

## Thermal characterization studies on Zinc, Cadmium and Mercury dithiocarbamate complexes

Arumugam Manohar<sup>1\*</sup>, Kuppukannu Ramalingam<sup>2</sup> and Kottamalai Karpagavel<sup>3</sup>

<sup>1</sup>Department of Chemistry, Kalasalingam University, Krishnankoil-626 190, India

<sup>2</sup>Department of Chemistry, Annamalai University, Annamalainagar – 608 002, India

<sup>3</sup>Department of Chemistry, Renganayagi Varatharaj College of Engineering, Sivakasi- 626128, India.

\*Corres.author: navmanohar@yahoo.co.in

**Abstract:** Thermal decomposition of N,N'-iminodiethylenebis(phthalimide)dithiocarbamate(padtc) and N-methyl-N-ethanoldithiocarbamate(nmedtc) complexes of Zinc, Cadmium and Mercury have been studied by thermogravimetry (TG). The decomposition pattern of Zn(nmedtc)<sub>2</sub> is similar to that of Zn(padtc)<sub>2</sub>, leaving ZnS as the final product. After 200° C, a single step decomposition was observed in both Cd(nmedtc)<sub>2</sub> and Cd(padtc)<sub>2</sub> complexes and the final residue was found to be CdS. A continuous mass loss was observed in both ligand complexes of mercury and only 10% initial mass remained at 650°C, owing to the volatile nature of mercury dithiocarbamates.

**Keywords:** Thermal characterization, Zinc, Cadmium and Mercury dithiocarbamate complexes.

### Introduction

Dithiocarbamates of zinc, cadmium, and mercury continue to attract attention for their industrial applications. Interest on the study of metal dithiocarbamates was aroused owing to the striking structural features shown by this class of compounds and also due to its diversified applications, such as high pressure lubricants in industry, antioxidants, insecticides, in the biochemical field, correction of chronic alcoholism, fungicides and pesticides, and also as accelerators in vulcanization[1-4]. Zinc, cadmium, and mercury dithiocarbamate complexes have proven to be very successful as single source precursors for the preparation of ZnS, CdS, and HgS nanoparticles respectively[5]. It is important to know the thermal properties of the dithiocarbamates for their applications.

Thermogravimetric technique is useful to evaluate the thermal stability of the various substances and also to establish the structure of insoluble and infusible compounds [6]. Today the technique has become an essential tool for material research and development. The conventional thermal techniques were applied more commonly for interpretation of the kinetics and mechanisms of thermal decompositions of inorganic solids [7]. Thermoanalytical methods have a great interest in the research community, due to their wide applicability in academic researches and mainly in the industrial processes that involving the thermal decomposition reactions of solids [8].

The thermal decomposition behavior of Tri(diethyldithiocarbamato)iron(III) was studied and found it to be a completely volatile complex by using thermogravimetry and differential thermal analysis [9]. It has been observed that most volatile compounds contain branched groups like *i*-butyl and *i*-propyl. The volatile behaviours of *N*-(*p*-ethoxyphenyl)dithiocarbamato iron(III) complexes beyond 823K were reported and showed three major thermal changes: formation of sulphide, its oxidation to sulphate and finally to oxide [10]. The decomposition pattern of metal *N*- $\alpha$ -methylbenzylidithiocarbamates was observed, whereby loss of hydrogen sulphide resulting in the formation of isothiocyanate and metal sulphides was reported [11]. TG analysis of dithiocarbamato complexes of Zn(II), Cd(II) and Hg(II) show that the possible stage of weight loss to give MS (M=Zn,Cd,Hg) indicating that they might be useful as single source precursors for the synthesis of metal sulphide nanoparticles and thin films [12-14].

