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METAL-HYDRAZINE HOMOPHTHALIC ACID COMPLEXES AS PRECURSORS OF NANOMETAL POWDER

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Hydrazine complexes, $M(N_2H_4)_{0.5}A_2$ where M=Co and Cu and $M(N_2H_4)A_2$ where M=Cd and Ni and $Cd(N_2H_4)A$ where A = homophthalic acid(H_2hp), $C_6H_4(CH_2COOH)(COOH)$ have been prepared by the reaction of aqueous solution of hydrazine hydrate, homophthalic acid and metal nitrate at pH = 5-7. The acid shows only mono ionic nature in the complexes by deprotonation from aliphatic carboxylic acid group. The elemental analysis of complexes, IR data shows $\upsilon_{N\text{-}N}$ in the range 933-987 cm^{-1} , $\upsilon_{C=O\ sym}$ & $\upsilon_{C=O\ assym}$ of the aliphatic carboxylate respectively in the range of 1620-1481 cm^{-1}& 1404-1381 cm^{-1} respectively and υ_{OH} of COOH group around 3400 cm^{-1} confirm the structure of complexes. UV-Visible & VSM data substantiate the geometry of complexes. Simultaneous TG-DSC data indicate that the complexes undergo decomposition to give nano metal powder.

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Keywords: Homophthalic acid, Hydrazine, IR, UV, TG-DSC

1. Introduction

Homophthalic acid,(2 carboxy phenyl acetic acid) possesses two types of carboxylic acids groups, aromatic and aliphatic, due to which it acts as a versatile ligand and forms polymeric complexes with transition metals with different structures[1,2]. Co-ordination polymers are nowadays popular and are being used as functional materials to form compounds with organic and inorganic hybrid architectures [3]. Jiema et al [4] have reported the structural and magnetic studies of a copper(II) coordination polymer containing homophthalic acid in which the acid binds to copper metal through bidental carboxylates. Photoluminescence studies of crystalline cadmium(II) coordination polymers containing homophthalic acid is also found in literature [5]. In this polymer the carboxylate group of homophthalic acid ligand adopt μ-η^1 chelating mode. A set of manganese(II) complexes using homophthalic acid and bipypiridine as ligands has also been reported [6]. In these complexes, the two manganese(II) ions are bridged by a homophthalic acid ligand using new bridging coordination mode. The manganese (II) ions and homophthalic acid ligand generate one dimensional coordination polymer. In the same report nickel complex forms a two dimensional supra molecule network through N-H-----O and O-H-----O hydrogen bonds between water molecule amino groups and carboxylate oxygen atoms. Another set of new cadmium coordination polymers has been synthesized under hydrothermal condition and its structural study indicates that it forms three dimensional interpenetrating dia array with a four

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connected 6^6Topology [7]. Another study reveals that homophthalic acid on reaction with a metal nitrate and piperazines derivative forms coordination polymer exhibiting two dimensional (4,4) grid topology [8]. New metal organic frameworks using Zn,Cd & Ni ions with homophthalic acid and N-donor auxillary ligand have also been synthesized by using hydrothermal methods by Yan Wang et al indicating a diversified coordination pattern adopted by homophthalic acid [9]. Simple layered and complex self penetrated networks of Cadmium homophthalate coordination polymers have been reported by G.A.Farnum et al.

The later complex has a complicated, unprecedented tetrahedral self penetrated cationic three dimensional network [10]. Further one dimensional, two dimensional layer structured cadmium complexes have also been reported by J.R.H.et al [11]. All the coordination polymers so far reported involves the ligation of homophthalic acid and co-ligation of nitrogen donor bases. Yet, no metal complexes of homophthalic acid with simplest diamine, hydrazine has not been reported so far. Hydrazine has two donor nitrogen atoms and possess capability of forming variety of complexes, with hydrazinium cationic ligand [12] and bridged bidentate neutral ligand. Inferring from the literature that hydrazine can also contribute to the formation coordination polymers of metal homophthalates, this work was undertaken. In this report, simple synthesis of polymeric complexes of Co,Cu,Ni and Cd using hydrazine and homophthalic acid and characterization by elemental, spectroscopic, XRD ,magnetic and thermal studies are presented.

