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Synthesis, spectral, thermal and X-ray diffraction studies on bis-hydrazine metal and mixed metal o-nitrobenzoates

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ABSTRACT

Bis-hydrazine metal o-nitrobenzoate, $[M(o\text{-}NO_2C_6H_4COO)_2(N_2H_4)_2]$, where M= Co, Ni, Zn or Cd have been prepared by mixing aqueous solution of respective metal nitrate hydrate with aqueous solution containing o-nitrobenzoic acid and hydrazine hydrate in 2:4 ratio. These complexes were analysed by chemical and CHN analyses. The IR spectrum of these complexes reveals the monodentate nature of carboxylate ions and bridged bidentate nature of hydrazine. Thermal behaviour of these complexes shows single step decomposition to give respective metal oxide as the final product except zinc complex which after dehydrazination in the first step undergo pyrolysis to give ZnO. X-ray powder patterns indicate that the complexes are isomorphism. The mixed metal complexes, $[M_{1/3}Co_{2/3}(o\text{-}NO_2C_6H_4COO)_2(N_2H_4)_2]$ have also been prepared using aqueous solution of mixture of metal ions in appropriate ratio. These precursors on thermal degradation yielded respective metal cobaltites as the end residue. The formations of these cobaltates were confirmed by chemical analysis, IR spectra and X-ray powder diffraction studies.

Key words: Bis-hydrazine, metal cobaltites, mixed metal complexes, o-nitrobenzoic acid, TG-DTA and X-ray powder diffraction.

INTRODUCTION

Nitro compounds are known for their explosive nature and undergo thermal degradation at much lower temperatures than other compounds. Simple metal complexes of nitrobenzoic acids and their derivatives have been thoroughly investigated [1-6]. In spite of a large number of such complexes are known, corresponding hydrazine derivatives have not been reported so far. The presence of hydrazine moiety in such system along with nitro group expected to highly enhance their thermal reactivity. Hydrazine due the presence of endothermic N-N bond undergoes exothermic degradation at lower temperatures. Hence, its presence in metal nitrobenzoates leads to undergo violent decomposition and hence this property could be exploited in the preparation of pure and fine metal oxides through hydrazine metal nitrobenzoate precursors. Such compounds can yield simple metal oxides and even mixed metal oxides at 200-300 ^{o}C with high degree of purity.

Hydrazine, besides its use in the synthetic organic chemistry has been utilised in the fields of inorganic chemistry, coordination chemistry and material science with different motives. Hydrazine, N_2H_4 can act as a neutral monodentate, bidentate and bridged bidentate ligand during its complexsation with metal carboxylates. Furthermore, even in weakly acidic medium it generates hydrazinium cation, $N_2H_5^+$ which is also capable of coordination with metal ions. The form and nature of hydrazine in complexes greatly influences the structure, thermal stability, solubility and biological activity of the hydrazine metal carboxylates.

Our through literature survey clearly reveals that plenty of hydrazine complexes of transition metal carboxylates [7-13] and hydrazine lanthanide carboxylates [14-17] have been prepared and their spectral and thermal properties have been exhaustively studied. However, only few aromatic carboxylic acid complexes have been investigated because of their complicated multi-stage thermal degradation patterns [18-20]. The presence of both nitro group and hydrazine in these complexes lead to one or two step decomposition at quite lower temperatures. Besides these the mixed metal complexes have 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 orthonitrobenzoate could be prepared and possibly used as the solid solution precursors for the fine mixed metal oxides.

In this article, we wish to report the synthesis, characterisation, spectral, thermal and X-ray studies of some new bis-hydrazine metal orthonitrobenzoates and the corresponding mixed metal complexes as precursors to the fine metal cobaltites.

EXPERIMENTAL SECTION

Preparation of bis- hydrazine metal o-nitrobenzoates and bis-hydrazine mixed metal o-nitrobenzoates

An aqueous solution (15 mL) containing a mixture of o-nitrobenzoic acid (3.3424 g, 0.02 mol) and hydrazine hydrate (2 mL, 0.04 mol) was added to an aqueous solution (20 mL) of respective metal nitrate hydrate (0.01 mol). The clear solution obtained was filtered and kept aside at room temperature. The precipitate formed was filtered washed with water then with alcohol and dried in air.

