

Synthesis and Spectroscopic Studies of Bivalent Transition Metal Complexes of Co(II), Ni(II), and Ti(II) with Hydrazone-Hydrazones

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Abstract

Presently some transition metal complexes of Co (II), Ni (II), and Ti (II) have been synthesized. Newly synthesized complexes having formula [Co (II) (EDPIDAH)] (BF₄)₂, [Ni (II) (EDPIDAH)] (BF₄)₂, and [Ti (II) (EDPIDAH)] (BF₄)₂. (Here M = bivalent metal ion and EDPIDAH = 4-Ethyl -2, 6-pyridinediacetyl-N,N'-iminodiacetic acid dihydrazone) were characterized by elemental analysis, IR, ¹H NMR and UV-Vis spectroscopy. All the complexes were found colored, stable in air. The coordinated water molecules were confirmed by IR and thermal data, while the geometry of the complexes was confirmed by electronic spectra, magnetic moment measurements and ESR analysis.. Schiff base and its metal complexes were screened for *in vitro* antimicrobial activity and it was observed that metal complexes show enhanced biocidal activities as compared to corresponding ligand and metal salts.

Key point; dihydrazone, antimicrobial, ida

1. Introduction

Hydrazones play an important central role in bioinorganic chemistry [1-7]. It is a category of organic substances having R₁R₂C=NNH₂ formula. They are related to aldehydes and ketones by the replacement of the oxygen with the N-NH₂ group. Hydrazones, generally derived by the reaction of hydrazides with aldehydes or ketones [8-9]. The α - H atom of hydrazones ligand is more nucleophilic than ketones because α - H atom of hydrazones ligand is ten times more acidic as compared to ketones [10-11]. Hydrazone moiety (ligand) shows diversity in biological activities. Since 1850 [12] thousands of thousand mono, di substituted acylhydrazones have been discovered. Hydrazones are synthesized by simple refluxing. Double bond between carbon and hydrogen of the hydrazones is responsible for showing isomerism (syn and anti isomers). Geometrical isomerism could play an important role in the biocidal activities of the hydrazones .they have an azomethine-NH-N=CH- proton. Due to this proton hydrazones plays an important role in the field of drug development. Presently, hydrazone-hydrazones seek a great attention of researchers due to their versatile biological properties.

2. Instruments and Reagents use -

The solvents and chemicals were used of A.R grade. Elemental analysis was carried out in (CDRI) lucknow .FTIR spectra, absorption spectra, Molar conductance, analysis were performed at Dr. H.S. Gaur University, Sagar-M.P.

3. Synthesis of macrocyclic Ligand and M(II) complex-

Compounds were synthesized by precursor condensation method [13,14] IDA dihydrazide have been synthesized from their corresponding dimethyl esters of IDA acid and hydrazine hydrate . The nickel (II) and Cobalt (II) Coplexes were synthesized by the following general method. Equimolar amounts of either IDA dihydrazide (1.01 M) or TPA acid dihydrazide (0.01 M) and Ethyl-2,2diacetylpyridine (1.70g .0.01M) was mixed in ethyl alcohol. The mixture refluxed over a water- bath around 5 hrs. When it was concentrated to 1/3 V of its original then solution was cooled overnight. Yellowish- white crystals precipitate out .The crystals were then washed repeatedly with ethyl alcohol and diethyl ether, dried in vacuum over anhy.CaCl₂ in a desiccator.

4. Physical measurements

Elemental analysis of carbon,hydrogen and nitrogen was carried on (carlo Erbal 1106) elemental analyzer .Magnetic susceptibility is determined at room temperature by Gao balance , CuSO₄.5H₂O is used as a calibrant. Hitachi FT-MMR model R-600 spectrophotometer is used for ¹H-NMR spectrum..Chemical shift calculated in PPM ,DMSO was used as a solvent and tetra metylsilane as a internal standered. IR spectram recorded by using FT-IR spectra

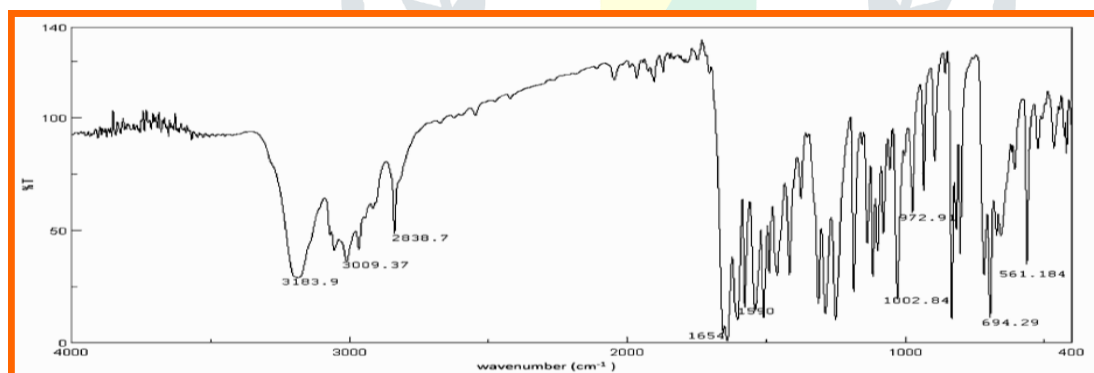
Table-1.-Analytical data of M(II) COMPLEXES

Compound	Colour	m.p.(°C)	% Analysis Found (Cal.)			Metal
			C	H	N	
Co[EDPIDAH]BF ₄) ₂ Co [C ₁₃ H ₁₉ N ₉ O ₇] (BF ₄) ₂	white	246	29.75 (29.82)	6.80 (6.83)	43.43 (43.47)	10.02 (9.85)
[TPADH]	White	120	33.24 (34.95)	6.74 (6.79)	34.71 (34.79)	

