermic peaks at 280° and 310°, accompanied by a shoulder at 300°, corresponding to the liberation of H_2O and the decomposition of oxalate, respectively. The split nature of the exotherm at 310° indicates that the oxalate decomposition is a multistep process. The exothermic breakdown of copper oxalate is due to the autocatalytic nature of the decomposition [13]. The loss of H_2O above 250° indicates that the water is bound in the inner coordination sphere of the copper(II) (presumably in the vacant 4*s* orbital in the square-planar, $3d4s4p^2$ hybridization). The absence of an endothermic peak due to liberation of the water may be explained by the masking of the endothermic decomposition by the exothermic breakdown of the copper oxalate.

The thermal decomposition of $CuC_2O_4(NH_3)_2$ (Fig. 2) shows two steps. The DTG peaks at 240° and 300° correspond to the loss of NH_3 (weight loss: found 18.55%; theoretical 18.37% and the decomposition of oxalate ion. The weight loss value from TG analysis shows that the final residue is Cu_2O (weight loss: found 61.5%; theoretical 61.45%). The DTA curve reveals the endothermic liberation of NH_3 at 220° and 260° and the exothermic decomposition of oxalate ion at 275° and 310°. Two well-defined endothermic peaks indicate the loss of NH_3 in two stages. The endothermic peak at 260°, accompanied by an exothermic peak at 275°, demonstrates that the loss of the

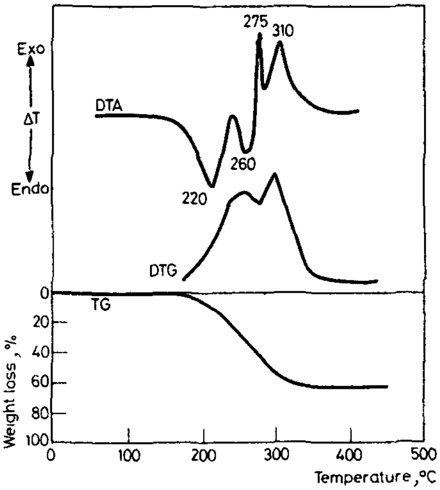


Fig. 2 TG, DTG and DTA curves of $CuC_2O_4(NH_3)_2$

second NH_3 molecule is accompanied by oxalate decomposition. The most probable stepwise thermal decomposition of the complex may be represented as:

$$CuC_2O_4(NH_3)_2 \xrightarrow{I} CuC_2O_4(NH_3) \xrightarrow{II} CuC_2O_4 \xrightarrow{III} Cu_2O$$

The complex $CuC_2O_4(NH_3)$ could not be isolated because it starts to decompose even before its formation is complete.

The thermal behaviour of $CuC_2O_4(py)$ (Fig. 3) indicates that the complex is stable up to 160°, after which it decomposes, the final residue of Cu_2O (weight loss: found 69%; theoretical 68.98%) being formed at 300°, as observed from its TG curve. The DTG curve shows two broad peaks at 220° and 280°, corresponding to the decomposition of pyridine and oxalate. The DTA curve (Fig. 2) of the complex displays one endothermic peak at 225°, due to the decomposition of pyridine, and two exothermic peaks at 260° and 290° (shoulder at 280°), due to oxalate decomposition. The endotherm at 225°, accompanied by a sharp exotherm at 260°, indicates the simultaneous decomposition of pyridines and oxalate.

The thermal curves of the ethylamine complex of copper oxalate are presented in Fig. 4. In the DTG curve, there are two peaks, at 140° and 340°, indicating a loss in weight. The first loss in weight, on heating from 60° to 280°, corresponds to the loss of ethylamine; after 280° the decomposition of oxalate begins, and a stable residue is formed at 380°, as confirmed by TG analysis. The weight loss from TG analysis reveals the formation of CuO (weight loss: found 66.50%; theoretical 67.0%), which is confirmed by X-ray diffraction using CuK_α radiation. The experimental *d* values and the corresponding relative intensities, calculated from the X-ray diffraction pattern of the final product of decomposition, are given in Table 2, along with the known diffraction

