TRANSITION METAL COMPLEXES OF PHENYLACETATES AND SUBSTITUTED PHENYACETATES WITH NEUTRAL HYDRAZINE AS A LIGAND

R. Manimekalai

Department of Chemistry, Kongunadu Arts and Science College, Coimbatore, Tamilnadu, India.

E mail: manimekalair@ymail.com

ABSTRACT : Some hydrazine carboxylates of the type $Co(PhAc)_2(N_2H_4)_2$, where M = Co, Ni, Cd and Mn , $M(Di-PhAc)_2 1.5N_2H_4.H_2O$, M = Co, Ni and Cd, $M(2,4 di-Cl PhAc)_2 1.5N_2H_4.H_2O$ where M = Co, Ni and Cd, have been prepared and studied. The compositions of the complexes have been determined by chemical analyses. The electronic spectra suggest the octahedral geometry for the metal complexes. The IR absorption bands of N-N stretching in the range $958 – 975$ cm^{-1} unambiguously prove the bidentate bridging nature of the N_2H_4 ligand. All prepared complexes undergo two, three or multi step decomposition and the final products are found to be the respective metal oxide, metal carbonate, metal of mixture of metal oxide and metal carbonate or metal as indicated by thermal analysis. In order to know the isomorphous nature among the complexes the X–ray patterns have been compared.

Key Words: IR; Electronic Spectra; Thermal analysis; X-ray pattern

INTRODUCTION

Hydrazine is a versatile ligand and forms a wide variety of complexes with various metal ions. The monodentate and bridging bidentate coordination of the hydrazine molecule on complexation has been well documented in the literature [1]. The emerging interest in these hydrazine complexes are mainly due to their structure and thermal behaviour.

Hydrazine complexes of the transition metal ions with variety of carboxylic acids have been reported [13, 12,17,15,2,18,20,4,16,7,6,9]. Recently Some new metal cinnamate monohydrazinate, $M(cin)_2 N_2H_4$ (M = Co or Zn), metal cinnamate dihydrazinates, $M(cin)_2(N_2H_4)_2$ (M = Co, Ni, Zn or Cd), metal crotonate dihydrazinates, $M(crot)_2(N_2H_4)_2$ (M = Co or Ni), nickel crotonate monohydrazinate monohydrate $Ni(crot)_2.N_2H_4.H_2O$ and $Cd(crot)_2(N_2H_4)_2.H_2O$ have been reported by R. Manimekalai [10]. Among the hydrazinate of metal carboxylates those of metal acetates and substituted acetates are least studied. The preparation and thermal reactivity of some metal acetate hydrazinates have been reported[19, 15]. Mixed ligand complexes of metal acetate with quinoline, isoquinoline and 3 – methyl pyridine have been reported [10]. However these appear to be few literature citations on metal phenylacetate [5] and substituted phenylacetate hydrazinates. Therefore in continuation of my work it is considered to be worthwhile and interesting to investigate with phenylacetate and substituted phenylacetates of a few typical divalent metal ions such as Co(II), Ni(II), Mn(II), Cd(II).

EXPERIMENTAL

The bis(hydrazine) metal Phenylacetates and sesqui(hydrazine) metal Dipheylacetates, 2,4-dichlorophenylacetates have been prepared by the reaction of the corresponding metal nitrate hydrate or metal acetate hydrate, respective acids and hydrazine hydrate in aqueous medium.

Preparation

M(PhAc)$_2$(N$_2$H$_4$)$_2$ M = Co(II) (or) Ni(II),

Phenylacetic acid (1.3614 g, 0.1 mol) is added to 100 mL distilled water containing 99 – 100 %, pure hydrazine hydrate (1 mL, 0.2mol). The mixture is stirred well and heated over water bath to get a clear solution. It is filtered and added slowly to an aqueous solution of the corresponding metal nitrate   hexahydrate (1.4550 g, 0.05 mol) with constant stirring. The clear solution obtained is kept aside for 45 minutes. This precipitates the complex, which is filtered washed with distilled water, alcohol and ether and air dried.

Cd(PhAc)$_2$(N$_2$H$_4$)$_2$

Phenylacetic acid (0.9076 g, 0.1 mol) is added to 50 ml water containing 99 – 100 %, pure hydrazine hydrate (1.3 mL, 0.53 mol). The mixture is stirred well and heated over water bath to get a clear solution. It is filtered and added slowly to an aqueous solution of the cadmium nitrate (1.028 2g, 0.01 mol) with constant stirring. The complex is precipitated slowly on the addition of the ligand to the metal ion solution. It is kept for sometime and filtered, washed with distilled water, alcohol and ether and air dried.

Mn(PhAc)$_2$(N$_2$H$_4$)$_2$

Phenylacetic acid (1.3614 g, 0.2 mol) is added to 50 ml of distilled water containing 99 – 100 % pure hydrazine hydrate(1 mL, 0.4 mol). The mixture is stirred well and heated over water bath to get a clear solution. It is filtered and added slowly to an aqueous solution of Mn(CH$_3$COO)$_2$.4H$_2$O(1.2250g, 0.2mol) with constant stirring. The mixture solution is concentrated over water bath at 80 – 90 ˚. When the volume is reduced to about 15 ml, few crystals of the complex is formed. When it is allowed to cool, the complex completely precipitated. Then it is filtered, washed with distilled water, alcohol and ether and air dried.

