

Thermolysis of some Nitrogen Ligated Complexes of Transition and non Transition metals

TAJ ALI, ABDUL WADUD, HAROON-AL-RASHID,
Department of Chemistry,
University of Peshawar, Peshawar, Pakistan

(Received 24th January, 1982)

Summary: Thermal dissociation of some nitrogen ligated complexes of 2-guanidinobenzimidazole (GBM), 1,2-dimorpholinoethane (DME) and 1,3-dimorpholinopropane (DMP) with Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Mn(II) have been studied by thermogravimetry and few compounds by differential thermal analysis. The thermal decomposition of GBM, DME and DMP complexes with transition metals was generally observed to occur in two stages. The dissociation sequence observed for GBM complexes was such that the ligand was lost in the second stage of dissociation. However DME and DMP chelates were found to follow entirely different decomposition mechanism. In DMP chelates the ligand was lost in the first stage of dissociation followed by the elimination of halogens. DME complexes, unlike DMP chelates, loses part of the ligand, one morpholine moiety, in the first stage and morpholino-ethane moiety in the second stage of dissociation. The non-transition metal complex of all the three ligands follow the same sequence of decomposition and analysis of Ni(II) complexes are also reported. The reactions found in DTA curves correspond well to those found in the TGA curves.

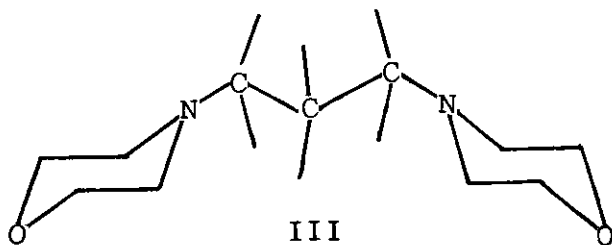
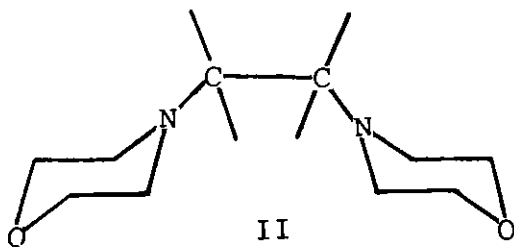
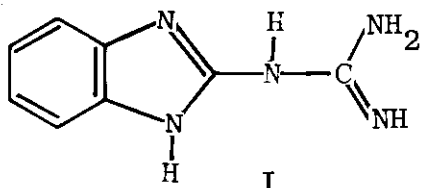
Introduction

During the last decade a large number of model coordination compounds containing imidazole and substituted imidazole ligands have been studied both spectroscopically and magnetically [1-2] and also by X-ray analysis [2-7]. Thermal properties of Ni(II) complex with imidazole and N-methyl imidazole have been studied to investigate the nature of linkage between the ligand and the transition metal [8-11], as such bonding is of considerable biological importance [12-13].

2-Guanidinobenzimidazole (GBM) (I) is considered an interesting derivative of imidazole. In recent years systematic investigations of the ability of this ligand to form complexes with transition and non-transition metals have been made [14-17]. In all these complexes GBM acts as a bidentate

ligand with the cyclic secondary amine and terminal imide groups engaged in metal nitrogen bonding [16-17]. The ligands 1,2-di-morpholinoethane (DME) (II) [18-21] and 1,3-dimorpholinopropane [DMP] (III) [23-24] have been shown to act as stereospecific chelating agents and form tetrahedral complexes with first row transition and non-transition metal ions. These chelating agents were observed to behave as bidentate ligands and coordinate through nitrogen atoms only [18-24]. The ligands were used as a selective reagent for gravimetric and spectrophotometric analysis of various metal ions [25-31] and DME as catalyst for the preparation of polyurethane foams [32]. However the thermal properties of coordination compounds of these ligands have not been studied so far with the exception of only Co(II) complexes [33]. Therefore, the

present investigation was undertaken with an objective to study the thermal behaviour of transition and non-transition metal complexes of these ligands.



Experimental

Thermobalance

The automatic recording thermobalance has previously been described [33]. The analyses were carried out in an open crucible under atmospheric pressure. Sample sizes ranged in weight from 36 mg to 98 mg and were pyrolysed at a furnace heating rate of about 5° per minute.

