Review

THERMAL STUDIES ON METAL DITHIOCARBAMATO COMPLEXES. A REVIEW

S.K. SENGUPTA *

Department of Chemistry, University of Gorakhpur, Gorakhpur 273001 (India)

SHYAM KUMAR

Oil and Natural Gas Commission, Bombay (India)

ABSTRACT

In the present review, the work done on thermal studies of metal dithiocarbamato complexes during the period 1969–1982 are given. The thermal studies include thermogravimetry, differential thermogravimetry, differential thermal analysis, differential scanning calorimetry and mass spectrometry. Fifty-two references are included.

INTRODUCTION

A number of metal dithiocarbamates have been synthesized and characterized in recent years. Special interest in the study of metal dithiocarbamates was aroused because of the striking structural features presented by this class of compounds and also because of its diversified applications, such as accelerators in vulcanization, high pressure lubricants in industry, and also as fungicides and pesticides. Dithiocarbamate ligands have been known to stabilize the higher coordination states of metals due to their low charge and relatively small bites (2.8–2.9 Å). The special features associated with the complexes containing sulphur donor ligands are attributed to the ability of sulphur to form multiple (π bonds) bonds caused by the presence of a vacant $d\pi$ orbital in sulphur. The σ donation and π back-donation of the sulphur atoms are assumed to be of the same order of magnitude as found in the case of 1,1-dithioates. An additional π electron flow from the nitrogen atom to the sulphur atom via a planar delocalized π orbital system contributes to the special features of the dithiocarbamate ligands. Several canonical forms may be written for the structure of the dithiocarbamate group in $M(S_2CNR_2)_n$, where M is the metal ion and n is the valency.

---

* To whom correspondence should be addressed.
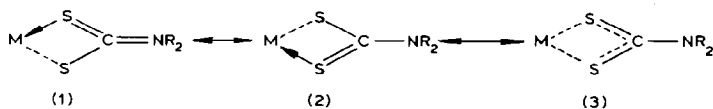
Thus, in the dithiocarbamates, the type of R group in the $-NH_2$ moiety is expected to influence the stability and other physico-chemical properties of a metal complex, depending on the inductive effect of the group(s) attached to the nitrogen atom. Till now, four reviews have appeared in the literature dealing with the properties, reactivities and analytical applications of such complexes [1–4].

HISTORICAL REVIEW

During the past decade, the thermal properties of metal dithiocarbamato complexes have been extensively investigated as one of the most interesting topics in the field of coordination chemistry. A large number of papers have appeared dealing with the applications of thermogravimetry, differential thermal analysis, differential scanning calorimetry, gas chromatography, and mass spectrometry to metal dithiocarbamates. Two reviews have appeared on the volatility and thermochemistry of metal complexes with sulphur donor ligands [5,6]. The present review incorporates some interesting papers on the thermal behaviour of metal dithiocarbamates.

In metal dithiocarbamates, thermal analyses data have been utilized to:

(a) investigate the limit of the horizontal stretch between which the complex retains the assigned formula;

(b) study the mode of thermal transformation of metal complexes;

(c) determine the correct temperature range for the resulting product to attain constant weight, thereby affording standardization of the conditions for the gravimetric evaluation of metal ions;

(d) confirm the purity of metal complexes in conformity with their stoichiometries,

(e) evaluate the activation energy and order of reaction for the decomposition reaction of the complex; and

(f) determine the enthalpies of fusion and sublimation of metal dithiocarbamate complexes.

The earliest works on thermoanalytical investigations of metal dithiocarbamates were reported by Bernard and Borel [7] and D'Ascenzo and Wendlandt [8] in 1969. After that, during the period 1969–1982, about 50 papers have appeared on the thermal behaviour of metal dithiocarbamates.

Bernard and Borel [7] studied the thermal behaviour of dithiocarbamates of lead, zinc and cadmium by TG and DTA and reported that these complexes, i.e., $M(S_2CNH_2)_2$, decompose with the evolution of hydrogen sulphide or carbon disulphide. They reported that the decomposition takes

place either via the formation of metal thiocyanate as an intermediate which finally gives the metal sulphide, or the complexes decompose in a single step, giving ammonium thiocyanate and the respective metal sulphides.

D'Ascenzo and Wendlandt [8] arrived at a different conclusion during the investigation of the thermal behaviour of some metal complexes of diethyldithiocarbamic acid by TG, DTA and HTRS (high temperature reflectance spectroscopy) techniques. They suggested that the Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Hg(II) diethyldithiocarbamate complexes were volatile in an inert atmosphere. The same authors [9] also reported Fe(Et$_2$dtc)$_3$ as a new volatile metal chelate on the basis of TG, DTA and vapour pressure studies. They also suggested that the partial decomposition of the complex takes place giving FeS which did not show weight loss in the region 350–800°C.

