Thermochimica Acta, 58 (1982) 231–243
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

BIS-*N*(*p*-ETHOXYPHENYL)DITHIOCARBAMATO COMPLEXES OF Cu(II), Zn(II), Cd(II), Sn(II), Sn(IV), Ni(II) AND Pd(II)

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(Received 25 March 1982)

ABSTRACT

Bis-*N*(*p*-ethoxyphenyl)dithiocarbamato complexes of copper(II), zinc(II), cadmium(II), tin(II), tin(IV), nickel(II) and palladium(II), abbreviated as $Cu(PED)_2$, $Zn(PED)_2$, $Cd(PED)_2$, $Sn(PED)_2$, $Sn(PED)_2Cl_2$, $Ni(PED)_2$ and $Pd(PED)_2$, have been synthesized. These complexes have been characterized on the basis of elemental analyses, molecular weight determinations, conductance measurements, IR and electronic spectral studies. Thermal studies of these complexes have been carried out in a static air atmosphere to determine their mode of decomposition. Kinetic parameters such as apparent activation energy and order of reaction have been determined using the graphical method of Coats and Redfern. Heats of reaction for different decomposition steps have been calculated from the DTA curves. The intermediates obtained at the end of various thermal decomposition steps were identified on the basis of elemental analyses and IR spectral studies.

INTRODUCTION

Dithiocarbamates form a class of sulphur–sulphur donor ligands, the metal complexes of which have been extensively studied for quite some years [1]. The interest in these complexes has been stimulated by their use in industry as vulcanization accelerators and as high pressure lubricants, whereas their use as fungicides and pesticides has induced a vast number of biological and biochemical studies [2]. A literature survey reveals that little work has been carried out on thermal studies of metal dithiocarbamato complexes [3–8]. In continuation of our previous work on metal dithiocarbamates [6–8], the present communication describes the preparation, characterization and thermal investigation on bis-*N*(*p*-ethoxyphenyl)dithiocarbamato complexes of Cu(II), Zn(II), Cd(II), Sn(II), Sn(IV), Ni(II) and Pd(II).

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0040-6031/82/0000–0000/$02.75

EXPERIMENTAL

Materials and methods

The ligand ammonium[*N*(*p*-ethoxyphenyl)dithiocarbamate] has been prepared by the reaction of equimolar amounts of the *p*-phenetidine, carbon disulphide and ammonia as described by Klopping and Vander Kerk [9]. All the materials used were of analytical grade. Extra pure *p*-phenetidine (Aldrich, U.S.A.) and carbon disulphide (B.D.H., England) were employed.

Preparation of the complexes

Bis-*N*(*p*-ethoxyphenyl)dithiocarbamate complexes of copper(II), zinc(II), cadmium(II), tin(II), tin(IV), nickel(II) and palladium(II) have been prepared by mixing an aqueous solution of the appropriate metal salt with an aqueous solution of the ligand in 1:2 molar ratio. The products were filtered off, washed with distilled water and dried over P_4O_{10} under vacuum; yield, 65–85%.

Analyses

The ligand was estimated by the method of Shankaranarayana and Patel [10]; copper, zinc, cadmium, tin, nickel and palladium were estimated by standard gravimetric methods [11] after digestion of the complexes, as reported by Erdey [12]. Nitrogen was estimated by Kjeldahl's method and sulphur as barium sulphate.

Physical measurements

Molecular weights were determined by a Gallenkemp (U.K.) ebulliometer. Conductance measurements were made in nitrobenzene at 25 ± 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 spectrophotometer. The electronic spectra were taken in acetone on the Perkin-Elmer 400 Å instrument in the region 400–750 nm. Magnetic measurements were carried out by Gouy's method using mercury tetrathiocyanate cobaltate(II), $Hg[Co(SCN)_4]$ as calibrant.

The thermogravimetric curves were obtained on a Stanton automatic thermorecording balance Model TR-I with a sample size ~ 100 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 (U.S.A.) using ceramic sample holders and a sample cell of Grimshaw pattern. The weight of samples used was ~ 100 mg and powdered α-alumina was used as a reference material. Rate of heating was 10 K min^{-1}.

