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THERMAL DECOMPOSITION OF Cu(II) COMPLEXES WITH SALICYLALDEHYDE S-METHYL THIOSEMICARBAZONE

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Abstract

The thermal decomposition of copper(II) complexes with salicylaldehyde S-methylthiosemicarbazone of general formula $Cu(HL)X\cdot nH_2O$ (X =Py +NO_3, NCS, $0.5SO_4$) and $[Cu(L)NH_3]\cdot H_2O$ was investigated in air atmosphere in the interval from room temperature to 1000°C. Decomposition of the complexes occurred in several successive endothermic and exothermic processes, and the residue was in all cases CuO.

Introduction

Copper(II) complexes with salicylaldehyde S-methylisothiosemicarbazone, H_2L, the subject of the present study, were synthesized earlier [1, 2]. They can be represented as $Cu(HL)X\cdot nH_2O$, where X =Py+NO_3, NCS, $0.5SO_4$ and $[Cu(L)NH_3]\cdot H_2O$.

All complexes are paramagnetic, and possess a square-planar configuration. In the cases when the synthesized complexes formed satisfactory monocrystals, their X-ray analysis was carried out [2, 3]. In this way, the postulated coordination was confirmed, and interatomic distances and angles were explicitly determined.

The results of studies of the complexes by electron spectroscopy have been presented in [4]. The obtained diffusion - reflection spectra were interpreted in accordance with the D_{4h} point group, which can be ascribed to the central ion surroundings. Spectral maxima were related to *d–d* and intraligand transitions, and also to charge-transfer transitions.

We have now undertaken a study of the thermal decomposition of these complexes, and the results are presented in this article.

Experimental

Thermogravimetric measurements were carried out on a Paulik-Paulik-Erdey derivatograph in air atmosphere, employing α-Al_2O_3 as a standard. The mass of the samples was 100 mg and the heating rate was 10 deg·min^{-1}.

Analysis of the final product was carried out with an automatic PW 1373 (Philips) powder diffractometer and by means of ASTM data.

Results and discussion

Figures 1–4 present thermal decomposition curves for the investigated compounds.

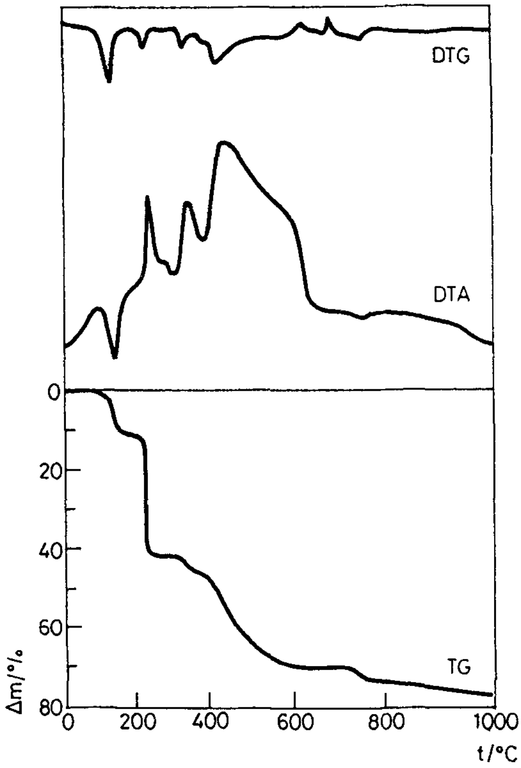

Fig. 1 TG, DTA and DTG curves of $[Cu(L)NH_3]\cdot H_2O$

It can be seen that the decomposition processes of the investigated complexes proceed with several analogous endothermic and exothermic effects. For the water-containing complexes, the first endothermic effect corresponds to water elimination. The endothermic effect observed for $Cu(L)NH_3$ at 403 K is