Differential thermal-analysis

The apparatus used has previously been described [34]. Sample size ranged in weight from 100 mg to 400 mg. The heating rate was 5°C per minute. The temperature rise

sensitivity of instrument was checked by quartz sample. Area of the peaks were calibrated by planimeter Sodium nitrate (Analar) having heat of fusion Hf 44.7 Cal/g at 325°C was used as the standard.

Preparation of Complexes

All GBM complexes studied in the investigation were prepared from partially dehydrated metal salts, and completely anhydrous solvents using the general procedure as previously described. The DME and DMP complexes were prepared by the procedure reported earlier [23] using completely anhydrous metal salts and solvents.

Results and Discussion

Thermogravimetric analysis (TGA) studies of 2-guanidinobenzimidazole complexes.

The TGA curves for the complexes are given in Fig.1 and data in Table-1.

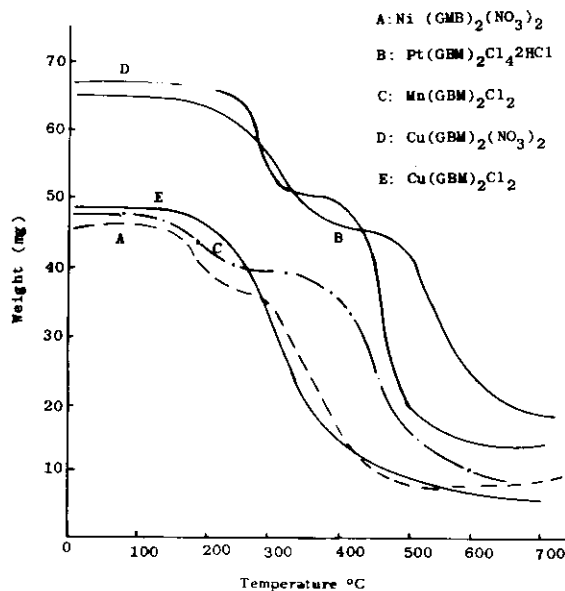
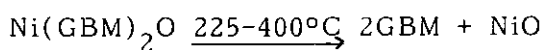
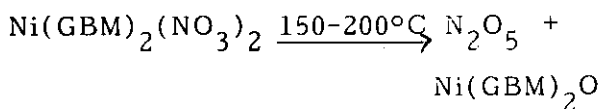


Fig. 1: Thermograms of GBM complexes

Table-1: Thermal Analysis data of GBM Complexes

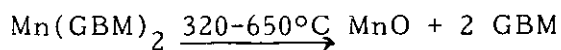
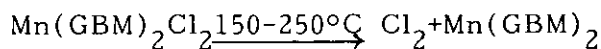
COMPLEX	DEGREE RANGE °C	SAMPLE MASS (mg)	MASS CHANGE(mg)		RESIDUE(mg)	
			Expected/Found	Expected/Found	Expected/Found	Expected/Found
Ni(GBM) ₂ (NO ₃) ₂	150-200	45.0	9.0	9.0		
	225-400		29.4	29.4	8.3	7.5
Mn(GBM) ₂ Cl ₂	150-250	47.4	7.1	7.5		
	320-650		35.1	39.0	6.7	6.4
Cu(GBM) ₂ (NO ₃) ₂	200-300	66.0	13.3	13.0		
	350-700		43.0	46.2	9.8	8.9
Cu(GBM) ₂ Cl	100-700	47.5	41.3	41.0	7.7	6.5

The dissociation of GBM complexes of the type M(GBM)₂X₂ when M=Ni (II), Mn(II) and Cu (II) and X=NO₃.Cl was accomplished in two stages. In all these chelated decomposition occurred in a particular sequence i.e. GBM ligand was evolved in the second stage of dissociation as was observed in case of Co(GBM)₂X₂ (23). The weight loss curve of Ni (GBM)₂ (NO₃)₂ given in Fig. 1/A indicate that one mole of nitrogen pentaoxide was lost per mole of the complex in the 150-200°C temperature range. The second weight loss, resulting in the curves break at 225°, approximated that for the loss of 2 moles of guanidinobenzimidazole. No further loss was observed and the weight remained constant which corresponded to the calculated value for NiO.