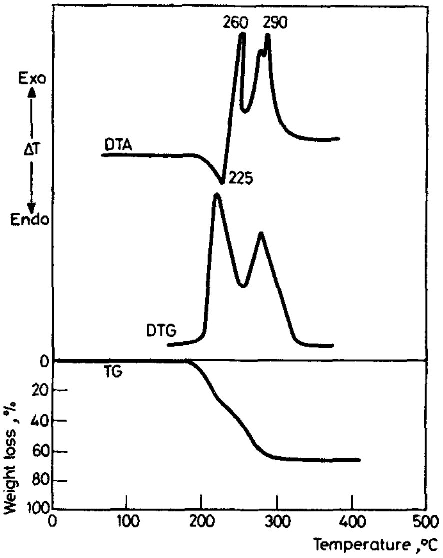


Fig. 3 TG, DTG and DTA curves of $CuC_2O_4(py)$

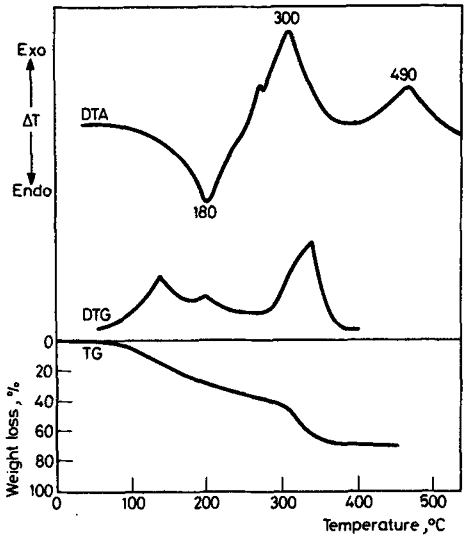


Fig. 4 TG, DTG and DTA curves of $CuC_2O_4(EtNH_2)_2$

Table 2 *d* values and the intensity the final decomposition product of copper-oxalate ethylamine calculated from X-ray diffraction pattern along with values reported for CuO

Final product		CuO	
d, A	Intensity	*d*, A	Intensity
2.520	50	2.53	49
2.508	100	2.51	100
2.320	95	2.32	96
1.970	5	1.96	3
1.870	30	1.86	25
1.780	10	1.71	8
1.720	20	1.58	14
1.585	15	1.50	20
1.505	30	1.41	12
1.420	20	1.37	19
1.410	30	1.30	7
1.380	35	1.26	6
1.308	10	1.09	6
1.265	10	0.90	1

data [14]. The DTA curve shows a broad endothermic peak at 180°, due to the liberation of ethylamine. The exothermic peak at 300° is due to the decomposition of copper oxalate, while the other exothermic peak, at 490°, may be due to oxidation of copper(I) to copper(II).

The thermal behaviour of $CuC_2O_4(MeNH_2)_2$ is comparable to that of $CuC_2O_4(EtNH_2)_2$, suggesting that the decomposition of this complex proceeds in a similar manner. Figure 5 shows the thermoanalytical curves of $CuC_2O_4(MeNH_2)_2$. The final residue formed after decomposition of methylamine and oxalate is CuO (weight loss: found 61.9%; theoretical 62.7%). The DTA results show exothermic peaks at 180° and 275°, due to the liberation of methylamine and the decomposition of copper oxalate. The other exothermic peak, at 425°, is similar in nature to the exotherm of $CuC_2O_4(EtNH_2)_2$.

The thermal curves of $CuC_2O_4(An)_2$ (An = aniline) are shown in Fig. 6. The DTG curve of the complex reveals two distinct ranges of decomposition, from 120 to 200° and from 280 to 380°, due to aniline and oxalate decomposition, respectively. The decomposition of aniline and oxalate is a continuous process and the TG curve does not indicate the formation of any stable intermediate. DTA studies of the complex (Fig. 6) demonstrate that this compound undergoes an endothermic reaction at 220°, with loss of aniline. The exothermic reaction takes place with a mass loss corresponding to oxalate at 230° and 320°, and the formation of CuO (weight loss: found 75.80%; theoretical 76.44%).