In 1971, D'Ascenzo et al. [10] reported the non-volatile nature of dichlorotin(IV)bis-diethyldithiocarbamate and proposed a two-step decomposition for this complex. In the same year, on the basis of TG/DTA studies [11], the diethyldithiocarbamato complexes of Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Cr(III) and Pb(II) were found to be partially volatile and undergo further decomposition, thus making analysis of these complexes by gas chromatography technique difficult.

In 1972, Lyalikov and Kitovskaya [12] used TG and DTA studies to characterize some active dithiocarbamate fungicides, viz., Ziram [bis(dimethyldithiocarbamato)zinc(II)], Ferbam [tris(dimethyldithiocarbamato)iron(III)], Zineb [ethylenebis(dithiocarbamato)zinc(II)], etc.

In 1973, Sceney and Magee [13] observed the volatility of a range of tri(dialkyldithiocarbamato)iridium(III) complexes and reported the maximum volatility for isopropyl and isobutyl derivatives.

During their studies on the thermal properties of Zn(II), Cd(II), Pb(II), Ni(II), Cr(III) and Co(III) chelates of bidentate sulphur-containing ligands by TG and DTA techniques in atmospheres of air and argon, Larionov and Kosareva [14] found that the thermal stability of these chelates decreased in the order $C_2H_5OCS_2^- < (C_2H_5O)_2PS_2^- < (C_2H_5)_2NCS_2^-$. Further, they observed that the metal dithiocarbamates decomposed mainly in argon atmosphere, though volatility of some chelates was quite evident. Nickel and zinc complexes were found to be partially volatile, whereas cobalt and chromium complexes were completely volatile in nature. Nickel, lead, zinc and cadmium complexes were found to give the corresponding metal sulphides on decomposition at about 350°C. According to Venkappayya and Brown [15], the N-α-methylbenzyldithiocarbamates of Cr(III), Co(III), Ni(II), Zn(II) and Cd(II) undergo thermal decomposition with the loss of hydrogen sulphide, resulting in the formation of the respective isothiocyanates and metal sulphides.

In 1974 Onuska and Boos [16] analyzed a series of S-alkyl-N,N-dialkyldithiocarbamate and S-alkyl-N-monoalkyldithiocarbamate complexes by

gas chromatography. In the same year, Annuar et al. [17] observed the thermal decomposition of Ni(II) and Cu(II) complexes of monoethanol and diethanol dithiocarbamic acids by TG, DTA and mass spectrometry and reported the formation of metal oxides. They also proposed the mechanism for nickel(II) monoethanoldithiocarbamate complex. The enthalpy change for the reaction

$$FeCl_3 + 3 NaS_2CN(C_2H_5)_2 \rightarrow Fe[S_2CN(C_2H_5)_2]_3 + 3 NaCl$$
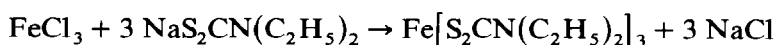
was found to be -82.7 ± 2.0 kJ mole^{-1} [18].

Copper(II) dithiocarbamates of the type Cu(R$_2$dtc)$_2$, where R$_2$ = Me$_2$, Et$_2$, n-Pr$_2$, n-Bu$_2$, EtPh, pyrrole and piperidine, were studied by Sceney et al. [19,20] and it was found that copper diethyldithiocarbamate was completely volatile under vacuum but in air and nitrogen only partial volatility was exhibited. Further, all these complexes in an atmosphere of nitrogen were found to decompose, with formation of Cu$_2$S. In air, copper diethyldithiocarbamate was found to yield Cu$_2$S as the product of the first step of decomposition, and this was further oxidized to CuSO$_4$ and CuO. Finally, it was found that CuSO$_4$ decomposed to CuO at 800°C. In 1975, Krupcik [21] studied the thermal stability of a series of bis(dialkyldithiocarbamato)-nickel(II) complexes and separated these complexes by gas chromatography. Hilderbrand and Pickett [22] determined Cr(III), Co(III), Cu(II), Mn(II) and Zn(II) by atomic absorption spectrometry which is based on the volatility of the respective dialkyldithiocarbamate complexes.

Larionov and Kosareva [23] studied the thermal decomposition of $[(C_2H_5)_2NCS_2]_2M(M = Ni, Zn, Cd, Pb)$ and obtained the corresponding metal sulphide residue at the end of decomposition. The residues were characterized by analyses and X-ray powder photography.