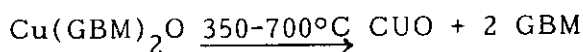
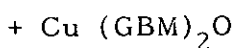
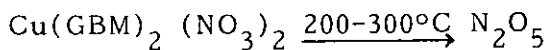


The weight loss curve for Mn(GBM)₂Cl₂ is given in Fig.1/B. The first weight loss resulting in a curve break at 150-250°C temperature range

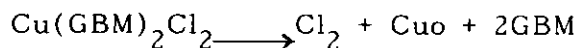
corresponding to evolution of 1 mole of chlorine per mole of complex. The second weight loss was observed above 320°C, resulting in the loss of 2 GBM moles. further heating caused oxidation of the Mn to give MnO residue.



The thermogram of Cu (GBM)₂ (NO₃)₂ and Cu (GMB)₂Cl₂ are given in Fig. 1/C and 1/D respectively. In both these complexes CuO was fomred as residue after complete dissociation. In case of Cu (GBM)₂ (NO₃)₂ first loss was observed at 200-300°C which is due to the elimination of N₂O₅. The second dissociation reaction occurred at 350-700°C resulting in the evolution of 2 mole of GBM per mole of the complex. No further loss was observed above 700°C resulting in the constant weight of CuO.



In case of $\text{Cu (GBM)}_2 \text{Cl}_2$, the decomposition started at a much lower temperature and occurred in a single step at $100\text{-}700^\circ\text{C}$, resulting in the formation of CuO as residue.



Thermogravimetric Studies of 1,2-Dimorpholinoethane (DME) Complexes.

The Thermograms of Ni(DME)Cl_2 and $\text{Ni(DME) (NO}_3)_2$ are given in Fig.2/A and 2/B respectively and data in Table-2. The weight loss curve of Ni(DME)Cl_2 indicates that the complex was stable upto 250°C . In first step at $250\text{-}350^\circ\text{C}$ temperature range the loss observed corresponded to the elimination of one morpholine moiety and chlorine. The intermediate product formed decomposed at $400\text{-}700^\circ\text{C}$; the residue found was NiO .

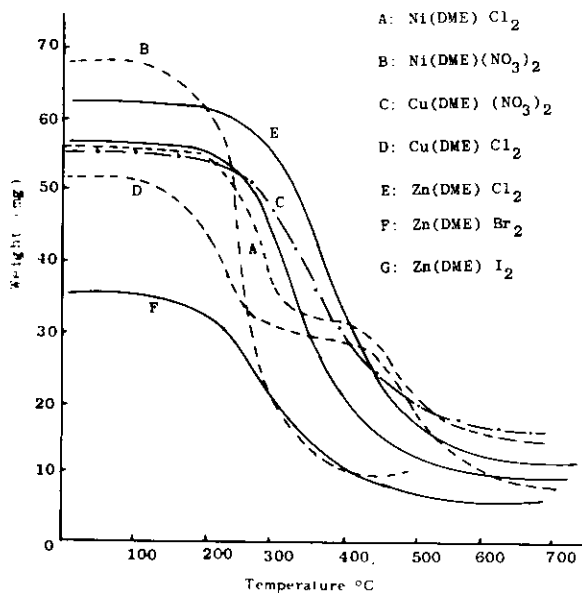
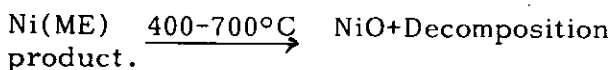
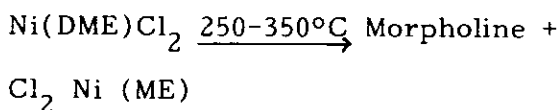
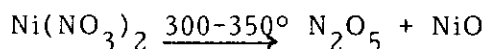
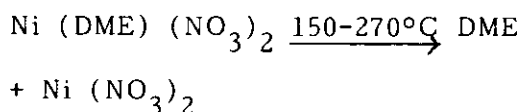
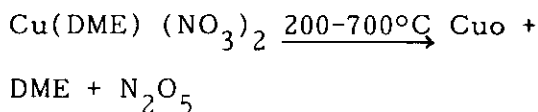


Fig.2: Thermobalance curves of DME complexes.