Thermal characterization studies on metal dithiocarbamate complexes were reported in several papers and reviews [15-61]. Thermal behaviours of alkyl, aryl groups substituted dithiocarbamates and aminoacids based dithiocarbamate complexes of Co(II), Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), As(III), Sb(III), Bi(III), Ag(I), Mn(II), Fe(II), Fe(III), Co(III), Mo(IV), Mo(V), Pt(II), Pd(II), UO<sub>2</sub>(II), Au(III), Ba(II) were reported [10,18,22, 24, 34,39,40,42,60]. The thermal properties of parent Zinc, Cadmium and Mercury dithiocarbamates and their nitrogenous bases involved adducts were studied extensively by our group [13,15,16,50-54,58] and also by research groups from other laboratories [23,27,30,33,45,55,56]. Zn(II) and Cd(II) dithiocarbamates and their adducts with nitrogenous bases such as 1,10-phenanthroline and 2,2'-bipyridine show similar thermal decomposition patterns. In the case of adducts, after the initial loss of solvent molecules, thermal decomposition of the nitrogenous bases is simultaneously followed by the decay of dithiocarbamate, leading to the formation of Zn(NCS)<sub>2</sub> or Cd(NCS)<sub>2</sub> as intermediates. Further increase in temperature results in the decomposition of Zn(NCS)<sub>2</sub> to ZnS in the case of Zn(II) adducts, and the observed trend is very similar in Cd(II) adducts also where the final residue corresponds to CdS. Thermally, 1,10-phenanthroline adducts were of higher stability than 2,2'-bipyridine adducts in both zinc and cadmium adducts. Comparatively, the 4,4'-bipyridine adducts are thermally more stable than the 2,2'-analogues probably because of the dimeric nature[54]. Thermal studies on mixed ligand complexes involving Ni(II) dithiocarbamates and free, chelated phosphines were reported extensively[47-49]. Chelated phosphine complexes are thermally more stable than free phosphine complexes with respect to their initial decomposition temperatures [47]. TG studies on nickel(II)aminoaciddithiocarbamates with triphenylphosphine were reported [21]. Thermal analyses of the nickel complexes are in keeping with the proposed formulae. All the complexes showed signs of decay above 170 °C and at around 390 °C, the final mass corresponded to NiS.

In the present work we report thermogravimetric studies on M(nmedtc)<sub>2</sub> and M(padtc)<sub>2</sub> (M = Zn, Cd, Hg; nmedtc = N-methyl-N-ethanoldithiocarbamate, padtc = N,N'-iminodiethylenebis (phthalimide) dithiocarbamate) complexes. In our earlier attempt in characterization studies on the above complexes, we have reported a very little information about their thermal behaviours [59]. In this paper we have discussed in detail with available thermograms.

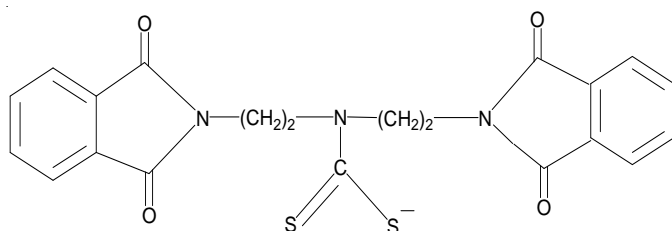
## **Experimental**

**Analytical and Physical measurements.** All the reagents and solvents employed were commercially available analytical grade materials, used as supplied, without further purification. STA 1500 PL and Perkin – Elmer TGA7 Thermal Sciences instrument were used for the thermogravimetric analysis. The heating rate of the furnace was fixed at 10°C per minute. About 5mg of the sample was taken in porcelain crucible for each thermogravimetric experiment.

### **Preparation of N,N'-(Iminodiethylene)bisphthalimide (paH)**

Preparations of “paH” and M(dtc)<sub>2</sub> (M= Zn, Cd, Hg; dtc = nmedtc, padtc) were reported earlier by our group [59]. In ‘paH’ preparation, phthalic anhydride (50 g, 0.35 mmol) was dissolved in boiling chloroform (500 mL) and the solution was filtered to remove phthalic acid. To this solution at 50°C, with stirring, a solution of “dien” in chloroform (16.3 mL, 0.15 mmol) in 100mL was added slowly (40 min). A white sticky solid precipitated immediately on addition and the solution turned yellow. Most of the chloroform was evaporated and the reaction was completed by heating the mixture at 140°C for 1 h in the oven. The resulting brittle yellow solid was powdered, dissolved in a minimum volume of hot chloroform (250 mL) and was filtered to remove traces of phthalic acid. The yellowish crude product was precipitated with ethanol (500 mL) and was filtered and dried at 100°C. It was recrystallized from hot chloroform containing decolorizing charcoal and precipitated

from the filtered solution by the addition of ethanol. The fluffy powder was filtered off, washed with cold ethanol, and dried at 100°C (yield: 60%). The structure of paH is given in Fig.1



**Fig. 1** N,N'-(iminodiethylene)bisphthalimidedithiocarbamate anion ( $\text{padtc}^-$ )

### Preparation of bis(N, N'-(iminodiethylene)bisphthalimidedithiocarbamate)M(II); $[\text{M}(\text{padtc})_2]$ (M = Zn, Cd, Hg)

Amine, ‘‘paH’’ ( 2 mmol) was dissolved in acetonitrile (75 mL), and carbon disulfide (40 mmol,) was added with continuous stirring; yellow dithiocarbamic acid was obtained. To this, aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{HgCl}_2$  (1 mmol) was added and stirred. The precipitate obtained was filtered, washed with water and acetonitrile, and finally dried in an oven at 100°C

### Preparation of bis(N-methyl,N-ethanoldithiocarbamate)M(II); $[\text{M}(\text{nmedtc})_2]$ (M = Zn, Cd, Hg)

Dithiocarbamic acid was prepared from 20 mmol of N-methyl,N-ethanolamine and 20 mmol of carbondisulphide in ethanol (20mL) under ice cold condition (5°C). To the yellow dithiocarbamic acid solution, aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{HgCl}_2$  (10 mmol) added with constant stirring. The complex was filtered and washed with alcohol and was then dried.

