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SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF $[M(CIN)_2(N_2H_4)_2]$ (M=NI/CD)

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ABSTRACT

Ni (II) and Cd (II) complexes containing hydrazine as ligand and cinnamic acid as co-ligand were synthesized and characterized by hydrazine and metal analyses, thermal analysis and FT-IR spectral studies. It has been found that hydrazine behaves as bidentate ligand and cinnamate as monodentate ligand in the complexes. The biological activities of complexes have been evaluated against two gram negative (Escherichia coli and Pseudomonas aeruginosa) and two gram positive (Bacillus subtilis and Staphylococcus aureus) bacteria by Agar diffusion disc method. It has been found that the complexes have potent activity against the bacteria.

Key words: nanoparticles, XRD, HRTEM, SAED, SEM.

1. INTRODUCTION

The field of bioinorganic chemistry, which deals with the study of role of metal complexes in biological systems, has opened a new horizon for scientific research in coordination compounds. A large number of compounds are important from the biological point of view. Hydrazine was historically used experimentally as a therapeutic agent in the treatment of tuberculosis, sickle cell anaemia, and non-specific chronic illnesses. (Premkumar and Govindarajan, 2005; Yasodhai and Govindarajan, 2000) Hydrazine and their metal complexes have played an important role in the development of co-ordination chemistry. A large number of publications ranging from synthetic to modern physiochemical and biochemical relevant studies of these complexes bear testimony to their importance. Hydrazine carboxylates of the transition metal ions with variety of acids have been reported. These include simple aliphatic mono carboxylic acid, (Sivasankar and Govindarajan, 1995; Sivasankar and Govindarajan, 1997; Sivasankar and Govindarajan, 1994) aliphatic dicarboxylic acids, (Gold, 1987; Govindarajan *et al.,* 1995; Sivasankar, and Govindarajan, 1994; Vikram and Sivasankar, 2007; Vogel, 1985) aromatic mono and dicarboxylic acids (Kuppusamy, and Govindarajan, 1995; Kuppusamy and Govindarajan, 1996) and heterocyclic acids. (Premkumar and Govindarajan, 2006; Von Burg and Stout, 1991) The present paper describes the synthesis, analytical, spectral, thermal studies of Ni (II) and Cd (II) metal complexes containing hydrazine and cinnamic acid.

2. EXPERIMENTAL

2.1. Preparation of $[M(cin)_2(N_2H_4)_2]$

$[M(cin)_2(N_2H_4)_2]$ (M=Ni/Cd) complex was prepared by the addition of an aqueous solution (50 mL) of hydrazine hydrate (1 mL, 0.01 mol) and cinnamic acid (0.74g 0.055 mol) to the corresponding aqueous solution (50 mL) of the corresponding metal nitrates $[Ni(NO_3)_2.6H_2O$, 0.73 g, 0.002 mol or cadmium nitrate hexahydrate, 0.77 g, 0.002 mol] . The complex formed immediately was kept aside for an hour for digestion, then filtered and washed with water, alcohol followed by diethylether and air dried.

2.2. Quantitative methods

The hydrazine content in the complexes was determined by titration using KIO_3 as the titrant (Von Burg and Stout, 1991). The percentage of metals in the complexes was estimated by the standard methods given in the Vogel's textbook (Von Burg and Stout, 1991).

2.2. Physico-chemical techniques

2.2.1. Infrared spectrum

The infrared spectrum of the solid precursor sample was recorded by the KBr disc technique using a Perkin Elmer 597/1650 spectrophotometer.

2.2.2. Thermal analysis

The simultaneous TG-DTA experiment was carried out in Shimadzu DT40, Stanton 781 and STA 1500 thermal analyzer. Thermal analysis was carried out in air at the heating rate of 10°C per minute using 5-10 mg of the sample. Platinum cups were used as sample holders and alumina as reference. The temperature range was ambient to 700°C.

2.2.3. Biological assay

The antibacterial activities of the prepared complexes were determined by the disc diffusion method. The bacteria were cultured in nutrient agar medium and used as inoculum for the study. The antibacterial activity of the synthesized compounds of 25µg, 50µg, 100µg and 200µg concentrations were tested against two gram positive bacteria *Staphylococcus aureus & Bacillus subtilis* and two gram negative bacteria *Pseudomonas aeruginosa & Escherichia coli*. The inhibition zones were calculated and recorded.

3. RESULTS AND DISCUSSION

Table 1 – Compositional analysis data of the prepared complexes

Complex	Hydrazine (%) Found (Calcd.)	Metal (%) Found (Calcd.)	Yield (%)
$[Ni(cin)_2(N_2H_4)_2]$	15.00 (15.36)	14.10 (14.08)	90
$[Cd(cin)_2(N_2H_4)_2]$	13.70 (13.61)	23.60 (23.90)	82

3.1. Chemical formula determination of the complexes

The chemical formula $[M(cin)_2(N_2H_4)_2]$ (M=Ni/Cd) has been assigned to the prepared complexes, based on the observed and calculated percentage of hydrazine and metals, which are found to match closely with the calculated values (Table. 1).