Comparatively $\text{Ni(DME) (NO}_3)_2$ is less stable as it began to lose weight at a lower temperature at about 150°C . The first decomposition starts by removal of the ligand at $150\text{-}270^\circ\text{C}$. The curve breaks showed the loss of one mole of DME per mole of the complex. In the second dissociation reaction N_2O_5 was evolved at $300\text{-}350^\circ\text{C}$. As indicated by the constant level of thermogram no further loss was observed above 550°C . The results is the formation of NiO .

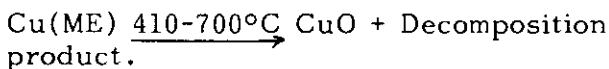
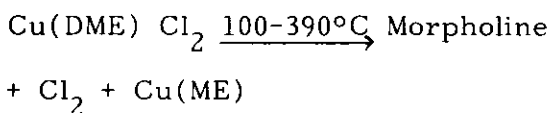


The thermobalance curve of $\text{Cu-(DME) (NO}_3)_2$ complex is given in Fig.2/C. The dissociation was completed in a single step at $200\text{-}700^\circ\text{C}$ temperature range. The residue found was CuO .



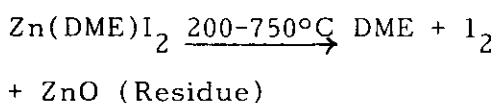
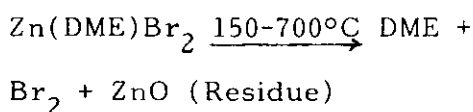
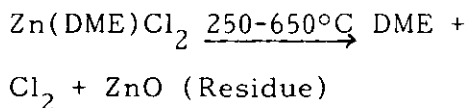
The weight loss curve of the complex Cu (DME) Cl_2 is given in Fig.2/D.

First dissociation occurred at $100\text{-}390^\circ\text{C}$ resulting in the loss which corresponded to the weight of morpholine and chlorine. In the second stage of dissociation at temperature $410\text{-}700^\circ\text{C}$ the observed loss was due to the elimination of morpholine ethane moiety of the intermediate product. Further heating caused oxidation of the copper to give a residue of CuO .



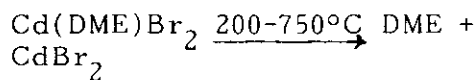
The weight loss curves for Zn(DME)Cl_2 , Zn(DME)Br_2 and Zn(DME)I_2 are

given in Fig.2/E, 2/F and 2/G respectively. In all these complexes decomposition was completed in a single step, resulting in formation of ZnO as residue.



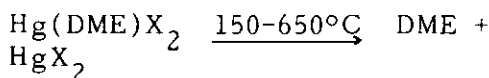
The weight loss curves for Cd-(DME)Br₂ and Cd(DME)I₂ are given in Fig.3/D and 3/E respectively which indicate that the complexes were decomposed and then all the content evaporated with no residue formation.

The decomposition occurred at 200-750°C temperature range. The probable decomposition sequence is:-



The TGA curves for Hg (DME)X₂ when X=Cl, Br, I given in Fig.3/A, 3/B and 3/C respectively showed that like Cd(DME) X₂ complexes these chelates started decomposing at 150°C and the whole product was then eliminated 650° with no residue formation. Experimental data indicate that Mercury DME complexes are thermally less stable than the corresponding Zinc and Cadmium complexes.

The probable sequence of decomposition may be



Thermogravimetric Studies of 1,3-dimorpholinopropane (DMP) Complexes

The thermograms of Ni(II), Cu(II) and Zn(II) complexes with 1,3-Dimorpholinopropane (DMP) are given in Fig.4 and data in Table-3.

The weight loss curve of Ni(DMP) (NO₃)₂ (Fig.4/A) shows that this complex is thermally less stable of all the complexes as its decomposition started at a much lower temperature (100°) and was complete at 350°C in a single step. The loss observed stoichiometrically equals to the elimination of the ligand (DMP) and N₂O₅. The weight of residue remained constant which corresponding to the calculated value of NiO.