The mixed metal bis-hydrazine o-nitrobenzoate complexes were prepared by reacting an aqueous mixture (50 mL) of o-nitrobenzoic acid (10.0272 g, 0.06 mol) and hydrazine hydrate (6 mL, 0.12 mol) with an aqueous solution (50 mL) containing cobalt nitrate hexahydrate (5.8209 g, 0.02 mol) and nickel nitrate hexahydrate (2.0790 g, 0.01 mol) or zinc nitrate hexahydrate (2.9748 g, 0.01 mol) or cadmium nitrate hexahydrate (3 g, 0.01 mol). The precipitated bis-hydrazine mixed metal o-nitrobenzoates were filtered washed first with water then alcohol and dried in air.

Physico-Chemical studies

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. The hydrazine content was estimated volumetrically using KIO_3 solution (0.025 mol) under Andrew's condition.

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 room temperature magnetic susceptibility measurements were carried out with 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. The simultaneous TG-DTA of the complexes in air was carried out using TG/DTA 6200 Thermal Analyser. The heating rate employed was 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.

RESULTS AND DISCUSSION

The bis-hydrazine metal o-nitrobenzoate complexes were prepared by slowly mixing an aqueous solution containing a mixture of o-nitrobenzoic acid (3.3424 g, 0.02 mol) and hydrazine hydrate (2 mL, 0.04 mol) to an aqueous solution (20 mL) of the respective metal nitrate hydrates (0.01 mol). The resultant solution thus obtained was filtered and the clear solution was allowed to stand at room temperature. The bis hydrazine complex precipitated after 2-3 hours were filtered using Buckner funnel in suction pump, washed first with water then with alcohol and dried in air.

The mixed metal o-nitrobenzoate complexes were also prepared by the above procedure by taking 0.02 mol of cobalt nitrate hexahydrate and 0.01 mol of nickel nitrate hexahydrate, zinc nitrate hexahydrate or cadmium nitrate hexahydrate. The ligand solution is prepared by mixing o-nitrobenzoic acid (10.0272 g, 0.06 mol) and hydrazine hydrate (6 mL, 0.12 mol). The precipitated mixed metal complexes were filtered, washed with water then with alcohol and dried in air. The reaction may be represented as follows

$$M(NO_3)_2.nH_2O + 2\ C_6H_4(NO_2)COON_2H_5 + 4\ N_2H_4.H_2O \longrightarrow M[o\text{-}C_6H_4(NO_2)COO]_2(N_2H_4)_2 + 2HNO_3 + (n+1)\ H_2O$$

Where M = Co, Ni, Zn or Cd

$$2\,Co(NO_3)_2.6H_2O + 2\,M'(NO_3)_2.xH_2O + 2\,C_6H_4(NO_2)COON_2H_5 + 4\,N_2H_4.H_2O \longrightarrow$$
$$M'Co_2[o\text{-}C_6H_4(NO_2)COO]_6(N_2H_4)_6 + 2HNO_3 + (n+1)\,H_2O$$

Where M' = Ni, Zn or Cd

The 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 analysis. The analytical data of bis-hydrazine metal o-nitrobenzoates and bis-hydrazine mixed metal o-nitrobenzoates are summarised in table 1.