## Results and Discussion

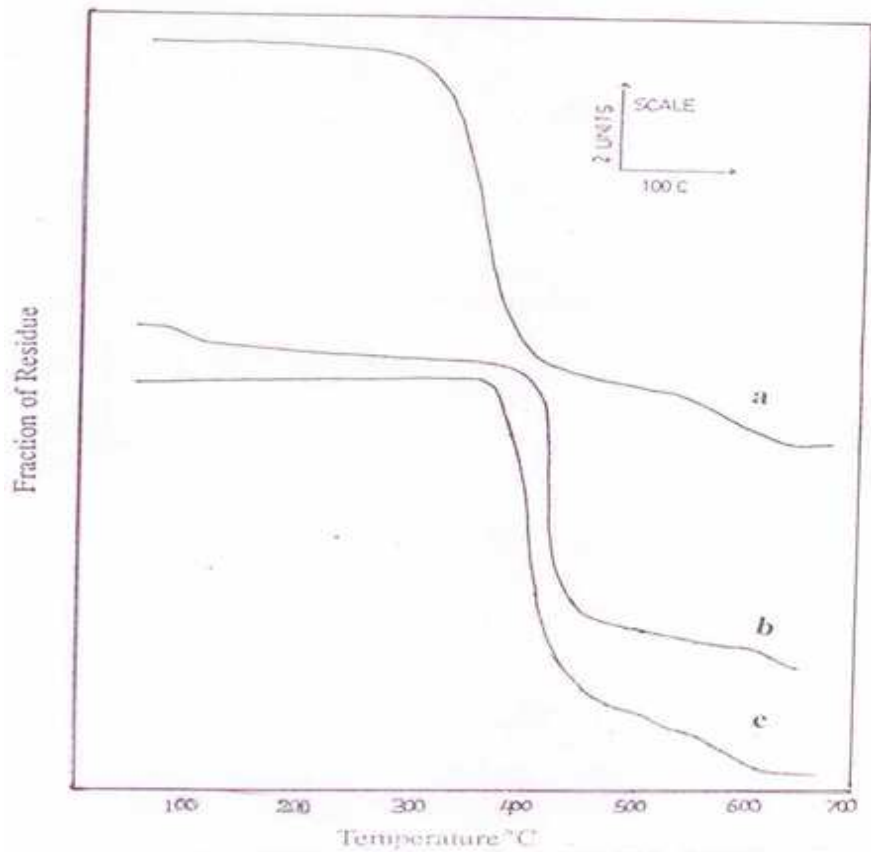
### Thermogravimetric studies on $\text{M}(\text{padtc})_2$ (M=Zn,Cd,Hg)

Thermograms of ‘‘paH’’,  $\text{Zn}(\text{padtc})_2$  and  $\text{Hg}(\text{padtc})_2$  are given Fig.2. The parent amine shows a small loss corresponding to the loss of solvent of crystallization but it is not stoichiometrically significant. However, the crystal structure solved for  $\text{paH}^+ \text{padtc}^-$  showed the presence of  $1/2\text{H}_2\text{O}$  per molecule as water of crystallization. The parent amine ‘pa’ itself is otherwise stable upto 350°C and almost 96% of the mass was lost in a single step leaving only a small percentage of unburnt carbonaceous material as expected of an organic compound.

