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Synthesis, Spectral, Thermal and X-ray Powder Diffraction Studies on Hydrazine Bridged Metal and Mixed Metal Para Nitrobenzoate Complexes

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Abstract:
Bis-hydrazine metal(II) p-nitrobenzoates, $[M(p\text{-}NO_2C_6H_4COO)_2(N_2H_4)_2]$, where M= Co, Ni, Zn or Cd have been prepared by mixing an aqueous solution of respective metal nitrate hydrate with an aqueous solution containing a mixture of p-nitro benzoic acid and hydrazine hydrate in appropriate ratio. These complexes have been characterised by analytical, spectral, thermal and X-ray powder diffraction studies. The IR spectra of these complexes indicate the bridging bidentate nature of hydrazine moieties and monodentate nature of carboxylate ions. On thermal degradation these complexes except zinc complex undergo one step decomposition to yield respective metal oxide as the final product. However, the zinc complex undergoes dehydrazination in the first step followed by ligand pyrolysis to give ZnO as the final residue. X-ray powder diffraction pattern indicates the isomorphism among the complexes.
The mixed metal complexes, $[M_{1/3}Co_{2/3}(p\text{-}NO_2C_6H_4COO)_2(N_2H_4)_2]$ have also been prepared using aqueous solution containing a mixture of metal nitrate hydrates and cobalt nitrate hexahydrate in 1:2 ratio instead of metal nitrate hydrate. These complexes on thermal degradation yield respective metal cobaltites with high degree of purity as the final product. The formations of these cobaltites were confirmed by chemical analysis, IR spectra and X-ray powder diffraction studies.

Keywords*: Bis-hydrazine, p-nitrobenzoic acid, mixed metal complexes, metal cobaltites, TG-DTA and X-ray powder diffraction*

1. Introduction

The carboxylate ion plays an important role in inorganic and bioinorganic compounds. Several natural compounds such as vitamins and drugs contains this kind of system especially six membered ring system in their structure [1, 2]. The chemistry of metal-aromatic six membered ring with nitro functional group act as hard hydrogen bond acceptors [3]. Moreover, these carboxylates of transition metals having different magnetic properties may be used in modern branches of science and technology as electronic materials. Serious efforts in metal carboxylate research are directed towards the development of new methods for the preparation of metal organic frame work materials using benzene based aromatic carboxylic acids as the organic part to bind the metal ions and study their structure and properties [4-11]. Many investigations including structural aspects are made on transition metals with p-nitrobenzoic acid [12-21], but there is no report on corresponding hydrazine analogue.

Hydrazine complexes gain much interest due to their thermal reactivity. Hydrazine forms complex with almost all metals including lanthanides with aliphatic and aromatic mono and di carboxylic acids and many amino acids. Hydrazine being a versatile ligand it forms mono, bis and tris hydrazine and also it forms hydrazinium complexes in weakly acidic solutions. The hydrazine complexes show high thermal reactivity than the corresponding hydrazinium complexes. Thermal behaviour of the complex is quite interesting because the hydrazine and nitro group are present in a same complex.

Our through literature survey clearly reveals that a large number of hydrazine complexes of transition metal carboxylates [22-27] and hydrazine lanthanide carboxylates [28-30] have been reported. In addition to this, the mixed metal complexes containing hydrazine have also been prepared and have been utilised as the precursors to the metal cobaltites and metal ferrites. However, only a few aromatic carboxylic acid complexes have been investigated. Hence, attempt has been made to prepare metal hydrazine and mixed metal complexes with para nitrobenzoic acid and the results are discussed in this paper.

2. Experimental

2.1. Preparation of Bis-Hydrazine Metal P-Nitrobenzoates and Mixed Metal P-Nitrobenzoates

An aqueous solution (50 mL) containing a mixture of p-nitrobenzoic acid (10g, 0.06 mol) and hydrazine hydrate (6 mL, 0.12 mol) was slowly added to an aqueous solution (50 mL) of respective metal nitrate hydrate (0.03 mol). The resulting clear solution

obtained was filtered and kept aside for crystallisation. The crystalline precipitate formed after 7-8 hours was filtered, washed with water then with alcohol and dried in air.

