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X-RAY *K*-ABSORPTION AS A PROBE FOR INVESTIGATING THERMAL BEHAVIOUR OF COMPLEXES: RELATED THERMAL AND X-RAY *K*-ABSORPTION STUDIES ON COPPER(II) SALICYLHYDROXAMATE

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ABSTRACT

The preparation and characterization of copper(II) salicylhydroxamate (CuSHA) is described. The compound was characterized on the basis of analytical and Fourier transform infrared (FTIR) spectral data. The thermal decomposition was investigated by thermal techniques (TG, DTG and DTA), whereas X-ray *K*-absorption was used as a probe for the investigation of the thermal degradation of CuSHA. The X-ray study showed that during thermal decomposition the symmetry of CuSHA changed from O_h to T_d with CuO as the end product. Formation of CuO as the end product was also confirmed by thermal, FTIR and X-ray studies.

INTRODUCTION

Very recently [1,2], we presented a preliminary report on the thermal decomposition of metal(II) salicylhydroxamates (MSHA). However, no information on the thermal behaviour of copper salicylhydroxamate (CuSHA) is available. In this paper a detailed thermal characterization of the CuSHA system is carried out for the first time using TG, DTG and DTA techniques. X-ray *K*-absorption was used as a probe for investigating thermal degradation. This was carried out by heat treating CuSHA in air at a constant temperature of 150 °C for a constant time of 30 min. It was found that the compound was thermally stable when heated up to about 160 °C for a constant time of 30 min, or when heated at a constant temperature of 155 °C for about 60 min. We also investigated the resulting products of this thermal decomposition.

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EXPERIMENTAL

All chemicals used were BDH AnalaR or equivalent quality.

Preparation of CuSHA

The chelate (CuSHA) was synthesized following the method described by Khadikar et al. [3,8]. A known amount of copper sulphate was dissolved in 0.1 M perchloric acid solution. This was diluted to 1 l and heated to 62 ± 2°C. A concentrated solution of salicylhydroxamic acid (SHA) was prepared in 50% (v/v) ethanol–water and was added to the copper sulphate solution in the presence of ammonium acetate. An olive-green product was obtained and the supernatant liquid was colourless. The compound was filtered, washed several times with boiling water, ethanol, then ether and dried. Finally, the compound was vacuum-dried overnight and ground to pass 300 mesh.

Elemental analyses

The elemental analyses (C, H and N) of CuSHA were carried out using a Colemann CHN-Analyzer-29. Copper was estimated iodometrically as usual [4]. The analyses led to the following results. Found: C = 41.63 (45.70), H = 3.96 (3.26), N = 6.93 (7.61), Cu = 15.74 (17.28); calculated: C = 41.77 (45.72), H = 3.99 (3.22), N = 7.12 (7.59), Cu = 15.67 (17.30). The values in parentheses are for thermally dehydrated products. Both sets are consistent with the composition $Cu(SHA)_2 \cdot 2H_2O$.

Heat treatment

The heat treatment was performed in air using an oil bath with a thermal stability within ±0.2°C. All the samples were cooled in water to room temperature.

FTIR spectra

Fourier transform infrared (FTIR) spectra of the sample and its thermal degradation products were recorded on a Polytech FIR-30 Fourier far-IR spectrometer with an estimated accuracy of ± 0.5 cm^{-1}.

Thermal studies

Thermogravimetry (TG) on 100 mg of the sample was carried out on a Stanton-Redcroft recording thermobalance (HT-model) of 1 mg sensitivity in static air at a heating rate of 4°C min^{-1}. The chart speed was maintained