Lyalikov and Kitovskaya [24] studied the thermal decomposition of divalent metal complexes with a series of ethylenebisdithiocarbamate ligands by TG/DTG and DTA and reported the loss of CS$_2$ molecule during the first step of decomposition.

The two-step thermal decomposition mechanism for bis(dialkyldithiocarbamato)tin(II) complexes was proposed by Perry and Greanangel in 1975 [25] on the basis of TG/DTA data. The first step represented the loss of one dithiocarbamate ligand followed by the other during the second decomposition step, resulting in the formation of tin metal.

$$Sn(S_2CNR_2)_2 \rightarrow Sn(S_2CNR_2) \rightarrow Sn$$
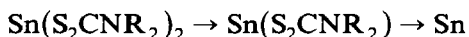
The above mechanism has been supported by mass spectra of the intermediate and final residues.

The thermal properties of silver(I) and gold(III) complexes, such as Ag(Et$_2$dtc), Au(dtc)Cl$_2$, and Au(dtc)$_3$, were studied by D'Ascenzo and Bica [26] in atmospheres of air and nitrogen using TG, DTA, and DRS (dynamic reflectance spectroscopy) techniques. In nitrogen the silver compound was

found to decompose to Ag_2S, whereas in air, it first decomposed to give a mixture of Ag_2S, Ag_2SO_4 and Ag. Further, Ag_2S was oxidized to Ag_2SO_4, and finally silver metal was obtained at 925°C. The gold complexes decomposed both in air and in nitrogen atmospheres giving metal as the residue. A comparative study was reported on the thermal behaviour (TG and DTG) of $Cu(S_2CNR_2)_2$ complexes with different R-groups (R = Me, Et, i-Pr, n-Bu) by Larionov et al. [27]. The reduction of Cu(II), when the chelates were heated, was studied by EPR. The chief product obtained by heating the chelates in argon was $Cu_{1.96}S$.

Bratspies et al. [28,29] reported the modes of thermal decomposition of tin(IV) complexes of the type $X_2Sn(Et_2dtc)$, where X = Cl, Br or I, $Ph_2Sn(Et_2dtc)_2$ and $Sn(Et_2dtc)_4$ in atmospheres of air and nitrogen by employing TG, DTA, EGA (evolved gas analysis) and P/GC–MS (pyrolysis/gas chromatography–mass spectroscopy) techniques. They proposed various mechanisms for the decomposition of these complexes but the final product obtained in all cases was SnS.

Mechanism I
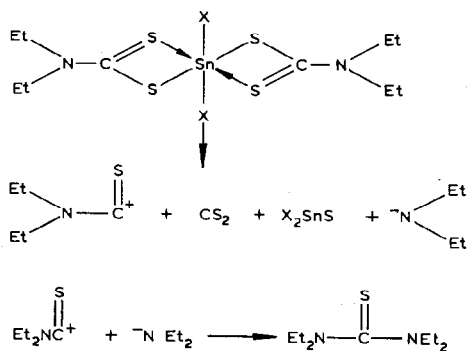
Mechanism II

The mechanism proposed below is consistent with a tetrahedral structure for the complex and monodentate behaviour of dithiocarbamate ligand.

Strivastava et al. [30] also carried out thermal investigations of $Ph_2Sn(X)dtc$, where X = Cl^-, I^-, N_3^-, NCS or NO_2^-, and dtc is $Et_2NCS_2^-$, and their results were similar to that reported by Perry and Greanangel [25] for $Sn(R_2dtc)_2$ complexes, i.e., loss of S_2CNR_2 moiety finally results in tin metal.