M(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O M= Co(II), Ni(II) or Cd(II)

Respective metal nitrate hydrates (0.5 g, 0.001 mol) in 50mL of water and 50 mL of aqueous solution containing a mixture of Diphenylacetic acid (0.72 g, 0.003 mol) and hydrazine hydrate (0.7 mL. 0.01 mol) are mixed and stirred well. The complexes are formed after few minutes, is filtered and washed with alcohol, diethylether and air dried.

M(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O M = Co, Ni or Cd

These complexes are also prepared by the same procedure by mixing aqueous solution of respective metal nitrate hydrates and an aqueous solution contains 2,4-dichloropheylacetic acid and hydrazine hydrate in the same molar ratio. Cobalt and nickel complexes formed slowly whereas cadmium complex settled down immediately. They are separated as mentioned above.

RESULTS AND DISCUSSION

Analytical data of the prepared complexes are given in table 1. They are best fit with the proposed compositions.

Table 1: Analytical data

Compound	Molecular Weight	Hydrazine %		Metal %	
		Observed	Calculated	Observed	Calculated
Co(PhAc)$_2$(N$_2$H$_4$)$_2$	395.42	17.54	16.21	13.65	14.12
Ni(PhAc)$_2$(N$_2$H$_4$)$_2$	395.13	17.94	16.22	15.99	14.35
Mn(PhAc)$_2$(N$_2$H$_4$)$_2$	391.32	17.28	16.38	14.30	14.22
Cd(PhAc)$_2$(N$_2$H$_4$)$_2$	448.82	14.59	14.24	23.30	23.27
Co(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	567.59	7.13	8.47	11.05	10.39
Ni(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	567.30	7.37	8.47	10.96	10.35
Cd(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	621.00	8.25	7.73	17.94	18.10
Co(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	533.00	9.05	9.01	11.22	11.06
Ni(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	532.88	8.75	9.03	11.79	11.01
Cd(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	586.17	8.25	8.20	19.13	19.17

Electronic spectra

The electronic spectrum of the above mentioned cobalt and nickel complexes are in support of octahedral coordination around the metal ions. For example cobalt complexes display a band at 28,330cm^{-1} which is assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. This band and pink colour of the compounds are in indicative of the octahedrally coordinated Co(II) ion [8]. Nickel complexes exhibit a band at 28,980cm^{-1}which is also attributed to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition, characteristic of octahedral geometry. The Electronic spectrum of Co(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O and Ni(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O are given in fig 1 and .2.
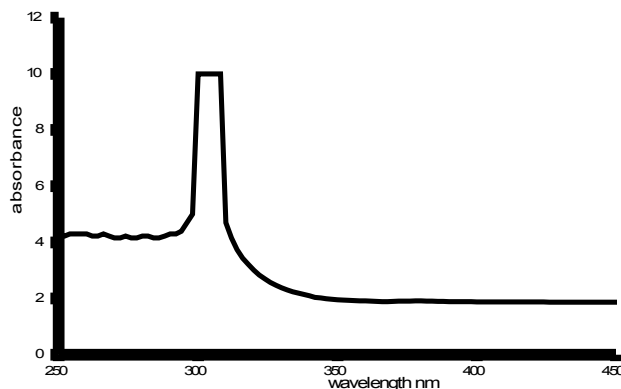
Fig 1 Electronic spectrum of Co(Di-PhAc)₂1.5N₂H₄.H₂O
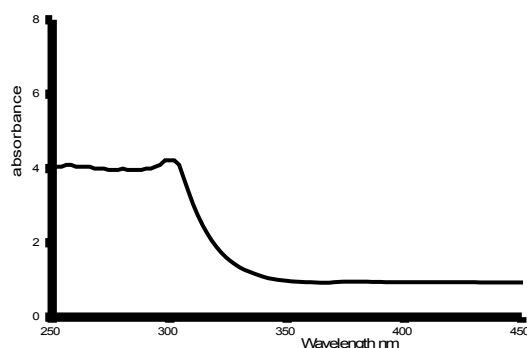
Fig 2 Electronic spectrum of Ni(Di-PhAc)₂1.5N₂H₄.H₂O

Infrared spectra

The important IR absorption frequencies of prepared complexes are listed in Table 2. All hydrated complexes shows band in the region 3321 – 3434 cm^{-1} due to O- H stretching of H$_2$O molecule [14]. All prepared complexes show bands in the region 3000 – 3308 cm^{-1} which are assigned to N – H stretching frequencies of the hydrazine moieties. However for the cobalt, nickel complexes of Diphenylacetic acid and cadmium complex of 2,4- diphenylacetic acid the O – H stretching frequencies overlap with N – H stretching frequencies of hydrazine and hence their individual assignments could not be made. The υ_{asymm} and υ_{sym} carboxylate stretching of all the complexes are seen in the region 1347 – 1402 cm^{-1} respectively, with $\Delta\upsilon$ is in between 206 – 257 cm^{-1}, showing the unidentate coordination [11] of carboxylate ions. The N- N stretching frequency of hydrazine moieties are observed at 958 – 975 cm^{-1} indicating their bridging bidentate nature [1]. In these compounds the monodentate coordination of hydrazine is ruled out for which the N – N stretching frequency normally is expected at 940 – 930 cm^{-1}. The IR spectra of Co(PhAc)$_2$(N$_2$H$_4$)$_2$, Cd(PhAc)$_2$(N$_2$H$_4$)$_2$,Co(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O, and Ni(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O are displayed in fig 3, 4, 5 and 6.

