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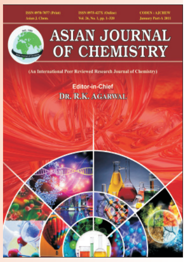

bis-Hydrazine Metal and Mixed Metal *m*-Nitrobenzoates: Synthesis, Spectral, Thermal and X-ray Diffraction Studies

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bis-Hydrazine metal(II) *m*-nitrobenzoates, $[M(m\text{-}NO_2C_6H_4COO)_2(N_2H_4)_2]$, where M = Co, Ni, Zn or Cd have been prepared by the stoichiometric reaction between the aqueous solution of respective metal nitrate hydrate with aqueous solution containing a mixture of *m*-nitrobenzoic 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 indicate the bridging bidentate nature of hydrazine moieties and monodentate nature of carboxylate ions. All 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 patterns indicate that the complexes are isomorphous. The mixed metal complexes, $[M_{1/3}Co_{2/3}(m\text{-}NO_2C_6H_4COO)_2(N_2H_4)_2]$ 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 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, *m*-Nitrobenzoic acid, Mixed metal complexes, Metal cobaltites, TG-DTA and X-ray powder diffraction.

INTRODUCTION

Aromatic compounds containing nitro group are used as an explosives due to their vigorous decompositions at lower temperatures. The coordination compound containing nitro group also exhibits the same thermal behaviours. There are a large number of simple metal complexes containing nitro benzoic acid and their derivatives are thoroughly investigated[1-7]. Despite this, there is no report on the corresponding hydrazine analogue.

Hydrazine is used in various fields for diverse applications. Coordination compounds containing hydrazine receive much attention during the recent year due to its ability to coordination and high thermal reactivity. This low temperature decomposition has been attributed to the endothermic nature of N-N bond of hydrazine, which release enormous amount of energy in the form of heat during its thermal cleavage. This energy is utilized for the decomposition of remaining part of the complex into oxides, mixed metal oxides even into metal powder. In coordination complexes hydrazine shows different behaviour towards metal ions such as neutral monodentate, bidentate and bridged bidentate ligand. In weakly acidic medium it also generates hydrazinium cation. The nature of complex formed mainly depends on the nature of hydrazine moiety in it. The presence of these two groups such as nitro group and hydrazine in a same complex largely enhances their thermal reactivity. These properties provide access for the preparation of fine metal oxides at much lower temperatures with high purity.

Review of literature clearly reveals that substantial amounts of work have been done on transition metal[8-14] and lanthanide carboxylates[15-17] containing neutral hydrazine and hydrazine cation. However, only a few aromatic carboxylic acid complexes have been investigated[18-20]. Besides this the mixed metal complexes containing hydrazine have also been prepared for a few hydrazine metal carboxylates and have been used as the precursors to the metal cobaltites and metal ferrites[21-24]. Hence, it is also expected that the hydrazine mixed metal *meta*-nitrobenzoate could be prepared and possibly used as the solid solution precursors for fine mixed metal oxides. In the present investigation attempt has been made to prepare metal hydrazine and mixed metal hydrazine complexes with *meta*-nitrobenzoic acid. In this paper, we wish to report the synthesis, characterization, spectral, thermal and X-ray diffraction pattern of *bis*-hydrazine metal and mixed metal *m*-nitrobenzoates.

EXPERIMENTAL

Preparation of *bis*-hydrazine metal *m*-nitrobenzoates and mixed metal *m*-nitrobenzoates: *bis*-Hydrazine metal *m*-nitrobenzoate complexes were prepared by adding an aqueous solution containing a mixture of *m*-nitrobenzoic acid (10 g, 0.06 mol) and hydrazine hydrate (6 mL, 0.12 mol) to an aqueous solution (50 mL) of respective metal nitrate hydrate (0.03 mol) slowly with constant stirring. The resulting solution obtained was filtered and allowed to stand at room temperature for crystallization. The crystalline precipitate formed after 5-6 h 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 hexahydrate (0.02 mol) instead of metal nitrate hydrate. The amounts of metal nitrates used are as follows. Cobalt nitrate hexahydrate (5.82 g, 0.02 mol), nickel nitrate hexahydrate (2.59 g, 0.01 mol), Zinc nitrate hexahydrate (2.97 g, 0.01 mol) and cadmium nitrate hexahydrate (3 g, 0.01 mol).