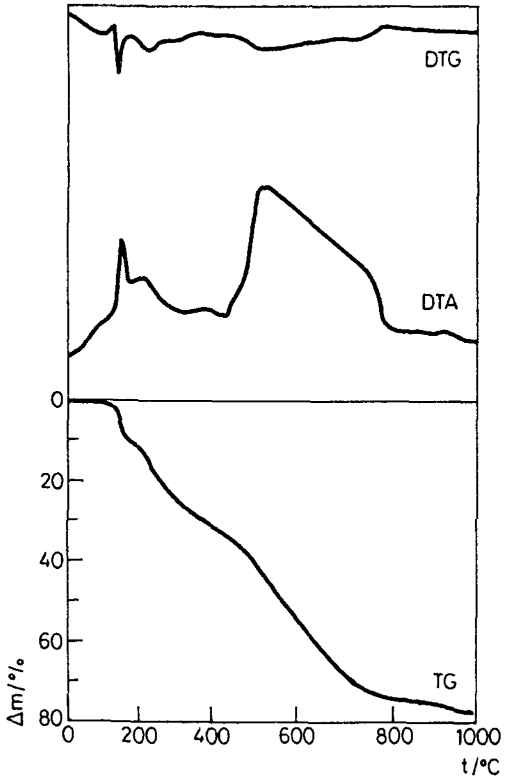

Fig. 2 TG, DTA and DTG curves of Cu(HL)NCS·H_2O

due to elimination of both water and ammonia. However, because of the presence of the close exothermic effect at 453 K, corresponding to the elimination of pyrazole, the weight losses for the two steps could not be separated, and a cumulative value is presented in the Table.

The subsequent effect is exothermic, and in all cases can be ascribed to elimination of the SMe group. The Table reveals that the temperatures of elimination of this group are similar for all the compounds and are close to the temperature of SMe elimination from the free ligand, H_2L [5], and also to the values observed for other complexes with similar ligands [6]. This could be explained in terms of the relatively large distance of the SMe group from the coordination polyhedron, and hence its weak binding to the rest of the ligand.

The next exothermic effect characterizes the elimination of the thiosemicarbazone fragment. However, for Cu(HL)PyNO_3·0.5H_2O, elimination of this fragment occurs in two stages. The fragment eliminated first contains the carbon atom connected to the SMe group and two nitrogen atoms bound to this carbon (thiosemicarbazone, part I, see Table 1), and then, after elimination of the salicylaldehyde fragment, the remaining thiosemicarbazone is eliminated. For $[Cu(HL)]_2SO_4{\cdot}H_2O$, the exothermic effects accompanying elimination of the thiosemicarbazone and the salicylaldehyde fragment can not be clearly separated. Table 1 therefore presents the temperature interval of the cumulative effect and the total weight loss. The exothermic effect in the decomposition of this compound is preceded by an endothermic effect due to elimination of the SO_4 group in the form of H_2SO_4.

Table 1 The characteristics of thermal decomposition of the complexes

	$[Cu(L)NH_3]{\cdot}H_2O$			
Effect	Fragment eliminated	T/K	Δm_{exp} / %	Δm_{cal} / %
endo	$H_2O + NH_3$	403	11.5	11.4
exo	SMe + Tsc	483-678	37	37.7
exo	Sal–O	678-1113	26	24.9
Residue	CuO		25.5	24.9

	$Cu(HL)NCS{\cdot}H_2O$			
Effect	Fragment eliminated	T/K	Δm_{exp} / %	Δm_{cal} / %
endo	H_2O	413	6	5.2
exo	SMe	508	15	13.5
exo	Tsc	548-788	19	19.8
exo	Sal + O + NCS	788-1173	37.5	38.6
Residue	CuO		23.5	22.9