But the recent work of Srivastava and Bhargava [31] on the TG study of tetrakis-morpholine-N-carbodithioate tin(IV) is slightly different. It is reported that the above complex loses three ligands consecutively and during
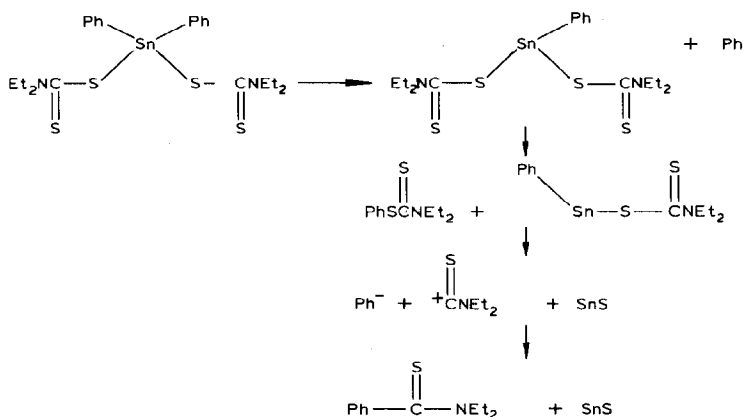
the fourth step of thermal decomposition it gives SnS_2 which finally results in tin metal at 300°C, whereas dichloro tin(IV) bis-(morpholine-N-carbodithioate) decomposes to tin metal via the formation of $Sn(NCS)_2Cl_2$ as an intermediate product.
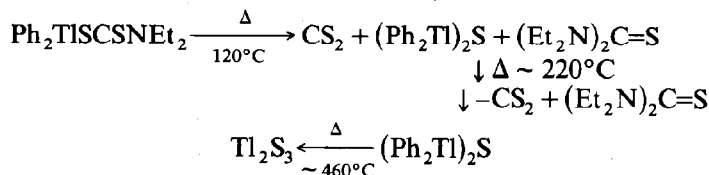
In 1978, Neeb and co-workers [32–34] reported the thermal stability of a series of metal dithiocarbamato complexes of Zn(II), Sb(III), Ni(II), Cu(II), Pb(II), Cd(II) and Bi(III). The melting points of tin dithiocarbamato complexes were reported [35] using their DTA data.

Janicki et al. [36] reported the thermal decomposition of chromium dithiocarbamato complexes, $Cr(S_2CX)_3$ [X = $(CH_3)_2N$, $(C_2H_5)_2N$, pyrollidine, hexamethylene, cyclohexyl, morpholine]. A gradual loss of organic fragments followed by the formation of Cr_2S_3 residue has been observed.

The thermal decomposition patterns for uranium(VI) dithiocarbamato complexes of the type $UO_2[(C_2H_5)_2NCS_2]_2 \cdot H_2O$ and $UO_2[(C_2H_5)_2-NCS]_3–NH_3$ have been reported by Dubrovin et al. [37]. The complexes decomposed in two steps, $UO_2[(C_2H_5)_2NCS_2]_2$ was formed at the end of the first decomposition step which decomposed to UO_2 at 500°C.

In 1979, two papers appeared [38,39] dealing with the DTA and differential scanning calorimetry of metal dithiocarbamato complexes. These techniques have been utilized to determine the melting points and enthalpies of fusion and sublimation of dithiocarbamato complexes. Kosareva and Larionov [40] studied the sublimation of a series of metal dithiocarbamato complexes. Two important conclusions were derived. It was observed that volatility increases as the oxidation state of the metal decreases and further, volatility increases as branching of the alkyl group of the dithiocarbamate ligand increases. In the same year, Baudis and Wieber [41] studied mono-arylthallium bis-dithiocarbamato complex by DTA and reported their melting points. Srivastava et al. [42] reported the thermal decomposition pathway for organothallium(III) dithiocarbamato complexes in which dithiocarbamate ligand acts as a monodentate. The compounds are thermally stable at

room temperature but decompose on heating above their melting points. The course of thermogravimetric analysis of diphenylthallium is given as

$$Ph_2TlSCSNEt_2 \xrightarrow[120°C]{\Delta} CS_2 + (Ph_2Tl)_2S + (Et_2N)_2C{=}S$$

$$\downarrow \Delta \sim 220°C$$

$$\downarrow -CS_2 + (Et_2N)_2C{=}S$$

$$Tl_2S_3 \xleftarrow[\sim 460°C]{\Delta} (Ph_2Tl)_2S$$

This behaviour is similar to that reported by Kupchik and Theisen [43] for organoantimony compounds. Chande [44] reported pyrolitic derangement of S-ethyl-*N*-disubstituted dithiocarbamates and ethylene was found to be one of the major products during the pyrolysis. The mechanism of thermal decomposition has been discussed. On pyrolysis of S-ethyl-*N*-ethylphenyl dithiocarbamate(I) at 285°C ethylaniline(II) and carbon disulphide were isolated along with the unreacted starting material. The gaseous products were mainly ethylene and smaller quantities of ethylmercapton.

(a)

(I)

(II)

(b)
(i)