The mixed metal complexes were prepared by the same procedure described as above by using mixture of respective metal nitrate hydrate (0.01 mol) and cobalt nitrate hexa hydrate (0.02 mol) instead of metal nitrate hydrate. The amounts of metal nitrates used are as follows. Cobalt nitrate hexahydrate (5.82g, 0.02 mol), Nickel nitrate hexahydrate (2.59g, 0.01 mol), Zinc nitrate hexahydrate (2.97g, 0.01 mol) and Cadmium nitrate hexahydrate (3g, 0.01 mol).

2.2 Physico-Chemical Studies

The compositions of the complexes were determined by hydrazine and metal analyses. The metal content in all the complexes were determined by EDTA complexometric titrations after decomposing a known amount of the complex with concentrated nitric acid [31]. The cobalt content in the mixed metal complexes and cobaltites was determined by separating cobalt as $Co(C_{10}H_6ONO)_3$ complex using α- nitroso β-naphthol after decomposing a known amount of the sample with concentrated nitric acid and evaporating the clear solution to dryness [32]. The hydrazine content in the complexes was determined volumetrically by titrating against 0.025 mol potassium iodate solution under Andrew's condition [33]. Room temperature magnetic measurements were determined by Gouy's method using $Hg[Co(SCN)_4]$ as a calibrant. The solid state electronic absorption spectra of the complexes in Nujol mull were recorded on a Varian Cary 5000 UV-Visible spectrophotometer in the range 200-800 nm. Infrared spectra of the complexes were recorded on a SHIMADZU spectrophotometer using KBr pellets in the range 4000-400 cm^{-1}. A Perkin-Elmer CHN analyser (Model 1240) was used for C, H and N analysis. The simultaneous TG-DTA of the complexes in air was carried out using TG/DTA 6200 Thermal Analyser. The thermal experiments were performed in air with heating rate of 10 ^oC min^{-1} using platinum cups as sample holders. X-ray powder diffraction pattern of samples were obtained using Bruker D8 Focus Diffractometer with scan speed 5 seconds per step, using CuKα radiation (λ= 1.540598 Å) and Scintillation counter as a detector.

3. Results and Discussion

Bis-hydrazine metal p-nitrobenzoates were prepared by the reaction between respective metal nitrate hydrate and para nitrobenzoic acid in the presence of excess of hydrazine hydrate in aqueous medium. The mixed metal p-nitrobenzoate complexes were prepared by the similar procedure using a mixture of metal nitrate hydrate and cobalt nitrate hexahydrate in appropriate ratio. The chemical reactions are represented as follows.

$3\ M(NO_3)_2.nH_2O + 6\ p\text{-}C_6H_4(NO_2)COOH + 12\ N_2H_4.H_2O \longrightarrow$

$3[M(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2] + 6\ N_2H_5NO_3 + (3n+12)\ H_2O$

Where M = Co, Ni, Zn or Cd

$2\ Co(NO_3)_2.6H_2O + M(NO_3)_2.xH_2O + 6\ p\text{-}C_6H_4(NO_2)COOH + 12\ N_2H_4.H_2O \longrightarrow$

$[MCo_2(p\text{-}C_6H_4(NO_2)COO)_6(N_2H_4)_6] + 6\ N_2H_5NO_3 + (x+24)\ H_2O$

Where M = Ni, Zn or Cd

These complexes are stable in air, insoluble in water and organic solvents such as alcohol and ether. The compositions of the complexes were assigned on the basis of hydrazine and metal analyses. The analytical data of these complexes are summarised in Table 1.

3.1. Magnetic Moments and Electronic Spectra

The room temperature magnetic moments of the cobalt and nickel complexes were found to be 4.6 BM and 3.2 BM respectively. These values are in accordance with the high spin nature of Co(II) and Ni(II) ions. As expected Zn(II) and Cd(II) complexes are diamagnetic. The electronic spectra of cobalt complex shows a band at 13,700 cm^{-1} which is assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition. The nickel complex shows two bands at 14,100 cm^{-1} and 20,000 cm^{-1} which are assigned to $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions respectively, which are characteristics of octahedral geometry around Co(II) and Ni(II) ions [34].