Table 2 : Infrared spectral data (cm^{-1})

Compound	ν_{OH} of water/acid cm^{-1}	ν_{N-H} cm^{-1}	ν_{asymm} (coo$^-$) cm^{-1}	ν_{sym} (coo$^-$) cm^{-1}	$\Delta\nu$ (ν_{asymm} -ν_{sym})cm^{-1}	N–N Streching cm^{-1}
Co(PhAc)$_2$(N$_2$H$_4$)$_2$	-	3247	1605	1391	214	967
Ni(PhAc)$_2$(N$_2$H$_4$)$_2$	-	3289	1616	1402	214	975
Mn(PhAc)$_2$(N$_2$H$_4$)$_2$	-	3000	1653	1396	257	960
Cd(PhAc)$_2$(N$_2$H$_4$)$_2$	-	3308	1576	1347	229	958
Co(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	3321	-	1614	1387	227	961
Ni(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	3416	-	1600	1390	210	976
Cd(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	3434	3283	1591	1385	206	973
Co(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	3371	-	1616	1387	229	972
Ni(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	3333	3149	1621	1376	245	973
Cd(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	3343	-	1627	1387	240	960
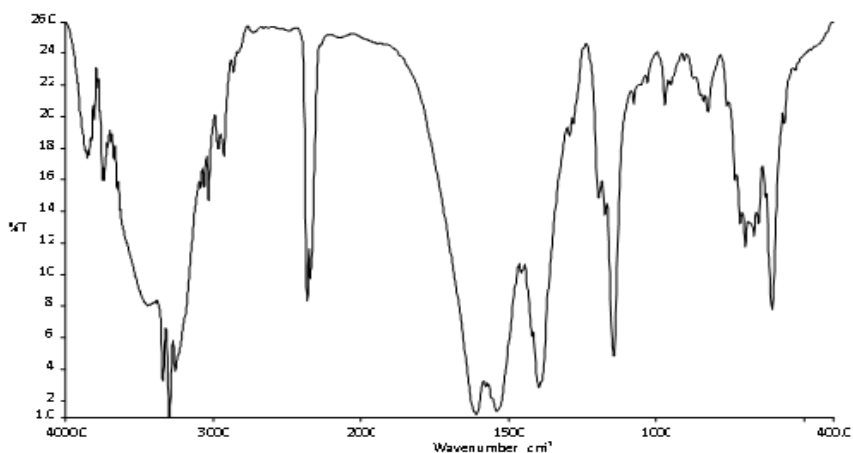
Fig 3 IR spectrum of Co(PhAc)$_2$(N$_2$H$_4$)$_2$
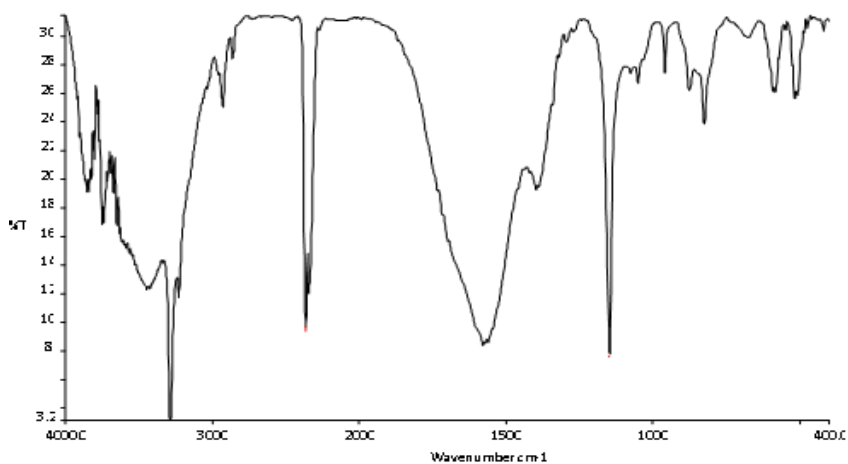
Fig 4 IR spectrum of Cd(PhAc)2(N2H4)2
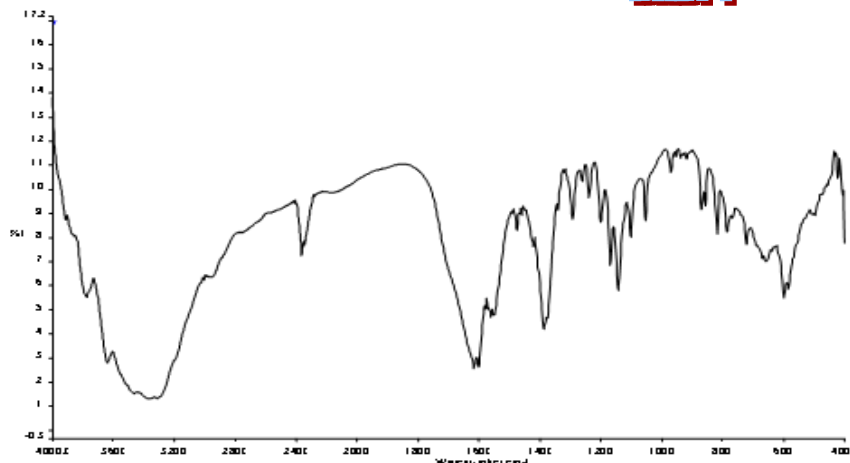
Fig 5 IR spectrum of Co(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O
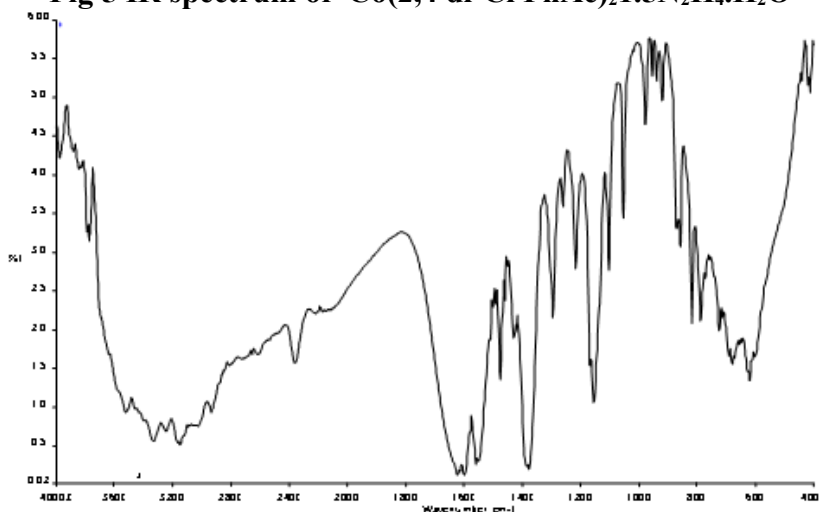
Fig 6 IR spectrum of Ni(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O