C_2H_5SH + $C_6H_5N{=}C{=}S$ $\xleftarrow{\Delta}$

ethyl mercapton   phenyl isothiocyanate
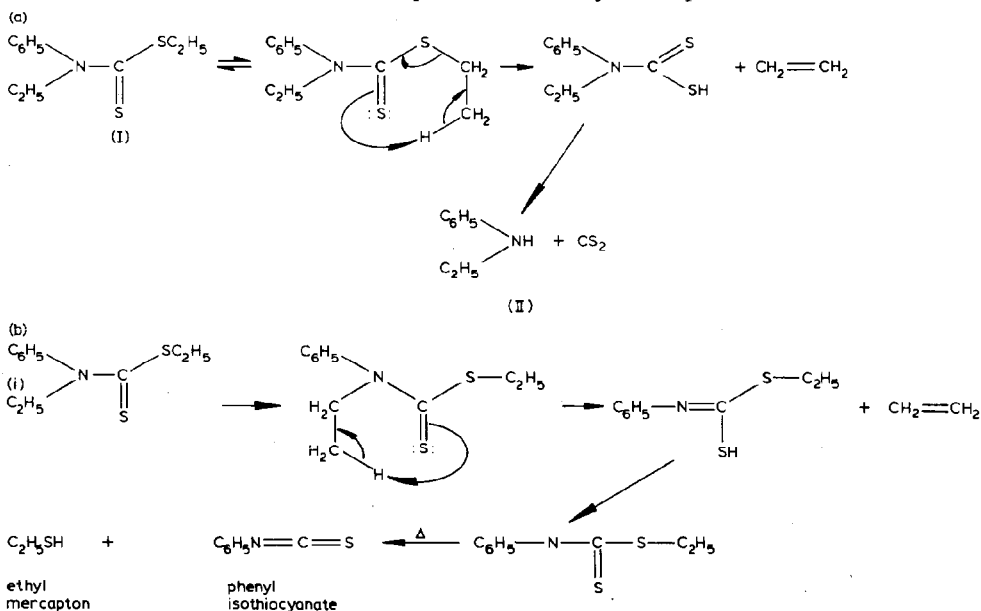
Kaushik and co-workers [45] studied the thermal decomposition (TG and DTG) of *N*(-ethyl, *m*-tolyl)dithiocarbamato complexes of Mn(III), Co(III), Ni(II), Cu(II) and Mo$_2$O$_3$. All these complexes are thermally stable up to 200°C except Ni(II) complexes, the thermal stability of which extended up to 320°C. Beyond this temperature, the organic portion of the ligand was decomposed, resulting in the formation of the respective metal thiocyanates at the end of the first step of decomposition, as evidenced by elemental analysis of the residue. However, in Mn(III) complex, two overlapping thermal decomposition reactions have been observed; the first decomposi-

tion in this case does not yield metal thiocyanate but one molecule of ligand is removed from the coordination sphere of the complex reducing it to a Mn(II) complex. Various thermal decomposition reactions for the above-mentioned complexes can be represented as

		Temp. range (°C)
(i)	$Mn(S_2CNRR')_3 \rightarrow Mn(S_2CNRR')_2$	205–250
	$Mn(S_2CnRR')_2 \rightarrow Mn(SCN)_2$	250–340
	$Mn(SCN)_2 \rightarrow$ Indefinite composition	460–810
(ii)	$Co(S_2CNRR')_2 \rightarrow Co(SCN)_3$	180–360
	$Co(SCN)_3 \rightarrow Co(SCN)_2$	400–530
	$Co(SCN)_2 \rightarrow CoS$	600–800
(iii)	$Ni(S_2CNRR')_2 \rightarrow Ni(SCN)_2$	325–390
	$Ni(SCN)_2 \rightarrow$ Volatile	455 onward
(iv)	$Cu(S_2CNRR')_2 \rightarrow Cu(SCN)_2$	200–290
	$Cu(SCN)_2 \rightarrow CuS$	300–600
(v)	$Mo_2O_3(S_2CNRR') \rightarrow Mo(SCN)_5$	200–370
	$Mo(SCN)_5 \rightarrow$ Volatile	380–670

Kinetic parameters like apparent activation energy and order of reactions were also reported for these complexes by making use of graphical methods of Coats and Redfern.

Johri and Venugopalan [46,47] carried out the systematic thermal decomposition studies of Cu(II), Zn(II), Cd(II), Co(II), Ni(II), Su(II), VO(IV) and UO_2(VI) with ammonium N,N-bis(dithiocarboxy)-o-phenylenediamine under non-isothermal temperature conditions. The decomposition range and residue obtained after decomposition are given.

Complex	Decomposition range	Final residue
CuL	60–800	CuO (black)
ZnL	50–870	ZnO (white)
CdL	50–855	CdO (yellowish brown)
CoL	60–830	Co_3O_4
NiL	50–760	NiO (black)
SuL	70–735	SnO_2 (white)
VOL	50–670	V_2O_5
(UO_2)L	65–760	U_3O_8 (olive green)

Bratspies et al. [48,49] reported the thermal decomposition of tetrakis(N,N-dialkyl dithiocarbamato) tin(IV) complexes. They also gave the thermal decomposition mechanism and proposed the formation of tetraalkylthiuram disulphide tetraalkylthiuram monosulphide, bis(dialkyldithio-

carbamato) tin(II) complex and a di-μ-sulphido bis[bis(N, N-dialkyldithio-carbamato)tin(IV)] complex as decomposition products.