3.2. Infrared Spectra

The infrared spectra of the complexes are almost superimposable. All the complexes show three bands in the region 3250-3350 cm^{-1} which are the characteristics of N-H stretching frequencies of hydrazine. All the bis-hydrazine complexes show two bands in the region 1590-1600 cm^{-1} and 1350-1390 cm^{-1} for ν_{asy} and ν_{sym} stretching respectively for carboxylate ions with $\Delta\nu$ separation of 210- 240 cm^{-1} indicating the monodentate nature of carboxylate ions [35]. In all the cases a sharp band is observed between 960-975 cm^{-1} which is typical for bridging bidentate nature of neutral hydrazine molecule [36]. The bands at 1520-1550 cm^{-1} and 1380-1390 cm^{-1} were assigned to asymmetric and symmetric vibration of the nitro group. The IR spectra of zinc and cadmium complexes are given in Fig.1and 2 as representative examples.

3.3. Thermal Degradation

The hydrazine complexes are expected to decompose at low temperature due to the endothermic nature of N-N bond in hydrazine. This thermal reactivity is further enhanced by the presence of nitro group in the complexes.

In the present serious of complexes, cobalt complex decomposes in a single step as shown by the TG curve to give Co_2O_3 as the final residue. The degradation takes place between 220-270 ^oC. The DTA shows a strong and sharp exotherm at 238 ^oC. The nickel complex decomposes in a similar pattern as the cobalt complex in a single step between 230-300 ^oC to give NiO as the end product. The DTA shows sharp exotherm at 273 ^oC for the above step. Unlike cobalt and nickel complexes, the zinc complex undergoes continuous decomposition in the temperature range 250-670 ^oC. The DTA shows an exotherm at 265 ^oC and another broad exotherm at 545 ^oC. In this degradation the first stage corresponds to the loss of two hydrazine molecules to form an intermediate which further undergo ligand pyrolysis to yield ZnO as the final residue. The cadmium complex exhibit single step

decomposition in the temperature range 200-260 ^{o}C and the DTA shows an exotherm at 233 ^{o}C. The final product obtained in this decomposition is CdO.

All the mixed metal complexes shows single step decomposition in the temperature range 200-260 ^{o}C with DTA peak temperature around 220 ^{o}C. The simultaneous TG-DTA of zinc and cobalt-nickel mixed metal complexes are given in Figs. 3 and 4 respectively. The thermal degradation patterns of these complexes are summarised in Table 2.

3.4. X-Ray Powder Diffraction

The isomorphism among the series of complexes is confirmed by their X-ray powder patterns, which are almost superimposable. The X-ray powder patterns of the mixed metal complexes shows sharp and intense signals which are identical with the simple complexes confirming the formation of solid solutions. The 'd' value for cadmium, zinc and cobalt-nickel mixed metal complexes are given in Table 3. The X-ray powder diffraction patterns of zinc and cobalt-nickel mixed metal complexes are shown in Figs. 5 and 6 respectively.

S. No	Molecular Formula (Mol.Wt)	Hydrazine Calc. (Found)	CHN Analysis			Yield %
			C % Calc. (Found)	H % Calc. (Found)	N % Calc. (Found)	
1	$Co(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.26)	14.08 (13.25)	36.94 (36.38)	3.54 (3.1)	18.46 (18.71)	87
2	$Ni(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.01)	14.09 (13.02)	36.96 (36.47)	3.54 (3.6)	18.47 (18.1)	86
3	$Zn(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (461.71)	13.88 (13.62)	36.42 (36.11)	5.49 (3.71)	18.2 (18.33)	83
4	$Cd(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (508.72)	12.64 (12.10)	33.05 (33.1)	3.17 (3.24)	16.52 (16.14)	85
5	$Co_{2/3}Ni_{1/3}(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.18)	14.08 (14.82)	36.94 (36.25)	3.54 (3.33)	18.46 (18.08)	82
6	$Co_{2/3}Zn_{1/3}(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (457.41)	14.01 (13.67)	36.76 (36.5)	3.53 (3.6)	18.37 (18.88)	84
7	$Co_{2/3}Cd_{1/3}(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (473.08)	13.55 (14.05)	35.54 (35.8)	3.41 (3.81)	17.78 (17.8)	83