3.2. FT-IR spectral analysis

From the IR spectrum of $[Ni(cin)_2(N_2H_4)_2]$ and $[Cd(cin)_2(N_2H_4)_2]$ complexes, it is observed that the N-N stretching frequency is seen at 962 cm^{-1} and 972 cm^{-1} respectively, which unambiguously proves the bidentate bridging nature of the hydrazine ligand (Sivasankar and Govindarajan, 1996). The asymmetric and symmetric stretching frequencies of the carboxylate ions in $[Ni(cin)_2(N_2H_4)_2]$ are seen at 1612 and 1384 cm^{-1}, respectively with the $\Delta\upsilon$ (υ_{asymm}- υ_{sym}) separation of 288 cm^{-1}. In $[Cd(cin)_2(N_2H_4)_2]$, the asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1600 and 1396 cm^{-1}, respectively with the $\Delta\upsilon$ (υ_{asymm}- υ_{sym}) separation of 204 cm^{-1}. From this, the monodentate linkage of carboxylate groups in the complexes is confirmed. The N-H stretching is observed around 3300 cm^{-1} in both the complexes.

Table 2 – FT-IR spectral data of the prepared complexes

Compound	υ N-H cm^{-1}	$\upsilon_{asym(OCO)}$ cm^{-1}	$\upsilon_{sym(OCO)}$ cm^{-1}	$\Delta\upsilon$ cm^{-1}	ν (C=C) cm^{-1}	$\upsilon_{(N-N)}$ cm^{-1}
$[Ni(cin)_2(N_2H_4)_2]$	3351 3270	1612	1384	288	1651	972
$[Cd(cin)_2(N_2H_4)_2]$	3300 3285	1600	1396	204	1638	962

Fig. 1 – FT-IR spectrum of $[Ni(cin)_2(N_2H_4)_2]$

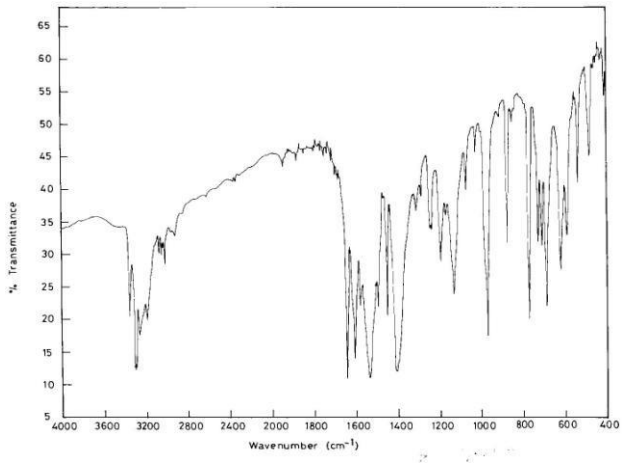
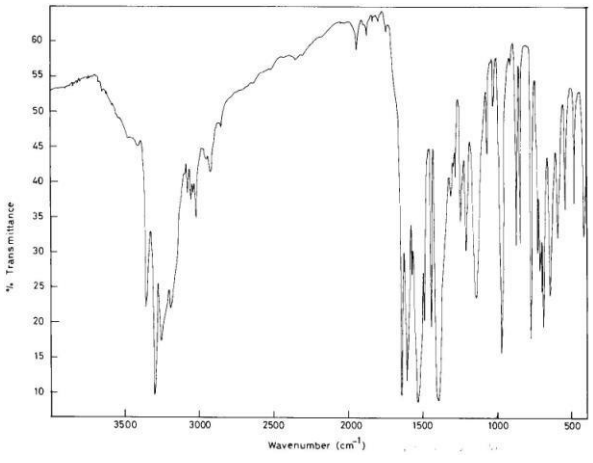


Fig. 2 – FT-IR spectrum of $[Cd(cin)_2(N_2H_4)_2]$



3.3. Thermal analysis

Figure. 3 depicts the TG-DTA curve of the prepared complex $[Ni(cin)_2(N_2H_4)_2]$. The complex undergoes two-step decomposition, the first step being the dehydrazination. In DTA, the corresponding decomposition is observed as an exotherm. The second step is the exothermic decomposition of the dehydrazinated compound, yielding nickel oxide as the final residue with in 250-470°C.