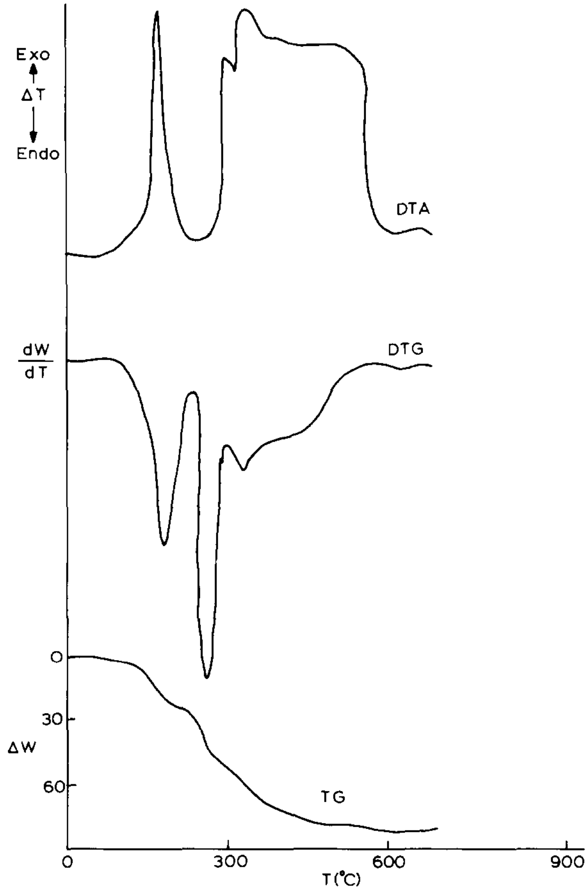

Fig. 1. TG, DTG and DTA curves for bis-(salicylhydroxamato)-diaquo copper(II) chelate (CuSHA·$2H_2O$).

at 3 in h^{-1}. The sample was packed as uniformly as possible in a platinum crucible of appropriate size. The same platinum crucible was used throughout the experiment. Before packing, the sample was homogenized by sieving below 300 mesh.

A differential thermal analysis (DTA) assembly with an F and M Scientific 240 Hewlett-Packard temperature programmer and a Platinel-II thermocouple (Engelhard, U.S.A.) was used. The DTA curve for the 50 mg sample was recorded by a Rikadenki Kogyo recorder in static air at a heating rate of 4°C min^{-1}. Alumina was used as a standard reference.

The TG, DTG and DTA curves for copper(II) salicylhydroxamate are shown in Fig. 1.

X-ray absorption studies

A molybdenum target X-ray tube was employed to supply continuous radiation at 30 kV and 10–12 mA. A 40 cm transmission type curved crystal

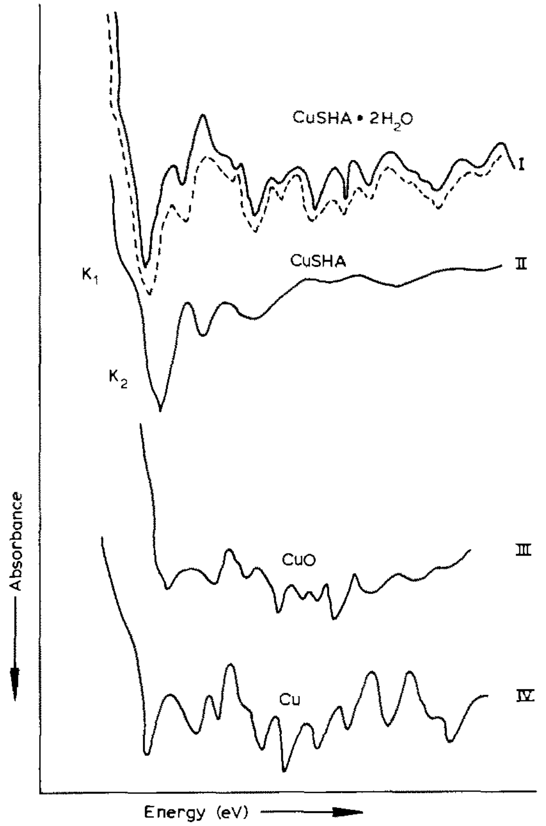

Fig. 2. X-ray *K*-absorption spectra for CuSHA·2H$_2$O, CuSHA, CuO, and Cu metal.

spectrograph was used to record the spectra photographically. The $(\bar{2}01)$ planes of mica, reflecting in the second order, gave a dispersion of about 12.4 × 4 mm^{-1} for the sample as described previously [5,6]. The spectra obtained for various samples are recorded in Fig. 2.

TABLE 1

Thermoanalytical data for copper(II) salicylhydroxamate

Complex [a]	DP [b]	Temp. range (° C)	Residual product	% Weight loss *w*	
				Calc.	Obs.
CuSHA [c]	I	80–200	Cu(SHA)$_2$	8.92	8.50
	II	220–280	Cu(SHA)	46.58	47.00
	III	280–600	CuO	84.22	84.00

[a] CuSHA denotes copper(II) salicylhydroxamate. The actual composition of the complex is Cu(SHA)$_2$·2H$_2$O, where SHA denotes the salicylhydroxamic acid moiety and Cu the divalent copper(II) ion.