2. Experimental

The compositions of the complexes were fixed by chemical analysis and confirmed by micro elemental analysis. Hydrazine content in the complex was determined by titrating against standard KIO_3 (0.025 mol L^{-1}) under Andrew's conditions [13]. Metal contents were determined by titrating with EDTA (0.025 mol L^{-1}) after decomposition the complexes with 1:1 nitric acid [14]. All the chemicals used were of analytical grade. Double distilled water was used as solvent. The IR spectra of the complexes in the region 4000-400 cm^{-1} were recorded as KBr pellets using a Shimadzu spectrophotometer. Electronic reflectance spectra for the solid state complexes were obtained using a Jasco U 530 UV-Visible spectrometer by dispersing the solid samples in nujol mull. The magnetic susceptibility of the complexes was measured using a vibrating sample magnetometer, VSM EG&G model 155 at room temperature and the data were corrected for diamagnetism. The X-ray powder patterns of the complexes were recorded using a Siemens D-5005 X Ray diffractometer and JEOL FDX 8P X-ray diffraction using Cu K_α Nickel filter. The simultaneous TG-DSC experiments were carried out using NETZSCH STA 449F3 STA449F3A-0929-M thermal analyzer and the curves obtained in air at the heating rate of 10 ^oC min^{-1} using 5 to 10 mg of the samples. Platinum cups were employed as sample holders and alumina as reference. The temperature range was ambient to 1100 ^oC.

2.1. Synthesis of $[Co(N_2H_4)_{0.5}(C_9H_8O_4)_2]$ (compound 1), $[Ni(N_2H_4)(C_9H_8O_4)_2]$ (compound 2), $[Cu(N_2H_4)_{0.5}(C_9H_8O_4)_2]$ (compound 3) & $[Cd(N_2H_4)(C_9H_8O_4)_2]$ (compound 4)

Compound (1), (2, 3) & (4) were prepared by the same procedure with metal:acid:base in the ratios, 1:1:8, 1:1:6 & 1:1:4 respectively at pH = 5-7. A clear solution became turbid and then turned out to be precipitate settled at the bottom. The above solution was mixed thoroughly over magnetic stirrer for 20 minutes under 40 ^oC. It was cooled, filtered and washed with distilled water, ethanol and then with ether. Then it was dried in a desiccators.

2.2. Synthesis of$[Cd(N_2H_4)(C_9H_8O_4)]$(compound5)

The compound 5 was prepared by the procedure with metal:acid:base in the ratio of 1:2:3 at pH = 5. The above solution was mixed thoroughly over magnetic stirrer for 20 minutes under 40 ^oC. It was cooled, filtered and kept aside for 15 days. A solid substance was formed after 15 days and it was washed with distilled water, ethanol and then with ether. Then it was dried in a desiccators.

3. Result and discussion

3.1. Infrared spectra

Broad features ranging from 3300-3450cm^{-1} in all the spectra indicate the presence of –NH_2 group of hydrazine molecules. The peaks observed in the range of 1550 to 1620 cm^{-1} and in the range of 1381-1481 cm^{-1} are due to asymmetric and symmetric C=O stretching modes of homophthalic acid ligand respectively [15,16] and the difference between the two being less than 170 cm^{-1} indicate that the carboxylate moiety of aliphatic carboxylate of homophthalic acid involve in bidental coordination modes with metals in all complexes except compound(5). Further, the presence of N_2H_4 in the bridged bidental mode is also revealed by the presence of N-N stretching in the range 964-987 cm^{-1}(Bribanti et al) [17], in the case of compound 1,2 and 4. In the case of copper complex compound(3) N-N stretching is shown at 933 cm^{-1} indicating that hydrogen is coordinated to metal in a mono dental fashion [18]. All the complexes show the sharp peak at the frequency range of 470-501 cm^{-1} which is ascribed as the characteristic vibration of M-O bond [19].Analytical data and IR data of all the compounds are given in Table 1.