Thermal Analysis

The thermal decomposition patterns of all the complexes are listed in Table 3. The observed mass losses from TG coincide well with the theoretical mass losses. Thermogravimetric results are in good agreement with the DTA data.

Co(PhAc)$_2$(N$_2$H$_4$)$_2$

The TG-DTA curves of this complex indicate that the weight loss begins at 150°C and 24 % of the mass lost with DTA exothermic peak at 179°C. In this stage of the carboxylate ligand is reduced to formate ligand. On further heating, hydrazine is completely lost with exothermic peak at 251°C. On further heating, the complex becomes cobalt formate which slowly decomposes to metal oxide as the final product.

Ni(PhAc)$_2$(N$_2$H$_4$)$_2$

The TG – DTA curves of this complex indicate that the weight loss begins at 191°C and 39% of the mass lost with DTA exothermic peak at 208°C. The reaction is made more exothermic by the loss of hydrazine to give the mixture of nickel oxide and nickel carbonate with DTA peak at 344°C.

Table 3 : Thermal decomposition data

Compound	DTA Peak (°C)	Thermogravimery (TG)		Decomposition Product
		Temp range(°C)	Mass Loss(%)	
Co(PhAc)$_2$(N$_2$H$_4$)$_2$	179 (-)	150- 220	24	Co(N$_2$H$_4$)$_2$(PhAc)HCOO$^-$
	251(-)	220- 261	42	Co(PhAc)HCOO-
	329(-)	261- 340	65	Co(HCOO$^-$)$_2$
	406(-)	340- 428	77	CoO.CoCO$_3$
	912(+)	428- 919	79	CoO$_{1.5}$
Ni(PhAc)$_2$(N$_2$H$_4$)$_2$	239(-)	191 - 292	39	Ni(PhAc)HCOO$^-$
	344(-)	292 - 376	75	NiO, NiCO$_3$
	404(-)	376 - 412	84	Ni
Mn(PhAc)$_2$(N$_2$H$_4$)$_2$	239(-)	202 – 278	15	Mn(PhAc)$_2$
	321(-)	278 – 346	45	Mn(PhAc)HCOO$^-$
	394(-)	346 - 484	73	MnCO$_3$, MnO
Cd(PhAc)$_2$(N$_2$H$_4$)$_2$	207(-)	141 – 240	20	Cd(N$_2$H$_4$)$_2$(PhAc)HCOO$^-$
	314(-)	240 – 389	58	Cd(HCOO$^-$)$_2$
	446(-)	389 – 525	67	CdCO$_3$
Co(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	175(+)	100 -228	12	Co(Di-PhAc)$_2$
	370(-)	228 – 407	36	CoO
Ni(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	200(-)	146 – 223	13	Ni(Di-PhAc)$_2$
	443(-)	223 – 496	86	NiO
Cd(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	215(-)	161 – 242	11	Cd(Di-PhAc)$_2$
	365(-)	242 – 444	73	CdCo$_3$
	510(-)	444 - 547	80	CdO
Co(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	229(-)	124 – 235	11	Co(2,4 di-Cl PhAc)$_2$
	495(-)	235 – 553	72	CoCO$_3$
	583(+)	553 - 972	91	Co
Ni(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	200(-)	100 – 205	11	Ni(2,4 di-Cl PhAc)$_2$
	378(-)	205 – 501	76	NiCO$_3$
	531(-)	501 – 561	91	Ni
Cd(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O	200(-)	165 – 210	12	Cd(2,4 di-Cl PhAc)$_2$
	481(-)	210 – 528	62	Cd(HCOO$^-$)$_2$
	550(-)	528 - 617	92	Cd

Cd(PhAc)$_2$(N$_2$H$_4$)$_2$

The TG – DTA pattern this is shown in fig 7.8. This complex shows three peaks in DTA curve. The first step corresponds to the formation of metal dicarboxylate intermediate similar to that of cadmium complex. Further, exothermic decompositions at 312°C and 394°C leads to equimolar mixture of manganese carbonate and manganese oxide of an end product.