RESULTS AND DISCUSSION

Analytical data and other physical characteristics of the compounds are listed in Table 1. On the basis of analytical results, all the complexes possess 1:2 metal-to-ligand stoichiometry. They are soluble in most of the common organic solvents, particularly chloroform, acetone, benzene and nitrobenzene. The molar conductances of 10^{-3} M solutions of all these complexes in nitrobenzene are found to be in the range 0.25–0.35 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mole}^{-1}$, 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

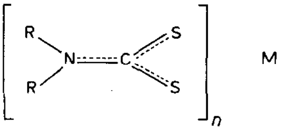
The IR spectral studies of the metal dithiocarbamates have been well established by Chatt et al. [13]. The spectra possess one medium intensity

TABLE 1

Analytical data and physical characteristics

Compound	Colour	M.p. (K)	Found (calcd.)%				M.W. Found (calcd.)
			M	N	S	Cl	
$Cu(PED)_2$	Dark brown	465	13.02 (13.03)	5.78 (5.74)	26.40 (26.26)		484 (487.5)
$Zn(PED)_2$	White	423	13.32 (13.36)	5.60 (5.72)	26.30 (26.16)		480 (489.37)
$Cd(PED)_2$	White	418	20.80 (20.95)	5.10 (5.20)	23.94 (23.86)		522 (536.4)
$Sn(PED)_2$	Yellow	408	21.92 (21.87)	5.24 (5.60)	23.40 (23.56)		534 (542.7)
$Sn(PED)_2Cl_2$	Yellow	430	19.40 (19.30)	4.50 (4.56)	20.90 (20.86)	11.50 (11.57)	608 (613.6)
$Ni(PED)_2$	Green	505	12.06 (12.16)	5.86 (5.80)	26.40 (26.52)		480 (482.7)
$Pd(PED)_2$	Light yellow	444	20.10 (20.06)	5.40 (5.28)	24.06 (24.13)		526 (530.4)

band at ~ 1000 cm^{-1}, indicating the presence of a four-membered ring system and supporting the bidentate nature of the dithiocarbamate ligand [14–18]. The thioureide band (C=N) near 1500 cm^{-1} is a very important characteristic of the dithiocarbamates. The frequency of this band lies between (C–N) 1250–1350 cm^{-1} and (C=N) 1640–1690 cm^{-1}, which suggests that it possesses some double bond character. Therefore, the general formula



may be assigned to these compounds where $R = p\text{-}OC_2H_5C_6H_4$, M = Cu(II), Zn(II), Cd(II), Sn(II), Sn(IV)Cl_2, Ni(II) and Pd(II), and *n* is the oxidation state of the metal. The weak band appearing at ~ 360 cm^{-1} in these complexes may be assigned to the ν(M–S) band [M = Cu(II), Zn(II), Cd(II), Sn(II), Sn(IV), Ni(II) and Pd(II)].

Magnetic moment and electronic spectra

Room temperature magnetic moment measurements show that the Cu(II) complex is paramagnetic, having a magnetic moment of 1.82 B.M. corresponding to one unpaired electron in this complex. Other complexes studied, viz. Zn(II), Cd(II), Sn(II), Sn(IV), Ni(II) and Pd(II), are diamagnetic. The electronic spectrum of the Cu(II) complex resembles that of a d^9 square-planar complex. This exhibits three bands at 15800, 18000 and 24800 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 [19].

Thermal analysis

Figures 1 and 2 present the TG and DTA curves of $Cu(PED)_2$, $Zn(PED)_2$, $Cd(PED)_2$, $Sn(PED)_2$, $Sn(PED)_2Cl_2$, $Ni(PED)_2$ and $Pd(PED)_2$ in a static air atmosphere.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*copper(II),* $Cu(S_2CNH(p\text{-}OC_2H_5C_6H_4))_2$

The TG and DTA curves of bis[*N*(*p*-ethoxyphenyl)dithiocarbamato]-copper(II) show that the compound decomposes in three steps. The first weight loss step corresponds to the formation of copper sulphide, Cu_2S. After this there is a sudden increase in the weight which is followed by a

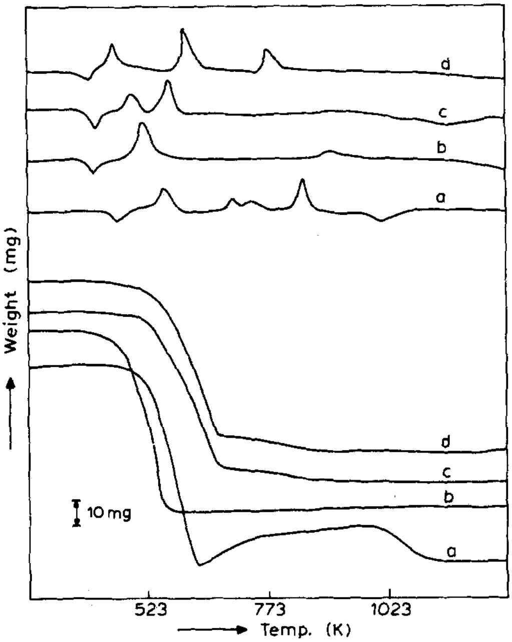


Fig. 1. TG and DTA curves of (a) $Cu(PED)_2$, (b) $Zn(PED)_2$, (c) $Cd(PED)_2$ and (d) $Sn(PED)_2$.

