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BIS[*N*(CHLOROPHENYL)DITHIOCARBAMATO] COMPLEXES OF Cu(II), Zn(II), Cd(II) AND Sn(II)

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ABSTRACT

Ammonium[*N*(*o*-chlorophenyl)dithiocarbamate], NH_4(OCD), ammonium [*N*(*m*-chlorophenyl)dithiocarbamate], NH_4(MCD) and ammonium [*N*(*p*-chlorophenyl)dithiocarbamate], NH_4(PCD) and their complexes with Cu(II), Zn(II), Cd(II) and Sn(II) have been synthesised. These complexes have been characterised on the basis of chemical analyses, molecular weight determinations, conductance measurements, electronic and IR spectral studies. Thermal behaviour of the compounds has been studied with the aid of TG and DTA techniques in static air atmosphere. Heats of reaction for different decomposition steps have been calculated from the DTA curves. The end products obtained after thermal decomposition of the complexes were identified by elemental analyses and IR spectral data.

INTRODUCTION

In recent years there has been considerable interest in the field of metal dithiocarbamates due to their diversified applications such as accelerators in vulcanisation, as high pressure lubricants in industries, and as fungicides and pesticides in biological and biochemical fields [1]. Although a large number of metal dithiocarbamates have been reported, only little attention has been paid to the study of the thermal behaviour of these metal complexes [2–13]. In continuation to our previous work on the thermal studies of metal dithiocarbamates [5–13], the present communication describes the preparation, characterisation and thermal investigation of ammonium[*N*(chlorophenyl)dithiocarbamates] and their copper(II), zinc(II), cadmium(II) and tin(II) complexes.

EXPERIMENTAL

The ligands ammonium[*N*(*o*-, *m*-, *p*-chlorophenyl)dithiocarbamates] have been prepared by the reaction of equimolar amounts of the *o*-, *m*- and

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p-chlorophenyl amine, carbon disulphide and ammonia as described by Klopping and Van der Kerk [14]. All the materials used were of analytical grade.

Preparation of the complexes

Bis[*N*(*o*-, *m*-, *p*-chlorophenyl)dithiocarbamato] complexes of copper(II), zinc(II), cadmium(II) and tin(II) have been prepared by mixing an aqueous solution of the appropriate metal salt with an aqueous solution of the ligand in 1 : 2 metal–ligand molar ratio. The products were filtered off, washed with distilled water, and dried over P_4O_{10} under vacuum (yield 60–80%).

Analyses

The ligand was estimated by the method of Shankaranarayana and Patel [15]. Copper, zinc, cadmium and tin were estimated by standard gravimetric methods [16] after digestion of the complexes, as reported by Erdey [17]. Nitrogen was estimated by Kjeldahl's method [16], and sulphur as barium sulphate.

Physical measurements

Molecular weights were determined by a Gallenkemp ebulliometer. Conductance measurements were made in nitrobenzene at $25 \pm 0.5°C$ with a Beckmann conductivity bridge (model RC-18A). Infrared spectra were recorded in the solid-state (KBr pellets) in the region 4000–200 cm^{-1} with a Perkin-Elmer 621 grating spectrometer. The electronic spectra were taken in acetone on the Perkin-Elmer 4000 Å instrument. Magnetic measurements were carried out by Gouy's method [16a] using mercury tetrathiocyanate cobaltate(II), $Hg[Co(SCN)_4]$, as calibrant.

The thermogravimetric curves were obtained on a Stanton-Redcroft automatic thermorecording balance (Model TR-I) with a sample size of 80–102 mg and a heating rate of 4 K min^{-1} in a self-produced air atmosphere. A silica crucible was used for these operations and the curve was recorded up to 1273 K. The sensitivity of the balance per small chart division was 1 mg. The differential thermal analysis was carried out with a Leeds and Northrup DTA unit using ceramic sample holders and a sample cell of Grimshaw pattern. The weight of samples used was 500 mg and powdered α-alumina was used as a reference material and the rate of heating was 10 K min^{-1}.

