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Research Paper

Synthesis, Characterization and Antimicrobial Studies of Novel Hydrazine Complexes with 2-Hydroxypyridine -3-Carboxylic Acid

CHEMISTRY

KEYWORDS : Hydrazine, 2-hydroxypyridine-3-carboxylic acid, IR spectra, TG-DTA and antimicrobial studies.

R.Anu Research Scholar, Department of Chemistry, PSGR Krishnammal College for women, Coimbatore

P.Kanchana Assistan Professor, Department of Chemistry, PSGR Krishnammal College for women, Coimbatore.

N. Arunadevi Assistan Professor, Department of Chemistry, PSGR Krishnammal College for women, Coimbatore.

ABSTRACT

A new complexes of formula, $[M(C6H3NO3)(N2H4)2]$ where M = Ni, Co &Cd, have been prepared by reacting 2-hydroxynicotinic acid and hydrazine with respective metal nitrates. The complexes were characterized by elemental analyses, IR, UV- visible spectra, TG-DTA , VSM studies and also by SEM with EDAX, AFM and TEM analysis. The acid shows dianionic nature in these complexes. IR data indicates the nature of hydrazine in the complexes. Simultaneous TG-DTA studies shows thermal degradation pattern for these complexes. All the complexes undergo three step decomposition. The SEM image of the complexes implies that the size of the particles is 40- 50 nm. Anti microbial studies revealed that the complexes are potential antimicrobial agents.

Introduction

Among the polyamines, hydrazine, N_2H_4, the simplest diamine, plays a major role in co-ordination chemistry due to the presence of lone pair of electrons each on their nitrogen atoms. It acts as a neutral, mono or bidentate bridging ligand leading to the formation of polymeric complexes [1-3]. A number of studies have been carried out on bivalent metal carboxylates [4-10]. Our current interest is on investigation of a series of bivalent transition metal complexes using hydrazine and heteroaromatic carboxylic acids as ligands with the aim of obtaining the information about the co-ordination and thermal reactivity of hydrazine in such complexes.

The present paper deals with the preparation and characterization of transition metal complexes of 2-hydroxynicotinic acid with hydrazine.

Experimental

All the chemicals used in the synthesis were in analytical grade while, 2-hydroxynicotinic acid, hydrazine hydrate, methanol, acetone, and chloroform have been purchased from Sigma Aldrich and used as received.

2.1 Preparation of $[M(C_6H_3NO_3)(N_2H_4)_2].H_2O$ where (M= Ni ,Co & Cd)

These complexes were prepared by stirring the aqueous solution of the ligands (60 mL) containing 2-hydroxynicotinic acid (0. 139 g, 0.001 mol) and hydrazine hydrate (2 ml, 0.002 mol) with an 20 mL of metal nitrate solution (for example, 0.291g of $Co(NO_3)_2.6H_2O$; 1mmol in 20mL of distilled water) at pH 8.

The above solution mixtures which appeared cloudy at first, turned out to be a micro crystalline solid on digestion when kept over a hot water bath at 90°C for 20 minutes. It was cooled, filtered and washed with distilled water, ethanol and then with ether. The crystals were dried in a desiccator over anhydrous $CaCl_2$.

2.2 Physicochemical Techniques

The compositions of the complexes were fixed by chemical analysis and confirmed by micro elemental analysis. Hydrazine content was determined by titrating against standard KIO3 (0.025mol L^{-1}) under Andrew's conditions. Metal Contents were determined by titrating with EDTA (0.01mol L^{-1}) after decomposing a known weight of the complex with 1:1 nitric acid for atleast three times to destroy the organic matter [11].

The infrared spectra of the complexes were recorded on a Perkin-Elmer 597 spectrophotometer in the range 4000–400cm^{-1} using KBr discs of the samples. The simultaneous TG-DTA experiments were carried out using SDT Q600 V8.3 instrument and Stanton 781 simultaneous thermal analyzer. Thermal analyses were carried out in air at the heating rate of 10 °C 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 700 °C. Surface morphology was studied by JEOL GSM – 6390 LV scanning electron microscope at 3-12 KV at different magnifications. The transmission electron micrographs were taken with a JEOL JEM -2010 electron microscope. The solid-state UV-visible absorption spectra of the complexes were recorded on a Varian, Cary 5000 recording spectrophotometer. The magnetic susceptibility data were determined for the powder samples over the temperature range 200-300 k by using John Foxx: Metamatic (Elka Rhapsody) magnetometer. Bacterial and fungal strains used for this study are *E. Coli, Staphylococcus Aureus, Candida Albicans & Aspergillus Fumigates.* The standardized disc agar diffusion method was followed to determine the activities of the synthesized compounds against the sensitive organisms.