Table 1- Analytical data of metal orthonitrobenzoate and mixed metal orthonitrobenzoate complexes

S. No.	Molecular Formula (Mol. Wt)	Hydrazine	CHN Analysis			Yield %
			C %	H %	N %	
		Calc. (Found)	Calc. (Found)	Calc. (Found)	Calc. (Found)	
1	$Co(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.26)	14.1 (13.87)	36.9 (36.24)	3.54 (3.14)	18.5 (18.26)	85
2	$Ni(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.01)	14.1 (14.02)	37 (36.12)	3.54 (3.33)	18.5 (18.58)	90
3	$Zn(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (461.71)	13.9 (12.5)	36.4 (36.3)	3.49 (3.19)	18.2 (18.60)	82
4	$Cd(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (508.72)	12.6 (12.82)	33.1 (33.15)	3.17 (3.11)	16.5 (16.12)	80
5	$Co_{2/3}Ni_{1/3}\ (o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.18)	14.1 (13.7)	36.9 (36.25)	3.54 (3.33)	18.5 (18.08)	90
6	$Co_{2/3}Zn_{1/3}\ (o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (457.41)	14 (12.5)	36.8 (36.5)	3.53 (3.60)	18.4 (18.88)	90
7	$Co_{2/3}Cd_{1/3}\ (o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (473.08)	13.6 (12.82)	35.5 (35.8)	3.41 (3.81)	17.8 (17.8)	85

Magnetic Moments and Electronic Spectra

The room temperature magnetic moments of Co and Ni complexes are found to be 4.6 BM and 2.92 BM respectively. These values indicate that the metal ions are of high-spin variety and the complexes are expected to be octahedral in nature. Zn and Cd complexes are diamagnetic as expected. The electronic spectra of bis-hydrazine cobalt and nickel o-nirobenzoate complexes were recorded. The cobalt complex shows a band at 20,500 cm^{-1} which is assigned to spin allowed $^4T_{1g}(F) \longrightarrow {}^4T_{1g(P)}$ transition thereby suggesting octahedral geometry around Co(II).

The nickel complex exhibit electronic spectral maxima around 17,000 and 27,000 cm^{-1} corresponding to $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transitions respectively which are characteristics of octahedral geometry [25].

Infrared Spectra

The IR spectra of the bis-hydrazine metal and mixed metal o-nitrobenzoates are similar and shows bands at 3650-3700 cm^{-1} due to N-H stretching. The asymmetric and symmetric carboxylate stretching are observed in the region 1610-1620 cm^{-1} and 1350-1390 cm^{-1} respectively with $\Delta\nu = \nu_{asy} - \nu_{sym} > 200\ cm^{-1}$ clearly indicating the monodentate coordination of carboxylate ions. The N-N stretching frequencies of hydrazine moieties are seen in the range 950-980 cm^{-1} are in conformity with bidentate bridging nature of hydrazine [26]. The N-O stretching for nitro group is also observed in the finger print region between 850-900 cm^{-1} [27]. The IR spectrum of nickel, cadmium and cobalt-nickel mixed metal complexes are given in figs.1-3 respectively.

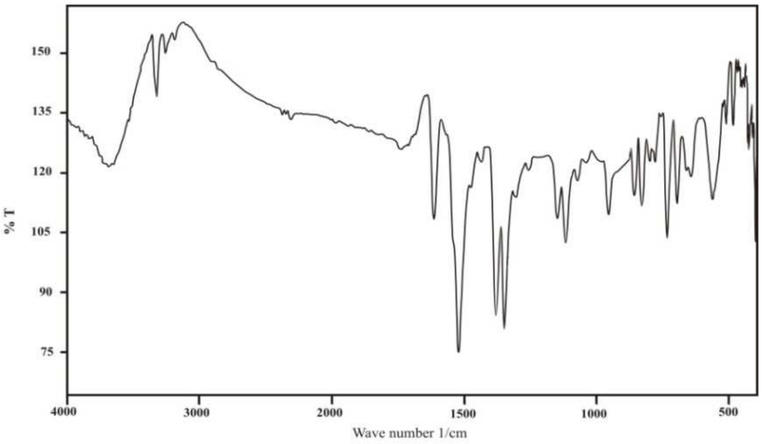

Fig. 1- IR Spectra of $Co(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)$