Ni[EDPIDAH]BF ₄) ₂ Ni[C ₁₃ H ₁₉ N ₉ O ₇] (BF ₄) ₂	(Yellowish- white)	260	38.24 (38.25)	3.28 (3.35)	11.10 (11.18)	9.32 (9.38)
Ti[EDPIDAH]BF ₄) ₂ Ti[C ₁₃ H ₁₉ N ₉ O ₇] (BF ₄) ₂	(Yellowish sky blue)	280	39.15 (39.46)	3.49 (39.36)	8.28 (8.34)	8.69 (8.75)

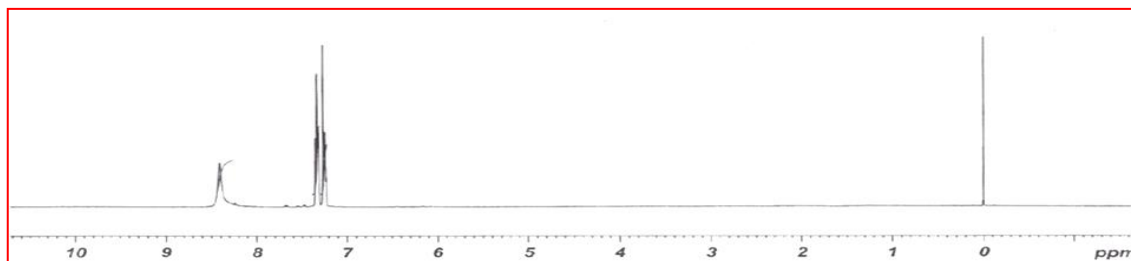
5. IR spectrum

Infrared Spectra of M (II) complexes have been recorded in KBr over the range 4000-400 cm⁻¹. In FTIR spectra Three characteristics bands are observed for ligand in range of 3160-3200, 300-3100, and 2800-2900 cm⁻¹ to (-N-H), and azomethine (-C=N), amide carbonyl (-C=O) stretching respectively. During complex formation deprotonation of bonded (-NH) group and the oxygen of amide carbonyl to metal ion is confirmed by the lower shifting of the band. The ν (C=N) band is shifted to lower region 3100-3180 cm⁻¹ that shows the formation of the complex. the N of azomethine group is coordinated to the Mⁿ⁺, which was again confirmed by observation of the red shift in the ν (N-N) and frequency from 850 to 976 cm⁻¹ region. A new band is appear in the complex at 2835.7 and 1654 cm⁻¹ are attributed the >C=N-N=C< group.



6. ¹H NMR spectral determinations

Spectrum (complex-1) was recorded at 500 mega hertz.. The objective is done on chemical shifts the basis of multiplicities and coupling constants J. We got 1 more singlet at 0-9.2, which is obtained to be coupled with a proton of H (12) (8-8.7) from the 1H.1H correlation spectra. It is assigned to be of H(13) to which a doublet is expected . One singlet of three protons at δ =2.2 was responsible to the CH₃group protons which are magnetically and chemically equivalent .Fig.1

Figure.1, ^1H NMR (complex-1)

7. Antimicrobial Activities

Antimicrobial activities were tested against *E. coli*, *S. aureus*, *A.niger* and *C. albicans* by disc/well diffusion method. NG Kandile et.al.[15] synthesized hydrazones and screened for antimicrobial sensitivity against *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*, *Streptococcus faecalis*. The synthesized compounds $[\text{Co}(\text{II})(\text{EDPIDAH})](\text{BF}_4)_2$, $[\text{Ni}(\text{II})(\text{EDPIDAH})](\text{BF}_4)_2$, and $[\text{Ti}(\text{II})(\text{EDPIDAH})](\text{BF}_4)_2$ also tested against these microbes as activity of salts, activity of ligands and then activity complexes checked against microbes. Ligands show much more reactivity than salts while complexes exhibit just double killing efficiency against these microbes.

Table-2. data of antimicrobial study of ligands, salts and complexes

S.No.	Compounds	Bacteria		Fungi	
		E. Coli	S. aureus	A. niger	C. albicans
1.	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.860	0.890	0.850	0.876
2.	(IDADH)	5.205	5.201	5.207	5.209
3.	[TDPH]	6.255	6.270	6.248	6.270
4.	$[\text{Co}(\text{EDPIDAH})](\text{BF}_4)_2$	7.485	7.520	7.590	0.520
5.	$[\text{Co}(\text{EDPTDPH})](\text{BF}_4)_2$	7.355	7.105	7.105	0.105
6.	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.816	0.816	0.826	0.836
7.	$\text{TiCl}_2 \cdot 6\text{H}_2\text{O}$	0.890	0.886	0.895	0.896
8.	$[\text{Ni}(\text{EDPIDAH})](\text{BF}_4)_2$	8.235	8.110	8.110	8.110
9.	$\text{Ti}[(\text{EDPIDAH})](\text{BF}_4)_2$	7.230	7.105	7.105	7.105

Results

Coordination compounds famous for their bioactivities but are also often rather toxic [16, 17] Coordination of metals with organic ligands would be an interesting planning for activity enhancement [18] or reduction of toxicity. In present work it is demonstrated that coordination of metal salts to hydrazones might improve

the pharmacological performance of both ligands as well as metal [19, 20] Physical and analytical data show that metal complexes have general composition [Co (II) (EDPIDAH)] (BF₄)₂, [Ni (II) (EDPIDAH)] (BF₄)₂, and [Ti (II) (EDPIDAH)] (BF₄)₂. All complexes are solid, colored, and stable towards air and moisture at room temp., All are soluble in DMF and DMSO .

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