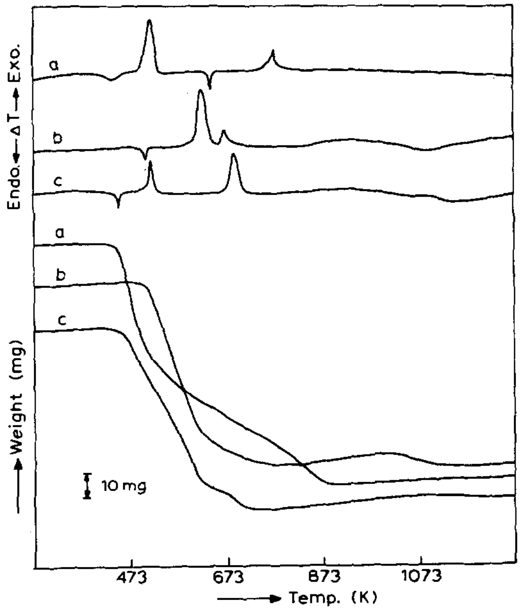


Fig. 2. TG and DTA curves of (a) $Sn(PED)_2Cl_2$, (b) $Ni(PED)_2$ and (c) $Pd(PED)_2$.

decrease in weight. The increase in weight is due to the oxidation of Cu_2S to $CuSO_4$ and CuO.

$$2\,Cu_2S + 5\,O_2 \xrightarrow{623-958\text{ K}} 2\,CuO + 2\,CuSO_4$$

The decrease in weight is due to the decomposition of the sulphate to the oxide.

$$CuSO_4 \xrightarrow{958-1173\text{ K}} CuO + SO_3$$

Thus a residue of CuO is the end product of the thermal decomposition of $Cu(PED)_2$.

The DTA profile of $Cu(PED)_2$ in air shows two endotherms and four exotherms. The first endotherm with a sharp maxima at 468 K is due to the melting of the complex. This is followed by an exotherm which may be assigned to the decomposition of $Cu(PED)_2$ into Cu_2S. Three exothermic peaks at 708, 738 and 848 K may appear due to the oxidation of Cu_2S to CuO and $CuSO_4$. The final endothermic peak at 1008 K is probably due to the decomposition of $CuSO_4$ to CuO.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*zinc(II)*, $Zn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2$

Bis[*N*(*p*-ethoxyphenyl)dithiocarbamato]zinc(II) shows two major changes in its thermal behaviour. The complex was stable up to 423 K. In the first step the compound decomposes rapidly into zinc sulphide which in the second step is converted slowly into zinc oxide. Furthermore, the thermolysis curve of the compound reveals that zinc sulphate is not formed at any stage. The end product ZnO may be obtained easily by heating the complex at 1080 K for 30 min. The mode of decomposition of the $Zn(PED)_2$ therefore may be represented by the following scheme.

$$Zn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \xrightarrow{423-558\text{ K}} ZnS$$

$$ZnS \xrightarrow{653-1073\text{ K}} ZnO$$

The DTA of $Zn(PED)_2$ shows one endotherm and two exotherms. A small endotherm having a sharp maxima at 423 K corresponds to the melting of the complex. The first exotherm can be ascribed to the decomposition of the complex into sulphide. The next exotherm having no sharp maxima may be due to the oxidation of zinc sulphide, formed after the first decomposition step to zinc oxide.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*cadmium(II)*, $Cd[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2$

From the thermogram of $Cd(PED)_2$, it is observed that the complex is thermally stable up to 398 K. Beyond this temperature the TG curve descends rapidly. This rapid mass loss may be due to the simultaneous destruction of the organic matter and oxidation of the sulphide and the metal formed to the sulphate and oxide, respectively. A mixture of cadmium sulphide and cadmium oxide is obtained at 1273 K. No horizontal level corresponds to cadmium sulphate, cadmium sulphide or cadmium oxide.