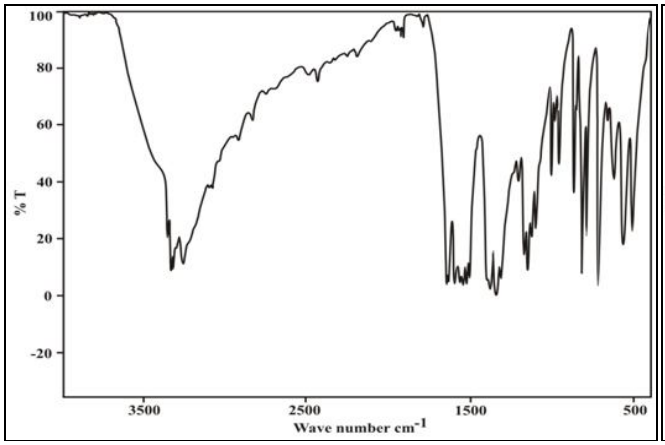
Table 1: Analytical data of metal p-nitrobenzoate and mixed metal p-nitrobenzoates

Compound	DTA Peak Temp (^{o}C)	TG- Temp. range (^{o}C)	weight loss Found (Calc.)	Residue
$Co(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	238 (exo)	220-270	81.80 (81.8)	Co_2O_3
$Ni(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	273 (exo)	230-300	83.10 (83.59)	NiO
$Zn(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	265 (exo)	250-270	13.60 (13.88)	$Zn(m\text{-}C_6H_4(NO_2)COO)_2$
	545 (exo)	530-670	83.10 (82.37)	ZnO
$Cd(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	233 (exo)	200-260	74.90 (74.76)	CdO
$Co_{2/3}Ni_{1/3}(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	217 (exo)	200-250	82.90 (82.38)	$NiCo_2O_4$
$Co_{2/3}Zn_{1/3}(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	220 (exo)	210-260	82.20 (81.98)	$ZnCo_2O_4$
$Co_{2/3}Cd_{1/3}(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	223 (exo)	200-240	79.90 (79.27)	$CdCo_2O_4$

Table 2: Simultaneous TG-DTA analysis data of metal p-nitrobenzoates and mixed metal p-nitrobenzoates

Zn			Cd			$Co_{2/3}Ni_{1/3}$		
2θ	Intensity	d value	2θ	Intensity	d value	2θ	Intensity	d value
10.45	50	8.4992	10.95	43	8.0735	10.14	27	8.7509
10.07	33	8.7769	11.05	31.5	8.0006	11.26	29	7.8938
12.50	49	7.0756	12.01	45.1	7.3632	11.94	32	7.4310
12.95	39	6.8571	13.11	39.4	6.7477	15.02	40	5.8937
13.03	100	6.7890	14.03	100	6.3073	15.98	100	5.5694
13.06	44	6.7735	14.53	40.3	6.0913	17.79	37.7	5.0069
17.04	49	5.1993	18.26	35.3	4.8546	24.31	30.3	3.6599
17.56	47.5	5.0637	18.91	36.4	4.6891	30.33	32.3	2.9446
30.17	44.5	2.9666	31.08	43.8	2.8752	33.06	18.3	2.7074
47.58	33.8	1.9126	45.50	34.2	1.9919	44.08	23.0	2.0527

Table 3: X-ray powder diffraction data of $M(p\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$



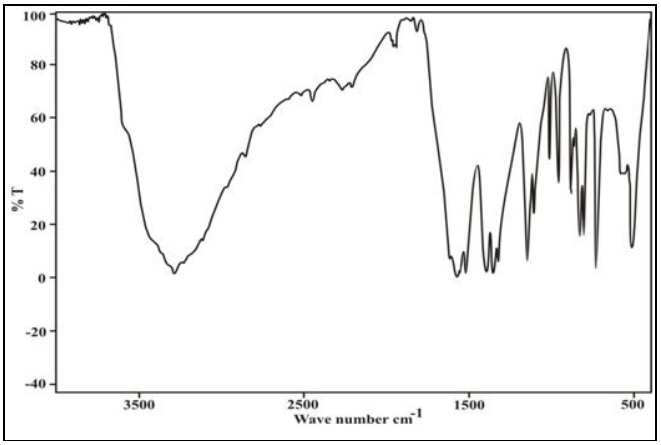
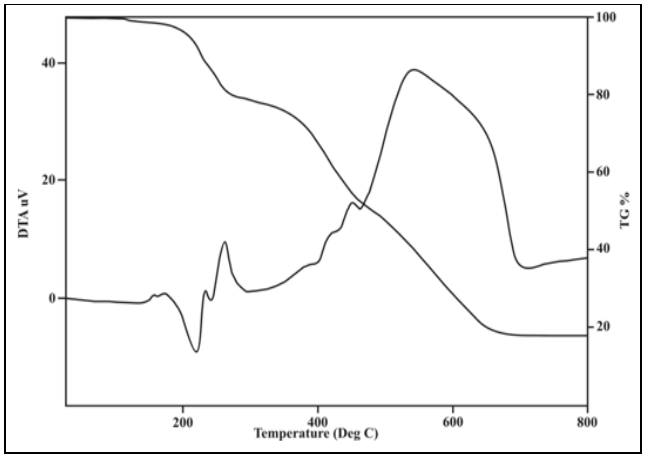