RESULTS AND DISCUSSION

Analytical data and physical characteristics of the compounds are listed in Table 1. On the basis of analytical results, all the complexes possess 1 : 2

TABLE 1

Analytical data and physical characteristics

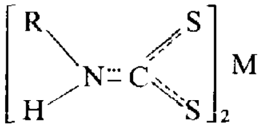
Compound	Colour	m.p. (K)	Found (calcd.) (%) N	S	Cl	M	Mol. wt. found (calcd.)
NH_4(OCD)	Pale white	345	12.50(12.70)	29.20(29.00)	16.30(16.10)		223.3(220.5)
NH_4(MCD)	Pale white	352	12.80(12.70)	29.20(29.00)	16.40(16.10)		219.6(220.5)
NH_4(PCD)	Pale white	368	12.90(12.70)	29.30(29.00)	16.30(16.10)		222.0(220.5)
Cu(OCD)$_2$	Dark brown	385	5.65(5.97)	27.34(27.32)	15.12(15.15)	13.60(13.56)	480.0(468.5)
Cu(MCD)$_2$	Brown	432	5.67(5.97)	27.30(27.32)	15.18(15.15)	13.50(13.56)	460.0(468.5)
Cu(PCD)$_2$	Dark brown	400	5.87(5.97)	27.32(27.32)	15.10(15.15)	13.06(13.56)	485.0(468.5)
Zn(OCD)$_2$	White	455(d)	5.90(5.95)	27.25(27.21)	15.12(15.09)	13.88(13.90)	450.0(470.4)
Zn(MCD)$_2$	White	480(d)	5.97(5.95)	27.10(27.21)	15.04(15.09)	13.80(13.90)	455.0(470.4)
Zn(PCD)$_2$	White	427(d)	5.90(5.95)	27.25(27.21)	15.25(15.09)	13.95(13.90)	454.0(470.4)
Cd(OCD)$_2$	Pale white	382	5.40(5.41)	24.77(24.74)	13.80(13.72)	21.78(21.72)	525.0(517.4)
Cd(MCD)$_2$	Pale white	460	5.46(5.41)	27.70(27.74)	13.80(13.72)	21.69(21.72)	530.0(517.4)
Cd(PCD)$_2$	Pale white	412	5.45(5.41)	24.76(24.74)	13.76(13.72)	21.75(21.72)	525.0(517.4)
Sn(OCD)$_2$	Yellow	377	5.40(5.35)	24.50(24.44)	13.65(13.56)	22.70(22.66)	540.0(523.7)
Sn(MCD)$_2$	Yellow	407	5.37(5.35)	24.48(24.44)	13.60(13.56)	22.70(22.66)	541.0(523.7)
Sn(PCD)$_2$	Yellow	363	5.37(5.35)	24.48(24.44)	13.62(13.56)	22.70(22.66)	500.0(523.7)

d = decomposition temperature.

metal–ligand stoichiometry. They are soluble in most of the common organic solvents, particularly chloroform, acetone, benzene and nitrobenzene. The molar conductance of 10^{-3} M solutions of all these complexes in nitrobenzene are found to be in the range 0.25–0.35 ohm^{-1} cm^2 mol^{-1}, indicating that they are nonelectrolytes. From the molecular weight determination in refluxing benzene, it follows that all the complexes are monomeric species.

IR spectral studies

The infrared spectral studies of the metal dithiocarbamates have been well established by Chatt et al. [18]. The spectra possess one medium intensity band at ~ 1000 cm^{-1}, indicating the presence of a four-membered ring system and supporting the bidentate nature of the dithiocarbamate ligand [19–23]. The thioureide band (C⎓N) near 1500 cm^{-1} is a very important characteristic of the dithiocarbamates. The frequency of this band lies between 1250–1350 cm^{-1} (C–N) and 1640–1690 cm^{-1} (C=N), which suggests that it possesses some double-bond character. Therefore, the general formula



may be assigned to these compounds, where R = *o*-, *m*- or *p*-ClC_6H_4; M = Cu(II), Zn(II), Cd(II) or Sn(II). The weak band appearing at ~ 360 cm^{-1} in these complexes may be assigned to the ν(M–S) band.