3. Results and Discussion

All the complexes are microcrystalline solids, stable in air and insensitive to light. They are sparingly soluble in water and insoluble in common organic solvents like ethanol, acetone and chloroform. The analytical data of the complexes are compatible with the proposed composition for the complexes (Table 1).

3.1 IR spectra of complexes

The N-N stretching frequencies (Table1) observed in the range 967-999cm^{-1} are the evidence for the presence of coordinated N_2H_4 in the complexes [12] which were not found for free acid. The carbonyl stretching frequency, which appears as a strong band at 1685 cm^{-1} in the free acid, vanishes upon the formation of the complex, indicating that the carboxylic groups are all deprotonated. In all the complexes (Fig. 1) the asymmetric and symmetric stretching frequencies of the carboxylate ions are seen in the range 1635 - 1651 cm-1 and 1554-1588 cm-1, respectively indicating the monodentate coordination of carboxylate group [13]. The N-N stretching frequency is observed in the range of 967-999 cm-1 which is the evidence for neutral, bridging hydrazine .The peak in the range 461-532 cm^{-1} is ascribed to the characteristic vibration of M-O bond [14].

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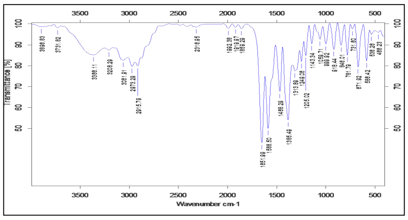


Fig. 1 IR Spectra of Nickel complex

3.2 Thermal Analysis

The TG – DTA experiment was carried out to explore the thermal stability of the complexes. The different decomposition stages of the complexes with percentage loss are represented in Table 2.

The compositions of the intermediates and the final products are those which best fit with the observed mass losses in the TG studies. Thermogravimetric results are in good agreement with the DTA data. As a representative example, TG-DTA of $Ni[(C_6H_3NO_3)(N_2H_4)_2].H_2O$ & $Co[(C_6H_3NO_3)(N_2H_4)_2].H_2O$ is shown in Fig. 2a and Fig.2b.

The TG curves reveal three step decomposition of the complexes. Dehydration takes place in the first step, exhibiting endotherms in the range of 125-160°C, followed by a decomposition of hydrazine in the second step with a display of an exothermic peak in the range of 220-280°C in DTA.During the last step, the intermediate degrades to the respective metal oxide showing a strong exothermic peak in the range of 390-470°C. The metal oxides formed after the incineration of the complexes at their decomposition points, followed by sintering at the same temperature for about 3 -4 hours were found to be pure and uniform in nano scale. The oxides obtained in this way are expected to be chemically more homogeneous, free of contamination by impurities and highly reactive.

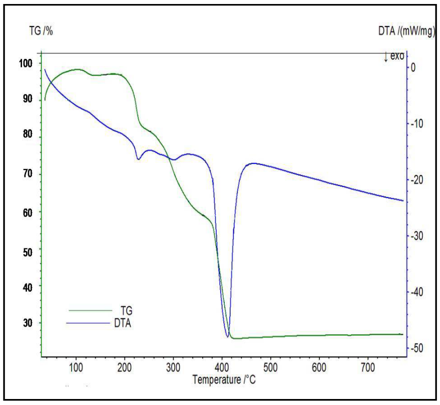


Fig.2a TG-DTA of $Ni[(C_6H_3NO_3)(N_2H_4)_2].H_2O$

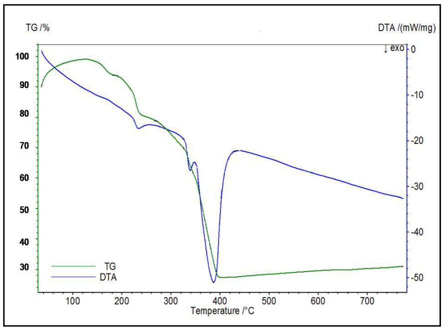


Fig.2b TG-DTA of $Co[(C_6H_3NO_3)(N_2H_4)_2].H_2O$

3.3 Scanning Electron Microscopy

Scanning electron micrography (SEM) is used to evaluate morphology and particle size of the metal oxide. The SEM micrographs and EDAX images are shown in Fig. 3 &4. The morphologies of metal oxides are found in different shapes and sizes, though they are synthesized from a same ligand. A very good and homogeneous dispersion of Nickel oxide was evidenced from the micrograph (Fig.3a) which shows jelly fish type structure i.e., seen as a bundle of fibres having diameter of 50 nm. The morphology of Cobalt oxide (Fig.4a) is found to be bead shape as well as appeared like stack of globule or droplet. From the EDAX spectra it was seen that only metal and oxide were present and it is free from other impurities like N, C etc. This indicates that hydrazine hydrate played a key role in the formation of well-dispersed nano particles due to co-ordination with metal nitrates that leads to the formation of uniform sized metal oxide during heat treatment.