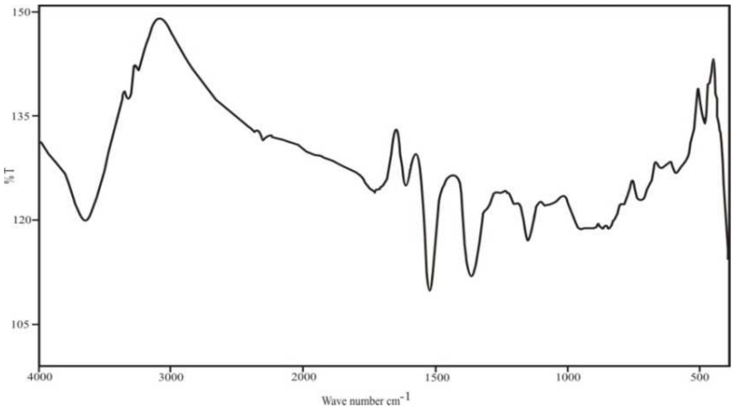

Fig. 2- IR Spectra of Ni(o-$C_6H_4(NO_2)COO)_2(N_2H_4)_2$

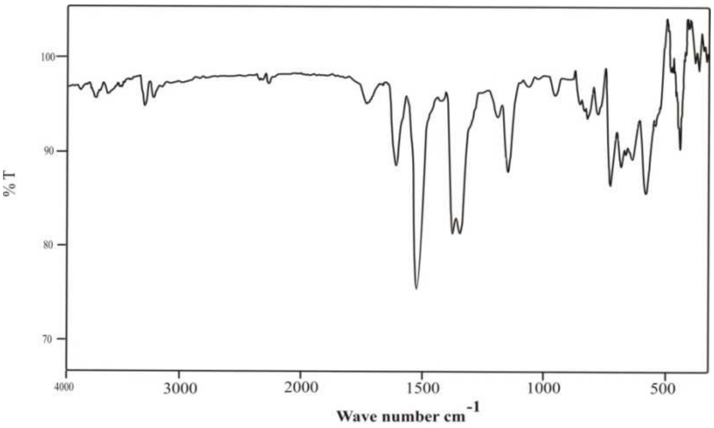

Fig. 3- IR Spectra of $Co_{2/3}Ni_{1/3}$(o-$C_6H_4(NO_2)COO)_2(N_2H_4)_2$

Thermal Degradation

Bis-hydrazine cobalt o-nitrobenzoate complex [Co(o-$C_6H_4(NO_2)COO)_2(N_2H_4)_2$] decomposes in a single stage as shown by the TG curve to give Co_2O_3 as the final residue. The degradation takes place between 180-220 ^oC. The DTA shows a strong and sharp exotherm at 218 ^oC. The nickel complex shows single step degradation between 220-270 ^oC to give NiO as final residue. The DTA shows a strong exotherm at 255 ^oC corresponding to the above stage. Unlike cobalt and nickel complexes, the zinc complex shows two stage decomposition in the temperature range 195-235 ^oC and 450-500 ^oC. The DTA shows an exotherm at 230 ^oC and also a sharp exotherm observed with peak temperature around 500 ^oC. In the first stage two hydrazine molecules are eliminated to give the zinc o-nitrobenzoate as an intermediate which subsequently undergoes pyrolysis to yield ZnO as the end residue. The thermal degradation of the cadmium complex also shows single step decomposition in the range 200-260 ^oC and the DTA shows an endotherm at 220 ^oC for the decomposition. The final product obtained was CdO.