Kumar and Kaushik [50] have also carried out thermal studies of $M(S_2CNRR')_3$ ($M = As$, Sb, Bi; $R = C_2H_5$, $R' = m\text{-}C_6H_4 \cdot CH_3$) complexes in nitrogen and air to determine their modes of decomposition. The apparent activation energy and order of reaction were also evaluated by the graphical method of Coats and Redfern.

Complex	1st Decompn. range (°C)	Product	2nd Decompn. range (°C)	Product	Activation energy for 1st decompn. reaction (kcal mole^{-1})
$As(S_2CNRR')_3$ in N_2	200–265	As_2S_3	275–700	Volatilization	47.16
$Sb(S_2CNRR')_3$ in N_2	200–290	$Sb(SCN)_3$	300–490	Sb_2S_3	24.34
$Bi(S_2CNRR')_3$ in N_2	160–280	$Bi(SCN)_3$	300–640	Bi_2S_3	13.51
$As(S_2CNRR')_3$ in air	180–250	As_2S_3	280–650	Volatilization	–
$Sb(S_2CNRR')_3$ in air	220–275	Sb_2S_3	–	–	–
$Bi(S_2CNRR')_3$ in air	120–285	$Bi_2(SO_4)_3$	400–500	Bi_2O_3	–

The first-step decomposition reactions in all cases in nitrogen atmosphere followed first-order kinetics. Recently, Kumar and Kaushik [51] reported the thermogravimetric study of Ru(III), Rh(III), Pd(II), Os(IV), Ir(III) and Pt(II) complexes of N-(ethyl, m-tolyl) dithiocarbamate under nitrogen atmosphere. Ru(III), Rh(III), Os(IV), Ir(III) complexes yielded the respective metal sulphides at the end of the first decomposition step, i.e., at 390, 520, 260 and 320°C, respectively. Beyond these temperatures, the TG curves showed a little arrest followed by continuous weight loss in each case. Except for Os_2S_3, which is completely volatile in the range 300–600°C, other sulphides lose sulphur, but even at 1000°C pure metals were not obtained. This was attributed either to incomplete decomposition of these sulphides or to the probability of formation of non-stoichiometric sulphides of these metals. Pd(II) and Pt(II) showed high thermal stabilities (250 and 200°C, respectively). After the step of first decomposition, metal thiocyanates were obtained at 370 and 340°C for Pd(II) and Pt(II) complexes, respectively. The respective thiocyanates undergo decomposition at higher temperatures and the respective metal sulphides are obtained. The metal sulphides on heating at higher temperature lose sulphur and form non-stoichiometric metal sulphides.

Kumar and Kaushik [52] also carried out thermogravimetric studies of $M(S_2CNRR')_2$ ($M = Zn$, Cd, Hg; $R = C_2H_5$, $R' = C_6H_4 \cdot CH_3$) complexes in atmospheres of nitrogen and oxygen. The thermal decomposition range and modes of thermal transformations for these complexes are given below.

Complex	Decompn. range (K)	Decompn. reactions
Zn(S$_2$CNRR')$_2$ in N$_2$	543–643	Zn(S$_2$CNRR')$_2$ → Zn(SCN)$_2$
	713–943	Zn(SCN)$_2$ → ZnS
Cd(S$_2$CNRR')$_2$ in N$_2$	548–613	Cd(S$_2$CNRR')$_2$ → Cd(SCN)$_2$
	718–943	Cd(SCN)$_2$ → CdS
Hg(S$_2$CNRR')$_2$ in N$_2$	453–553	Hg(S$_2$CNRR')$_2$ → HgS
	573–728	Volatilization
Zn(S$_2$CNRR')$_2$ in O$_2$	543–633	Zn(S$_2$CNRR')$_2$ → ZnS
	728–923	ZnS → ZnO
Cd(S$_2$CNRR')$_2$ in O$_2$	523–628	Cd(S$_2$CNRR')$_2$ → CdS
	728–883	CdS → CdO
Hg(S$_2$CNRR')$_2$ in O$_2$	443–543	Hg(S$_2$CNRR')$_2$ → HgS
	543–728	volatilization

The intermediate and final residues were identified by analyses and spectral studies.