Cd(PhAc)$_2$(N$_2$H$_4$)$_2$

It also gives three exothermic peaks in DTA curve. In the first stage it is decomposes to Cd(N$_2$H$_4$)$_2$ (PhAc)HCOO$^-$. In the second step, this intermediate undergoes decomposition at 314°C to give the cadmium formate, which undergoes decomposition at 446°C in the final step to form cadmium carbonate.
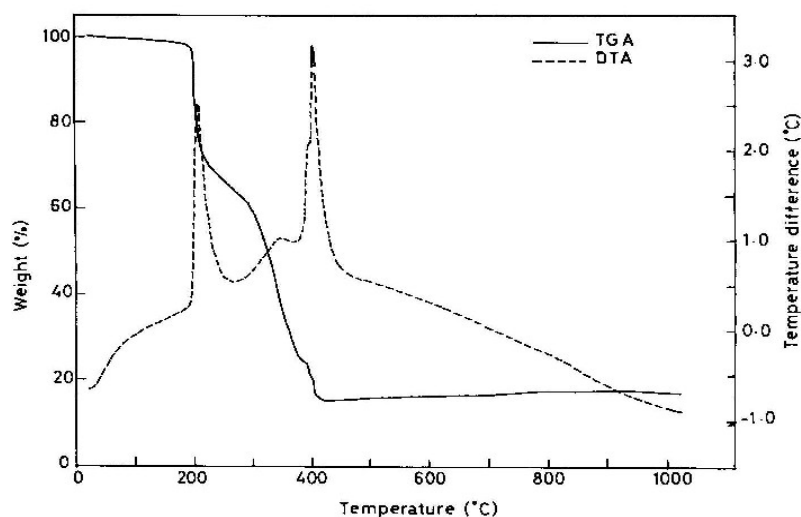
Fig 7 TG – DTA of Co(PhAc)$_2$(N$_2$H$_4$)$_2$

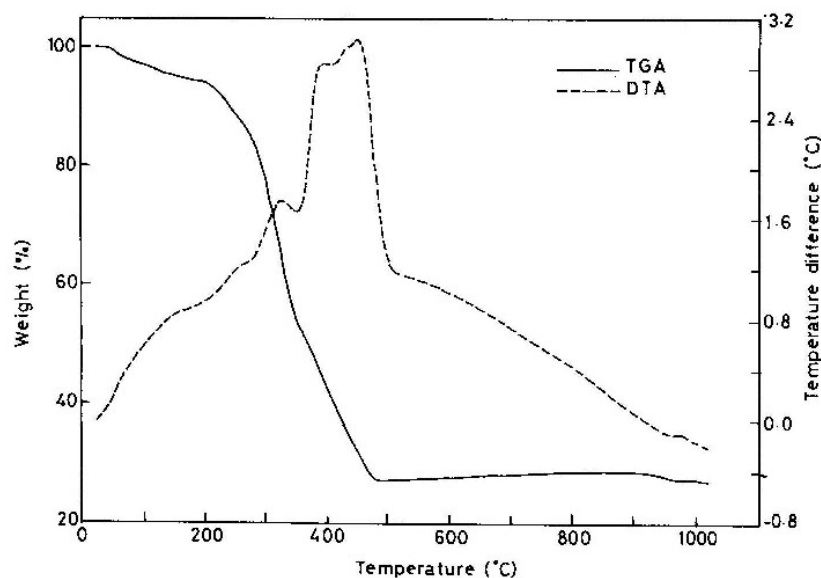**Fig 8 TG – DTA of Mn(PhAc)$_2$(N$_2$H$_4$)$_2$**

Co(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O

This complex decomposes exothermically in the temperature range 100 – 228 ˚C with loss of H$_2$O and 1.5 N$_2$H$_4$ molecules to form metal carboxylate intermediate. In DTA this decomposition is observed above 175˚C. Such high temperature dehydration and dehydrazination suggests the presence of metal bounded water molecules [3]. The metal carboxylate intermediate further decomposes in the temperature range 228 – 407 ˚C to give CoO as the residue. The weight loss in TG is also in accordance with he formation of CoO. DTA shows an exotherm art 370 ˚C for the second stage of decomposition.

Ni(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O

The nickel complex also decomposes in tow stages similar to that of cobalt cojmpled to give NiO as the final product. DTA shows two exotherms at 200 and 443 ˚C corresponding to the two stages.

Cd(Di-PhAc)₂1.5N₂H₄.H₂O

In the cadmium complex, decomposition takes place through $CdCO_3$ intermediate. In the first stage loss of H_2O and 1.5 N_2H_4 molecules takes place in the temperature range 161 – 242 ˚C to form metal carboxylate similar to that of cobalt and nickel complexes. In the second stage the metal carboxylate decomposes in the temperature range 242 – 444 ˚C to form $CdCO_3$ as an intermediate. Finally $CdCO_3$ decomposes in the temperature range 444 – 547 ˚C to give CdO as the residue. The TG – DTA pattern of this complex is shown in fig 9.
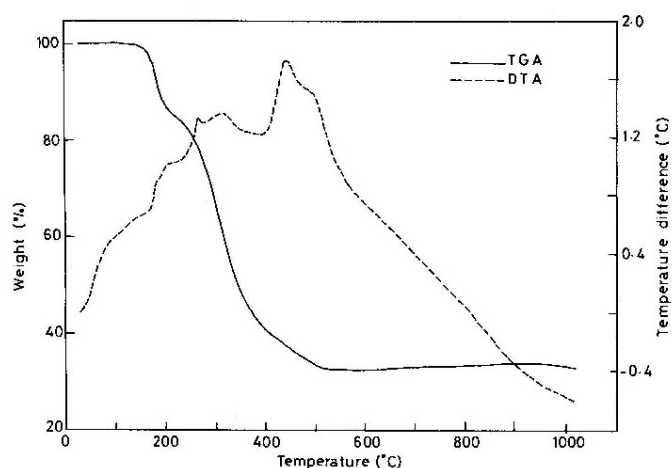

