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Syntheses, characterization and thermal decomposition studies of hydrazine complexes of transition metal phthalates

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ABSTRACT

Metal complexes with a general formula $M(C_8H_4O_4)(N_2H_4)_2$, where $M=Mn(II)$, $Fe(II)$, $Co(II)$, $Ni(II)$, $Zn(II)$ or $Cd(II)$ were prepared and characterised by elemental analysis, IR-, electronic spectral- and magnetic studies and X-ray diffraction techniques. The polymeric nature of the complexes through hydrazine bridges and octahedral geometry around the metal ions were established. The thermal reactivity of the $Co(II)$ complex was ascertained by thermogravimetric(TG) technique. The decomposition was subjected to kinetic analysis using Coats-Redfern, Horowitz-Metzger- and MacCallum-Tanner equations.

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KEYWORDS

Hydrazine;
Phthalate;
Synthesis;
Characterisation;
Thermal studies.

INTRODUCTION

The ligational properties of hydrazine were extensively studied from the beginning of the 20th century but it took momentum in the latter half of the century^[1]. The potent N-N bond has a positive heat of formation ($\Delta H_f \sim 12 \text{ kcal mole}^{-1}$) and is thus thermodynamically unstable^[2]. The presence of carboxyl group adjacent to the hydrazine molecule in metal complexes gives interesting thermal behaviours like low-temperature oxide formation. This can produce oxide-particles of desirable properties in solid-state applications^[1,3-9]. Among the reported thermal decomposition studies of metal complexes of hydrazine and carboxylates, complexes with dicarboxylates were only a few and aromatic dicarboxylates were not at all found. The kinetic analyses of the thermal decomposition studies were also scanty^[10-13]. In this context, we selected the hydrazine

complexes of transition metal phthalates, which is a part of a series of works being carried out in our laboratory.

EXPERIMENTAL

Materials

All the chemicals used were BDH/EMerck/Qualigen products, AnalaR-, Exceller or equivalent grade. Solvents used were purified by reported methods^[14].

Preparation of complexes

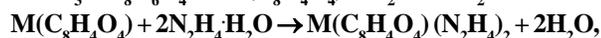
For the preparation of the complexes, phthalic acid (8.3g, 50mmol) in ethanol (50mL) was used. To this solution, freshly prepared metal carbonate (50 mmol) was added slowly with constant stirring, at 30°C, until saturation and boiled. The mixture was filtered hot and hydrazine monohydrate (5g, 100mmol) in ethanol

TABLE 1 : Analytical and magnetic data

Compd. ^a	Yield (%)	Colour	Melting point/ Decomposition temp.(°C)	Found (calculated) %					μ_{eff} (B.M)
				Metal	Hydrazine	C	N	H	
MnL ₂ X	75	Pale-pink	> 369	19.91 (19.43)	22.28 (22.61)	33.42 (33.92)	19.19 (19.78)	4.21 (4.24)	5.71
FeL ₂ X	95	Brown	> 360	19.24 (19.67)	22.71 (22.54)	34.08 (33.82)	19.86 (19.72)	4.15 (4.22)	5.00
CoL ₂ X	87	Pale-pink	> 360	20.84 (20.55)	22.45 (22.30)	32.98 (33.45)	19.73 (19.57)	4.25 (4.18)	4.88
NiL ₂ X	88	Light-blue	300	20.91 (20.41)	22.64 (22.33)	33.42 (33.50)	19.19 (19.54)	4.21 (4.18)	2.56
ZnL ₂ X	79	Off-white	> 360	22.65 (22.68)	22.12 (21.81)	32.36 (32.72)	19.45 (19.08)	4.33 (4.09)	D
CdL ₂ X	84	Off-white	> 320	33.58 (33.02)	18.32 (18.80)	28.70 (28.20)	16.33 (16.45)	3.73 (3.72)	D

^aL = N₂H₄ -hydrazine, X = C₈H₄O₄²⁻ -phthalate, D = diamagnetic

(20mL) was added drop by drop with constant stirring and allowed to cool to room temperature. The complexes precipitated after keeping for 24 h, were filtered, washed with water, ethanol and ether and dried under reduced pressure and kept in vacuum over fused calcium chloride. The formation of the complexes can be represented by the following equations.



where C₈H₆O₄ = phthalic acid and M=Mn(II), Fe(II), Co(II), Ni(II) or Cd(II).