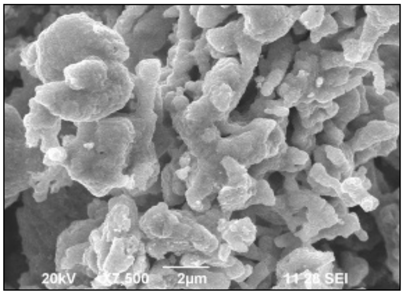


Fig. 3a SEM image of Nickel Oxide

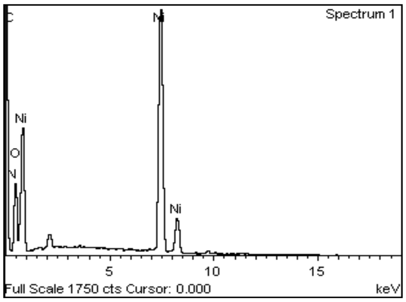


Fig. 3b EDAX of Nickel Oxide

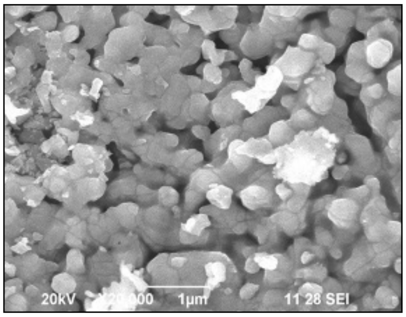
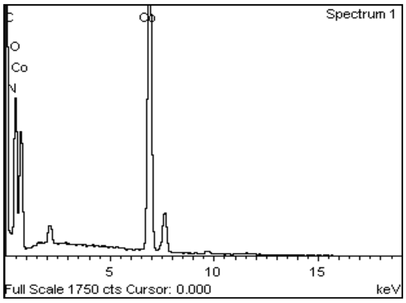


Fig. 3a SEM image of Nickel Oxide



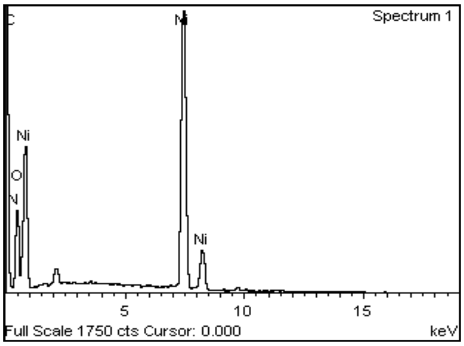


Fig. 3b EDAX of Nickel Oxide

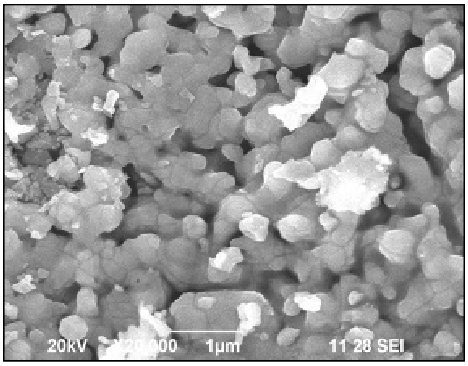


Fig. 4a SEM image of Cobalt Oxide

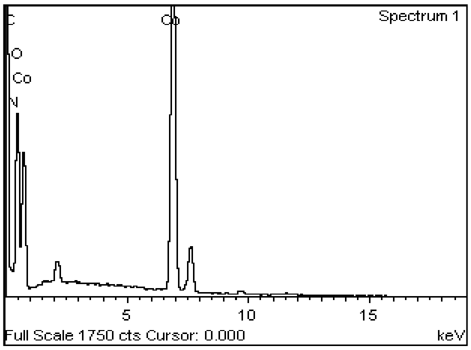


Fig. 4b EDAX of Cobalt Oxide

3.4 Transmission electron microscopy

TEM photos (Fig. 5a) revealed the presence of a large number of cobalt oxide particle with hexagonal shape and uniform size around 40-50nm .No aggregation of particles was found in TEM image. Fig.5 b shows selected area diffraction pattern of nano particles. The appearance of strong diffraction spots confirmed the formation of single crystalline cubic nature of cobalt oxide.