Table 1. Analytical and IR data of the complexes.

S.No	**Molecular formula**	**%C Found (cald)**	**%H Found (cald)**	**%N Found (cald)**	**N_2H_4 Found (cald)**	**Metal Found (cald)**	υ_{O-H}	υ_{N-H}	$\upsilon_{c=o}$ free acid	υ_{coo}^{-} (asym)	υ_{coo}^{-} (sym)	υ_{N-N}	**Bridging**
1	$[Co(N_2H_4)_{0.5}(C_8H_8O_4)_2]$	49.7 (48.6)	4.1 (3.8)	3.2 (2.8)	3.68 (3.93)	13.53 (11.95)	3450	3309	1604	1481	1381	972	bridging
2	$[Ni(N_2H_4)C_8H_8O_4)_2]$	47.9 (46.0)	4.4 (3.6)	6.2 (5.5)	7.10 (7.30)	13.01 (12.40)	-	3317	-	1620	1389	987	bridging
3	$[Cu(N_2H_4)_{0.5}(C_8H_8O_4)_2]$	49.1 (48.2)	4.1 (3.5)	3.2 (2.5)	3.63 (3.90)	14.45 (14.00)	-	3402	-	1551	1381	933	bridging
4	$[Cd(N_2H_4)(C_8H_8O_4)_2]$	42.8 (41.1)	4.4 (3.1)	5.5 (4.6)	6.34 (6.23)	22.26 (24.05)	3448	3302	-	1550	1404	964	bridging
5	$[Cd(N_2H_4)(C_8H_8O_4)]$	33.3 (32.5)	3.7 (3.0)	8.6 (7.2)	9.90 (5.40)	34.62 (29.50)	3395	3394	1697	1550	1396	948	unidentate