Physico-chemical studies: The hydrazine content in the complexes was determined volumetrically using KIO_3 solution (0.025 mol) under Andrew's condition. 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[25]. The cobalt content in mixed metal complexes were determined by separating cobalt as $Co(C_{10}H_6ONO)_3$ complex using α-nitroso β-naphthol after decomposing a known amount of sample with concentrated nitric acid and evaporating the clear solution to dryness[26]. The filtrate during the separations containing Ni, Zn or Cd has treated with chloroform to remove excess α-nitroso β-naphthol and the metal ions were estimated by titration with standard EDTA solution[25].

Room temperature magnetic measurements were carried out by Gouy balance 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. A Perkin-Elmer CHN analyser (Model 1240) was used for C, H and N analysis. The IR spectra of the complexes were recorded on a SHIMADZU spectrophotometer using KBr pellets in the range 4000-400 cm^{-1}. 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 °C 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 CuK_α radiation (λ = 1.540598 Å) and Scintillation counter as a detector.

RESULTS AND DISCUSSION

bis-Hydrazine metal *m*-nitrobenzoates were prepared by the reaction between respective metal nitrate hydrate and *m*-nitrobenzoic acid in the presence of excess of hydrazine hydrate in aqueous medium. The mixed metal *m*-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.

$$3M\,(NO_3)_2{\cdot}nH_2O + 6C_6H_4(NO_2)COOH + 12N_2H_4{\cdot}H_2O \rightarrow 3[M(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2] + 6N_2H_5NO_3 + (3n{+}12)H_2O$$

where M = Co, Ni, Zn or Cd

$$2\,Co(NO_3)_2{\cdot}6H_2O + M\,(NO_3)_2{\cdot}xH_2O + 6C_6H_4(NO_2)COOH + 12\,N_2H_4{\cdot}H_2O \rightarrow [MCo_2(m\text{-}C_6H_4(NO_2)COO)_6(N_2H_4)_6] + 6N_2H_5NO_3 + (x{+}24)H_2O$$

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 summarized in Table-1.

Magnetic moments and electronic spectra: The magnetic moments of the cobalt and nickel complexes were found to be 4.8 BM and 3.1 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 23,500 cm^{-1} which is assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. The nickel complex shows two bands at 14,300 cm^{-1} and 20,400 cm^{-1} which are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, which are characteristics of octahedral geometry around Co(II) and Ni(II) ions[27].

Infrared spectra: All the *bis*-hydrazine metal and mixed metal complexes show similar IR spectra which are almost superimposable. All the complexes show bands in the region 3650-3700 cm^{-1} due to the N-H stretching of hydrazine molecules. The ν_{asy} and ν_{sym} stretching of carboxylate ions are observed in the regions 1600-1620 and 1380-1390 cm^{-1} respectively with $\Delta\nu$ separation > 200 cm^{-1} which clearly indicates the monodentate coordination of carboxylate ions[28]. The N-N stretching frequencies of hydrazine moieties are observed in the region 960-950 cm^{-1} and are in conformity with the bidentate bridging nature of hydrazine[29]. The bands at 1540-1530 and

TABLE-1
ANALYTICAL DATA OF THE COMPOUNDS

m.f.	m.w.	Hydrazine		Elemental analysis (%): Found (calcd.)			Yield (%)
		Found	Calcd.	C	H	N	
$Co(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	455.26	13.50	14.08	36.22 (36.94)	3.60 (3.54)	18.04 (18.46)	90
$Ni(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	455.01	13.62	14.09	36.52 (36.96)	3.38 (3.54)	18.14 (18.47)	85
$Zn(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	461.71	13.20	13.88	36.19 (36.42)	3.54 (3.49)	18.32 (18.20)	90
$Cd(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	508.72	12.34	12.60	33.50 (33.05)	3.07 (3.17)	16.22 (16.52)	85
$Co_{2/3}Ni_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	455.18	13.82	14.08	36.25 (36.94)	3 .33(3.54)	18.08 (18.46)	80
$Co_{2/3}Zn_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	457.41	13.65	14.01	36.50 (36.76)	3.60 (3.53)	18.88 (18.37)	85
$Co_{2/3}Cd_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	473.08	13.14	13.55	35.80 (35.54)	3.81 (3.41)	17.80 (17.78)	83

1350-1340 cm^{-1} were assigned to asymmetric and symmetric vibrations of the NO_2 group. The IR spectra of zinc and cobalt-nickel mixed metal complexes are given in Fig.1 and 2 as representative examples.