Physical measurements

The percentages of metals were estimated by standard methods^[15]. The percentage of hydrazine was estimated by titration with 25 mM solution of KIO₃ under Andrews' conditions^[15]. Carbon, hydrogen, nitrogen and oxygen were estimated using a Hitachi C, H, N, O rapid analyzer. Electrical conductances of the saturated solutions of the complexes in DMSO were measured at room temperature in a direct-reading Systronix-305 conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy-type magnetic balance using Co[Hg(NCS)₄] as calibrant. Uv-Vis spectra of the complexes were recorded by the Nujol mull technique in a Shimadzu Uv-Vis1601 spectrophotometer. IR spectra were recorded on a Shimadzu FTIR-8101A spectrophotometer. X-ray diffraction in the powder method was done on a Bruker AXS-D5005 model diffractometer. Thermogravimetric analysis in static air was done on a Mettler Toledo Star system thermobalance, with a heating rate of 10°C min⁻¹ and a sample size of 5

mg. Independent pyrolytic studies were also conducted to verify the TG results. A computer programme in Fortran 77 was used to calculate the kinetic parameters of the decomposition processes.

RESULTS AND DISCUSSION

All the complexes were non-hygroscopic, air- and photostable and sparingly soluble in methanol, ethanol, DMF, DMSO etc. The analytical- and magnetic data are given in TABLE 1. The non-conducting nature of the saturated solutions of the complexes in DMSO indicated the formation of neutral complexes.

Magnetic behaviour

The magnetic moment-values indicated the formation high-spin octahedral complexes for all the metals^[16]. The Zn(II) and Cd(II) complexes were found diamagnetic indicating their d¹⁰ configuration.

Electronic spectra and ligand field parameters

The prominent electronic spectral bands and the ligand field parameters calculated are given in TABLE 2. The data corresponded to the formation of high-spin octahedral complexes in all the cases. In the case of the Mn(II) complex, observed bands and the pale-pink color supported this view. For the Fe(II), Co(II) and Ni(II) complexes also, the data were in good agreement with the prediction^[17]. The ligand field parameters calculated were ligand field stabilization energy (LFSE), ligand field splitting (Δ_o) and Racah parameter (B^1). The ratio B^1/B , where B is the Racah parameter for free ion, is expressed as β ^[18]. The $\beta\%$ were also calculated

TABLE 2 : Electronic spectral bands, assignments and ligand field parameters

Compound ^a	Bands(cm ⁻¹)	Assignments	Δ_0 (cm ⁻¹)	LFSE (kcal/mole)	B ¹ (cm ⁻¹)	B (cm ⁻¹)	β	$\beta\%$
FeL ₂ X	10101	⁵ E _g (D)← ⁵ T _{2g} (D)	10101	-9.62	-	-	-	-
	9852 (v ₁)	⁴ T _{2g} (F)← ⁴ T _{1g} (F)						
CoL ₂ X	15873(v ₂)	⁴ A _{2g} (F)← ⁴ T _{1g} (F)	6021	-11.46	506	1120	0.45	54.82
	21276(v ₃)	⁴ T _{1g} (P)← ⁴ T _{1g} (F)						
NiL ₂ X	9436 (v ₁)	³ T _{2g} (F)← ³ A _{2g} (F)	9436	-26.96	662.73	1080	0.61	3872
	15903(v ₂)	³ T _{1g} (F)← ³ A _{2g} (F)						
	22346 (v ₃)	³ T _{1g} (P)← ³ A _{2g} (F)						

L = N₂H₄ -hydrazine, X = C₈H₄O₄²⁻ -phthalateTABLE 3: Prominent IR spectral bonds (cm⁻¹) and their assignments