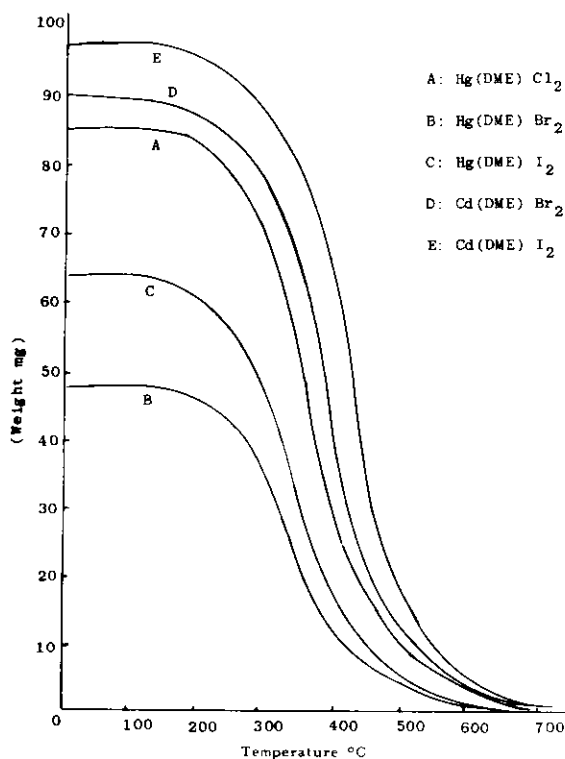
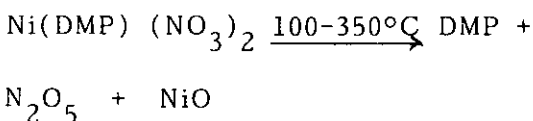


Fig.3: Thermobalance curves of DME complexes.

Table-2: Thermal Analysis data of DME Complexes

COMPLEX	DEGREE RANGE(°C)	SAMPLES MASS(mg)	MASS CHANGE(mg) Expected /Found		RESIDUE(mg) Expected /Found	
Ni(DME)Cl ₂	250-350	56.2	26.7	25.0	-	-
-	400-700	-	19.5	19.0	13.1	12.8
Ni(DME)(NO ₃) ₂	150-270	68.0	35.5	38.0	-	-
-	300-550	-	19.1	17.8	13.4	13.0
Cu(DME)(NO ₃) ₂	200-700	54.8	45.8	46.0	11.2	11.0
Cu(DME) Cl ₂	100-390	51.4	23.9	22.0	-	-
-	410-700	-	17.3	17.0	12.8	12.0
Zn(DME) Cl ₂	250-650	62.2	50.0	50.0	15.2	15.0
Zn(DME)Br ₂	150-700	35.6	30.2	29.0	6.0	5.0
Zn(DME)I ₂	200-750	65.1	49.0	47.0	8.8	9.0
Cd(DME) Br ₂	200-750	90.0	90.0	9.0	NIL	NIL
Cd(DME) Cl ₂	200-700	98.0	98.0	98.0	NIL	NIL
Hg(DME) Cl ₂	150-650	85.7	85.7	85.7	NIL	NIL
Hg(DME) Br ₂	150-650	48.0	48.0	48.0	NIL	NIL
Hg(DME)I ₂	150-650	63.9	63.9	63.9	NIL	NIL

Table-3: Thermal Analysis data of DMP Complexes

COMPLEX	DEGREE RANGE °C	SAMPLE(mg)	MASS CHANGE(mg) Expected / Found		RESIDUE(mg) Expected /Found	
Ni(DMP)(NO ₃) ₂	100-350	68.3	55.4		12.9	10.5
Ni(DMP) I ₂	150-350	50.8	20.6	20.0		
	400-650	-	24.5	23.0	7.5	6.0
Cu(DMP) Br ₂	130-320	67.0	32.8	29.5		
	350-600	-	24.5	25.0	12.5	12.0
Zn(DMP) Cl ₂	150-750	60.8	49.5	47.8	14.0	12.0
Zn(DMP) Br ₂	130-700	70.9	60.4	62.0	13.0	12.0
Zn(DMP) I ₂	120-700	85.0	75.6	73.0	12.9	11.0
Mg(DMP) Cl ₂	200-600	79.2	79.2	79.2	NIL	NIL
Mg(DMP) Br ₂	180-600	70.5	70.5	70.5	NIL	NIL
Cd(DMP) I ₂	150-700	65.0	65.0	65.0	NIL	NIL