Magnetic moment and electronic spectra

Room-temperature magnetic-moment measurements show that the Cu(II) complexes are paramagnetic having a magnetic moment of ~ 1.82 BM; corresponding to one unpaired electron and indicative of square planar geometry for these complexes. The electronic spectra of Cu(II) complexes exhibit three bands at ~ 15 800, ~ 18 000 and ~ 24 800 cm^{-1}. The first two bands may be assigned to ${}^2A_{1g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ transitions, respectively, whereas the third band corresponds to the charge transfer transition [24].

Thermal analysis

The thermal stability data and heats of reaction are given in Table 2. Figures 1–5 present the TG and DTA curves of ammonium[*N*(*o*-, *m*-, *p*-chlorophenyl)dithiocarbamate] and bis[*N*(*o*-, *m*-, *p*-chlorophenyl)dithiocarbamato]copper(II), zinc(II), cadmium(II) and tin(II), in a static air atmosphere.

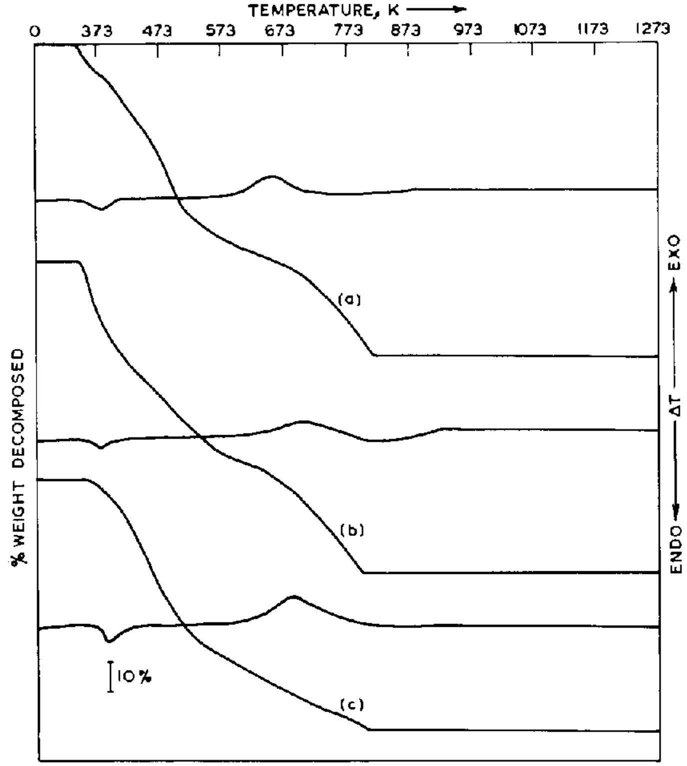


Fig. 1. TG and DTA curves of (a) NH_4(OCD), (b) NH_4(MCD) and (c) NH_4(PCD).

*Ammonium[*N-(o-, m-, p-*chlorophenyl)dithiocarbamate],* $NH_4[S_2CNH$(o-, m-, p-$ClC_6H_4)]$

The TG and DTA curves of ammonium[*N*-(*o*-, *m*-, *p*-chlorophenyl)dithiocarbamate] are shown in Fig. 1. The TG curve of NH_4(OCD) shows that the ligand is stable up to 338 K. Beyond this temperature a one-step decomposition of the compound started, and at 813 K the crucible was completely empty.

The DTA curve shows one endotherm and one exotherm, the first endotherm might be attributed to the fusion as well as partial decomposition of the fused ligand. This is followed by an exotherm which may be due to the complete decomposition of NH_4(OCD).

The TG and DTA curves of both NH_4(MCD) and NH_4(PCD) follow the same pattern of decomposition as that of NH_4(OCD).