Fig 9. TG – DTA of Cd(PhAc)₂(N₂H₄)₂

M(2,4 di-Cl PhAc)₂1.5N₂H₄.H₂O M = Co(II) or Ni(II)

These complexes undergo three stages of decomposition. The first stage corresponds to dehydration and dehydrazination, which is seen as an exotherm at 200 and 209 ˚C, confirming the coordination of water similar to that of cobalt, nickel and cadmium complexes of Diphenylacetic acid. In the second stage, the metal carboxylate decomposes with DTA peak at 495 and 378 ˚C to form respective metal carbonates. In the final stage, the metal carbonates decomposes exothermically o form respective metal as the residue.The TG – DTA pattern of Ni(2,4 di-Cl PhAc)₂1.5N₂H₄.H₂O is given in fig 10.
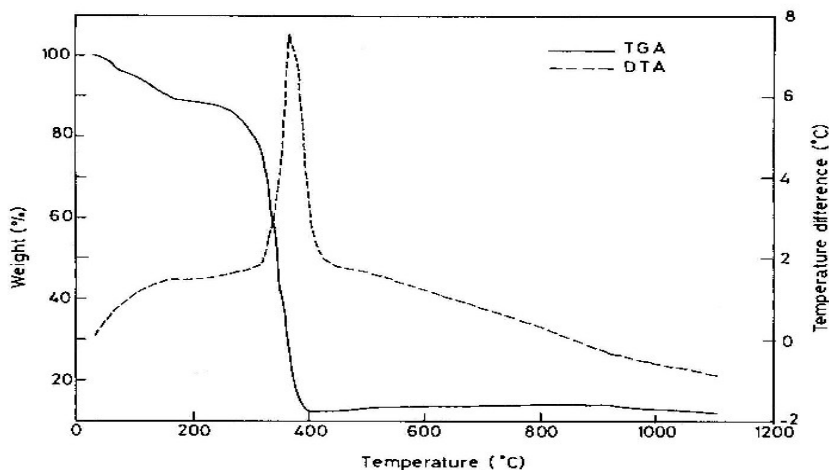
Fig 10 TG – DTA of Co(Di-PhAc)₂1.5N₂H₄.H₂O

Cd(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O

The TG – DTA pattern of this complex is given in fig 11. This is also undergoes three stage of weight loss through cadmium formate intermediate similar to that of cadmium complex prepared by using phenylacetic acid. In the first stage dehydration and dehydrazination takes place in the temperature range 165 – 210 °C to form metal carboxylate intermediate similar to that of cobalt and nickel complexes. In the second stage the metal carboxylate decomposes with DTA peak at 481 °C to give cadmium formate. In the final stage the cadmium formate decomposes to cadmium with DTA peak at 550 °C. The TG – DTA pattern of the some prepared complexes are given in fig 7– 13
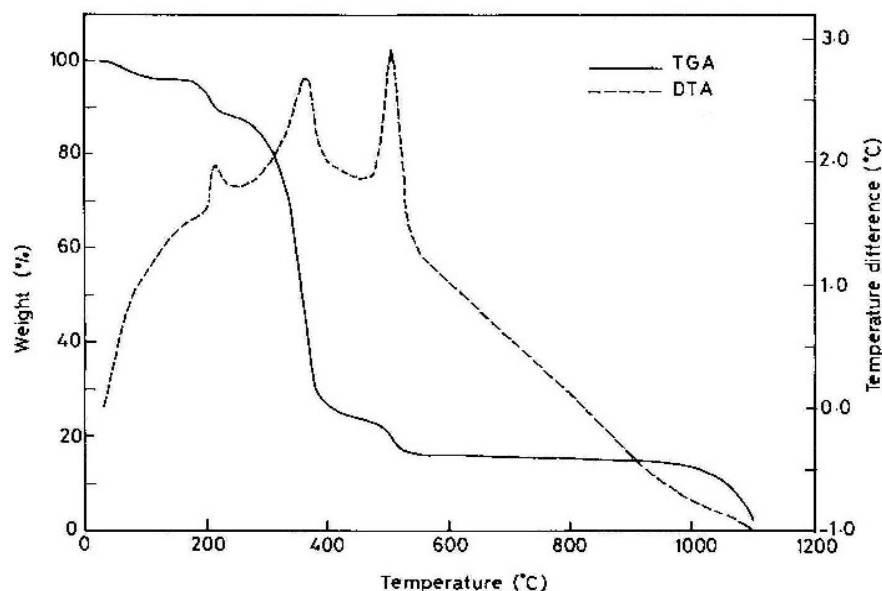