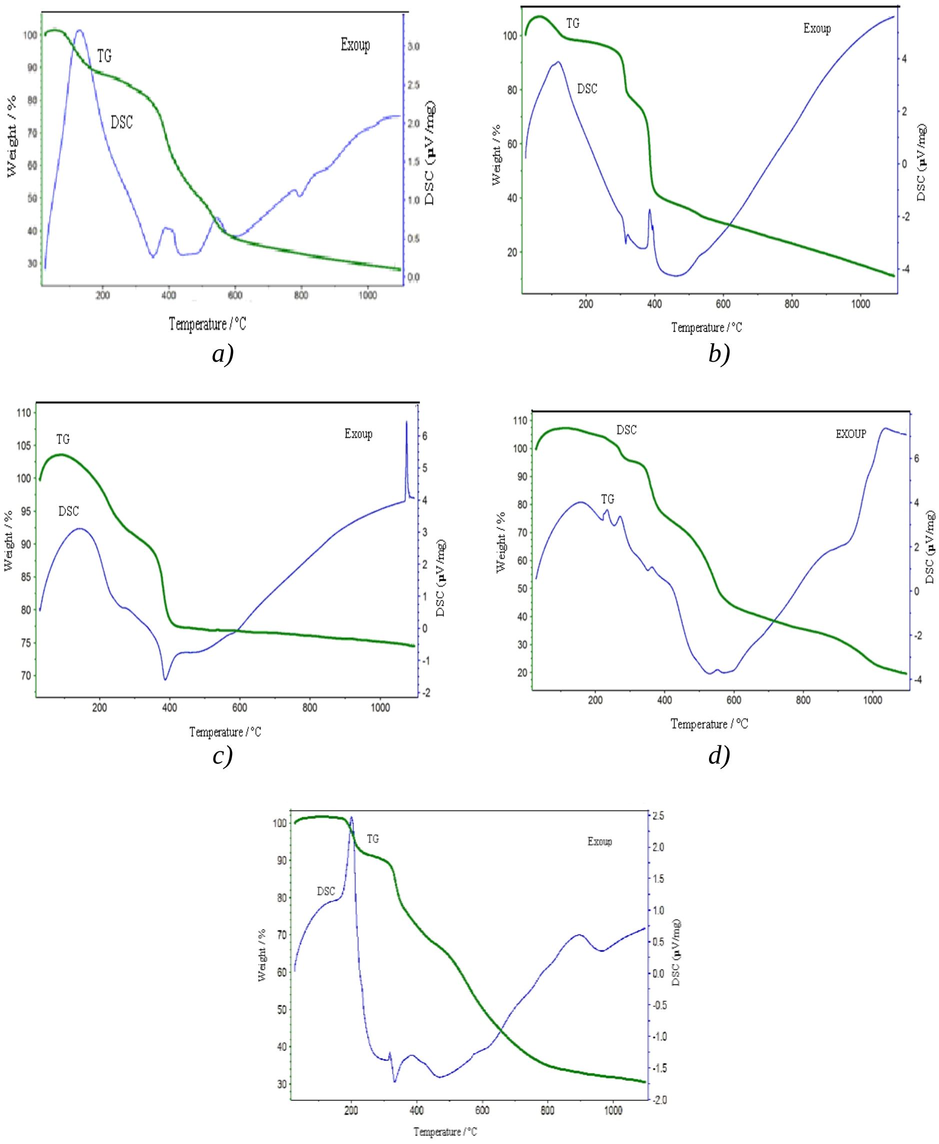
3.2. Thermal analysis

The thermal decomposition of compound(1) and (2) indicates that endothermic dehydrazination takes place at 133 ^{o}C(Cobalt complex) and 150 ^{o}C(Copper complex) in the first step.In the second step exothermic decomposition takes place at 400 ^{o}C(Cobalt complex) and 267 ^{o}C(Copper complex) followed by further exothermic decomposition at 550 ^{o}C(Cobalt complex) and 388^{o}C(Copper complex) to form the respective carbonates [20] the intermediate cobalt phthalate by its XRD collected after the decomposition at 400 ^{o}C whereas this intermediate could not be identified for copper complex but in the both the cases the final product cobalt carbonate could be identified by its spectrum.

In the case compound(3) it undergoes decomposition to eliminate hydrazine endothermally at the temperature 231 ^{o}C,262 ^{o}C and –CH_2 groups at 369 ^{o}C in the next step it undergoes exothermic decomposition at 583 ^{o}C to form cadmium carbonate. On further heating the carbonate formed decomposes at 839 ^{o}C exothermally to form metal as residue. Nickel complex shows a different type of decomposition in the first step it undergoes exothermic decomposition showing dehydrazination and decarboxylation. In the second step further decomposition occur to oxalate [21,22]. The oxalate intermediate undergoes decomposition at 539 °C to form metal as residue [23].

In the case of compound 4(cadmium complex), the first step involves endothermic dehydrazination at 262 °C first, and in second step another hydrazine and $-CH_2$ groups are removed. Further, exothermic decomposition occurs at 583 °C which corresponds to the decomposition of carbonate and at 839 °C endothermic decomposition occurs which results in metal powder. Compound(5) undergoes decomposition to eliminate hydrazine endothermally at the temperature 318 °C. On further heating it decomposes at 470 °C exothermally to form metal as residue.

