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Transition Metal Complexes of 3,5-Dihydroxy-2-naphthoic Acid and its Nano Metal Oxides: Synthesis and Characterization

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Synthesis of Cd(II), Cu(II), Mn(II) and Zn(II) complexes are achieved by adding hydrazine hydrate and 3,5-dihydroxy-2-naphthoic acid in the ratio 1:4 to the corresponding metal nitrates. The synthesized complexes are characterized by elemental analysis, IR, UV, TG-DTA and XRD analysis. The nano metal oxides are obtained by decomposing the complexes at 800 °C in the muffle furnace. The nano metal oxides are characterized by IR and XRD studies. The surface morphology and quantative analysis of metal oxides were determined by using SEM analysis. The shape of nano zinc oxide is rock like hexagonal structure while that of nano Mn oxide is rod like structure which was confirmed by transmission electron microscopy analysis.

Keywords: SEM images, Hexagonal structures, TEM images, TG-DTA.

INTRODUCTION

The hydroxynaphthoate ion has a variety of dentation modes in which both carboxylate and phenolic oxygen atoms participate [1-4]. Lanthanide complexes [5,6] with *ortho* substituted naphthoic acid show that the hydroxynaphthoate ion is monodentate, coordinated to the metal through the carboxyl group. A study of $(\mu\text{-L})_4[Nd(H_2O)(EtOH)L]_2{\cdot}2H_2O{\cdot}2EtOH$, (L is 1-hydroxy-2-naphthoate ligand) indicates that, two ligands act as bidentates and the two other as terdentates [7]. Gupta *et al.* [8] have prepared complexes of Fe, Ti, V, Al, Cu and Be using hydroxynaphthoic acid as a chelating agent and have studied the thermodynamic properties of complex of Fe(III) also with the same acid in ethanolic solution [9]. These complexes were found to decompose to their oxides with the intermediate formation of the respective naphthoates [10]. A detailed investigation of photophysics of 1-hydroxy-2-naphthoic acid has been carried out [11]. The investigation of structure of magnesium salts of 1-hydroxy-2-naphthoic acid was also reported [12]. These molecules are used as chelating agents, fluorescent indicators and the manufacturing of dyestuffs.

A study of isomeric hydroxynaphthoic acid with transition metals and hydrazine has not been attempted so far. Hence, it was decided to prepare the transition metal complexes with 3,5-dihydroxy-2-naphthoic acid and hydrazine and to study various spectral properties.

EXPERIMENTAL

3,5-Dihydroxy naphthoic acid was purchased from Sigma Aldrich. All other reagents were of AR grade and the solvents were purified by using standard methods. Micro analysis of C, H and N were obtained using elemental analysis. The IR spectra in the range 4000-400 cm^{-1} were obtained with KBr pellet using ATR Shimadzu model spectrometer. The UV spectra were run on Lad India UV-visible spectrometer using nujol mull. The TG-DTA analysis was obtained on Perkin-Elmer STA 600 thermal analyzer. The XRD pattern was taken with X-ray diffractometerBurker advanced D8 X-ray at room temperature using Cu K_α radiation over a wide range of Bragg angles. The surface morphologies of ZnO and MnO nanoparticles were observed by using SEM at room temperature. To confirm the size of the particles, further the metal oxides was analyzed with JEOL JEM 2100 high resolution transmission electron microscope (HRTEM).

Synthesis of $[M(C_{11}H_6O_6)(N_2H_4)_2{\cdot}2H_2O$ where M = Cd(II), Cu(II), Mn(II) and Zn(II): To the solution of 3,5-dihydroxy-2-naphthoic acid (0.2049, 0.001 mol), 10 % hydrazine hydrate was added. The solution was kept over the water bath for about 30 min to get transparent, homogeneous solution and the pH of the ligand solution was found to be 9.

The metal nitrate [Cd(II), Cu(II), Mn(II) and Zn(II)] solution (0.001 mmol in 10 mL H_2O) was then added to the prepared ligand solution, with slow and constant stirring. The

reaction mixture was heated over a water bath for 2 h and kept as such in a dark room for 24 h. A polycrystalline substance which obtained was washed with alcohol and dried.

Synthesis of nano Zn and Mn oxide particles: The metal oxides were synthesized by incineration of the complex in muffle furnace at 800 °C for 5 h. The nano metal oxides obtained by this method are free from organic impurities and expected to be homogeneous.

RESULTS AND DISCUSSION

The elemental analysis data were in good agreement with the calculated values and shows the formation of 1:1:2 [M:A:B] ratio. The hydrazine content was determined by titrating against KIO_3 (0.025 mol/L) under Andrew's condition. Metal content were estimated by titrating with standard EDTA (0.01 mol/L) after decomposing 60 mgm of the complex with 1:1 nitric acid for three times to destroy the organic content [13].

