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THERMAL ANALYSIS OF SOME TRANSITION METAL COMPLEXES OF DITHIOCARBAMATES

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Abstract

Some selected transition metal Copper(II), Nickel(II) and Cobalt(II) complexes have been synthesized and characterized with the help of IR, elemental, magnetic, NMR and thermogravimetric analysis. After characterization and structural determination, the detailed thermogravimetric analysis ofthese complexes for stability, activation energy(E), frequency factor(Z), entropy of activation(ΔS), free energy of activation (ΔG) has also been investigated, with the help of conventional and Freeman and Caroll's equation and discussed in the present work.

Keywords: *Dithiocarbamates, Thermogravimetry, Freeman and Caroll's equation*

Introduction:

After the preparation and the structural determination of the prepared dithiocarbamate complexes, selected complexes of Dithiocarbamatehave also been investigated by thermal analysis (fig1: for nickel dithiocarbamate complex as a representative). The chemistry of the dithiocarbamic acid and their metal derivatives have been investigated to a considerable extent (Delepine, 1907; Nqombola, 2016). In recent years several papers have been published on dithiocarbamate complexes (both transition and non-transition elements), on their physico-chemical aspects such as IR (Randle, 1949;Sorwar, 2007), magnetic (Febretti, 1984) and thermal analysis (Kaushik, 1985; Swiderski, 2016; Joblonska-Wawrzycka, 2012). The IR studies of the complexes prepared showed the bidentate nature of the complexes (Jung, 1988; Safaa, 2017). The thermal studies showed the two-step decomposition mechanism of the prepared complexes (Bajpai, 2004; Sakhare, 2015).

Results and Discussion

Detailed thermogravimetric studies have been carried out in order to find out the stoichiometry and thermal nature of the prepared complexes. The data of TG analysis gave evidence for 1:2 metal ligand ratio as also indicated by elemental analysis. The pattern of thermal decomposition suggests that cobalt(II) chelate contain two water molecules whereas the rest of the dithiocarbamate complexes i.e., Copper (II), Nickel(II), Manganese (II) are found to be anhydrous in nature.

Further, the decomposition of the organic part takes place in two steps, the major part of the organic moiety probably goes out in the first step. A little change is observed in the second step which may be attributed to the change of metal sulphides to metal oxides on further oxidation. The surveying of the literature(Bajpai, 2004; Sakhare, 2015) reveals that the products formed during the thermal decomposition of dithiocarbamate complexes include volatile H_2S metal sulphide which finally gets oxidised forming oxide as an end product. That residue obtained in the end corresponds to the weight of respective metallic oxides. The reaction for cobalt dithiocarbamate can be interpreted as follows.

(1) $(C_5H_8S_2NO)_2Co.2H_2O \xrightarrow[------>]{air} (C_5H_8S_2NO)_2Co + 2H_2O$

(2) $(C_5H_8S_2NO)_2Co \xrightarrow[------>]{air} CoS + 3H_2S + 10CO_2 + 2NO_2 + 5H_2O$

(3) $3CoS \xrightarrow[------>]{air} 1/3\ Co_3O_4 + 3SO_2$

The other complexes follow the same pattern except the first dehydration step.

The data of thermal analysis of metal complexes are recorded in table (3).

Calculation of thermodynamic parameters:

Mathematical analysis of TG curves was carried out using Freeman Caroll's equation (Madhusudan, 1975) which can be written in the form:

$$\frac{\Delta \log\left(\frac{\mathrm{dw}}{\mathrm{dt}}\right)}{\Delta \log \mathrm{Wr}} = -\frac{\mathrm{E}}{2.303\mathrm{R}} \cdot \frac{\Delta\left(\frac{1}{\mathrm{T}}\right)}{\Delta \log \mathrm{Wr}} + \mathrm{n}$$

Where, T = temperature on absolute scale

R= gas constant

E= Energy of activation

n= order of reaction

Wr= difference between the total loss in weight and the loss in weight at time t, i.e., Wo - Wtdw/dt= value of the rate of weight loss obtained from the loss in weight vs time curve at appropriate times

Wr and T can be directly obtained from the TG traces. From the TG curves (i.e., weight loss versus T), the heating rate per minute can be calculated. From the linear plots, Δlog (dw/dt)/Δlog(Wr) vs(1/T)/Δlog(Wr) having intercept equal to one fig(2) and table(2) it is therefore concluded that the order of thermal decomposition reaction of the metal complexes of dithiocarbamate is one. The temperature slope dw/dT were converted into time slopes dw/dt using the relationship(Patel, 2013)

$$\frac{\mathrm{dw}}{\mathrm{dt}} = \frac{dw}{dt} . \frac{dT}{dt} = \left(\frac{dw}{dt}\right) . \emptyset$$

The usual first order rate law expression:

dw/dt =k (a - x)