[b] DP = decomposition steps (period).

[c] Before thermal dehydration the complex is olive green in colour; it changes to dark grey on subsequent dehydration.

PRESENTATION OF THE DATA

The TG, DTG and DTA traces for CuSHA are presented in Fig. 1. The thermal analysis is given in Table 1. The X-ray *K*-absorption spectra of the sample together with its thermal decomposition products are shown in Fig. 2.

RESULTS AND DISCUSSION

The observed TG weight loss (Fig. 2, Table 1) of 8.5% when heating up to 458 K is consistent with the loss of two water molecules per molecule of the chelate. A very sharp exotherm at 453 K indicates that at this temperature dehydration is followed by decomposition of the organic moieties associated with the chelates. Another exothermic decomposition occurs at about 578 K as evidenced by the sharp peak in DTA and by an abrupt weight loss in the TG curve. A very broad exothermic peak is finally obtained in the range 650–930K.

Typical X-ray *K*-absorption spectra obtained at room temperature for the unheated sample and for the sample heated in air for 30 min at 450 and 570 K, respectively, are shown in Fig. 2. The solid line represents the spectrum for the unheated chelate while the broken line represents the same for the heated chelate.

The X-ray *K*-absorption spectrum of CuSHA (I) is similar to that of the curve I(a) reported by Van Nostrand [7], thereby indicating an octahedral stereochemistry for the hydrated product. However, the spectrum for the thermally dehydrated chelate (II) resembles the type IV(b) curve of Van Nostrand, i.e. the curves for tetrahedrally surrounded metal ions. The observed curve II also shows splitting of the principal absorption edge into two components K_1 and K_2, which is observed in tetrahedrally coordinated metal ions [8–10]. Thus, the X-ray *K*-absorption indicates that $Cu(SHA)_2$ is formed as a result of thermal dehydration and that during thermal degradation the octahedral stereochemistry changes to tetrahedral. The results are consistent with the thermal analytical data recorded in Tables 1 and 2.

It is interesting to note that the chemical shift of the hydrated chelate (10.49 eV) changes to 7.22 eV as a result of thermal dehydration. This is in accordance with our earlier results [10] on metal chelates of salicylic acid and with the results obtained by Glen and Dradd [11]. It was argued that the covalent character of the metal–ligand bond increases as a consequence of distortion of octahedral complexes and that the chemical shift is smaller for the compounds with lower symmetry features. The observed results, in the present case, are in fair agreement with these findings.

Further evidence for the formation of a thermally dehydrated product and the consequent change to tetrahedral symmetry is obtained from the

TABLE 2

TG horizontal, maxima and range of DTG and DTA peaks of copper(II) salicylhydroxamate

Complex [a]	DP [b]	Range of TG horizontal (°C)	Maxima of DTG trace (°C)	Range of DTG effect (°C)	Maxima of DTA trace (°C)	Range of DTA effect
CuSHA	I	80–200	185	100–220	190	Exo [c]
	II	220–280	300	220–335	305	Exo
	III	280–600	350	–		Exo

[a] The composition of the complex is $Cu(SHA)_2 \cdot 2H_2O$, where SHA denotes salicylhydroxamate anion and Cu divalent copper ion.

[b] DP = decomposition period (steps).

[c] Exo = exothermic peak.

estimation of the edge-width of the X-ray *K*-absorption spectra of the hydrated and thermally dehydrated chelates. A higher edge-width for the dehydrated product is consistent with the formation of tetrahedral coordination.

Finally, the X-ray *K*-absorption spectrum obtained for the end product of the thermal decomposition of CuSHA (II) was found to be identical with that of CuO (III). This indicates that the final residue of the thermal decomposition is CuO and is consistent with the thermal analytical data recorded in Table 1. Bands at 610, 500 and 410 cm^{-1} obtained in the FTIR spectrum of the residue also confirm the formation of CuO.