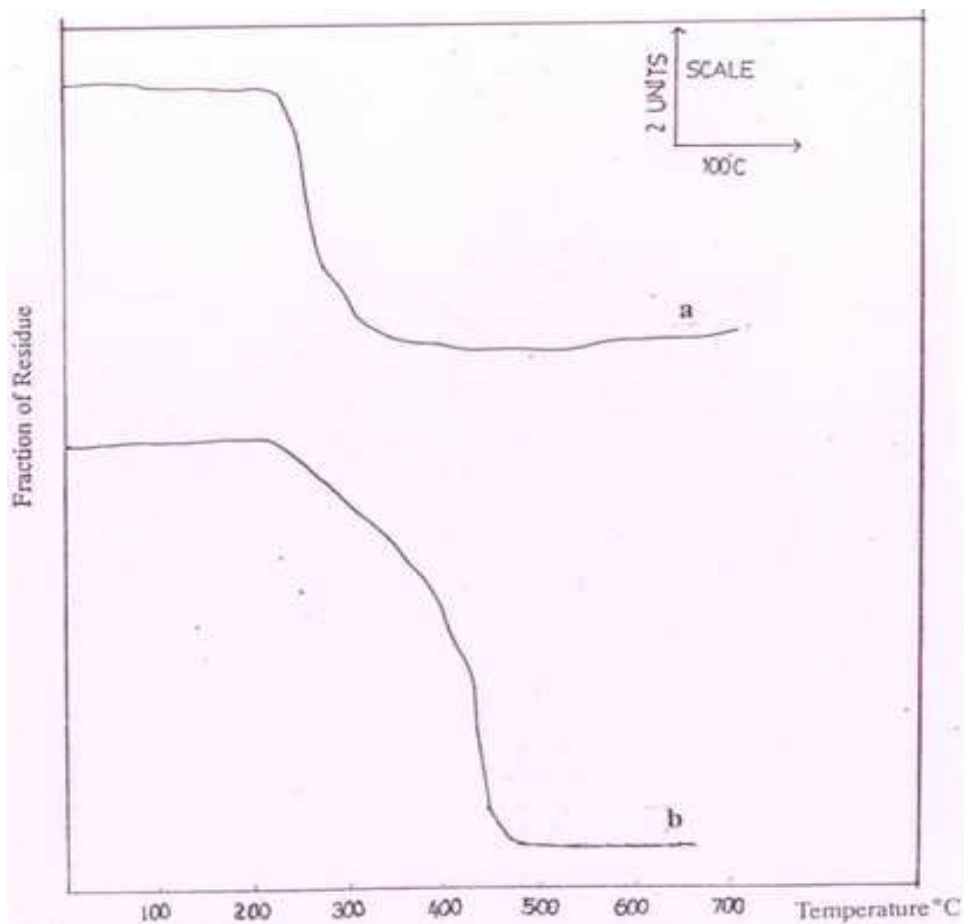
$\text{Zn}(\text{padtc})_2$  is also stable up to 400°C and then in a single step there was a weight loss . The final residue corresponds to the formation of ZnS as observed in other similar such compounds [61].  $\text{Cd}(\text{padtc})_2$  also showed a similar pattern of thermal decomposition. The complex was stable upto 400°C and then a single step decomposition led to CdS as the final product.  $\text{Hg}(\text{padtc})_2$  also was thermally stable upto 350°C and sharp loss in mass occurred after that temperature. Residue at the end of the decomposition around 650°C did not correspond to the sulphide. But volatilization of the mercury dithiocarbamates around 650°C is well documented[61].  $\text{Zn}(\text{padtc})_2$  as observed in other zinc complexes should be of tetrahedral geometry [59]. However, mercury and cadmium complexes should be polymeric. The tetrahedral structure of zinc complex and polymeric structures of cadmium, mercury complexes are given in Fig. 4.

### Thermogravimetric studies on $\text{M}(\text{nmedtc})_2$ (M = Zn,Cd,Hg)

Thermal decomposition of the  $\text{Zn}(\text{nmedtc})_2$ ,  $\text{Cd}(\text{nmedtc})_2$  complexes confirmed the proposed formulae. The decomposition pattern of  $\text{Zn}(\text{nmedtc})_2$  is similar to the decomposition of  $\text{Zn}(\text{padtc})_2$  leaving ZnS as the final product. Thermograms of  $\text{Cd}(\text{nmedtc})_2$  and  $\text{Hg}(\text{nmedtc})_2$  are shown in Fig. 3.