Figure 1: Infrared spectrum of bis-hydrazine zinc para nitrobenzoate
Figure 2: Infrared spectrum of bis-hydrazine cadmium para nitrobenzoate



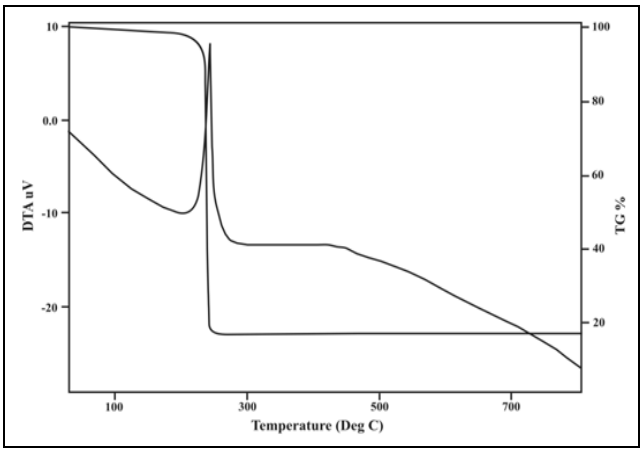
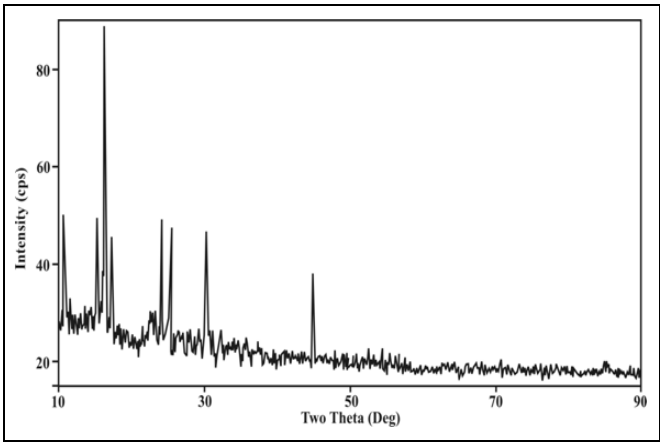


Figure 3: Simultaneous TG-DTA of bis-hydrazine zinc para nitrobenzoate
Figure 4: Simultaneous TG-DTA of bis-hydrazine cobalt nickel para nitrobenzoate



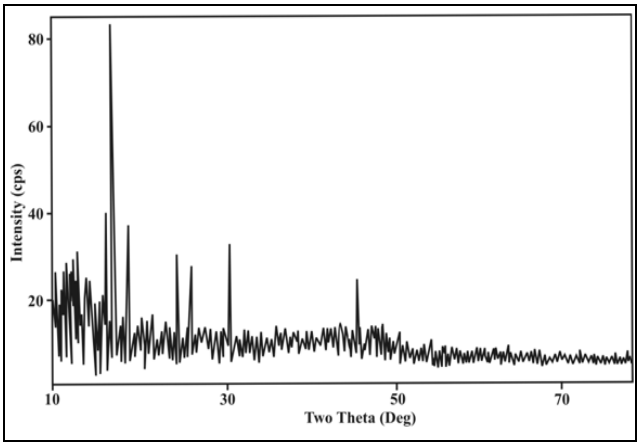


Figure 5:- X-ray powder diffraction pattern of bis-hydrazine zinc para nitrobenzoate
Figure 6: X-ray powder diffraction pattern of bis-hydrazine cobalt-nickel para nitrobenzoate

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