*Bis[*N(o-, m-, p-*chlorophenyl)dithiocarbamato]copper(II),* $Cu[S_2CNH$(o-, m-, p-$ClC_6H_4]_2$

The TG and DTA curves of $Cu[S_2CNH$(*o*-, *m*-, *p*-$ClC_6H_4]_2$ are shown in Fig. 2. All three complexes show a three-step decomposition. The first

TABLE 2

Thermal stability data and heats of reaction

Compound	TG			DTA (initial wt. = 500 mg)		
	Initial wt. (mg)	Decomp. range (K)	% wt. loss obs. (calcd.)	Oxidation range (K)	Peak temp. (K)	ΔH (kcal mol^{-1})
$NH_4(OCD)$	100.0	338–813	100.0(100.0)	338 403	b	
				563 783	b	
$NH_4(MCD)$	80.0	343–793	99.8(100.0)	333–433	b	
				543–793	b	
$NH_4(PCD)$	100.0	368–803	99.8(100.0)	360–468	b	
				548–803	b	
$Cu(OCD)_2$	100.0	373–1168	83.0(83.1)	368–423	398	2.61
				473–528	498	14.94
				598–688	653	54.32
				788–823	808	43.54
				848–973	873	91.07
				1013–1153	b	
$Cu(MCD)_2$	90.0	423–1133	83.0(83.1)	423–478	448	5.18
				503–558	543	37.13
				598–743	618	17.11
				823–968	b	
				1073–1125	1103	30.73
$Cu(PCD)_2$	100.0	393–1183	82.5(83.1)	388–443	408	2.75
				493–548	513	14.26
				618–673	643	22.87
				673–748	678	58.46
				798–858	833	88.88
				1083–1123	1103	21.51
$Zn(OCD)_2$	85.0	453–1223	83.0(82.7)	453 513	b	
				513–573	548	
				748–823	788	
				823–898	878	

$Zn(MCD)_2$	90.0	468–1123	83.0(82.7)	488–513	b
				538–583	573
				758–823	803
				878–948	918
$Zn(PCD)_2$	90.0	413–1073	83.5(82.7)	423–473	448
				488–558	528
				773–823	798
				893–1073	923
$Cd(OCD)_2$	100.0	373–1273		378–423	b
				468–508	493
				548–598	573
				718–788	758
				1023–1223	b
$Cd(MCD)_2$	90.0	453–1223		448–518	b
				513–618	b
				478–773	753
				813–883	858
				1073–1223	b
$Cd(PCD)_2$	80.0	403–1273		433–548	b
				648–723	698
				723–798	763
				1073–1273	b
$Sn(OCD)_2$	102.0	368–873	71.0(71.2)	380–413	398
				423–483	463
				533–673	623
				733–833	783
$Sn(MCD)_2$	100.0	398–873	71.0(71.2)	413–448	423
				448–473	473
				523–668	578
				773–833	808
$Sn(PCD)_2$	100.0	403–1273	71.0(71.2)	338–418	408
				418–468	438
				528–673	613
				673–798	748

b = broad peak.

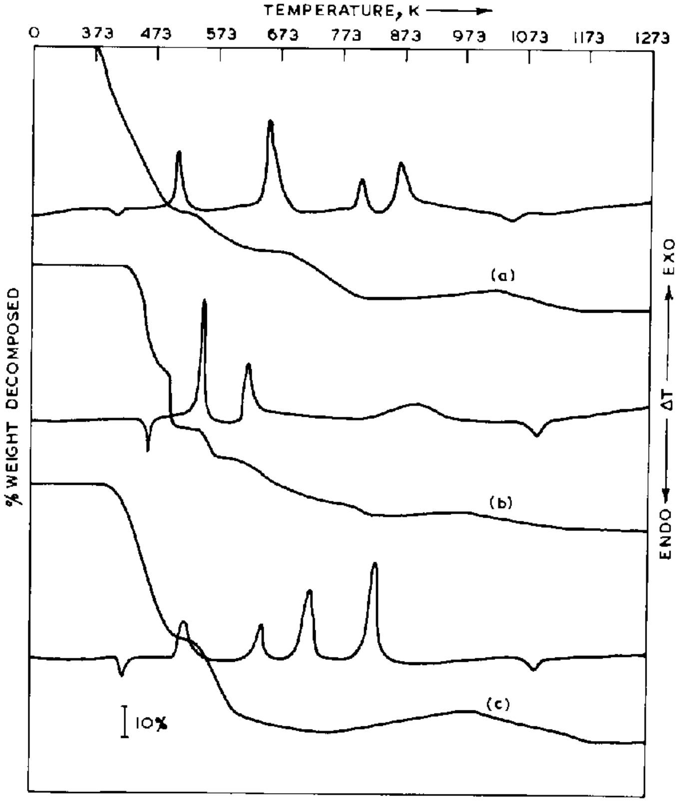


Fig. 2. TG and DTA curves of (a) $Cu(OCD)_2$, (b) $Cu(MCD)_2$, and (c) $Cu(PCD)_2$.