Fig 11 TG – DTA of Cd(Di-PhAc)$_2$1.5N$_2$H$_4$.H$_2$O
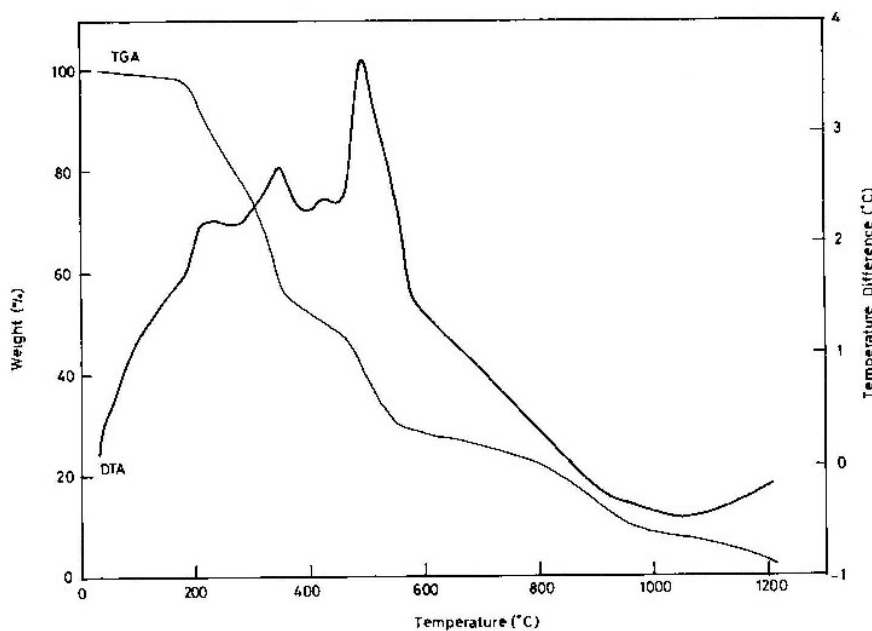
Fig 12 TG – DTA of Co(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O
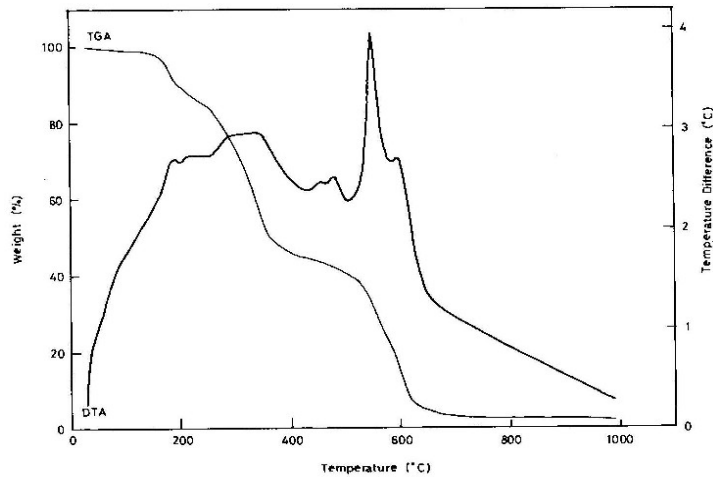
Fig 13 TG – DTA of Cd(2,4 di-Cl PhAc)$_2$1.5N$_2$H$_4$.H$_2$O
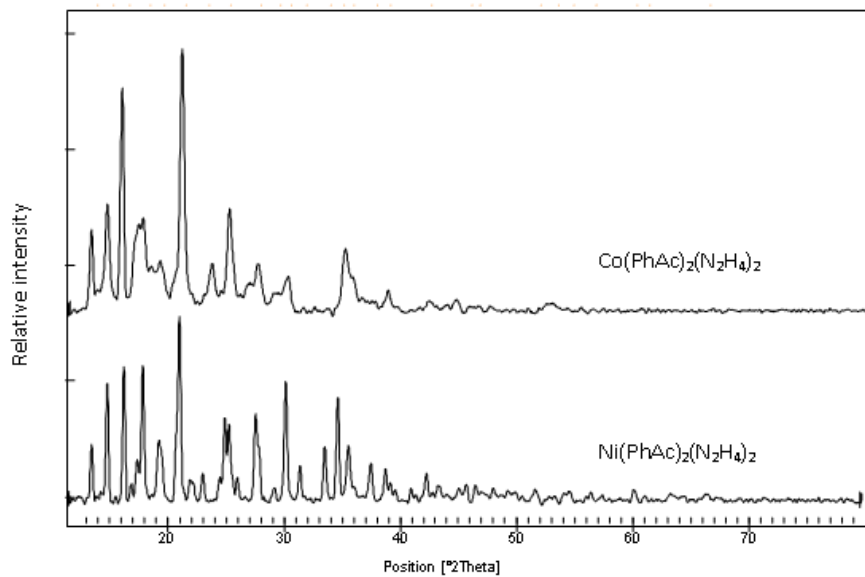
Fig 14 The X – ray patteren of Co (PhAc)$_2$(N$_2$H$_4$)$_2$ and Ni(PhAc)$_2$(N$_2$H$_4$)$_2$
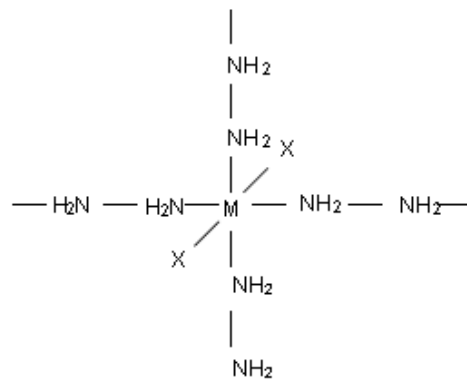
Fig 15 Structure of MX$_2$(N$_2$H$_4$)$_2$ Where X = C$_6$H$_5$CH$_2$COO$^-$ M = Co, Ni, Mn or Cd