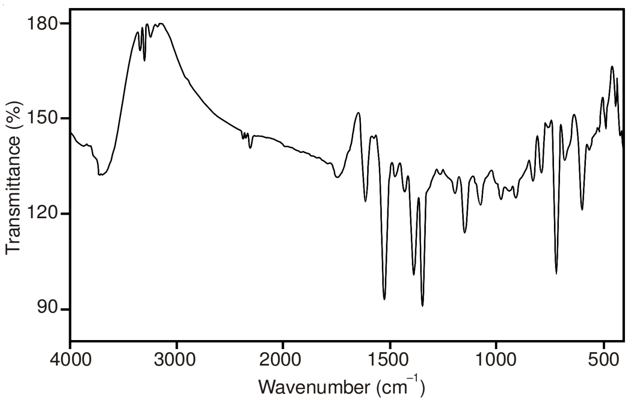

Fig. 1. IR Spectrum of $Zn(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

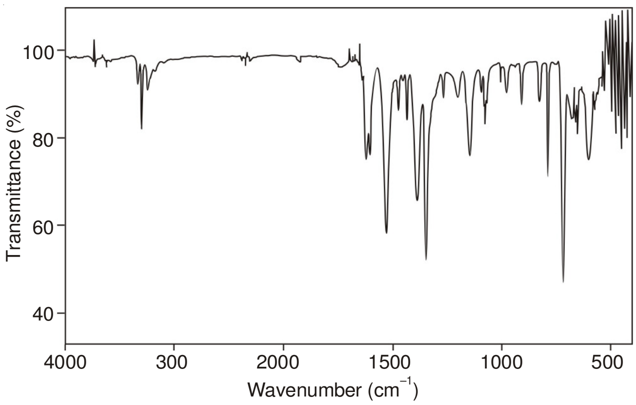

Fig. 2. IR spectrum of $Co_{2/3}Ni_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

Thermal degradation: Hydrazine is sensitive to heat due to the presence of endothermic N-N bond. The nitro group is also capable of enhancing the thermal reactivity, hence the present series of complexes are expected to decompose exothermically and vigorously at lower temperature. The *bis*-hydrazine cobalt *m*-nitrobenzoate decomposes in a single step in the temperature range 225-270 °C results in the formation of Co_2O_3 as final residue. DTA shows an exotherm at 220 °C corresponding to this step. The nickel(II) complex decomposes similar to the cobalt(II) complex in single step between 280-300 °C to give NiO as the end product. The DTA shows a sharp exotherm at 295 °C for the above step. The zinc(II) complex undergoes decomposition in a different pattern in this series. It decomposes in two stages, both sharp exothermic with the DTA peak temperatures 240 and 420 °C. The first step corresponding to the loss of two hydrazine molecules to give zinc *m*-nitro-benzoate as the intermediate which further decomposes in the temperature range 350-450 °C to give ZnO as the final residue.

The single step decomposition of cadmium(II) complex was also observed which leads to the formation of cadmium oxide. DTA shows an exotherm at 240 °C. The TG mass loss is observed in the temperature range 200-250 °C is 76 % which is close to the theoretical value.

The thermal degradation pattern of all the *bis*-hydrazine mixed metal *m*-nitrobenzoate complexes shows single step decomposition in the temperature range 250-300 °C with DTA peak temperatures around 260 °C. The simultaneous TG-DTA of nickel and zinc complexes are given in Figs. 3 and 4 respectively. The thermal degradation data of the complexes are given in Table-2.

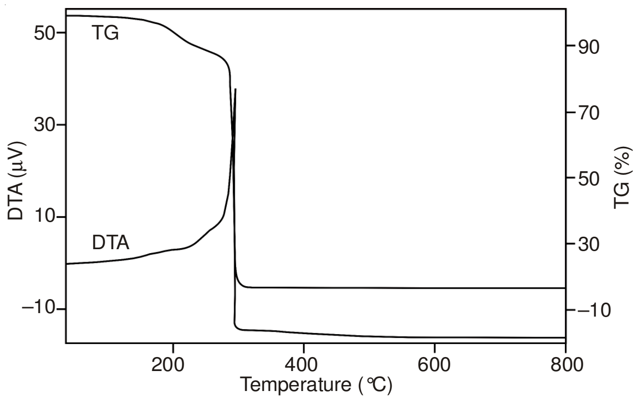

Fig. 3. Simultaneous TG-DTA of $Ni(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