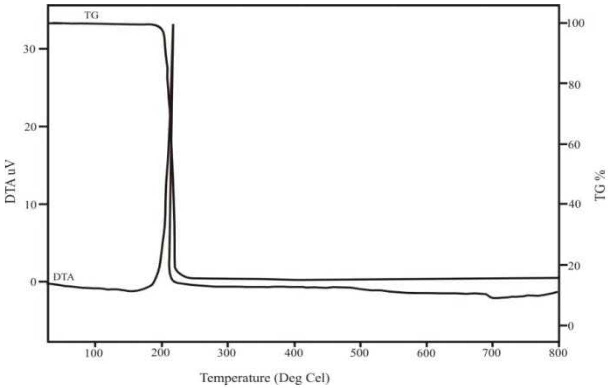

Fig. 4-Simultaneous TG-DTA of Co(o-$C_6H_4(NO_2)COO)_2(N_2H_4)_2$

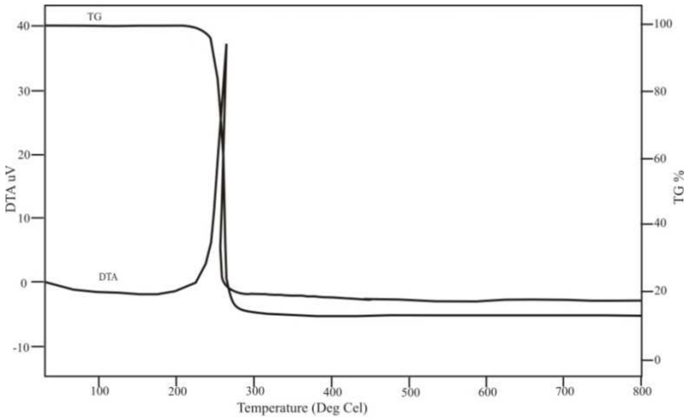

Fig. 5- Simultaneous TG-DTA of $Ni(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

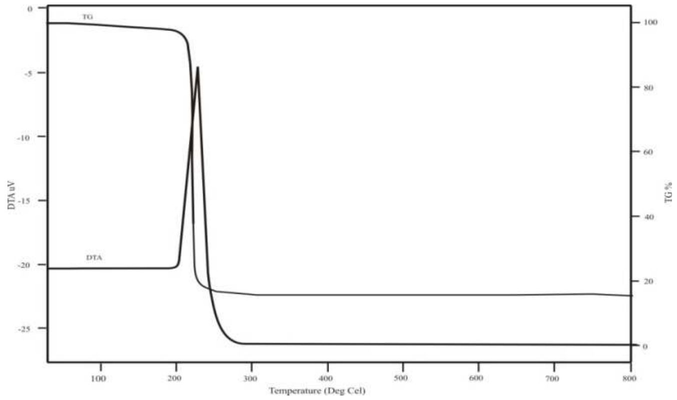

Fig. 6- Simultaneous TG-DTA of $Co_{2/3}Ni_{1/3}(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

The thermal degradation of all the bis-hydrazine mixed metal orthonitrobenzoate complexes shows single step decomposition in the temperature range 200-260 °C with the DTA peak temperature around 220 °C. The simultaneous TG-DTA of nickel, cobalt and cobalt-nickel mixed metal complexes are given in figs.4-6 respectively. The thermal degradation data of the complexes are given in table-2.

Table 2-Simultaneous TG-DTA analysis data of metal orthonitrobenzoate and mixed metal orthonitrobenzoate complexes

S. No.	Compound (Mol.Wt)	DTA Peak Temp(°C)	TG- Temp. range (°C)	weight loss Found (Calc.)	Residue
1	$Co(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.26)	218 (exo)	180-220	83 (81.8)	Co_2O_3
2	$Ni(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.01)	255 (exo)	220-265	85 (83.59)	NiO
3	$Zn(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (461.71)	227 (exo)	195-235	14 (13.88)	$Zn(o\text{-}C_6H_4(NO_2)COO)_2$
		502 (exo)	450-505	82 (82.37)	ZnO
4	$Cd(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (508.72)	235 (exo)	210-260	76 (74.76)	CdO
5	$Co_{2/3}Ni_{1/3}(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (455.18)	217 (exo)	200-260	83 (82.38)	$NiCo_2O_4$
6	$Co_{2/}Zn_{1/3}(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (457.41)	220 (exo)	200-230	83 (81.98)	$ZnCo_2O_4$
7	$Co_{2/}Cd_{1/3}(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$ (473.08)	222 (exo)	200-240	81 (79.27)	$CdCo_2O_4$

X –ray powder diffraction

The X-ray powder diffraction patterns of the complexes were recorded and found to show sharp and intense signals. The patterns are almost superimpossible which indicates isomorphism among these complexes. The X-ray powder patterns of the mixed metal complexes are also comparable with the simple complexes which also confirm the formation of solid solutions. The d values of cadmium, zinc and cobalt-nickel mixed metal complexes are given in table-3. The X-ray powder patterns of the cadmium complex and cobalt-nickel mixed metal complex are shown in fig.7 and fig.8 respectively.