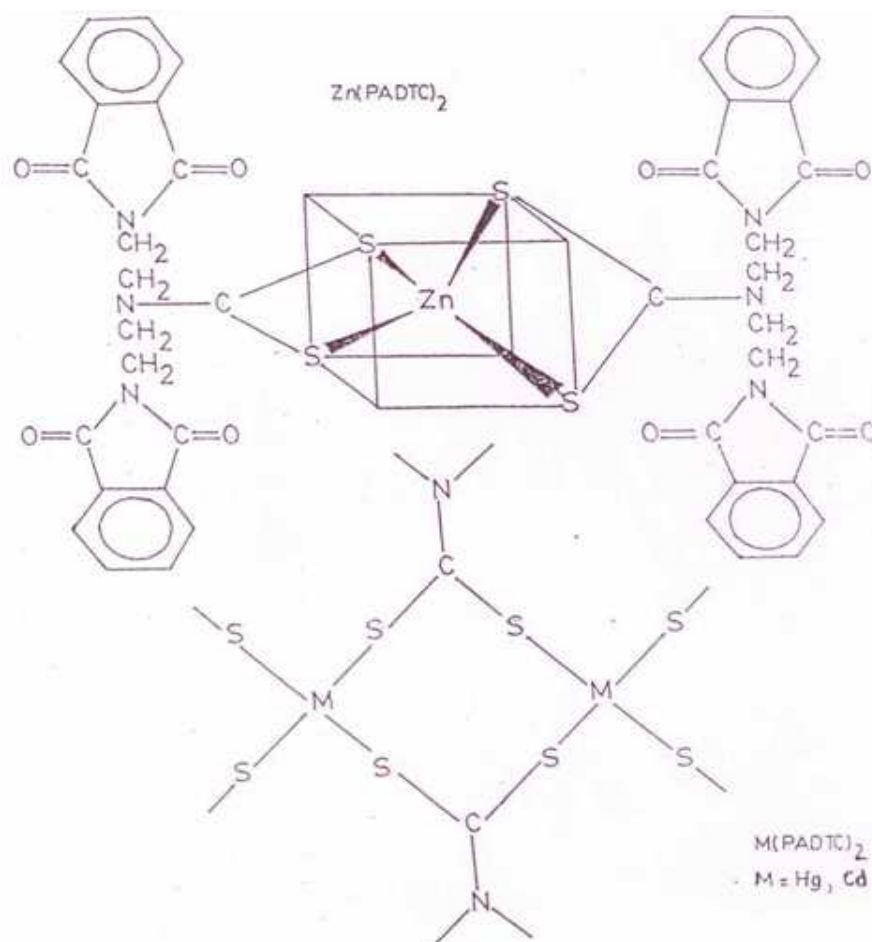


**Fig.2** Thermograms of a) paH, b) Zn(padtc)<sub>2</sub> and c) Hg(padtc)<sub>2</sub>



**Fig.3** Thermograms of a) Zn(nmedtc)<sub>2</sub> and b) Hg(nmedtc)<sub>2</sub>

Both the complexes are stable upto 200°C and above there is a single step decomposition. In the case of  $\text{Cd}(\text{nmedtc})_2$  the final residue is not mere  $\text{CdS}$  or  $\text{CdO}$  as observed [61] but it agrees well for a 1:1 mixture of  $\text{CdS}$  and  $\text{Cd}(\text{SCN})_2$ . However, X-ray powder pattern could not be recorded due to paucity of residue and hence could not be confirmed. In the case of  $\text{Hg}(\text{nmedtc})_2$  there is a continuous loss of mass and only 10% of the initial mass remained at 650°C, an identical behavior observed in the case of  $\text{Hg}(\text{padtc})_2$  and shows volatilization.



**Fig.4** Structures of Zinc, Cadmium and Mercury dithiocarbamate complexes

Infrared and electronic spectral data of the above  $\text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Hg}(\text{II})$  complexes were reported earlier [59]. All the complexes are colourless to pale yellow in complexation and are diamagnetic. IR spectral studies confirm the contribution of thioureide form to the complexes, which determine the physical and chemical properties of the complexes depending upon the nature of alkyl or aryl substituents present on nitrogen. Since other than Zinc complexes, the other two Cadmium and Mercury dithiocarbamates are highly insoluble in almost all organic solvents and their crystal structures could not be completed.

## Conclusion

Metal dithiocarbamate complexes involving N'-iminodiethylenbis(phthalimide)- dithiocarbamate and N-methyl-N-ethanoldithiocarbamate ligands and  $\text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Mg}(\text{II})$  were prepared and their decomposition patterns were investigated by using thermogravimetry. Thermal decomposition of both ligand complexes confirmed the proposed formulae. The decomposition pattern is similar in both  $\text{Zn}(\text{nmedtc})_2$  and  $\text{Zn}(\text{padtc})_2$  complexes with  $\text{ZnS}$  as the final product. A single step decomposition was observed in both  $\text{Cd}(\text{nmedtc})_2$  and  $\text{Cd}(\text{padtc})_2$  complexes after 200°C, and the final residue was found to be  $\text{CdS}$ . In the case of  $\text{Hg}(\text{nmedtc})_2$  and  $\text{Hg}(\text{padtc})_2$ , a continuous mass loss was observed and only 10% initial mass remained at 650°C, due to the volatile nature of mercury dithiocarbamates.

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