Can be written in the following form using the term W and Wr (where Wr=a-x) Combining this with Arrhenius equation:

K =Z exp(-Ea/ RT)

We obtain :

$$\frac{\log\left(\frac{dw}{dt}\right)}{Wr} = -\frac{E}{2.303RT} + logz$$

Activation energy (E) and frequency factor (Z):

Linear plot of log{[(dw/ dt)/Wr]/Wr} vs 1/T in all the cases under investigation with slope Ea/2.303R were obtained from which Ea values were found out. Z (frequency factor values)were also calculated from the intercept of the plots figure(3)

Entropy of activation (ΔS):

If activation ΔS were obtained from the relationship(Patel, 2013)

ΔS=2.3 03R log

(Zh/kT$_s$) Where k=

Boltzman constant h=

Plank constant

T$_s$= temperature for peak decomposition from TG curves

Free energy of activation (ΔG):

The free energy of activation ΔG was calculated using the following equation(Patel, 2013)

G =E - Ts ΔS

The kinetic parameters thus obtained are recorded in tables(3)

It can be seen from the tables that the trends of activation energy values of dithiocarbamate are in the order

Co > Ni > Cu

The trend in the free energy change ΔG in the case of metal complexes of dithiocarbamate complexes under investigation is different and simply throw light on the thermal stability of respective complexes. The trend observed is different from the behaviour of metal complexes in solution where stability is connected to the ionic potential (φ= charge/radius) of the metal ions (i.e., the stability of the complexes increases with φ) the difference in behaviour in E may be due to some factor other φ.

The trend in the value of Z and entropy of activation (ΔS) observed in the dithiocarbamate metal complexes under investigation are different. Negative values of entropy of activation (ΔS) and low values of frequency factor (Z) simply reflect upon the fact that the activated complex has a more ordered structure than the reactants(13) and the thermal decomposition reaction are slower than normal.

The fact however remains that the trends observed in kinetic parameters are different from the trends observed in the thermal stability of the complexes. It may be attributed to the fact that decisive criteria on which kinetic parameters depend are different from the criteria on which the thermal stability depends.

Experimental:

All the chemicals used were AR grade unless stated otherwise. All complexes were prepared and re-crystallised, the thermal measurements were carried out using a 'Mettler TG 50 thermal analyser.' The sample weighing 8-15 mg was heated at the rate of 20°/min in silica crucible to a temperature of 1000^0C in static air atmosphere and maintained the similar condition throughout the investigation. A thermo balance of 0.01mg sensitivity was used (MettlerMT-5).

Table 1: Thermogravimetric analysis of Ni (Morpholine-dtc)

S. No.	**Time t (sec)**	**Temp. T (^{0}A)**	**Wr x 10^3 (gm)**	**dw x 10^3 (gm)**	**(dw/dt) x 10^6 (gm/sec)**	**-log[(dw/dt)/wr]**	**1/T x 10^3 (^{0}A)**
1.	150	323	6.980	-	-	-	-
2.	300	373	6.980	-	-	-	-
3.	450	423	6.920	0.060	0.133	4.716	2.364
4.	600	473	6.920	0.060	0.100	4.840	2.114
5.	750	523	6.860	0.120	0.160	4.632	1.912
6.	900	573	6.674	0.306	0.340	4.293	1.745
7.	1050	623	3.245	3.735	3.557	2.960	1.605
8.	1200	673	0.796	6.184	5.153	2.189	1.486
9.	1350	723	0.612	6.368	4.717	2.113	1.383
10.	1500	773	0.612	6.368	4.245	2.159	1.294
11.	1650	823	-	6.980	4.230	-	-

Table 2 : Freeman-Carroll's treatment of thermogravimatric data of Morpholine-dtc.

S. No.	**1/T x 10^3 (^{0}A)**	**-Δ (log Wr)**	**-Δ [log(dw/dt)]**		
1.	2.114	2.160	7.000	0.979	3.241
2.	1.745	2.176	6.468	0.270	2.972
3.	1.486	3.099	5.288	0.281	1.706
4.	1.383	3.213	5.326	0.260	1.658
5.	1.294	3.213	5.372	0.241	1.672

Morpholine-dtc= Sodium morpholine dithiocarbamate

Table 3: Thermodynamic parameters of metal complexes of Morpholine-dtc.