MnL ₂ X ^a	FeL ₂ X	CoL ₂ X	NiL ₂ X	ZnL ₂ X	CdL ₂ X	Assignments
3333	3320	3339	3300	3326	3333	NH stretching
3272	3292	3265	3260	3285	3280	NH stretching
3023	3070	3045	3060	3075	3050	NH stretching
1660	1640	1645	1660	1650	1620	COO asy. stretching
1613	1620	1615	1614	1605	1595	NH ₂ bending
1580	1580	1595	1590	1573	1555	NH ₂ bending
1560	1553	1560	1560	1550	1553	C=O stretching
1458	1446	1470	1470	1470	1485	COO sym.stretching
1398	1385	1320	1356	1350	1404	NH ₂ wagging
1280	1270	1270	1280	1280	1298	NH ₂ wagging
1162	1169	1125	1160	1169	1155	NH ₂ twisting
1050	1050	1100	1115	1088	1081	NH ₂ twisting
966	993	960	965	960	975	N-N stretching
850	858	870	899	870	865	OCO deformation
656	660	663	650	697	703	NH ₂ asy. rocking
630	643	650	622	610	615	COO rocking
569	562	550	595	580	590	NH ₂ sym. rocking
480	498	481	481	460	475	M-O stretching
425	430	440	440	450	430	M-N stretching

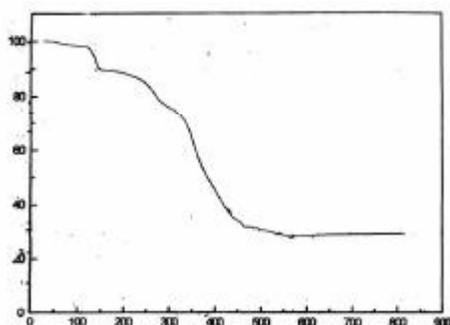
^aL = N₂H₄ -hydrazine, X = C₈H₄O₄²⁻ -phthalate

Figure 1: Thermogram of the Co(II) complex

and reported. All these values indicated to the highly covalent character of the metal-ligand bonds^[17].

Infra red spectra

The significant IR spectral bands and assignments are given in TABLE 3. All the characteristic bands of the NH₂ and carboxyl groups are observed^[19]. The large difference between the asymmetric- and symmetric

stretching frequencies of carboxyl groups ($\Delta\nu\sim 200$ cm⁻¹) indicated the monodentate behaviour of them towards the metals^[19]. All the complexes exhibited distinct absorptions in the 993-960 cm⁻¹ region that were due to the N-N stretching^[20]. This indicated the presence of bridging hydrazine^[20]. This observation along with the insoluble nature indicated the polymeric nature of the complexes. The M-O stretching- and M-N stretching frequencies appeared in the 498-475 and 450-425cm⁻¹ regions respectively^[19].

X-ray diffraction

The XRD analysis of the complexes in the powder method exhibited diffractograms with no specific signals characteristic of perfectly crystalline compounds. The lack of solubility in any solvents prevented the preparation of a perfect single crystal for analysis. The insoluble- and non-crystalline nature also indicated the polymeric nature of the complexes.

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TABLE 4: Thermal decomposition pattern of hydrazine complex of Co(II) phthalate

Stage	Mass-loss percentage			TG Temperature range (°C)	Decomposition pattern
	TG	Ind. pyrolysis	Theoretical		
I	11.20	--	11.04	105-150	$\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{N}_2\text{H}_4)_2 \rightarrow \text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{N}_2\text{H}_4) + \text{N}_2\text{H}_4$
II	22.88	--	22.08	207-293	$\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{N}_2\text{H}_4)_2 \rightarrow \text{Co}(\text{C}_8\text{H}_4\text{O}_4) + \text{N}_2\text{H}_4$
III	71.90	72.01	72.20	320-540	$\text{Co}(\text{C}_8\text{H}_4\text{O}_4) \rightarrow \text{Co}_3\text{O}_4/3$

TABLE 5: Kinetic parameters^a of the thermal decomposition reactions of hydrazine complex of Cobalt(II) phthalate

Stage	Method	ΔE (kcal mole ⁻¹)	Z (sec ⁻¹)	ΔS (kcal deg ⁻¹ mole ⁻¹)	r
I	Coats-Redfern	25.29	1.33×10^4	-48.11	0.998
	Horowitz-Metzger	32.13	3.79×10^5	-45.62	0.998
	MacCallum - Tanner	28.55	2.32×10^5	-38.25	0.997
II	Coats-Redfern	31.95	9.32×10^7	-28.59	0.999
	Horowitz-Metzger	35.20	8.16×10^6	-32.90	0.995
	MacCallum-Tanner	37.14	6.75×10^7	-27.95	0.996
III	Coats-Redfern	52.08	1.80×10^9 ¹²	-11.20	0.997
	Horowitz-Metzger	45.32	3.72×10^{11}	-17.21	0.995
	MacCallum-Tanner	43.19	4.23×10^{10}	-22.04	0.996

