

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF NICKEL (II) COMPLEXES WITH SCHIFF BASES

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Abstract

The synthesis and spectroscopic studies of some Ni(II) complexes with poly dentate Schiff bases are reported here. These Schiff bases were derived by condensing carbonyl oximes-like isonitrosoacetophenone, α -benzyl monoxime, isonitroso acetyl acetone with amines like sulphanilic acid.. The characterization of the complexes was done on the basis of elemental analysis, molar conductivity, spectral studies like and (ir uv ,visible, pmr) Anti-bacterial activity.. On the basis of these analysis it was concluded that Ni(II) complexes exhibit Octahedral binuclear geometry with $M_2L_2Cl_2 \cdot 4H_2O$ stoichiometry. The metal complexes have been screened for their antibacterial activity.

Keywords: Ni(II) complexes, Schiff bases, Structural analysis, HPEIBSA, HBEIBSA, HAMEIBSA.

Introduction

Progress in the field of Coordination chemistry has received considerable significance because of its importance in chemical industry and life itself. Schiff bases contain azomethine ($>C=N$) group as functional group and hence act as an effective ligand. Transition metal complexes of Schiff bases have witnessed a great deal of interest in the recent years because of their chemical, pharmacological [1-3]. and analytical applications [4]. In addition the presence of nitrogen and oxygen donor atoms in the complexes act as stereospecific catalyst for many reactions like oxidation ,reduction .hydrolysis and possess antibacterial activity .In this paper, Co andNi(II) the synthesis, characterization of some complexes with polydentate Schiff base ligands are reported.

Methodology

Chemicals

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) & used without further purification. Distilled solvents were used throughout the experiments.

Techniques

Metal content was determined in the laboratory by the reported methods [5]. C, H and N analysis were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the 4000-400 cm^{-1} region using a FTIR spectrum one supplied by Perkin Elmer instrument. The electronic spectra were recorded on Beckman Spectrophotometer, diffuse reflectance spectra of solid complexes taken on Carl-Zeiss VSU -2P spectrophotometer. The 1H NMR spectra were recorded on a VXR-300S Varian Super Nuclear Magnetic Resonance spectrophotometer using TMS as an internal standard. ESR Spectra recorded on a variance-Line-112 using TCNE as standard. TGA analysis was carried out using a Shimadzu DT-30 recording thermal analyser in an inert atmosphere of nitrogen, from room temperature to 900 $^{\circ}C$.

Synthesis of Schiff bases complexes

The Metal complexes of Schiff base were synthesized *in situ* condensing ethanolic solution of 0.01 mol of carbonyl oximes, namely Isonitrosoacetophenone HINAP [6]. α -Benzyl monoxime, HBMO [6]. Isonitrosoacetylacetone HINAA [6]. respectively with 0.01 mol of aqueous solution of sulphanilic acid and metal salt in 1:1:1 stoichiometric ratio and pH of the solution was raised to ~8 with 0.1 N NaOH solution when 1-phenyl 1-hydroimino ethylidene iminobenzene 4-sulphonic acid (HPEIBSA), 1,2diphenyl 1-hydroxyimino ethylidene iminobenzene 4-sulphonic acid (HBEIBSA) and 1-acetyl 2-methyl 1-hydroimino ethylidene imino benzene 4-sulphonic acid (HAMEIBSA) complexes of Ni(II) were respectively obtained digested on water bath for about half an hour. The solid precipitated was filtered off, washed with repeatedly with hot water followed by 50% alcohol and dried in vacuum and elemental analysis.

Results and Discussion

All the metal complexes are intensely coloured. They are thermally quite stable, as shown by their high decomposition temperatures, which indicate strong metal to ligand bonding solids. The complexes are insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride etc. but soluble in DMF and DMSO. The complexes dissolve in alkali like sodium hydroxide giving colour, indicating the presence of a free oxime group, suggesting oximino proton is not replaced during complexation. The elemental analysis show 1:1 ligand metal stoichiometry for all the complexes. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1. The molar conductivities of 1×10^{-3} mhos $\text{cm}^2 \text{mol}^{-1}$ solutions of the complexes in nitro benzene indicate their non-electrolytic nature [7].

The elemental analysis suggest 1:1 (metal: ligand) stoichiometry for all the metal complexes. They are formulated as $\text{M}_2\text{L}_2 \text{Cl}_2$. Here L represents HPEIBSA, HBEIBSA and HAMEIBSA.