IR spectra: The IR spectra of the free ligand were shifted upon complex formation. The ligand shows a band of OH group at 3300 cm^{-1} and it disappeared in the complex. This indicates the deprotonation of the hydroxyl group and coordinates to the metal atom through oxygen. Two new bands in the region 762-740 cm^{-1} and 3311-3200 cm^{-1} are assigned to ν(N-N) and ν(N-H) respectively [14]. The appearance of new band in the range of 3379-3278 cm^{-1} is due to O-H stretching vibration which indicates the presence of lattice water (Table-1).

Thermal studies: The simultaneous TG-DTA (Table-2) was recorded for the complexes in order to explore their thermal stability. The TG-DTA curves of the complexes of Cd(II), Mn(II), Zn(II) and Cu(II) were shown in Fig. 1. All the complexes show three stage decomposition patterns. Initially it showed endothermic band around 77-120 °C with a mass corresponding to loss of water molecules in the complex. Secondly, it shows strong exothermic band around 130-300 °C which may be due to the formation of unstable metal naphthoate. In the final step it decomposes continuously leading to the formation of corresponding metal oxides in the range of 350-700 °C.

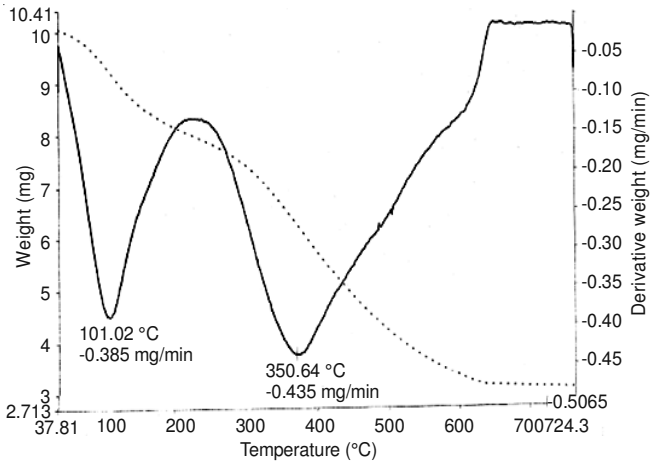

Fig. 1. TG-DTA curve of $[Cd(C_{11}H_8O_4)(N_2H_4)_2]\cdot 2H_2O$

TEM: TEM analysis of cross-sectional samples were carried out for the prepared nanometal oxides. It was apparent from the Fig. 2a and 2b that the metal oxides are in good distribution with evenness and there is formation of agglomerates. The SEM images of the metal oxides were shown in Fig. 3. Fig. 4 represents EDX spectra of the zinc oxide which is used to determine the composition of the metal oxide. The strong signals from Co confirm the presence of metals in nano oxide.