CONCLUSIONS

Studies on the thermal behaviour of the majority of the transition metal dithiocarbamates along with some non-transition metal dithiocarbamato complexes have been discussed in this review. But the insufficient data available have made it difficult to establish any straightforward relation between the thermal behaviour of the complexes and the nature of the metal ion. Although only a few metal dithiocarbamates have been reported to be volatile, it has given the scope for the use of gas chromatography for the separation of metals as the corresponding dithiocarbamate complexes. Thus, information and data on volatility of metal dithiocarbamates with different R-substituent groups and different metals (in one or more valence state) have become important considerations in an attempt to extract some general trends.

It was observed [40] that volatility increases as the oxidation state of the metal decreases and further, volatility increases as branching of the alkyl group of the dithiocarbamate ligand increases. As a result of insufficient data available, it is premature to establish any correlation between the volatility of metal dithiocarbamates and the structure of the complexes, although volatility may increase as the degree of association in the solid state increases.

In an attempt to make a comparative study, it was found that the thermal stability of some group V metal dithiocarbamates, in an inert atmosphere, decreases as the cation size increases [50]. With the same ligand, it was found that zinc, cadmium and mercury exhibit a decreasing trend of thermal stability in air from Zn to Hg.

Among the first-row transition metal complexes, no definite trend of

thermal stability data was observed, whereas some second- and the third-row transition metals (Pt metals) showed an increasing trend of thermal stability from Ru to Pd and from Os to Pt. A point worth noting is that the decomposition residue in the majority of platinum metal dithiocarbamate up to 1000°C did not correspond [51] to either metal or pure sulphide, which may be attributed to the possibility of the formation of non-stoichiometric platinum metal sulphides at that temperature.

Among the majority of the recently studied metal dithiocarbamates in an inert atmosphere, the common feature observed is that during thermal decomposition of these complexes, formation of the corresponding metal thiocyanate is an essential step.

So far, except in a few cases [28,29], no thermal decomposition mechanism for the thermal decomposition reactions of metal dithiocarbamate has been reported. The majority of those referred to in the literature as thermal decomposition mechanisms would be more appropriately described as thermal decomposition pathways. A DTA study of metal dithiocarbamate has been made to obtain data on melting points and phase changes, but the results obtained for the melting points are often different from those obtained by other methods. Enthalpies of fusion are known for only a limited number of complexes.

Only a little work has been done [45,50] in the area of thermal decomposition kinetics for the decomposition reactions of metal dithiocarbamates. In all cases the first-step decomposition reaction followed first-order kinetics.

Thus, it is obvious from the work reviewed here that there is great scope for further interesting and valuable investigations in all aspects of thermal studies of metal dithiocarbamato complexes, such as determination of thermal decomposition mechanism, thermal decomposition kinetics, etc. Further, a wide range of possible investigations can be made in this field, such as the investigation of the thermal behaviour of metal complexes with one metal and the ligands with a series of different substituent R groups or the complexes of a particular ligand with different metal atoms, so as to obtain a close insight into the significance of factors such as inductive effect, structures, etc., of the ligand and the thermal behaviour. Similarly, the effect of the cationic size of the metal on the thermal behaviour of the complexes may be studied to derive useful information for group classification. Such studies may open up more interesting areas of investigation which may be related to the effect of the above parameters on the mechanism of thermal decomposition reactions and their kinetics.