Table 3- X-ray Powder diffraction data of cadmium, zinc and cobalt-nickel mixed metal complexes

$Cd(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$			$Zn(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$			$Co_{2/3}Ni_{1/3}(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$		
2θ	Intensity	d value	2θ	Intensity	d value	2θ	Intensity	d value
11.91	81.95	7.4248	13.23	29.2	6.6868	11.42	81.91	7.7422
13.29	114.56	6.6567	14.95	30.61	5.9211	13.21	90.14	6.6969
14.82	109.8	5.9748	18.02	33.53	4.9187	14.65	91.22	6.0417
17.90	102.57	4.9514	20.25	21.43	4.3818	17.93	82.94	4.9432
19.52	73.33	4.5430	21.68	30.38	4.0959	21.56	75.17	4.1184
20.88	82.26	4.2510	26.57	32.88	3.3521	25.16	68.02	3.5367
24.61	73.13	3.6145	29.71	32.34	3.0046	26.49	63.1	3.3621
26.55	65.79	3.3547	34.85	28.57	2.5723	29.66	54.87	3.0095
29.07	64.84	3.0693	37.72	26.75	2.3829	32.79	40.14	2.7291
34.42	64.6	2.6035	41.09	21.9	2.1949	42.42	47.05	2.1292
36.95	47.63	1.6462	45.42	25.35	1.9952	44.20	35.03	2.0474
38.72	45.89	1.6733	48.48	20.21	1.8762	47.07	36.06	1.9291
39.72	45.89	2.2037	51.35	23.66	1.7779	50.60	36.06	1.8025
40.92	46.19	2.2674	52.32	20.44	1.7472	52.86	34.09	1.7306
45.86	54.1	1.9771	57.62	18.44	1.5984	56.45	32.13	1.6288
48.06	46.7	1.8916	63.22	18.27	1.4697	58.89	31.07	1.5670
50.80	40.1	1.7958	72.05	18.9	1.3097	59.85	29.03	1.5441
52.75	38.7	1.7340	74.62	18.85	1.2709	60.72	28.95	1.5240
54.82	36.45	1.6733	77.65	17.65	1.23	62.04	29.01	1.4947
55.80	36.49	1.6462	85.01	16.35	1.14	65.95	33.06	1.4153
60.97	32.75	1.5184	89.58	16.54	1.09	79.09	35.01	1.2099