S. No.	**Compound**	**E (K Cal mol^{-1})**	**Z (S^{-1})**	**-ΔS (e.u.)**	**G (k Cal mol^{-1})**	**Ts (^{0}A)**
1.	Cu(Mdtc)	11.440	10.000	55.430	45.973	623
2.	Ni(Mdtc)	14.643	2.089 x 10^2	49.437	47.914	673
3.	Co(Mdtc)	15.238	3.981 x 10^2	48.437	47.718	673

Morpholine-dtc= Sodium morpholine dithiocarbamate

Fig 1

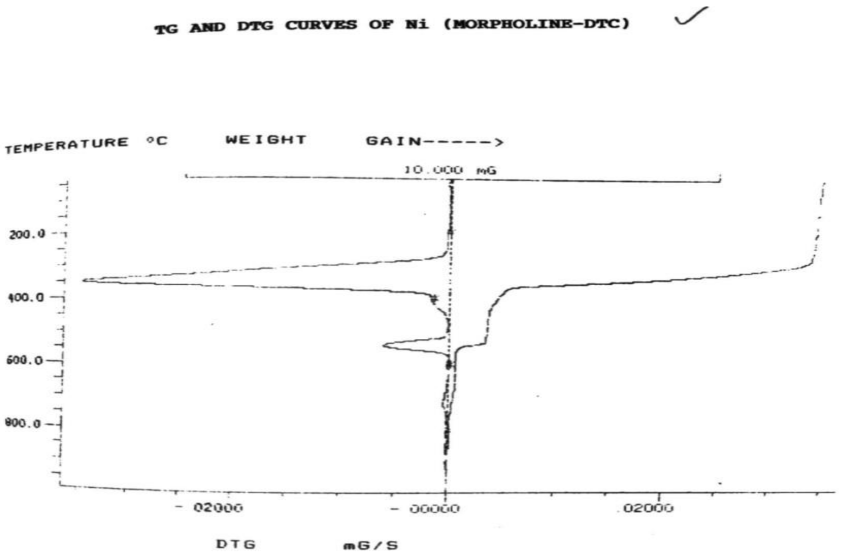
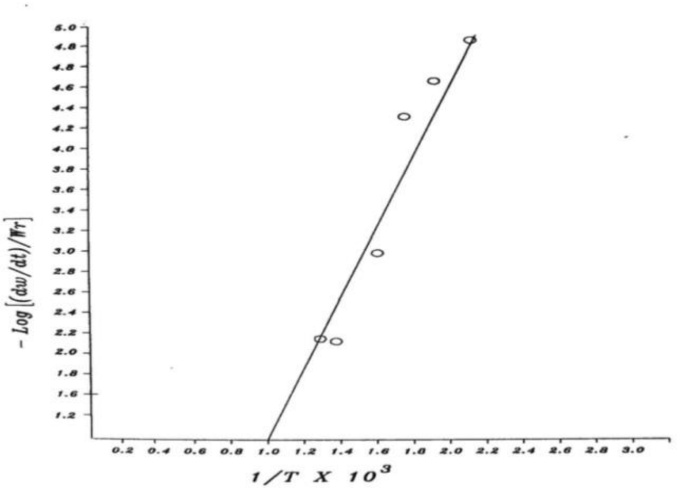
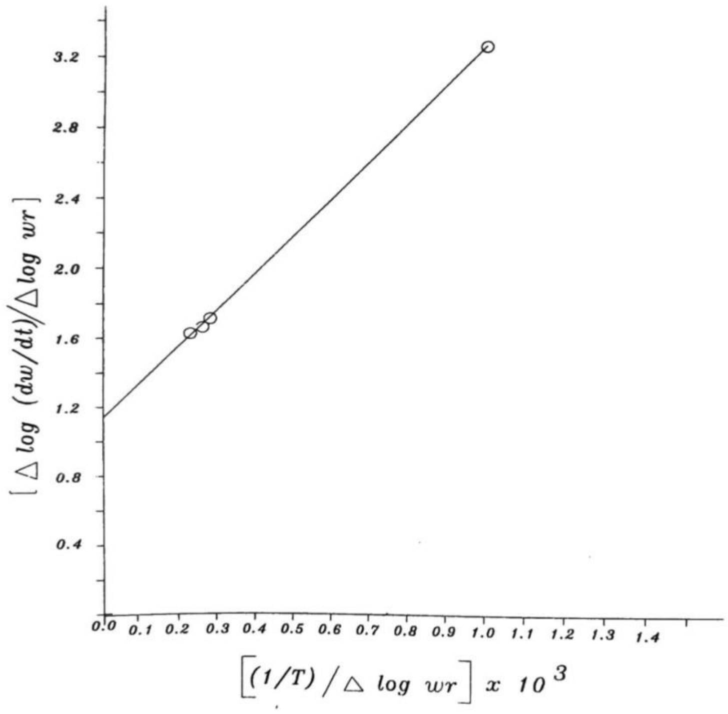


Fig 2



PLOT FOR Ni (MORPHOLINE–DTC) BETWEEN – Log [(dw/dt)/Wr] AND [1/T X 10^3]

Fig 3



FREEMAN AND CAROLL'S TYPE PLOT OF Ni – (MORPHOLINE–DTC)

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