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STUDIES ON TRIS N[(CHLOROPHENYL)DITHIOCARBAMATO] COMPLEXES OF Au(III) AND As(III)

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ABSTRACT

Tris[N(o-, m-, p-chlorophenyl)dithiocarbamato] complexes of Au(III) and As(III) have been synthesized and characterized. Thermal behaviour of these complexes have been investigated by TG and DTA techniques in static air atmosphere.

INTRODUCTION

In view of the interesting spectral aspects and diversified industrial applications, interest in the study of dithiocarbamate complexes continues to increase. However, only little is known about their thermal behaviour (1). The present work describes the preparation and thermal decomposition of some gold(III) and arsenic(III) complexes.

EXPERIMENTAL

The ligands ammonium N(o-, m-, p-chlorophenyl)dithiocarbamates were prepared by the literature method (2). Au(III) complexes were prepared by adding an aqueous solution of chloroauric acid to an aqueous solution of the ligand. While the As(III) complexes were isolated by adding an aqueous solution of ligand to sodium arsenite solution acidified with dilute hydrochloric acid at 0°C (pH 3-4).

The TG curves were obtained on a Stanton's Automatic Thermorecording Balance model TR-I and DTA was carried out with a Lead and Northrup DTA unit [with a sample size ≈ 100 mg (TG), ≈ 500 mg (DTA), heating rate 4 K/min in a self produced air atmosphere].

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RESULTS AND DISCUSSION

The TG and DTA curves of Au(III) and As(III) complexes are given in figure 1 and 2 respectively. From the TG and DTA curves almost a similar pattern of decomposition is observed for o-, m- and p-complexes with a slight difference in the temperature ranges (Table 1).

TG curves of Au(III) complexes show the two step decomposition. The first step decomposition corresponds to the formation of gold sulphide while the second step results in the formation of metallic gold. A slight arrest in the thermogram during the first step decomposition is observed, this is probably due to the fusion of the complexes. The DTA curves of the complexes show one endotherm and two exotherms. The first endotherm corresponds to the fusion of the complexes while the two exotherms are due to the decomposition of dithiocarbamate to sulphide and conversion of sulphide to metallic gold, respectively.

The thermogram of As(III) complexes show two major thermal changes, viz., the decomposition of the dithiocarbamate to the sulphide, As_2S_3 and the volatilization of the sulphide. The crucible was completely empty at 883K. The DTA profile of the complexes show two endotherms and two exotherms. The first endotherm might be due to the fusion of the complexes. The next two exotherms could be due to the decomposition of the complexes to the sulphides which probably take place in two consecutive steps, not resolved in TG curves. The last endothermic band might be called for the sublimation of the sulphide, As_2S_3 formed after first step weight loss.

On the basis of above results the following decomposition mechanisms may be proposed for Au(III) and As(III) complexes.

Decomposition of Au(III) complexes:

$$Au[S_2CNH(ClC_6H_4)]_3 \longrightarrow Au_2S_3$$

$$Au_2S_3 \longrightarrow Au$$

Decomposition of As(III) complexes:

$$As[S_2CNH(ClC_6H_4)]_3 \longrightarrow As_2S_3$$

$$As_2S_3 \longrightarrow \text{Volatilisation}$$

REFERENCES

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TABLE 1

Thermal stability data of the complexes (K)

Compound	m.p.	TG	DTA	
		Decomp. range	Temp. range	Peak maxima
$Au(OCD)_3$	396	383-533 663-733	363-408 423-483 553-723	388 448 608
$Au(MCD)_3$	427	418-583 583-728	413-448 473-548 613-718	433 528 b
$Au(PCD)_3$	405	393-533 633-768	388-483 498-573 608-673	423 553 648
$As(OCD)_3$	477	463-548 598-863	478-538 538-613 613-698 793-873	503 573 668 823
$As(MCD)_3$	496	488-598 655-883	483-553 553-613 613-768 808-873	498 593 648 818
$As(PCD)_3$	385	378-538 623-873	408-458 503-593 593-653 773-873	438 558 628 828

OCD, MCD, PCD = o-, m- and p-chlorophenyl dithiocarbamate, respectively

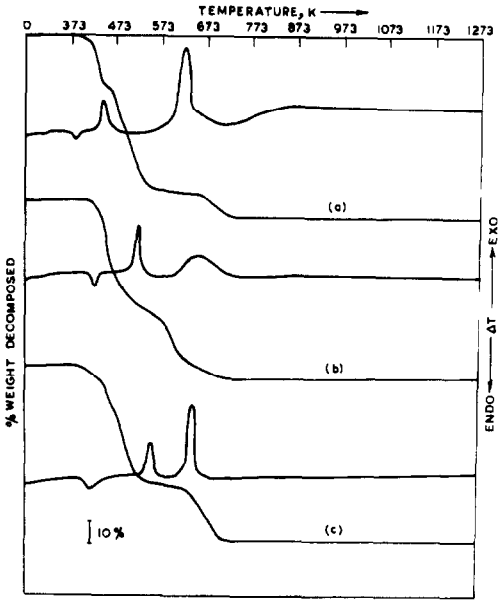

FIG 1 TG AND DTA CURVES OF (a) $Au(OCD)_3$, (b) $Au(MCD)_3$ AND (c) $Au(PCD)_3$

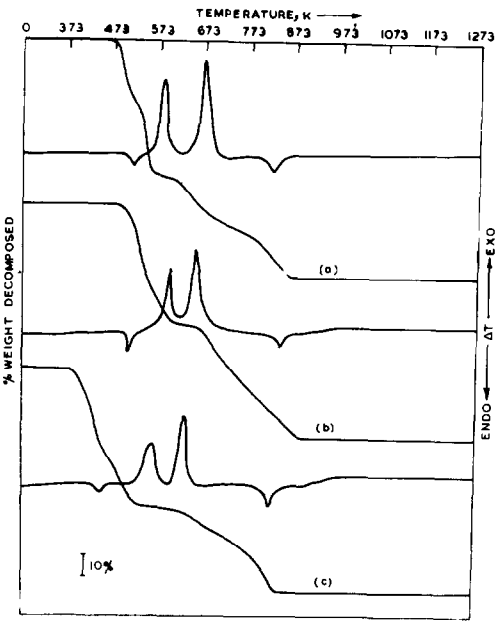

FIG 2 TG AND DTA CURVES OF (a) $As(OCD)_3$, (b) $As(MCD)_3$ AND (c) $As(PCD)_3$