weight-loss corresponds to the formation of copper sulphide, Cu_2S. After this there is a sudden increase in weight, which is followed by a decrease in weight. The increase in weight is due to the oxidation of Cu_2S to $CuSO_4$ and CuO. In the next step, the decrease in weight is due to the decomposition of the sulphate to CuO.

The DTA profile of the complexes shows two endotherms and four exotherms. The first endotherm is due to the melting of the complex. This is followed by an exotherm which may be assigned to the decomposition of the complex to the sulphide, Cu_2S. Three exothermic peaks may appear, due to the oxidation of Cu_2S to CuO and $CuSO_4$. The final endothermic peak is probably due to the decomposition of $CuSO_4$ to CuO.

The mode of decomposition of $Cu[S_2CNH(o\text{-}, m\text{-}, p\text{-}ClC_6H_4]_2$ may, therefore, be represented by the following scheme

$$Cu[S_2CNH(ClC_6H_4)]_2 \rightarrow Cu_2S$$

$$2\,Cu_2S + 5\,O_2 \rightarrow 2\,CuO + 2\,CuSO_4$$

$$CuSO_4 \rightarrow CuO + SO_3$$

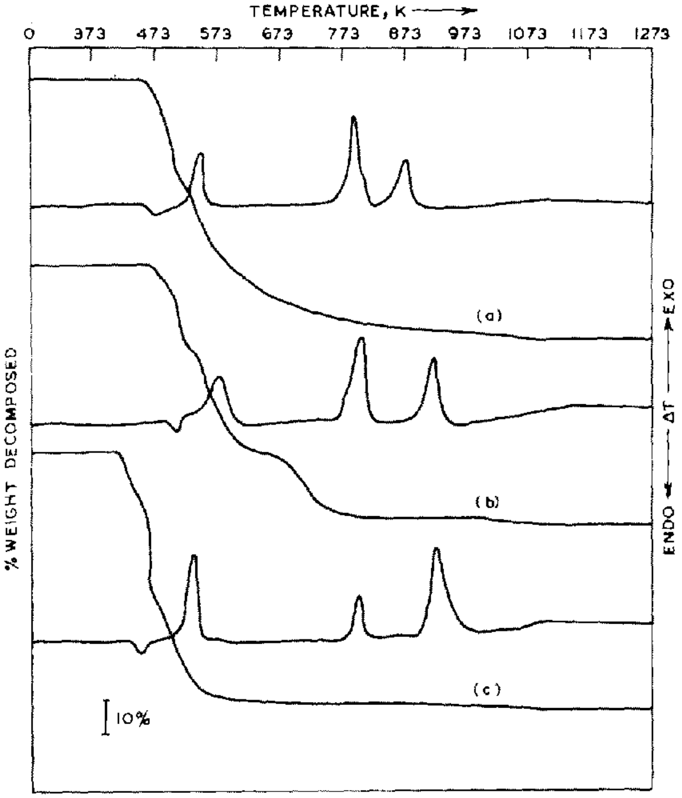


Fig. 3. TG and DTA curves of (a) $Zn(OCD)_2$, (b) $Zn(MCD)_2$, and (c) $Zn(PCD)_2$.