REFERENCES

1 G.D. Thorn and R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, Amsterdam, 1962.
2 D. Coucouvanis, Prog. Inorg. Chem., 11 (1970) 233.
3 R.J. Magee, Rev. Anal. Chem., 1 (1973) 333.
4 D. Coucouvanis, Prog. Inorg. Chem., 26 (1979) 301.
5 S.V. Larionov, Zh. Neorg. Khim., 24 (1979) 1446.
6 J.O. Hill and R.J. Magee, Rev. Inorg. Chem., 3 (1981) 141.
7 M.A. Bernard and M.M. Borel, Bull. Soc. Chim. Fr., (1969) 3066.
8 G. D'Ascenzo and W.W. Wendlandt, J. Therm. Anal., 1 (1969) 423.
9 G. D'Ascenzo and W.W. Wendlandt, J. Inorg. Nucl. Chem., 32 (1970) 2431.
10 G. D'Ascenzo, V. Carunchio, A. Messunei and W.W. Wendlandt, Thermochim. Acta, 2 (1971) 211.
11 B. Flaherty and G. McCutcheon, J. Therm. Anal., 3 (1971) 75.
12 Y.S. Lyalikov and M.I. Kitovskaya, J. Therm. Anal., 4 (1972) 271.
13 C.G. Sceney and R.J. Magee, J. Inorg. Nucl. Chem., Lett., 9 (1973) 595.
14 S.V. Larionov and L.A. Kosareva, Thermal Analysis, Proc. IVth ICTA, Budapest, 1 (1974) 877.
15 D. Venkappyya and D.H. Brown, Indian J. Chem., 12 (1974) 838.
16 F.I. Onuska and W.R. Boos, J. Chromatogr., 99 (1974) 291.
17 B. Annuar, J.O. Hill and R.J. Magee, Thermochim. Acta, 8 (1974) 439.
18 B. Annuar, J.O. Hill, D. McIvor and R.J. Magee, Thermochim. Acta, 9 (1974) 143.
19 C.G. Sceney, J.O. Hill and R.J. Magee, Thermochim. Acta, 11 (1975) 301.
20 C.G. Sceney, J.F. Smith, J.O. Hill and R.J. Magee, J. Therm. Anal., 9 (1976) 415.
21 J. Krupcik, J. Garaj, S. Holotik, D. Oktavee and M. Kosik, J. Chromatogr., 112 (1975) 189.
22 D.C. Hilderbrand and E.E. Pickett, Anal. Chem., 47 (1975) 425.
23 S.V. Larionov and L.A. Kosareva, Thermal Analysis, Proc. Vth ICTA, Budapest, 2 (1975) 287.
24 Y.S. Lyalikov and M.I. Kitovskaya, J. Therm. Anal., 7 (1975) 301.
25 D. Perry and R.A. Greanangel, Inorg. Chim. Acta, 13 (1975) 185.
26 G.D'Ascenzo and T. Bica, Thermochim. Acta, 18 (1977) 301.
27 S.V. Larionov, L.A. Kosareva, A.F. Malikova and A.A. Shklyaev, Zh. Neorg. Khim., 22 (1977) 2401.
28 G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 19 (1977) 335, 349, 361.
29 G.K. Bratspies, J.F. Smith and J.O. Hill, Thermochim. Acta, 19 (1977) 373.
30 T.N. Srivastava, V. Kumar and A. Bhargava, J. Indian Chem. Soc., 54 (1977) 591.
31 T.N. Srivastava and A. Bhargava, Indian J. Chem., 16A (1978) 148.
32 A. Tavlaridis and R. Neeb, Z. Anal. Chem., 292 (1978) 135.
33 A. Tavlaridis and R. Neeb, Z. Anal. Chem., 293 (1978) 211.
34 V. Gemmer-Colos and R. Neeb, Z. Anal. Chem., 293 (1978) 290.
35 G.K. Bratspies, J.F. Smith, J.O. Hill and R.J. Magee, Thermochim. Acta, 27 (1978) 307.
36 H. Janicki, G. Blotny and B. Botor-Sawicka, J. Therm. Anal., 14 (1978) 203.
37 A.V. Dubrovin, K.M. Dunaeva and V.I. Spitsyn, Zh. Neorg. Khim., 23 (1978) 3066.
38 M. Wieber and A. Basel, Z. Anorg. Allg. Chem., 448 (1979) 89.
39 K.J. Cavell, J.O. Hill and R.J. Magee, Thermochim. Acta, 34 (1979) 155.
40 L.A. Kosareva and S.V. Larionov, Z. Neorg. Khim., 24 (1979) 2834.
41 U. Baudis and M. Wieber, Z. Anorg. Allg. Chem., 448 (1979) 79.
42 T.N. Srivastava, O.P. Agarwal and R.S. Kapoor, J. Indian Chem. Soc., LVI (1979) 204.
43 E.J. Kupchik and C.T. Theisen, J. Organomet. Chem., 11 (1968) 627.

44 M.S. Chande, J. Indian Chem. Soc., LVI (1979) 386.
45 S. Kumar, N.K. Kaushik, I.P. Mittal, Thermal analysis, Proc. VI Int. Conf., Bayreuth, 1980.
46 K.N. Johri and K.A. Venugopalan, Rev. Roum. Chim., 25 (1980) 215.
47 K.N. Johri, in W. Hemminger (Ed.), Thermal Analysis, Proc. VI ICTA, Birkhauser-Verlag, Basel, 2 (1980) 129.
48 G.K. Bratspies, J.F. Smith and J.O. Hill, J. Anal. Appl. Pyrol., 2 (1980) 35.
49 G.K. Bratspies, J.F. Smith and J.O. Hill, in W. Hemminger (Ed.), Thermal Analysis Proc. VI ICTA, Birkhauser-Verlag, Basel, 2 (1980) 147.
50 S. Kumar and N.K. Kaushik, Thermochim. Acta, 41 (1980) 19.
51 S. Kumar and N.K. Kaushik, Indian J. Chem., 20A (1981) 512.
52 S. Kumar and N.K. Kaushik, J. Therm. Anal., 21 (1981) 3.