TG-DSC curves of complexes are shown in Fig. 1 (a), (b), (c), (d) & (e) and the thermal data are given in Table 2.



a) *b)* *c)* *d)* *e)*

Fig. 1. (a) TG-DSC curve for $[Co(N_2H_4)_{0.5}C_8H_8O_4)_2]$*; (b) TG-DSC curve for*$[Cu(N_2H_4)_{0.5}C_8H_8O_4)_2]$*; (c) TG-DSC curve for* $[Ni(N_2H_4)C_8H_8O_4)_2]$*; (d) TG-DSC curve for* $[Cd(N_2H_4)C_8H_8O_4)_2]$*; (e) TG-DSC curve for* $[Cd(N_2H_4)C_8H_8O_4)]$*;*

Table 2. Thermal data of the complexes

S.NO	Complex	DTA Temp^{o}c	Thermogravimetry				Nature of Decomposition
			Temp range		Weight loss%		
			From	To	Obsd.	Cald.	
1	$[Co(N_2H_4)_{0.5}(C_8H_8O_4)_2]$	133^{o}C (+)	60	260	13.7	13.8	Removal of $-CH_2$& Dehydrazination
		400 ^{o}C (-)	260	470	44.0	43.8	Decomposition to Cobalt phenolate
		550 ^{o}C (-)					
		800 ^{o}C (-)	470	1100	71.7	72.7	Decomposition to Cobalt carbonate
2	$[Ni(N_2H_4)C_8H_8O_4)_2]$	318 ^{o}C (-)	138	335	25.6	26.0	Dehydrazination & removal of CO_2
		383 ^{o}C (-)	335	529	67.5	67.4	Decomposition to Oxalate
		539 ^{o}C (-)	529	900	87.0	82.0	Decomposition to metal
3	$[Cu(N_2H_4)_{0.5}(C_8H_8O_4)_2]$	150 ^{o}C (+)	60	231	9.5	10.0	Removal of $-CH_2$& Dehydrazination
		267 ^{o}C (-)					
		388 ^{o}C (-)	231	440	71.9	72.1	Decomposition to Copper carbonate
4	$[Cd(N_2H_4)(C_8H_8O_4)_2]$	231 ^{o}C (+)	174	328	6.2	6.3	Dehydrazination
		262 ^{o}C (+)					
		369 ^{o}C (+)	328	390	12.0	11.9	Removal of $-CH_2$& Dehydrazination
		526 ^{o}C (-)					
		583 ^{o}C (-)	390	800	66.0	65.8	Decomposition to Carbonate
		839 ^{o}C (+)	800	1100	87.1	87.0	Decomposition to metal
5	$[Cd(N_2H_4)(C_8H_8O_4)]$	200 ^{o}C (+)	169	253	9.8	9.8	Dehydrazination
		318 ^{o}C (+)					
		335 ^{o}C (-)					
		470 ^{o}C (-)	253	900	66.0	65.4	Decomposition to metal

3.3. UV-visible spectroscopy and magnetic susceptibility

The absorptions in electronic spectra for cobalt complex at 28371 cm^{-1},26731cm^{-1} assigned to xz ,yz and xy states → x^2 and y^2 state [24] corresponding to low spin square pyramidal environment for the metal ion. In nickel complex, the absorptions in electronic spectra at 26700 cm^{-1},26688 cm^{-1} assigned to $^3T1_g(P)$, suggesting a six coordinate complex[25]. The absorptions in electronic spectra for copper complex at 25544 cm^{-1} and 25640 cm^{-1} correspond to square pyramidal environment for the metal ion [26]. The effective magnetic moment values, 4.3 BM for compound 1, 3.3 BM for compound 2 and 1.4 BM for compound 3, respectively. ESR spectra of copper complex exhibits g// (parallel) value of 4.19 and $g_{\perp}$ (perpendicular) value of 3.61 which is associated with square pyramidal coordination.

3.4. Powder XRD study and SEM

Fig. 2 shows the powder XRD pattern of Nickel nano particle remained after the thermal decomposition of compound 5. The 2θ values in the XRD pattern are in good agreement with the JCPDS card no.45-1027 and 04-0850 [27] corresponding to nickel metal. Using the measured full width at half width at half maximum of the peaks and Scherrer formula, $D = K\lambda / B \cos \theta$, where λ is the X-ray wavelength, B is the full width at half maximum(FWHM) of a diffraction angle and K is Scherrer constant of the order of 0.89, and the average particle diameter was estimated to be about 90-150nm. The SEM images of nickel metal formed from nickel complex are shown in Fig**.** (3a and 3b) implying that the complexes may be used as a precursors for nanometal powder.