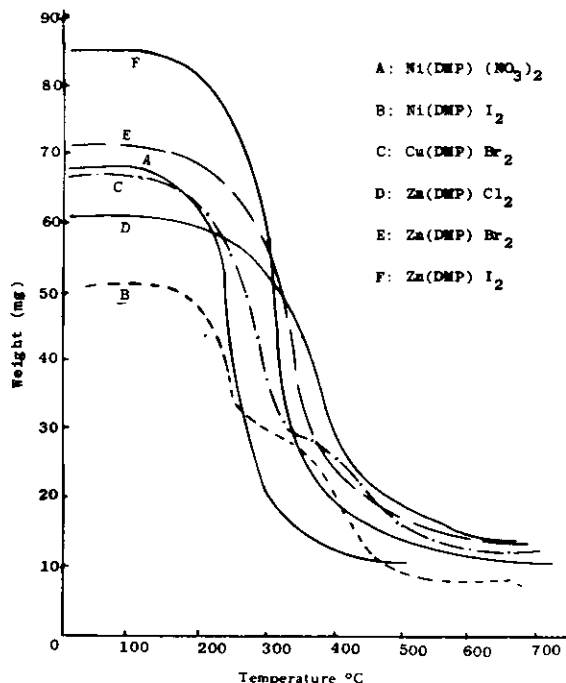
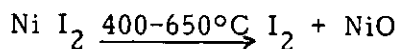
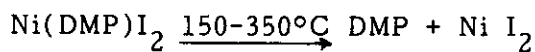
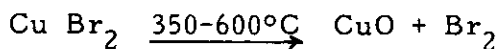
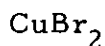
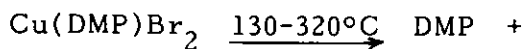


Fig.4: Thermograms of DMP complexes.

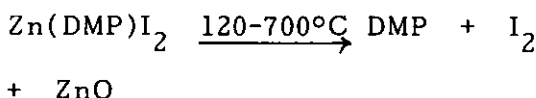
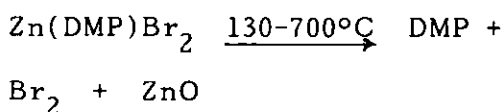
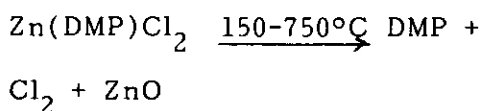
The weight loss curve of Ni(DMP)I₂ is given in Fig. 4/B. In the first stage, the decomposition starts by removal of the ligand DMP at 150-350°C. In the second stage of decomposition at 400-650°C, a loss which corresponded to the elimination of one mole of iodine per mole of the intermediate occurred. No further loss was noted above 650°C, resulting in the constant weight of NiO.



The decomposition sequence for the Complex Cu(DMP) Br₂ (Fig.4/C) is similar to that of Ni (DMP)I₂.

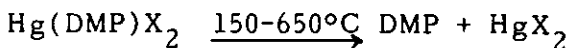
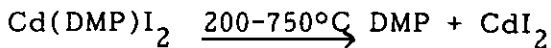


The thermogram of Zn(DMP) X₂ when X=Cl, Br, and I are given in Fig.4/D and 4/E and 4/F respectively. Thermally all the three complexes behave similarly. The decomposition was completed in one step. Experimental results indicate that the chloride complex is the most thermally stable while the iodine complex is the least stable; ZnO was found as the residue.



The observed values corresponded well to the stoichiometric calculated values.

The thermogram of Cd(DMP)I₂ Hg-(DMP)Cl₂ and Hg(DMP) Br₂ complexes given in Fig.5/A, 5/B and 5/C respectively indicated that these complexes behaved exactly like corresponding DME complexes. The decomposition takes place in a single step with no residue formation.



When X = Cl and Br.