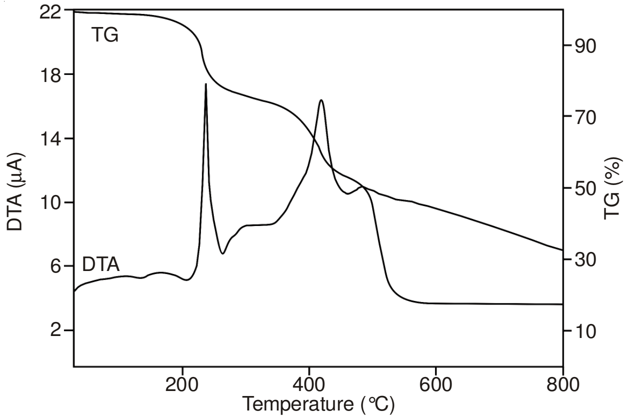

Fig. 4. Simultaneous TG-DTA of $Zn(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

TABLE-2
SIMULTANEOUS TG-DTA ANALYSIS DATA

Compound	DTA Peak temp. (°C)	TG Temp. range (°C)	Weight loss Found (calcd.)	Residue
$Co(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	255 (exo)	225-270	80.50 (81.80)	Co_2O_3
$Ni(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	295 (exo)	280-300	84.40 (83.59)	NiO
$Zn(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	240 (exo)	200-275	14.80 (13.88)	$Zn(m\text{-}C_6H_4(NO_2)COO)_2$
	420 (exo)	350-450	82.00 (82.37)	ZnO
$Cd(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	240 (exo)	200-250	75.90 (74.76)	CdO
$Co_{2/3}Ni_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	260 (exo)	250-270	82.10 (82.38)	$NiCo_2O_4$
$Co_{2/3}Zn_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	265 (exo)	260-280	82.80 (81.98)	$ZnCo_2O_4$
$Co_{2/3}Cd_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$	263 (exo)	250-280	81.10 (79.27)	$CdCo_2O_4$

X-ray powder diffraction: The isomorphism among the series of complexes is confirmed by their X-ray patterns, which are almost superimposable. The X-ray powder patterns of the mixed metal complexes shows sharp peaks 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(II) and cadmium(II) complexes are shown in Figs. 5 and 6, respectively.

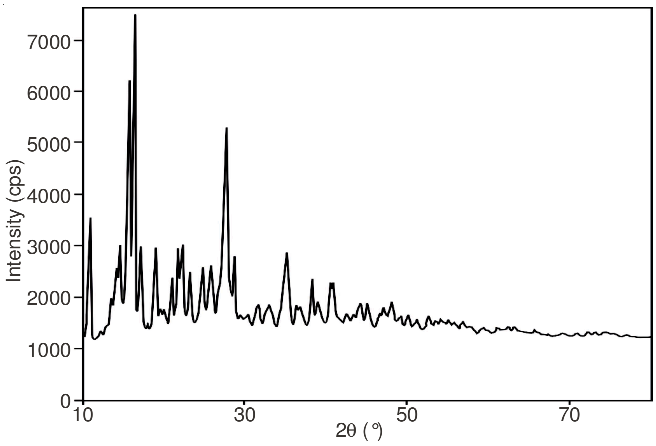

Fig. 5. X-ray powder diffraction pattern of $Zn(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

Metal cobaltites: The metal cobaltites were prepared by slowly heating the respective mixed metal complexes in a closed silica crucible at 260 °C for 10 min. The products formed were confirmed by their IR spectra and X-ray powder diffraction patterns. The metal analyses clearly indicate the ratios between cobalt to metal in the complexes are 1.98 to 2.1. The analytical, spectral and X-ray powder data of the metal cobaltites are summarised in Table-4. The line broadening indicates the fine particle nature of these cobaltites. The cell