	$Cu(HL)PyNO_3{\cdot}0.5H_2O$			
Effect	Fragment eliminated	T/K	Δm_{exp} / %	Δm_{cal} / %
endo	$NO_3 + 0.5H_2O$	413	36	36.6
exo	Py	453		
exo	SMe	573	10	11.4
exo	Tsc - part I	613-683	10	10.3
exo	Sal–O	683-803	18	18.6
exo	Tsc - part II	803-1018	7	6.6
Residue	CuO		19	19.4

	$Cu(HL)0.5SO_4{\cdot}H_2O$			
Effect	Fragment eliminated	T/K	Δm_{exp} / %	Δm_{cal} / %
endo	H_2O	413-473	5	5.3
exo	SMe	493	15	13.9
exo	H_2SO_4	593	16	14.5
exo	Tsc + Sal–O	593-1178	41	42.7
Residue	CuO		23	23.6

*Tsc – thiosemicarbazide, Sal – salicylaldehyde

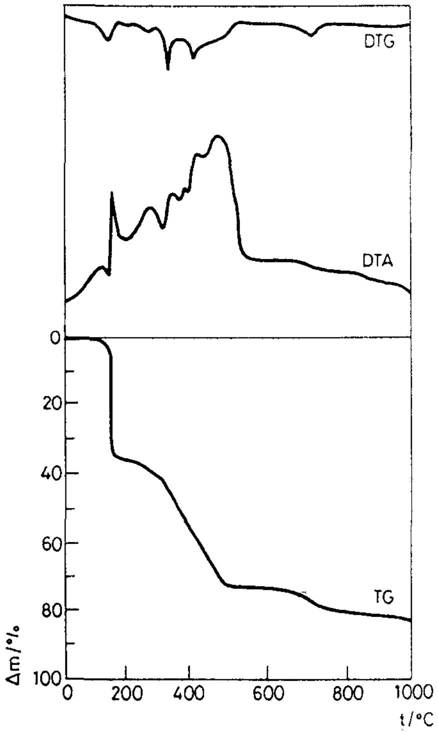

Fig. 3 TG, DTA and DTG curves of Cu(HL)PyNO$_3$·0.5H$_2$O

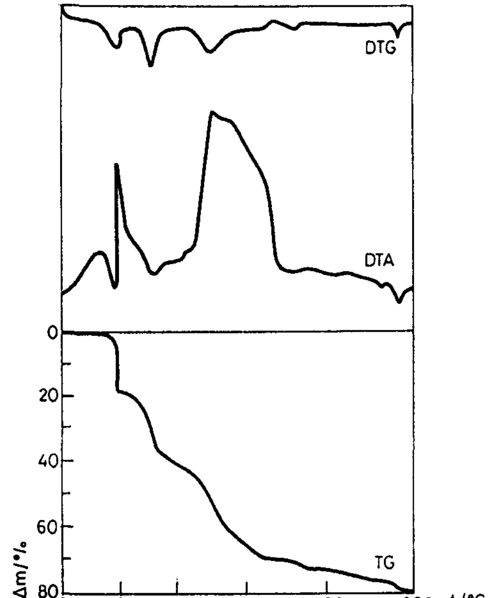

Fig. 4 TG, DTA and DTG curves of Cu(HL)0.5SO$_4$·H$_2$O

The last exothermic effect accompanies elimination of the salicylaldehyde fragment and the formation of copper oxide. The residual product of decomposition for all the investigated complexes was CuO, which was confirmed by X-ray analysis.

References

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Zusammenfassung — In Luft wurde im Temperaturbereich von Raumtemperatur bis 1000°C die thermische Zersetzung von Kupfer(II)-komplexen mit Salizylaldehyd S-Methylthiosemikarbazon der allgemeinen Formel $Cu(HL)X \cdot nH_2O$ (X =Py+NO_3, NCS, $0.5SO_4$) und $[Cu(L)NH_3] \cdot H_2O$ untersucht. Die Zersetzung der Komplexe erfolgt in verschiedenen nacheinanderfolgenden endothermen und exothermen Prozessen, der Rückstand war in allen Fällen CuO.