Bis[N(o-, m-, p-chlorophenyl)dithiocarbamato]zinc(II), $Zn[S_2CNH(o\text{-}, m\text{-}, p\text{-}ClC_6H_4)]_2$

The TG curves of $Zn[S_2CNH(o\text{-}, m\text{-}, p\text{-}ClC_6H_4)]_2$ show two major changes in their thermal behaviour. In the first step, rapid decomposition corresponds to the formation of zinc sulphide which, in the second step, converted slowly into the zinc oxide.

$$\begin{aligned} &Zn[S_2CNH(ClC_6H_4)]_2 && \rightarrow && ZnS \\ &ZnS + O_2 && \rightarrow && ZnO \end{aligned}$$

The DTA of $Zn[S_2CNH(o\text{-}, m\text{-}, p\text{-}ClC_6H_4)]_2$ shows one endotherm and three exotherms. The first small endotherm having no sharp maxima corresponds to the fusion and partial decomposition of the complex. The next two exotherms may be due to the oxidation of the zinc sulphide to zinc oxide. The final exotherm may be assigned to the oxidation of the sulphide to sulphate and its decomposition.

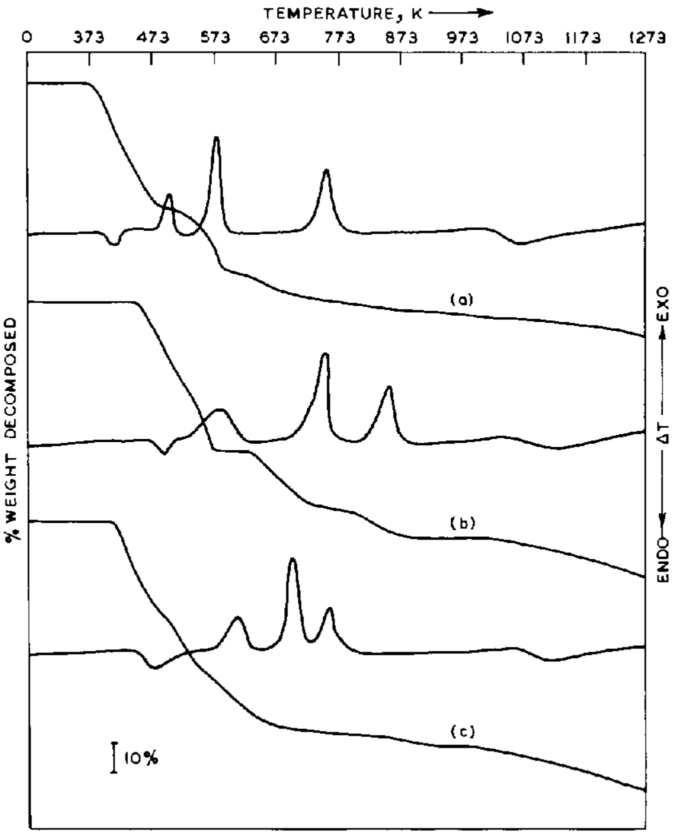


Fig. 4. TG and DTA curves of (a) $Cd(OCD)_2$, (b) $Cd(MCD)_2$, and (c) $Cd(PCD)_2$.

*Bis[*N(o-, m-, p-*chlorophenyl)dithiocarbamato]cadmium(II),* $Cd[S_2CNH$(o-, m-, p-$ClC_6H_4)]_2$

The complex $Cd(OCD)_2$ is stable up to 373 K. Beyond this temperature the TG curve descends rapidly with the destruction of organic matter. The simultaneous destruction of organic matter and the oxidation of the sulphide and the metal forming sulphate and oxide, respectively, resulted in an arrest (478–583 K) in the decomposition rate of complex. A mixture of cadmium sulphate, cadmium sulphide and cadmium oxide was obtained at 1273 K. No horizontal level corresponding to cadmium sulphate, cadmium sulphide or cadmium oxide is obtained. This is probably due to the partial volatilization of CdS and CdO at elevated temperatures.

The DTA curve for $Cd(OCD)_2$ showed two endotherms and three exotherms. The first peak is a shallow endotherm due to the melting of the complex. The next three exotherms may be attributed to the destruction of the organic matter with the simultaneous oxidation of the sulphide and metal forming sulphate and oxide, respectively. The last endotherm may be due to the partial volatilization of CdO and CdS.