ΔE =energy of activation, Z= pre-exponential factor, ΔS = entropy change, r= correlation coefficient

Thermal behaviour

The thermogram for the decomposition of the Co(II) complex is exhibited in figure 1. The thermal decomposition pattern is explained in TABLE 4 and the kinetic parameters calculated are given in TABLE 5. The complex exhibited a three-stage decomposition pattern. The first stage started at 105°C and was complete by 150°C. The percentage mass-loss was found to be 11.20. One coordinated hydrazine molecule was expected to be eliminated in which the theoretical mass-loss was 11.04%. The second stage started at 207°C and was complete at 293°C. In this stage, the second hydrazine molecule was expected to be eliminated. The experimental mass-loss of 22.88% agreed well with the theoretical mass-loss of 22.08%. The third stage of decomposition started at 320°C and was complete at 540°C. In this stage, the cobalt phthalate was expected to have decomposed to Co_3O_4 . The experimental mass-loss was 71.90% and the expected mass-loss, 72.02%. The decomposition pattern perfectly agreed with the proposed structure of the compound.

Decomposition kinetics

The non-isothermal method was used for the kinetic studies. The basic equations used for the calculation of kinetic parameters are given below.

Coats-Redfern equation^[21]

$$\ln\{[1-(1-\alpha)^{(1-n)}]/(1-n)T^2\} = \ln[(ZR/\phi\Delta E)(1-2RT/\Delta E)] - \Delta E/RT$$

Horowitz – Metzger equation^[22]

$$\ln\{[1-(1-\alpha)^{(1-n)}]/(1-n)\} = \ln(ZRT_s^2/\phi\Delta E) - \Delta E/RT_s + \Delta E\theta/RT_s^2$$

MacCallum–Tanner equation^[23]

$$\ln\{[1-(1-\alpha)^{(1-n)}]/(1-n)\} = \log(Z\Delta E/\phi R) - 0.483\Delta E^{0.435} - (0.449 + 0.217\Delta E \times 10^3)/T$$

In these equations, α is the ratio w/w_∞ , where w is the weight-loss at time t and w_∞ , the maximum weight-loss from the TG-curve. n is the order-parameter, Z is the pre-exponential factor, ΔE the energy of activation, R the universal gas constant, T the absolute temperature, ϕ the heating rate, T_s the temperature of maximum decomposition and θ is $T-T_s$.

ΔS , the entropy of activation is calculated from the expression $Z = kT_s \exp(\Delta S/R)/h$,

where k is the Boltzmann constant and h the Planck's constant. In all the three methods, the equations represent straight lines and from the slope and intercepts, the parameters are calculated. The order parameter n was calculated by the method reported by Horowitz-Metzger^[22, 24].

The kinetic parameters calculated by the three different methods, Coats-Redfern, Horowitz-Metzger and MacCallum-Tanner, were in perfect agreement with good correlation coefficients. The large negative values of entropy of activation indicated that the activated states are more ordered than the initial states in all the steps of decomposition.

The final decomposition stage leading to the formation of metal oxide shows higher values of activation energy (~ 50 kcal mol⁻¹) than of the initial two steps (\sim

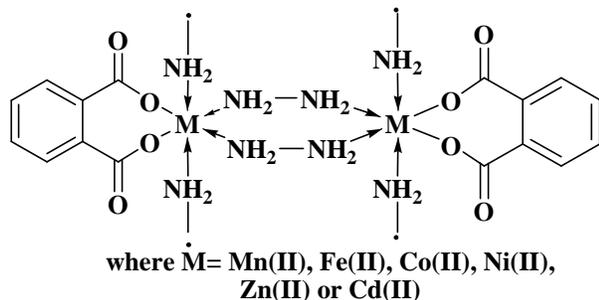


Figure 2 : General structure of complexes

30 kcal mol⁻¹). This is expected because the final stage involved the rupture of stronger bonds than the initial steps involving dehydrazination. We have calculated pre-exponential factor values ($Z \text{ sec}^{-1}$) for the process, they are in the limits $10^4 < Z < 10^{12}$. A value $Z \leq 10^{24}$ is believed to be real for the solid-state decomposition processes [25].

CONCLUSION

All the complexes were octahedral in stereochemistry with metal ion in the high-spin state. Polymeric nature was also established. Based all the data, the general structure of the complexes is given in figure 2.

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