The DTA curve for $Cd(PED)_2$ shows two endotherms and three exotherms. The first peak at 419 K is endothermic due to 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 formed to the sulphate and oxide, respectively. The last endotherm between 1113 and 1208 K may be due to the partial volatilization of CdO and CdS.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*tin(II)*, $Sn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2$

The complex $Sn(PED)_2$ shows two major thermal changes, and is stable up to 408 K. Beyond this temperature it starts to decompose and continues up to 673 K. The rate of decomposition of this complex is very slow up to 473 K, after which it is accelerated until a perfectly horizontal level in the temperature range 673–723 K appears which corresponds to the formation of SnS_2. Beyond 723 K the conversion of the sulphide to the oxide starts which is complete at 883 K. A horizontal level corresponding to SnO_2 then appears which is stable up to 1273 K.

$$Sn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \xrightarrow{408-673\ K} SnS_2$$

$$SnS_2 + O_2 \xrightarrow{723-883\ K} SnO_2$$

The DTA profile of $Sn(PED)_2$ reveals one endotherm and three exotherms. The first endothermic band corresponds to the melting of the complex. The next two exothermic bands may be due to two consecutive decomposition steps, viz. decomposition of dithiocarbamate to thiocyanate and decomposition of thiocyanate to sulphide, which are not resolved from the TG curve. The last exothermic band may be attributed to the conversion of SnS_2 to SnO_2.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*dichlorotin(IV)*, $Sn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]Cl_2$

Bis[*N*(*p*-ethoxyphenyl)dithiocarbamato]dichlorotin(IV) shows a three-step decomposition, viz. the decomposition of dithiocarbamate to thiocyanate, $Sn(CNS)_2Cl_2$, the decomposition of thiocyanate to sulphide, SnS_2, and the oxidation of sulphide to oxide SnO_2.

$$Sn[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2Cl_2 \xrightarrow{433-503\ K} Sn(CNS)_2Cl_2$$

$$Sn(CNS)_2Cl_2 \xrightarrow{523-678\ K} SnS_2$$

$$SnS_2 + O_2 \xrightarrow{718-893\ K} SnO_2$$

The intermediates $Sn(SCN)_2Cl_2$ and SnS_2 may be obtained by heating the complex at 513 K and 693 K, respectively, for about 30 min. Analysis of the residue at 513 K and 693 K clearly confirms the viewpoint that chlorine is eliminated in the temperature interval 523–678 K.

The DTA of $Sn(PED)_2Cl_2$ shows two endotherms and two exotherms. The first endotherm having maximum at 433 K may be correlated to the fusion as well as the decomposition of the complex. The exotherm in the temperature interval 483–533 K may be attributed to the decomposition of the organic portion of the complex, leading to the formation of $Sn(CNS)_2Cl_2$. The next endotherm having a maximum at 648 K is due to the decomposition of $Sn(CNS)_2Cl_2$ into SnS_2. The last exothermic band corresponds to the conversion of SnS_2 into SnO_2.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*nickel(II)*, $Ni[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2$

The complex $Ni(PED)_2$ decomposes in four well-defined steps. The first decomposition step, with rapid mass loss, leads to the formation of nickel thiocyanate. The intermediate nickel thiocyanate, $Ni(SCN)_2$, then decomposes into nickel sulphide in the second decomposition stage, after which the TG curve shows a sudden increase in the weight due to oxidation of some nickel sulphide to nickel sulphate. After the third decomposotion step, there again occurs a mass loss due to the decomposition of nickel sulphate to nickel oxide.

$$Ni[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_2 \xrightarrow{508-638\ K} Ni(CNS)_2$$

$$Ni(CNS)_2 \xrightarrow{638-823\ K} NiS$$

$$NiS + O_2 \xrightarrow{823-1023\ K} NiSO_4$$

$$NiSO_4 \xrightarrow{1023-1183\ K} NiO$$

From the DTA of Ni(PED)$_2$ two endotherms and three exotherms are observed. The first endotherm is due to the melting of the complex while the second endotherm is attributed to the decomposition of nickel sulphate to nickel oxide. The first, second and third exotherms are due to the decomposition of dithiocarbamate to thiocyanate, the decomposition of thiocyanate to sulphide, and finally the oxidation of nickel sulphide to nickel sulphate, respectively.