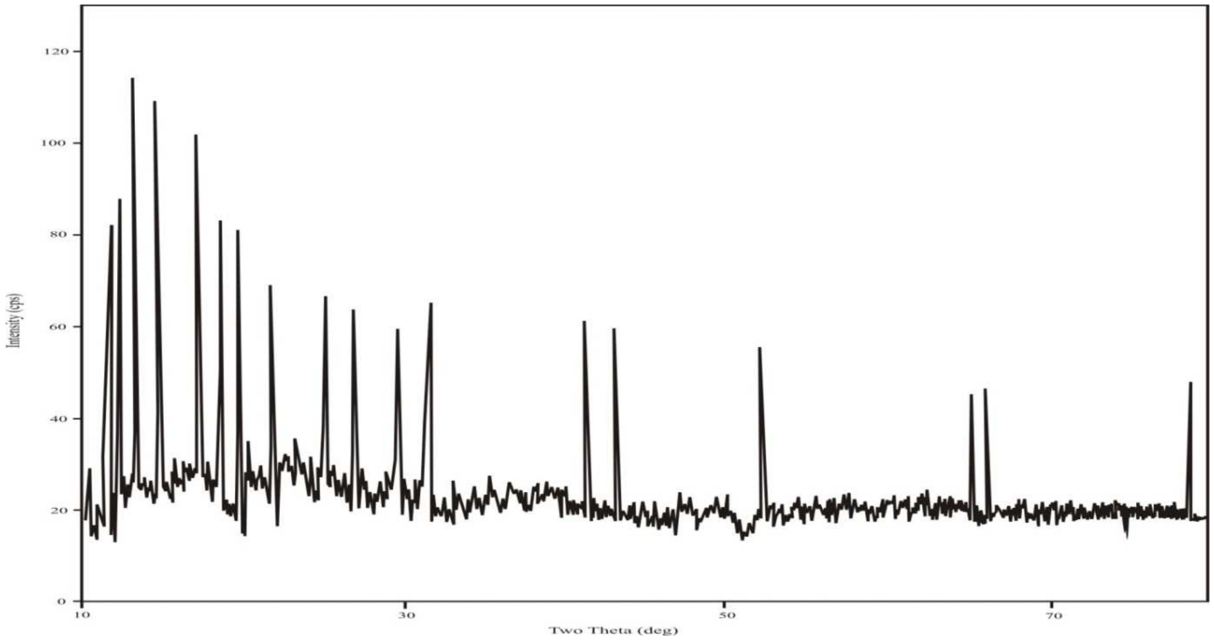

Fig.7- X-ray powder diffraction pattern of $Cd(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

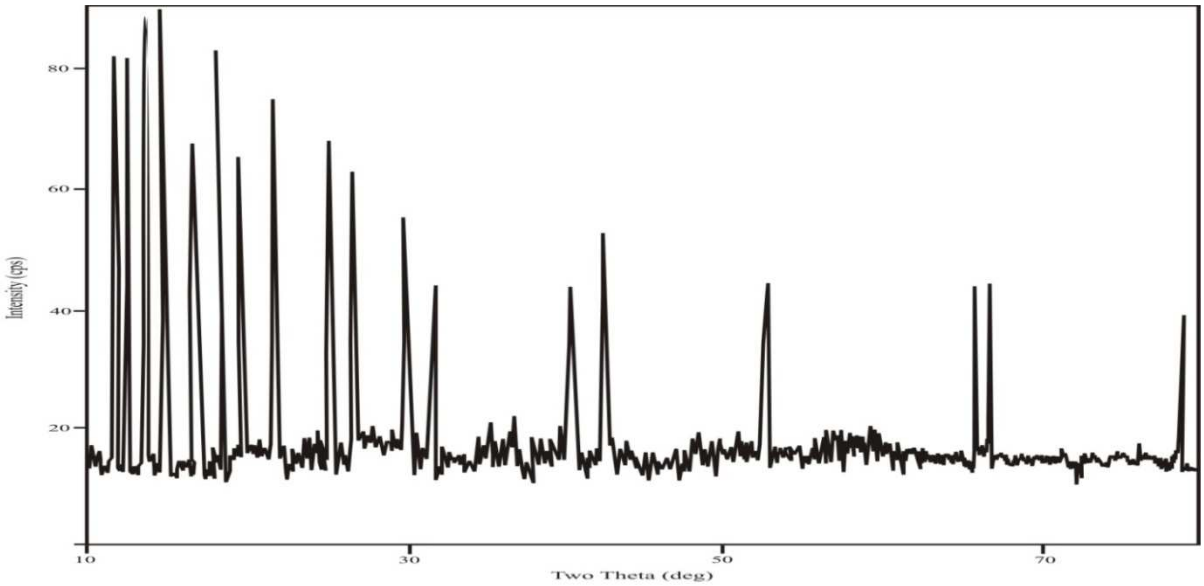

Fig. 8- X-ray powder diffraction pattern of $Co_{2/3}Ni_{1/3}(o\text{-}C_6H_4(NO_2)COO)_2(N_2H_4)_2$

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