Differential Thermal Analysis (DTA)- Studies of Some GBM and DME Complexes

The DTA curves of Ni(GBM)₂ (NO₃)₂ is given in Fig.6/A the reactions found in the DTA curves corresponded to those previously found in the TGA curves. The DTA curves indicated two

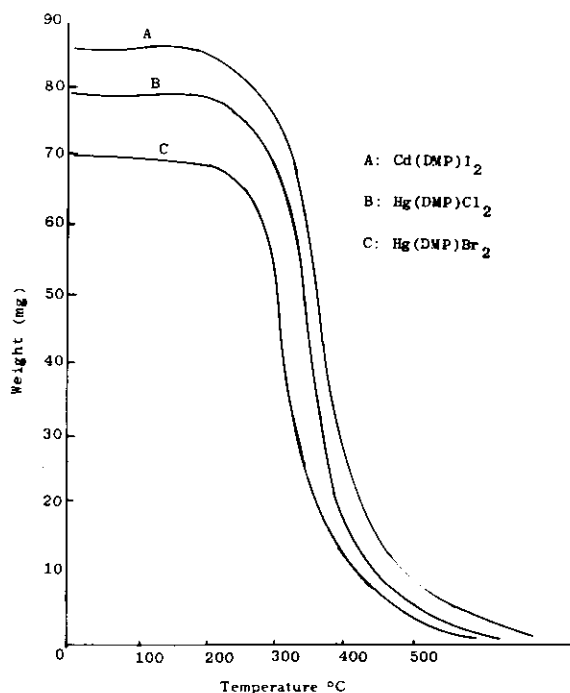


Fig. 5: Thermograms of DMP complexes.

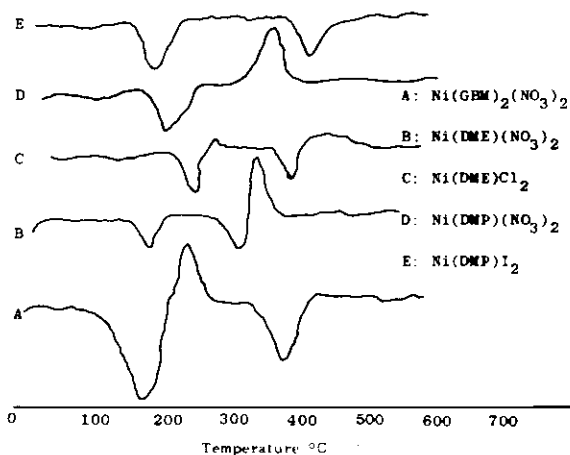
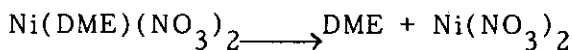


Fig. 6: A. Ni(GBM)₂(NO₃)₂ B. Ni(DME)(NO₃)₂
C. Ni(DME)Cl₂ D. Ni(DMP)(NO₃)₂ E. Ni(DMP)I₂

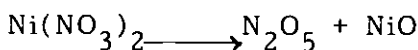
endothermic and one exothermic peak. The first endothermic peak at 180°C corresponded to the loss of N₂O₅. The exothermic peak at 225°C just following the endothermic peak may be due to the evolution of N₂O₅ (35-36) or some rearrangement reaction. The second

endothermic peak at temperature 400°C is due to the evolution of the ligand (GBM) as shown in TGA curves.

The DTA curves of Ni(DME)(NO₃)₂ as shown in Fig. 6/B gave two endothermic peaks, with peak maximum at temperature 200 and 300°C, the reactions found in these curves corresponded to those found in the TGA curves Fig. 2/B.



The second small endothermic peak at 320°C, is due to the dissociation reaction as concluded by the TDA data.



The exothermic peak at 360°C may be due to the evolution of N₂O₅ as observed in the case Ni(GBM)(NO₃)₂.

The DTA curves for Ni(DME)Cl₂ complex is shown in Fig. 6/C. It also indicate two endothermic peak maximum at 260°C and 400°C. The reactions found in DTA curves corresponded with TGA curves.