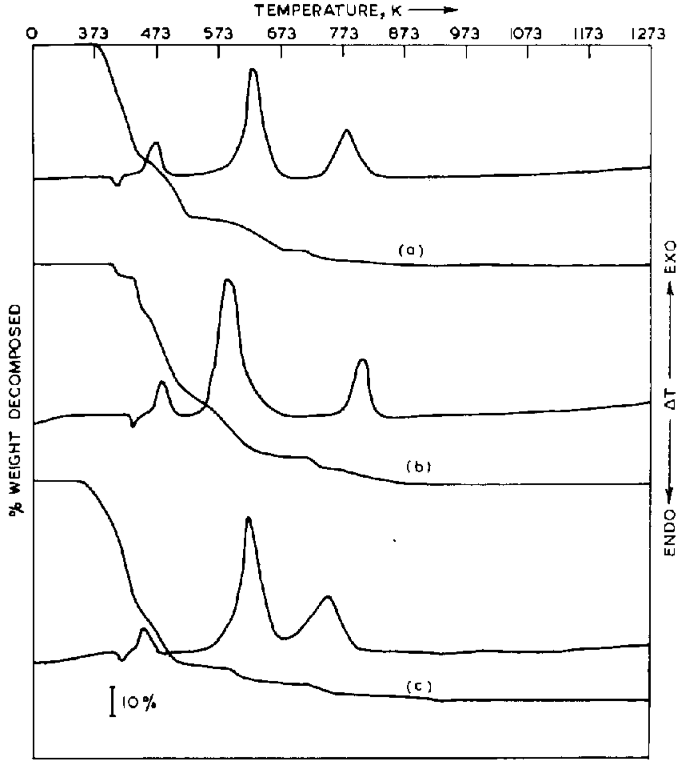


Fig. 5. TG and DTA curves of (a) $Sn(OCD)_2$, (b) $Sn(MCD)_2$, and (c) $Sn(PCD)_2$.

The TG and DTA profiles of the *m*- and *p*-analogues, $Cd(MCD)_2$ and $Cd(PCD)_2$, are of similar nature as that described for the *ortho* complex, $Cd(OCD)_2$. No definite product was obtained after the decomposition in any of these cases.

*Bis[*N-(o-, m-, p-*chlorophenyl)dithiocarbamato]tin(II), Sn[S₂CNH(*o-, m-, p-*ClC₆H₄)]₂*

The complex $Sn(OCD)_2$ shows two major thermal changes and is stable up to 373 K. Beyond this temperature it starts to decompose and continues up to 668 K. The rate of decomposition of this complex is very slow up to 573 K and a slight arrest in the rate of decomposition is observed in the temperature range 428–573 K. After 573 K the rate of decomposition is accelerated until a perfectly horizontal level appeared, in the temperature range 668–713 K, corresponding to the formation of SnS_2. Beyond 713 K the conversion of sulphide into oxide starts which completes at 873 K. A horizontal level corresponding to SnO_2 then appeared, which continues up to 1273 K.

The DTA of $Sn(OCD)_2$ shows one endotherm and three exotherms. The first endothermic band could be ascribed to the melting of the complex and the next two exotherms might be due to the decomposition of the complex to sulphide which probably takes place in two steps, not resolved from the TG curve. The last exothermic peak might be attributed to the conversion of SnS_2 to SnO_2.

From the TG and DTA curves an almost similar pattern of decomposition is observed for $Sn(MCD)_2$ and $Sn(PCD)_2$, as that described for $Sn(OCD)_2$.

The mode of decomposition of $Sn[S_2CNH(ClC_6H_4)]_2$ may be represented by the following scheme

$$Sn[S_2CNH(ClC_6H_4)]_2 \rightarrow SnS_2$$
$$SnS_2 + O_2 \rightarrow SnO_2$$

The heats of reaction from DTA curves have been calculated using the simple expression

$$\Delta H = KA/N_0$$

where ΔH is the heat of reaction, K is the calibration constant, A is the area under the peak and N_0 is the initial number of moles of the specimen.

CONCLUSION

Thermoanalytical data of the complexes reveal that the decomposition of most of the complexes proceeds through two major steps, viz., the decomposition of the metal dithiocarbamate to metal sulphide and the decomposition of metal sulphide to metal oxide. The formation of metal sulphate as the intermediate oxidation product is observed in case of Cu(II) complexes.

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