Bis[N(p-*ethoxyphenyl)dithiocarbamato*]*palladium(II),* $Pd[S_2CNH(\text{p-}OC_2H_5C_6H_4)]_2$

The complex Pd(PED)$_2$ is thermally stable up to 448 K. Beyond this temperature, decomposition of the complex starts and continues up to 703 K, having a slight arrest in the temperature interval 598–648 K. A plateau between 703 and 823 K appears which corresponds to metallic palladium. After 823 K the platinum metal undergoes partial oxidation and this continues up to 1023 K. After 1073 K the decomposition of the oxide starts, resulting the formation of metallic palladium at 1223 K.

$$\mathrm{Pd[S_2CNH(\mathit{p}\text{-}OC_2H_5C_6H_4)]_2} \xrightarrow{448-598\ \mathrm{K}} \mathrm{PdS}$$

$$\mathrm{PdS} \xrightarrow{648-703\ \mathrm{K}} \mathrm{Pd}$$

$$\mathrm{Pd} + \tfrac{1}{2}\,\mathrm{O_2} \xrightarrow{823-1073\ \mathrm{K}} \mathrm{PdO}$$

$$\mathrm{PdO} \xrightarrow{1073-1273\ \mathrm{K}} \mathrm{Pd}$$

The DTA curve of Pd(PED)$_2$ shows two endotherms and three exotherms. A small endothermic band having a maximum at 448 K corresponds to the melting of the compound. The next two endotherms are due to the decomposition of the complex into sulphide, followed by its conversion into palladium metal. The next broad endotherm corresponds to the oxidation of metallic palladium to palladium oxide. The last small exotherm is attributed to the decomposition of the oxide into metallic palladium.

Evaluation of kinetic parameters and heats of reaction

Kinetic parameters such as apparent activation energy and order of reaction for the first thermal decomposition step of Cu(PED)$_4$, Zn(PED)$_2$, Sn(PED)$_2$ and Sn(PED)$_2$Cl$_2$ have been determined (Table 2) using the graphical method of Coats and Redfern [20]. The order of reaction in all cases was found to be one (Fig. 3). The reason behind the calculation of the kinetics for the first thermal decomposition step is exclusively thermal since the rate equation used is quite sensitive to the thermal properties of the

TABLE 2

Temperature range, weight loss, activation energy and heat of reaction for different decomposition steps of $Cu(PED)_3$, $Zn(PED)_2$, $Cd(PED)_2$, $Sn(PED)_2$, $Sn(PED)_2Cl_2$, $Ni(PED)_2$ and $Pd(PED)_2$

Compound	TG					DTA		
	Decomposition range (K)	%wt. loss		Order of reaction	*E* (Kcal $mole^{-1}$)	Oxidation range (K)	Peak temp. (K)	ΔH (Kcal $mole^{-1}$)
		Obsd.	Calcd					
$Cu(PED)_3$	463– 623	67.02	67.38	1st	26.15	453– 488	468	4.33
	623– 958					533– 583	563	13.80
						673– 723	710	12.42
						723– 768	738	12.55
						808– 898	848	67.80
	958–1173	16.16	16.31			993–1033	1008	12.40
$Zn(PED)_2$	423– 558	80.32	80.10	1st	16.18	413– 443	423	2.97
						488– 558	518	34.07
	653–1073	3.09	3.27			823–1023		
$Cd(PED)_2$	398–1273					408– 438	419	3.38
						473– 523	498	9.69
						538– 588	565	16.18
						848–1053		
						1113–1208		

$Sn(PED)_2$	408– 673	66.50	66.33	1st	12.64	398– 423	410	2.52
						438– 478	463	5.38
						573– 648	613	33.24
	723– 883	6.02	5.90			773– 808	788	12.79
$Sn(PED)_2Cl_2$	433– 503	50.32	50.20	1st	22.88	408– 473	433	6.26
						483– 533	515	31.22
	523– 678	19.92	20.04			633– 668	648	6.70
	718– 893	5.30	5.22			748– 824	778	6.71
$Ni(PED)_2$	508– 638	64.04	63.81			488– 523	508	2.82
						583– 658	623	
	638– 823	17.32	17.41			658– 728	673	17.84
	823–1023					848–1033		
	1023–1173	3.32	3.30			1033–1173		
$Pd(PED)_2$	448– 598	73.80	73.91			433– 468	448	2.80
						478– 538	515	10.18
	648– 703	6.08	6.03			673– 703	693	17.50
	823–1073					863–1023		
	1073–1273					1088–1223	1128	47.35