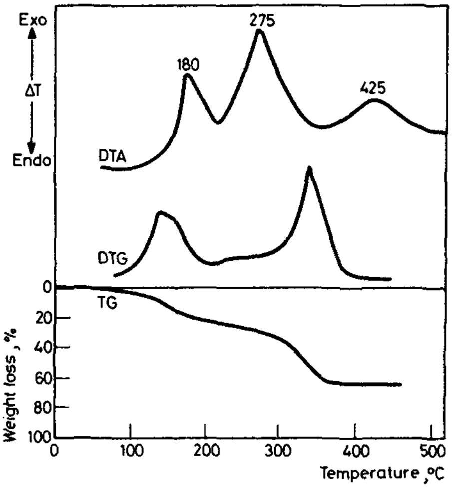


Fig. 5 TG, DTG and DTA curves of $CuC_2O_4(MeNH_2)_2$

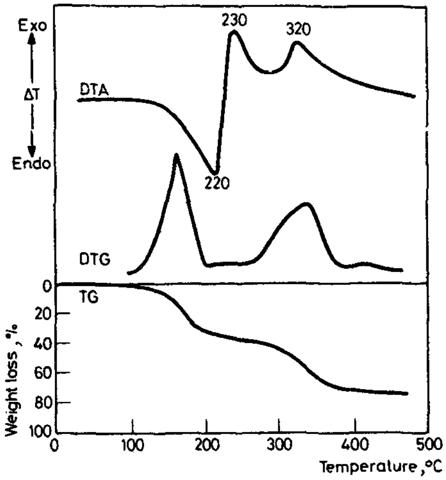


Fig. 6 TG, DTG and DTA curves of $CuC_2O_4(An)_2$

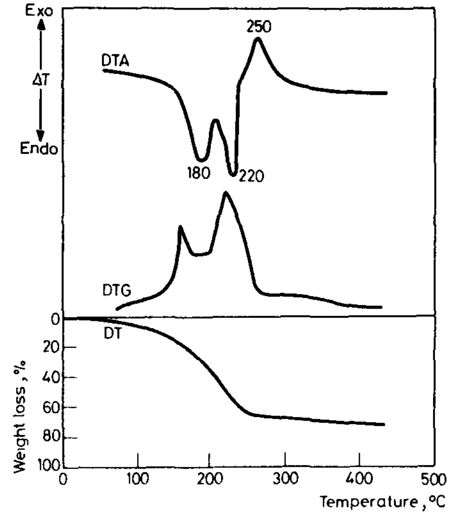
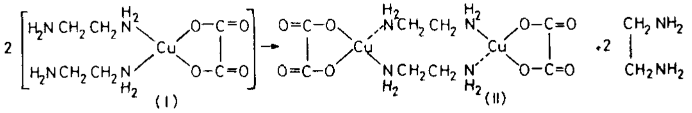


Fig. 7 TG, DTG and DTA curves of $CuC_2O_4(en)_2$

Thermal decomposition curves of $CuC_2O_4(en)$ are shown in Fig. 7. In the DTG curve, there are two peaks, at 160° and 220°, indicating a loss in weight. The first loss in weight corresponds to the liberation of one ethylenediamine molecule (loss in weight: found 21.85%; theoretical 22.09%) up to 170°. The curve exhibits a definite plateau after the loss of one ethylenediamine molecule, indicating the formation of stable intermediate complex with one ethylenediamine ligand. The ethylenediamine ligand is monodentate in the square-planar $CuC_2O_4(en)_2$ complex (structure I). The proposed intermediate complex (structure II) is dimeric in nature: ethylenediamine acts as a bridge between two copper atoms, to give a coordination number of four for each of the Cu(II) ions. Elemental analysis of the intermediate complex $(CuC_2O_4en)_2$ (Cu: found 29.85%; theoretical 30.04%) and the monodentate nature of the ethylenediamine ligand support the bimolecular structure of the intermediate complex.



On further heating of the intermediate complex, the simultaneous decomposition of ethylenediamine and oxalate occurred up to 260°, with CuO as final product. The DTA curve shows a broad endothermic peak at 180°, due to the evolution of an ethylenediamine molecule. A further endothermic peak at 220°, accompanied by a small exothermic peak at 250°, corresponds to the decomposition of the other ethylenediamine molecule, together with oxalate.