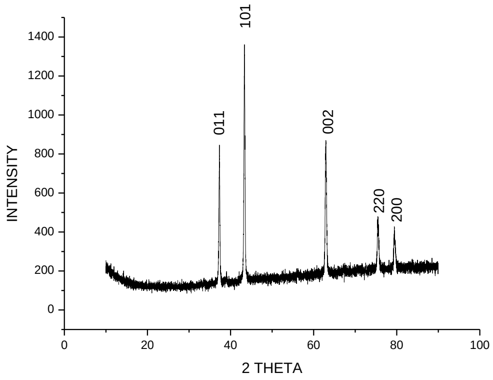
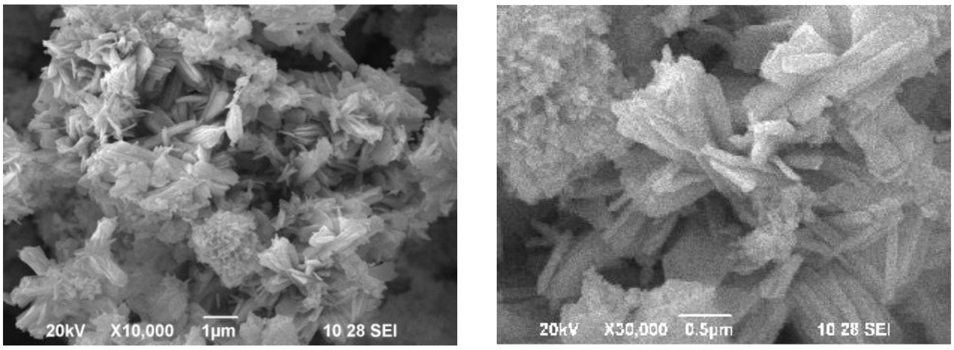
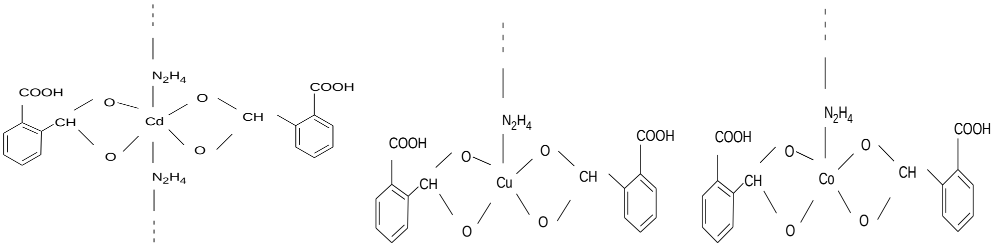


Fig. 2. Powder XRD pattern of Nickel metal.



(a) *(b)*

Fig. 3. (a) SEM image for Nickel metal; (b) SEM image for Nickel metal.



(a) *(b)* *(c)*

Fig. 4. (a) Structure of [Cd(N_2H_4)($C_8H_8O_4$)$_2$]; (b) Structure of [Cu(N_2H_4)$_{0.5}$($C_8H_8O_4$)$_2$]; (c) Structure of [Co(N_2H_4)$_{0.5}$($C_8H_8O_4$)$_2$].

4. Conclusions

The reaction of metal nitrate with homophthalic acid and hydrazine hydrate yields the complexes of formula. Analytical data confirm their formulations. The $\upsilon_{\text{(N-N)}}$ frequencies in IR spectra of the complexes in the range of 933-987 cm-1 evidence the presence of hydrazine as a neutral bidentate ligand. Based on analytical spectroscopy and thermal analysis data the following structure are proposed for the complexes as shown in figure(4a, 4b and 4c). The complexes undergo decomposition to form carbonates (cobalt and copper) and metals as final products for nickel and cadmium complexes.

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