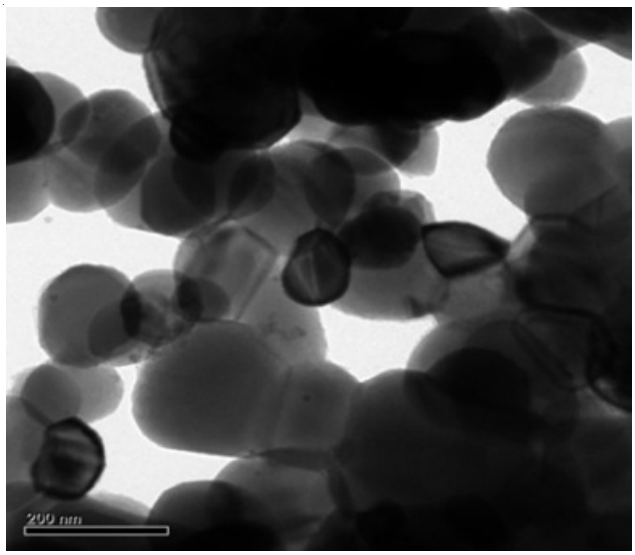

Fig. 2a. TEM image of zinc oxide

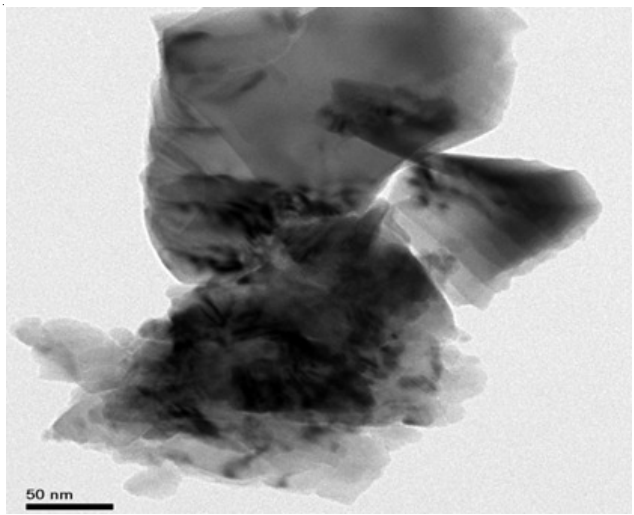

Fig. 2b. TEM image of manganous oxide

TABLE-1
PHYSICO-CHEMICAL AND IR DATA OF THE COMPLEXES

Complexes	Colour	Yield (%)	Decomposition temperature	ν(O-H)	ν(H_2O)	ν(N-H)	ν_{asym}(COO)	ν_{sym}(COO)	ν(N-N)
3,5-Dihydroxy-2-naphthoic acid	Yellow	–	272	3300	–	–	1663	1517	–
$[Mn(C_{11}H_8O_4)(N_2H_4)_2]\cdot H_2O$	Light brown	75	120	–	3379	3300	1500	1421	750
$[Cu(C_{11}H_8O_4)(N_2H_4)_2]\cdot H_2O$	Blue	70	172	–	3752	3311	1561	1436	762
$[Zn(C_{11}H_8O_4)(N_2H_4)_2]\cdot 2H_2O$	Dull brown	75	165	–	3330	3200	1591	1545	740
$[Cd(C_{11}H_8O_4)(N_2H_4)_2]\cdot 2H_2O$	White	85	174	–	3278	3200	1550	1421	750

TABLE-2
THERMAL ANALYSIS OF THE COMPLEXES

Complexes	DTA peak temperature (°C)	Thermogravimetry			Nature of decomposition
		Temperature range (°C)	Moss loss (%)		
			Found	Calculated	
$[Cu(C_{11}H_8O_4)(N_2H_4)_2]\cdot H_2O$	88	40-160	5	59.15	Dehydration
	248	190-250	20	19.29	Dehydration
	335	350-600	75	77.36	Formation of CuO
$[Zn(C_{11}H_8O_4)(N_2H_4)_2]\cdot 2H_2O$	77.27	50-150	10	9.74	Dehydration
		160-350	30	27.05	Formation of metal naphthoate
		390-600	78	77.87	Formation of ZnO
$[Cd(C_{11}H_8O_4)(N_2H_4)_2]\cdot 2H_2O$	120	50-130	9	8.64	Dehydration
	245	150-300	25	24.00	Formation of metal naphthoate
	430	350-650	80	8.00	Metal oxide formation
$[Mn(C_{11}H_8O_4)(N_2H_4)_2]\cdot H_2O$	123	80-140	5	60.00	Dehydration
	300	140-650	78	76.00	Metal oxide formation

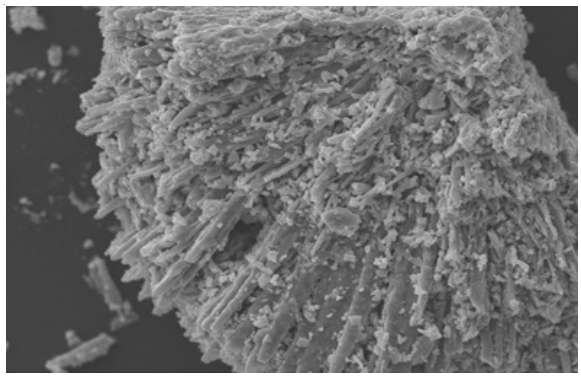

Fig.3a. SEM image of zinc oxide

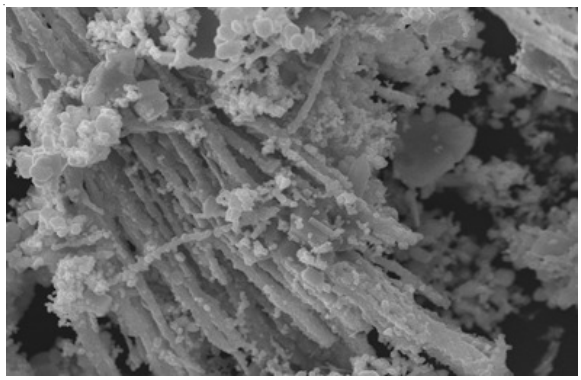

Fig. 3b. SEM image of manganous oxide

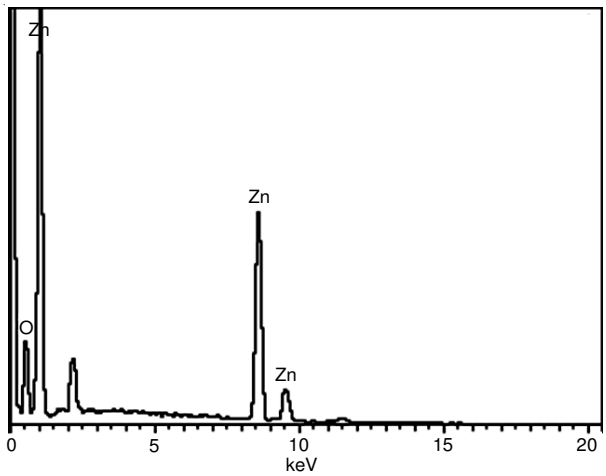

Fig. 4. EDX spectra of zinc oxide

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