The experimental results demonstrate that the studied complexes fall into two groups. The first group [$CuC_2O_4 \cdot 0.5\ H_2O$, $CuC_2O_4(NH_3)_2$ and $CuC_2O_4(py)$] produce copper(I) oxide as a result of decomposition in nitrogen atmosphere. The decomposition may be described by the equation:

(I) $2\ CuC_2O_4L_n \longrightarrow Cu_2O + 3\ CO_2 + CO + 2nL$

The other group comprises the complexes $C_2O_4(MeNH_2)_2$, $CuC_2O_4(EtNH_2)_2$, $CuC_2O_4(An)_2$ and $CuC_2O_4(en)_2$, for which the weight loss corresponds to the formation of CuO in nitrogen. The decomposition scheme may be written:

(II) $CuC_2O_4L_2 \longrightarrow CuO + CO + CO_2 + 2L$

This latter reaction leads to the evolution of equimolar amounts of CO and CO_2. The decomposition of copper oxalate can occur through rupture either of the Cu–O bond or of the C–O linkage in the carboxylate group. Breaking of the C–O bond would lead to the formation of an oxide of copper and the evolution of CO_2 [15]. The decomposition results for the above complexes favour the breaking of the C–O link during their thermal decomposition.

The thermal decomposition results reveal that the amine molecules are lost at a lower temperature than that of oxalate decomposition, indicating that the Cu–N bonds are weaker than the Cu–O bond. This is in agreement with findings for other mixed ligand complexes [16]. It can be inferred that the decomposition of the complexes is influenced by the axial base, i.e. the amines. The thermal behaviour of the pyridine, ammonia and aquo complexes is different from that of the aniline and primary amine complexes. The amines form complexes involving the donation of a nitrogen lane pair of electrons to the metal, whereas in the case of pyridine the nitrogen atom is incorporated into a conjugated ring system and therefore acts as a π-acceptor (through a delocalized orbital) as well as a σ-donor ligand.

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Zusammenfassung — Das thermische Zersetzungsverhalten des Hemihydrats von Kupferoxalat, sowie seine Komplexe mit verschiedenen Aminen wurden mit den TG- und DTA-Methoden in Nitrogen- und Luft-Atmosphere untersucht. Die Komplexe $CuC_2O_4 \cdot 0.5\,H_2O$, $CuC_2O_4(NH_3)_2$ *und* $CuC_2O_4(py)$ *ergaben nach der Zersetzung* Cu_2O *als Endprodukt*, wogegen eine andere Gruppe der Komplexe, d.h. $CuC_2O_4(EtNH_2)_2$, $CuC_2O_4(MeNH_2)_2$, $CuC_2O_4(en)_2$ und $CuC_2O_4(An)_2$ ein Endprodukt von CuO ergaben. All diese Komplexe zersetzten sich keine isolierbare, stabile Zwischenprodukte geformt zu haben, mit einer Ausnahme des $CuC_2O_4(en)_2$, welches ein binukleares Zwischenkomplex, das $[CuC_2O_4en]_2$ bildete.

Резюме — Методами ТГ и ДТА изучено в атмосфере кислорода и азота термическое разложение полугидрата оксалата меди и его комплексов с различными аминами. При разложении комплексов $CuC_2O_4 \cdot 0.5\,H_2O$, $CuC_2O_4(NH_3)_2$ и $CuC_2O_4(py)$ в качестве конечного продукта реакции образуется Cu_2O, тогда как при разложении комплексов $CuC_2O_4(EtNH_2)_2$, $CuC_2O_4(MeNH_2)_2$, $CuC_2O_4(en)_2$ и $CuC_2O_4(An)_2$ — образуется CuO. Все комплексы разлагаются без образования каких-либо выделяемых стабильных промежуточных продуктов. Исключение составлял комплекс $CuC_2O_4(en)_2$, который образует двухядерный комплекс $[CuC_2O_4en]_2$.