References

1. J. Reedijk, *Rec. Trav. Chem.*, **88** 1451 (1969)
2. R.J. Sundberg and R.B. Martin, *Chem. Rev.*, **74**, 471 1974.
3. A. Santoro, A.D. Michell, M. Zocchi and C.W. Reimann, *Acta. Cryst.*, **B 25**, 842 (1969)
4. J. Redijk and G.C. Verschoor, *Acta. Cryst.*, **B 29**, 721, (1973)
5. G.J.M. Ivarsson and W. Forling, *Acta. Cryst.*, **B 39** 1896, (1979)
6. J.C. Janson, H. Vonkoningseld and J.A.C. Vanocijen, *Cryst. Struct. Comm.*, **7** 637, (1978)
7. B.K.S. Lundberg, *Acta. Chem. Scotnd.*, **26**, 3977 (1972)
8. J.C. Van Dam, G. Harkvoort, J.C. Jansen and J. Readkijk, *J. Inorg. Nucl. Chem.*, **37**, 713, (1975)

- 9 C.Dash and P.Pujari,
J.Inorg.Nucl.Chem., **40**, 173 (1978)
10. G.Hakvoort, J.E.Van Dam and J. Reedijk, Thermal analysis, Proc.5th ICTA, Kyoto P.186 (1977)
11. J.C.Van.Dam, C.Harkvoort and J. Reeduck,
J.Thermal Analysis **20** 2 (1981)
12. D.M.Dooley R.A.Scot. J. Ellinghaus, E.J.Soloman and H.B. Gray
Proc.Nat.Acd.Sci., (USA) **75**, 3019 (1978)
13. M.E.Tweedle, L.J.Wilson, L. Garcila Iniguez, G.T.Balcock & G. Palmer
J.Biol.Chem., **253**, 8065 (1978)
14. A.K.Bennerjee and S.P. Ghosh,
J.Indian.Chem.Soc., **38**, 237 (1961)
15. S.M.Ali, N.Ahmad & M.S. Hussain,
Pak.J.Sci.Ind.Res., **18**, 29 (1966)
16. N.Ahmad,
Pak.J.Sci.Ind.Res., **12**, 342 (1969)
17. M.S.Hussain, Taj Ali & S.M.Ali,
Pak.J.Sci.Ind.Res., **16**, 344 (1973)
18. S.M.Ali, M.S.Hussain and M. Akhtar,
Pak.J.Sci.Ind.Res., **6**, 174 (1963)
19. A.L.Lott and P.G.Rasmussen,
J.Org.Nucl.Chem., **32**, 101 (1969)
20. W.R.Schiedt, J.C. Hason and P. G.Rasmussen,
Inorg.Chem., **8**, 2398 (1969)
21. A.L.Lott,
J.Am.Chem.Soc., **93**, 5313 (1971)
22. A.L.Lott and G.P.Ramussen,
J.Am.Chem.Soc., **91**, 6502 (1969)
23. M.S.Hussain, Taj Ali and S.M. Ali,
Proc.Pak.Acad.Sci., **13**, 1 (1976)
24. M.S.Hussain, Taj Ali and S.M.Ali
Pak.J.Sci.Ind.Res., **19**, 2 (1976)
25. E.Asmus, and K.Ohls,
Z.Analyst.Chem., **177**, 100 (1960)
26. E.Asmus, H.Halne and K.Ohls,
Ibid, **196**, 161 (1963)
27. E.Asmus, and J.Sarfert,
Ibid, **198**, 412 (1963)
28. E.Asmus, and D.Ziesche,
Ibid, **210**, 177 (1967)
29. E.Asmus and J.Peters,
Ibid, **203**, 409 (1964)
30. E.Asmus and H.D.Lunkwitz,
Ibid, **226**, 171 (1967)
31. M.S.Hussain, Taj Ali, Falak Naz and S.M.Ali,
Pak.Sci.Ind.Res., **19**, 56 (1976)
32. F.A.Kryuchkov, S.T.Pyshago, L.I.Parkouskii, L.A. Kulikova, YU.M.Mogedevskii, A.M. Egorov & A.V. Liven,
CAA, **77**, 2081 (1972)
33. Taj Ali, A.Wadood & S.M. Hussain,
J.Chem.Sco.Pak., **4**, 1 (1982)
34. M.A.Qaiser, M.K.Ali and A.U.Khan
Pak.J.Sci.Ind.Res., **11**, 1 (1968)