Thus, on the basis of changes in edge-structure edge-width and edge-shift, it can be concluded that the thermal decomposition of CuSHA proceeds through the mechanism

$$Cu(SHA)_2 \cdot 2H_2O \rightarrow Cu(SHA)_2 + 2H_2O$$

$$Cu(SHA)_2 \rightarrow CuSHA + SHA$$

$$CuSHA \rightarrow \underset{\substack{\downarrow \\ \text{CuO + other combustion processes}}}{CuCO_3} + SO_2 + SO_3 + H_2O,\ CO + CO_2$$

Hence, the results show that X-ray *K*-absorption can be used as a probe for investigating the thermal behaviour of complexes. Further studies in this direction are under way.

Further evidence for the change in symmetry and composition of the thermal degradation products

In an effort to verify the change in stereochemistry as a result of thermal dehydration and to obtain further evidence for the estimation of the composition of the thermal decomposition products, Fourier transform infrared

(FTIR) spectra of SHA, $Cu(SHA)_2 \cdot 2H_2O$, CuSHA and CuO (final residue) were obtained.

The carbonyl group frequency in SHA (1610 cm^{-1}, doublet) shifts to lower frequencies in hydrated copper chelate ($CuSHA,2H_2O$) and in the thermally dehydrated product (CuSHA): 1595 and 1590 cm^{-1}, respectively. If the lowering of the carbonyl group frequency is correlated with the stability of the chelate then the dehydrated product would be the most stable. In view of possible Jahn–Teller distortion [12] for the system this is only possible by a lowering of symmetry, indicating the change from O_h to T_d symmetry as a consequence of thermal dehydration. The absence of frequencies 1620, 795 and 515 cm^{-1} (due to coordinated water molecules) in the thermal product confirms the formation of CuSHA.

The presence of bands at 610(m), 500(s) and 410(m) cm^{-1} in the FTIR spectrum of the residue indicate the formation of CuO as end product.

The results are in agreement with the composition and structure of the chelate.

Characteristic features of the thermal decomposition of copper(II) salicylhydroxamate

From the discussion so far, it is clear that the thermal decomposition of copper(II) salicylhydroxamate is a three-step decomposition. The first step is dehydration. The dehydrated chelate then undergoes pyrolysis. The pyrolysis of the chelate is stepwise and leads to the formation of CuO as the end product.

The endothermic peak (438 K) on the DTA curve suggests dehydration and the exotherms (553 and 593–823 K) correspond to the decomposition of the dehydrated chelate. The water molecules lost are of coordinated type as indicated by their temperature of dehydration (Tables 1 and 2).

The chelate is fairly stable up to 353 K and then starts losing the water molecules followed by decomposition starting at 523 K. The metal oxide was obtained at 873 K. The three decomposition ranges are 353–473, 493–553 and 550–873 K, respectively.

The elimination of the two water molecules in a single step indicates that they are bound equally to the central copper ion. The temperature range in which these water molecules are lost indicates that they are coordinated water molecules. It is worth noting that near the completion of the elimination of water an intermediate CuSHA moiety is formed. The results provide a large amount of information regarding the mechanism of the thermal degradation processes of copper salicylhydroxamate. A study is under way and the estimated kinetics will be published elsewhere. However, the occurrence of several peaks in the DTG and DTA curves indicates a multi-step mechanism.

The recorded DTA curve for CuSHA has an exothermic peak with an unusual shape. This is analogous to our earlier observations [5,6,12] as well as those of other workers [13–15]. The occurrence of such an abnormal exothermic peak may be attributed to the formation of various combustion products as a consequence of the decomposition of the organic skeleton (SHA in the present case). A large, broad exothermic peak over a wide temperature range on the DTA curve for the decomposition of dehydrated $Cu(SHA)_2$ indicates, besides the decomposition, oxidation and combustion processes.

Finally, it is worth mentioning that in the last step, copper carbonate finally decomposes to CuO with the elimination of CO_2. This decomposition is always endothermic. However, the oxidation of a product of cracking from the preceding decomposition process, or of carbon, probably produces an exothermic effect shown on the DTA curve.

CONCLUSIONS

The thermal decomposition of copper(II) salicylhydroxamate is a multi-step decomposition. The first step is the dehydration of the chelate followed by a step-wise decomposition with CuO as the end product.

As a consequence of dehydration the octahedral stereochemistry changes to tetrahedral. This change in stereochemistry and the presence of the consequent thermal degradation products is indicated by IR, FTIR and X-ray *K*-absorption studies.

Finally, the results show that X-ray *K*-absorption can be used as a probe for investigating the thermal behaviour of the chelate.

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