X - ray diffraction studies

In order to compare and also to confirm the structural similarity among the complexes, the d spacing' of Cobalt and nickel phenylacetate hydrazinates have been compared. Similar complexes have almost same values of d-spacing and number of peaks. Hence these are isomorphous in nature. The X – ray patteren of $Co(PhAc)_2(N_2H_4)_2$ and $Ni(PhAc)_2(N_2H_4)_2$ are given fig 14.
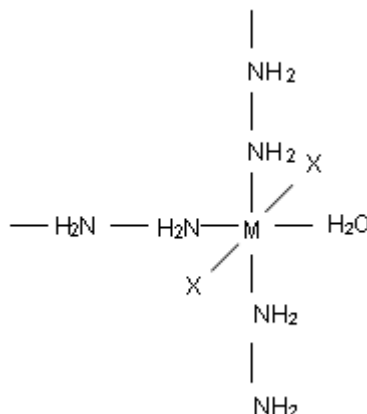
Fig 16 Structure of MX_2 $1.5N_2H_4.H_2O$ Where X = $(C_6H_5)_2CHCOO^-$ or $C_6H_3Cl_2CH_2COO^-$ M = Co, Ni or Cd

CONCLUSION

  I. From the present investigations, the following general observations may be made.
 II. Only phenylacetate complexes form bis- hydrazine complexes, whereas Dipheynlacetic acid and 2,4-dichloropheylacetate compolexes form sesqui- hydrazine complexes.
III. While manganese form only phenylacetate complex.
 IV. Physico – chemical and spectral studies indicate that all carboxylate ions act as unidentate ligand and hydrazine in all complexes coordinates to the metal as a bidentate ligand.
  V. Phenylacetate complexes decompose to give respective metal, metal oxide, metal carbonate or mixture of metal carbonate and metal oxide as the final product. Diphenylacetate complexes give respective metal oxide as the final product. 2,4 dichlorophenylacetate complexes give respective metal as the final product.
 VI. All the above studies indicate that the complexes are all of high spin octahedral geometry. In bis- hydrazine complexes of phenylacetate two coordination are satisfied by two unidentate carboxylate ions and remaining four coordination are satisfied by two bidentate bridging hydrazine moieties. In sesqui- hydrazine complexes of Diphenylacetate and 2,4-dichlorophenylacetate octahedral geometry is satisfied by two unidentate carboxylate ions, 1.5 bidentate hydrazine moieties and one coordinated water molecule.
VII. The X-ray diffraction powder diffraction data indicate isomorphism among cobalt and nickel complexes of phenylacetate.
VIII. Based on the above facts polymeric structure with octahedral geometry around the metal (Fig 15 and 16) has been tentatively assigned for the complexes.

REFERENCES

1. Braibanti, F. Dallavalle, M.A. Pellinghelli, E. Laporti (1968). The nitrogen – nitrogen stretching band in hydrazine derivatives and complexes, Inorg. Chem: vol 7, 1430 – 1433.
2. D. Gajapathy, S. Govindarajan, K. C. Patil and H. Manohar (1983). Polyhedron: vol 2, 865.
3. S. Govindarajan, K.C. Patil, H. Manohar, P.E. Werner (1984). J. Chem., Soc., Dalton Trans, 119.
4. S. Govindrajan, S.U. Nasrin Banu, N. Saravanan, B. N. Sivasankar (1995). Proc. Indian Acad. Sci (Chem. Sci.): vol 107, 559.
5. E.R. Jiji, K.K. Aravindakshan (1993). 'Synth React. Inorg. Met.-Org. Chem: vol 3(1),119.
6. K. Kuppusamy, S. Govindrajan (1995). Eur.J.Solid State Inorg.Chem: vol 32, 997.
7. K. Kuppusamy, S. Govindarajan (1996). 'Synth React. Inorg. Met.-Org. Chem: vol 26, 225.
8. A.B.P. Lever, Inorganic Electronic Spectroscopy (1894).Second Edn., Elsevier, Amsterdam,
9. G. V. Mahesh, K.C. Patil (1986). Thermochim. Acta: vol 93, 153.
10. R. Manimekalai (2011). International Journal of Applied Biology and Pharmacauetical Technology: vol .2(2), 268 – 278.
11. R.N. Mallick, N.K. Ranigrahi, B.K. Mohapatra (1987). J. Indian Chem., Soc: vol 64, 690.
12. K. Nakamoto (1978)." Infrared and Raman spectra of Inorganic and Coordination compounds", Wiley, Newyork,.
13. P. Ravindranathan, K. C. Patil (1983). Thermochim. Acta: vol 71, 153.
14. E.W. Schmidt (1984). Hydrazine and its Derivatives-Preparation, Properties and Applications, Wiley Interscience, New York,.
15. K. Saravanan, S. Govindarajan, D. Chellappa (2005).'Synth React. Inorg. Met.-Org. Chem: vol 34(2), 353.
16. N. Sivasankar, S. Govindarajan (1994). Z. Naturforsch: vol 49b, 950.
17. N. Sivasankar, S. Govindarajan (1994). Synth. React. Inorg. Met.-Org. Chem:Vol 24, 1573.
18. B.N. Sivasankar, S. Govindarajan (1995). Synth. React. Inorg. Met.-Org. Chem: vol 25, 31.
19. B. N. Sivasankar, S. Govindarajan (1996). Mater. Res . Bull vol 31, 47.
20. B. N. Sivasankar, S. Govindarajan (1997).J. Therm. Anal., vol 48, 1401.
21. S. Yasodhai, S. Govindarajan, Synth. React. Inorg. Met.-Org. Chem., 29 (1999) 919.24 (1994)1573.