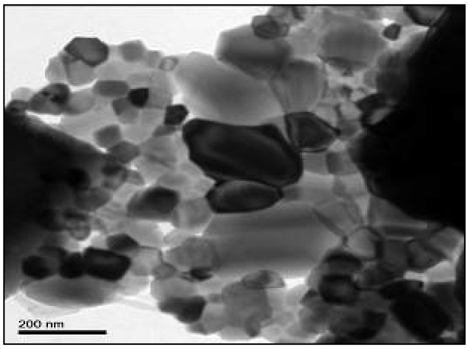


Fig.5a TEM image of CoO nanoparticles

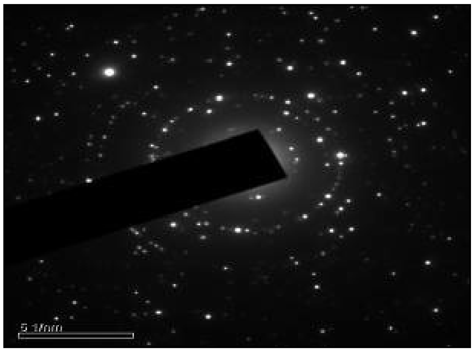


Fig.5b SAED of CoO nanoparticles

3.5 UV- Visible spectra and magnetic susceptibility

The Ni(II) & Co(II)complexes show magnetic moments of 3.12 and 3.88 B.M. respectively which is characteristic of mononuclear, octahedral, Ni(II) (d8, 2 unpaired electrons), Co(II) (d7, 3 unpaired electrons) complexes. The electronic spectrum of Ni(II) complexes showed peaks characteristic of octahedral geometry. The reflectance spectra of Ni(II) complex consist of the transition bands at 9980, 16800 and 26350 cm−1 assignable to the transitions 3A2g →3T2g and 3A2g →3T1g(F)15 respectively. The three transitions observed in the electronic spectra of the Co(II) complex indicate the octahedral environment around the metal ion. The electronic spectrum of the Co(II) complexes show strong peaks at 8250, 16220 and 20360 cm−1 assignable to the transitions 4T1g(F) →4A2g(F) and 4T1g(F) →4T2g(F).

3.6 Antimicrobial Studies

Antimicrobial activities of complexes at different concentrations were tested on are *E. Coli, Staphylococcus Aureus, Candida Albicans & Aspergillus Fumigates.* After incubation at 37°C for 24h, inhibition of the organisms was measured and used to calculate mean of inhibition zones. Activity index of all the synthesized compounds was also calculated against the corresponding standard drug (Table.3). The products showed various activities against all species of microorganisms, which suggest that, the variations in the structure affect the growth of the microorganisms. Among the prepared complexes, cobalt complex shows the most effective against both gram positive and gram negative organisms. Thus we conclude that, all the compounds have been fully characterized and they showed a moderate to high antimicrobial activity towards the species of bacteria and fungi. Therefore, these compounds may be considered promising for the development of new antimicrobial agents.

Conclusions

In this investigation at first, $[M(C_6H_3NO_3)(N_2H_4)_2].H_2O$ where M= Ni(II), Co(II) &Cd(II), complexes were synthesized and the structure of these compounds was confirmed by different techniques. The FT- IR and TG-DTA analysis confirmed that the synthesized complexes contain hydrazine and 2-hydroxy nicotinic acid along with metal. Then nano oxides are prepared from above complexes and their surface morphology was studied using SEM and TEM analysis. The magnetic moment and electronic spectra reveal that the metal ions are in octahedral environment. All complexes are tested by antibacterial and antifungal activities which show fine result with enhancement of activity on complexation with metal ions.

Table 2 Thermal Analysis of the complexes

Molecular formula of the Complexes	DTA Peak Temp(°C)	Thermogravimetry			Decomposition Products
		Temp. Range(°C)	Weight loss		
			Obs.	Calc.	
$[Ni(C_6H_3NO_3)\ (N_2H_4)_2].H_2O$	125 (+)	100-250	6.50	6.47	Dehydration
	220 (-)	150-300	23.21	23.03	Dehydrazination
	410 (-)	320-500	73.21	73.11	Formation of Nickel Oxide
$[Co(C_6H_3NO_3)(N_2H_4)_2].H_2O$	160 (+)	100-200	6.50	6.47	Dehydration
	225 (-)	200-300	23.12	23.01	Dehydrazination
	390 (-)	300-600	73.21	73.15	Formation of Cobalt Oxide
$[Cd(C_6H_3NO_3)(N_2H_4)_2].\ H_2O$	160 (+)	150-200	5.43	5.42	Dehydration
	280 (-)	260-330	19.27	19.30	Dehydrazination
	470 (-)	420-600	61.34	61.26	Formation of Cadmium Oxide
(+),endotherm ; (-) ,exotherm ;					

Table 3. Antimicrobial activities of the complexes

Complex	Diameter of inhibition zone in mm (activity index)			
	E. Coli	S.aureus	c. albicans	a.fumigates
Ni	12	20	12	12
Co	21	21	20	17
Zn	15	18	10	08

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