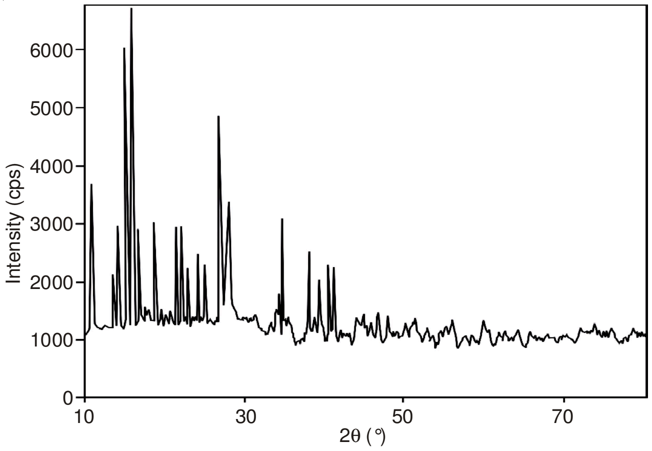

Fig. 6. X-ray powder diffraction pattern of $Cd(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

parameter 'a' calculated from the X-ray powder diffraction patterns are also presented in Table-4. The X-ray powder diffraction pattern of nickel cobaltite is shown in Fig. 7.

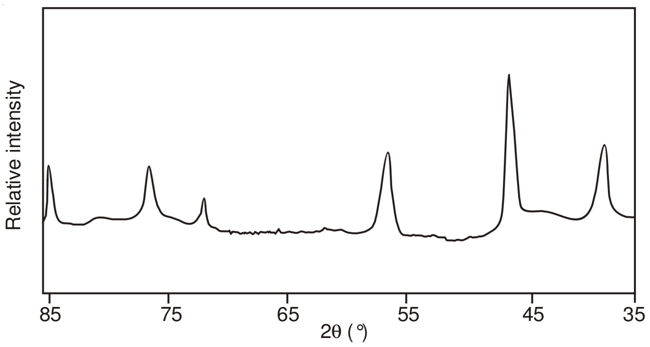

Fig. 7. X-ray powder diffraction pattern of $NiCo_2O_4$

TABLE-3
X-RAY POWDER DIFFRACTION DATA

$Cd(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$			$Zn(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$			$Co_{2/3}Ni_{1/3}(m\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$		
2θ	Intensity	d value	2θ	Intensity	d value	2θ	Intensity	d value
10.52	100	8.4025	10.76	47	8.2156	10.52	94.6	8.4025
11.28	92.6	7.8380	13.48	26.3	6.5633	11.49	100	7.6952
14.88	61.4	5.9488	14	34.6	6.3207	14.05	100	6.2983
15.2	58.4	5.8243	14.5	40.2	6.1039	14.7	95.7	6.0213
15.97	54	5.5452	15.5	82.7	5.7122	15.34	92.4	5.7715
16.4	52.6	5.4007	16.1	100	5.5007	16.1	89.1	5.5007
17.2	48	5.1513	17	39.7	5.2114	16.46	96.7	5.3812
18.44	42.9	4.8076	18.9	39.5	4.6916	17.4	78.3	5.0925
19.24	39.7	4.6095	20.9	32	4.2469	18.32	70.7	4.8388
21.11	35.8	4.2052	21.71	39.4	4.0903	21	65.2	4.2269
22.75	31.1	3.9056	22.2	40.1	4.0011	22.49	66.3	3.9502
24.46	30.1	3.6363	23.1	33.1	3.8472	23.8	67.4	3.7356
28.3	33.1	3.1510	24.75	34.6	3.5943	25.8	69.6	3.4504
31.27	22.1	2.8582	25.7	35.1	3.4636	27.81	69.6	3.2054
34.43	27.8	2.6027	27.48	70.9	3.2431	30	53.3	2.9762
38.05	22.8	2.3630	28.62	37.5	3.1165	32.8	51.1	2.7283
39.4	24.7	2.2851	35.08	38.3	2.5560	34.49	48.9	2.5983
41.3	19.5	2.1843	38.16	31.6	2.3565	36.1	46.7	2.4861
45.6	22.1	1.9878	40.45	30.4	2.2282	39.3	45.7	2.2907
48.09	21.4	1.8905	47.98	25.6	1.8946	50.1	48.9	1.8193

TABLE-4
ANALYTICAL AND SPECTRAL DATA OF METAL COBALTITES

S. No	Oxide	Cobalt (%)		Metal (%)		IR Spectra (cm^{-1})		XRD (Å)
		Found.	Calc.	Found.	Calc.	ν_1	ν_2	
1	$NiCo_2O_4$	49.20	49.00	24.80	24.40	660	565	8.098
2	$ZnCo_2O_4$	46.90	47.67	26.00	26.45	665	560	8.120
3	$CdCo_2O_4$	39.60	40.05	38.50	38.22	660	555	8.110

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