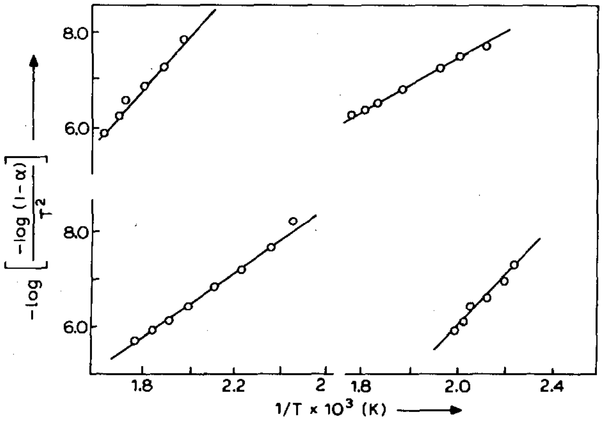


Fig. 3. Coats and Redfern linearization curves of (a) $Cu(PED)_2$, (b) $Zn(PED)_2$, (c) $Sn(PED)_2$ and (d) $Sn(PED)_2Cl_2$.

sample and it is quite obvious that various thermal properties do not remain the same for the sample at the beginning and after the first thermal decomposition.

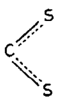
Calculation of the heats of reaction from DTA curves has been done using the simple expression

$$\Delta H = KA/N_0$$

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

The above results are suggestive of bidentate coordination of the ligand through sulphur [7,14].



Thermoanalytical data of the complexes reveal that the decomposition of most of the complexes proceeds through two major steps, viz. the decomposition of metal dithiocarbamate to metal sulphide to metal oxide/metal. However, for $Cd(PED)_2$ a single decomposition step is observed. In the case of $Sn(PED)_2Cl_2$ and $Ni(PED)_2$, however, the decomposition of metal dithiocarbamate to metal sulphide is observed in two substeps; the first weight loss corresponds to the formation of metal thiocyanate followed by the formation of metal sulphide after the second weight loss. The formation of metal sulphate as an intermediate oxidation product is observed in the case of $Cu(PED)_2$ and $Ni(PED)_2$. The first stage decomposition reactions in the case of $Cu(PED)_2$, $Zn(PED)_2$, $Sn(PED)_2$ and $Sn(PED)_2Cl_2$ in a static air atmosphere follow first order kinetics.

REFERENCES

1 D. Coucouvanis, in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. XI, Interscience, London, 1970, p. 233.
2 G.D. Thorn and R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, New York, 1962.
3 M.A. Par Bernard and M.M. Borel, Bull. Soc. Chim. Fr., (1969) 3066.
4 G. D'Ascenzo and W.W. Wendlandt, J. Therm. Anal., 1 (1969) 423.
5 S.V. Larionov and L.A. Kosareva, Thermal Analysis, Proc. 4th ICTA, Budapest, 1974, p. 877.
6 S. Kumar, N.K. Kaushik and I.P. Mittal, Thermal Analysis, Proc. 6th ICTA, Bayreuth, 1980, p. 137.
7 S. Kumar and N.K. Kaushik, Thermochimica Acta, 41 (1980) 19.
8 S. Kumar and N.K. Kaushik, Indian J. Chem., 20 (1981) 512.
9 H.L. Klopping and G.J.M. Vander Kerk, Rec. Trav. Chim., 70 (1951) 917.
10 M.L. Shankaranarayana and C.C. Patel, Anal. Chem., 33 (1961) 1398.
11 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans Green, London, 1964.
12 L. Erdey, Gravimetric Analysis, Vols. I and II, Pergamon, New Uork, 1965.
13 J. Chatt, L.A. Duncanson and L.M. Venanzi, Nature (London), 117 (1956) 1042.
14 F. Bonati and R. Ugo, J. Organomet. Chem., 10 (1967) 257.
15 G.E. Monoussakis, C.A. Tsipis and C.C. Hadjkostas, Can. J. Chem., 53 (1975) 1530.
16 T.N. Srivastava and V. Kumar, J. Organomet. Chem., 107 (1976) 55.
17 G. St. Nikolov, N. Jordanov and K. Daskadova, Inorg. Nucl. Chem. Lett., 33 (1971) 1059.
18 C. O'Connor, J.D. Gilbert and G. Wilkinson, J. Chem. Soc. A, (1969) 84.
19 B.N. Figgis, Introduction to Ligand Fields, Wiley Eastern Ltd., New Delhi, Indian Reprint, 1976.
20 A.W. Coats and J.P. Redfern, Nature (London), 68 (1964) 201.