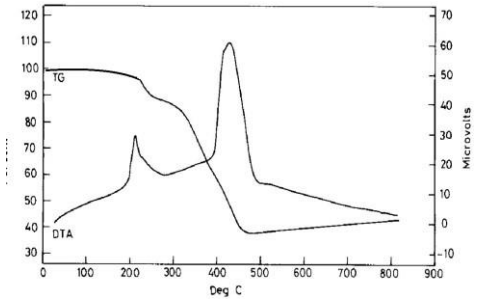


Fig. 3 – TG-DTA curve of $[Ni(cin)_2(N_2H_4)_2]$

From the TG-DTA curve of the cadmium complex shown in figure 4, it is evident that the complex loses weight in three steps. The first step is the endothermic dehydrazination reaction between 166-297°C. In the second step, the dehydrazinated compound gives cadmium acetate as the intermediate exothermically in the temperature range, 297-395°C. Our attempt to separate the intermediate was unsuccessful since the decomposition was continuous. In the third step, the proposed intermediate undergoes exothermic decomposition to give CdO as the end product.

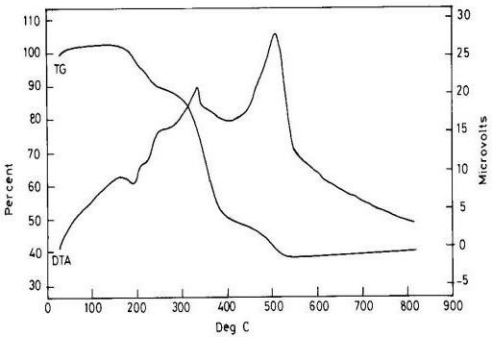


Fig. 4 – TG-DTA curve of $[Cd(cin)_2(N_2H_4)_2]$

Table 3 – Antibacterial activity of the prepared complexes

Complex	Concentration of the complex µg/ml	Zone of inhibition in mm			
		Gram positive bacteria		Gram negative bacteria	
		SA	BS	PA	EC
$[Ni(cin)_2(N_2H_4)_2]$	200	15	14	14	14
	100	12	10	11	11
	50	9	NA	9	8
	25	NA	NA	NA	NA
$[Cd(cin)_2(N_2H_4)_2]$	200	15	14	13	16
	100	13	10	10	13
	50	10	NA	8	10
	25	8	NA	NA	NA

SA - *Staphylococcus aureus;* BS - *Bacillus subtilis;* PA - *Pseudomonas aeruginosa;* EC - *Escherichia coli*

3.4. Antibacterial activity

The antibacterial activity of the synthesised complexes at different concentrations have been studied and recorded in Table 3.

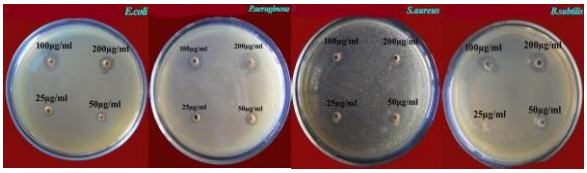


Fig. 5 – Antibacterial activity of $[Ni(cin)_2(N_2H_4)_2]$

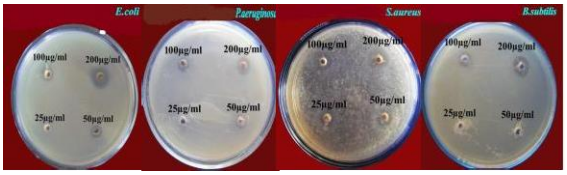


Fig. 6 – Antibacterial activity of $[Cd(cin)_2(N_2H_4)_2]$

It is seen from the figures that the synthesised complexes exhibit antibacterial activity against tested pathogens used in this study. For the Ni (II) complex, in gram negative bacteria the minimum inhibition concentration (MIC) value was exhibited with 50µg/ml for *E.coli and P.aeruginosa*. In gram positive bacteria, the MIC value was identified with 25µg/ml for *S.aureus* and 100µg/ml for *B.subtilis.* For the Cd (II) complex, in gram negative bacteria the minimum inhibition concentration (MIC) value was exhibited with 50µg/ml for *E.coli and P.aeruginosa*. In gram positive bacteria, the MIC value was identified with 25µg/ml for *S.aureus* and 100µg/ml for *B.subtilis.*

4. CONCLUSION

Ni (II) and Cd (II) complexes containing hydrazine and cinnamic acid were synthesized and physico-chemically characterized by FT-IR spectra

and thermal analysis. Antibacterial analysis of the complexes was evaluated among the different bacterial strains such as *Escherichia coli, Pseudomonas aeruginosa, Bacillus subtilis and Staphylococcus aureus.* Among the pathogens, *Staphylococcus aureus* was highly susceptible to both the metal complexes. The present study concluded that synthesised complexes will be used as good drug of choice to manage the bacterial and fungal diseases after evaluating the in-vivo effect of metal complexes on experimental animal and clinical trials.

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