Table 1. Physical and Analytical Data of the metal complexes

COMPLEX	Colour	M.P. ($^{\circ}\text{C}$)	Elemental Analysis							Molar conductance	eff
			M	C	H	N	S	Cl			
$\text{Ni}_2(\text{L}_1)_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Green	162	13.2 (13.56)	38.2 (38.82)	3.0 (3.46)	6.2 (6.47)	7.0 (7.39)	7.8 (8.08)	.156	2.90	
$\text{Ni}_2(\text{L}_2)_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Dirty green	170	11.3 (11.54)	46.8 (47.17)	3.6 (3.73)	5.4 (5.50)	6.0 (6.29)	6.20 (6.88)	.701	3.20	
$\text{Ni}_2(\text{L}_3)_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Green	230	14.0 (14.23)	31.6 (32.1)	3.2 (3.63)	6.5 (6.78)	7.3 (7.75)	8.2 (8.48)	.130	4.48	

The infrared spectra of the free carbonyl oximes were compared with those of their complexes to determine the bonding mode of the ligands to the metal in the complexes. The strong C=O stretching vibrations, in HINAP is absent in the spectra of the metal complexes corresponding ligands. The observations confirm the successful replacement of carbonyl oxygen by imino nitrogen during Schiff base formation prior to the *in situ* formation of the complexes. The spectra of the parent carbonyl oximes shows strong and broad absorption band in the region 3300 cm^{-1} , which is due to $\nu_{\text{O-H}}$ band due to =NOH. The FT-IR spectra of the metal complexes reveal a band in the region $3246\text{-}3398$ attributed to O-H stretching vibrations of free =NOH group. It is also corroborated by PMR spectra of complexes. It may be concluded that sulphonic group is deprotonated on the basis of P_k values of $-\text{SO}_3$ group, The N-O stretching vibrations in the spectra of complexes are in the range of $883\text{-}1024 \text{ cm}^{-1}$ indicating a shift bonding through deprotonated free oxime. The coordination of azomethine nitrogen is confirmed by the presence of bands in the $1590\text{-}1598 \text{ cm}^{-1}$ region in the ligand which underwent a shift to a lower frequency after complexation [8]. All complexes show extra bands in the $515\text{-}618 \text{ cm}^{-1}$ and $413\text{-}492 \text{ cm}^{-1}$ region assigned to $\nu(\text{M-N})$ [9], and $\nu(\text{M-O})$ [10]. stretching vibrations. The medium or weak intensity bands at $355\text{-}380 \text{ cm}^{-1}$ is due to terminal M-Cl. This data is in good agreement with literature values [11]. Thus these

Schiff bases behave as multi-dentate ligand coordinating through the deprotonated sulphonic group and azomethine nitrogen. The presence of an ionised $-\text{SO}_3^-$ is indicated by 1120-1160 cm^{-1} . Selected IR bands for the ligands and their metal complexes are represented in Fig. 1 along with the IR spectral data (cm^{-1}) in Table 2.

Table 2. I.R. Spectral data of Co and Ni(II) complexes (cm^{-1})

Complexes	$\nu_{\text{O-H}}$ $\text{H}_2\text{O}/\text{NOH}$ (cm^{-1})	$\nu_{\text{C=N}}$ Azomethi ne (cm^{-1})	$\nu_{\text{C=N}}$ Oximino (cm^{-1})	$\nu_{\text{N-O}}$ (cm^{-1})	$\nu_{\text{M-N}}$ (cm^{-1})	$\nu_{\text{M-O}}$ (cm^{-1})
$\text{Ni}_2(\text{L}_1)_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	3543/3390	1596	1556	892	562	418
$\text{Ni}_2(\text{L}_2)_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	3545/3340	1595	1560	912	580	416
$\text{Ni}_2(\text{L}_3)_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	3540/3275	1598	1570	1024	523	453

PMR Spectral Data

COMPOUNDS	SOLVENT	OBSERVED SHIFT IN PPM	ASSIGNMENT
HINAP	DIOXAN	11.40	=NOH
		8.40	-CH
		7.80	-C₆H₅
	CDCl_3	9.06	=NOH
		8.13	-CH
		8.04	C₆H₅
HBMO	CDCl_3	11,1	=NOH
		7.8-8.3	-C₆H₅

HINAA	DIOXAN	11.35	=NOH -CH ₃
Ni ₂ (HPEIBSA) ₂ Cl ₂ 4H ₂ O	DMSO	12.6 6.9-7.7 8.2	=NOH C ₆ H ₄ -CH

The metal complexes indicate that oximino proton of HINAP observed at 11.4 δ in dioxan or at 9.06 δ in CDCl₃ is shifted to 12-12.6 δ this positive shift indicates the proton of the =NOH is not replaced. The μ eff.) complexes was found in the range of 4.03-4.48 B.M. which is greater than spin – only moment of 3.87 expected for three unpaired electron in high spin cobaltous complexes.

The actual value depends on the extent of orbital angular momentum(L) remaining associated with the ground state orbital triplet. Taking in to consideration the analytical data ,the observed magnetic moments of the complexes appear to be consistent with their expected octahedral geometry . Relatively lower observed magnetic moments values indicate the possibility of some antiferromagnetic exchange interaction which may be responsible, at least in part, for the observed magnetic moments. if so, it could be explained as due to the presence of unpaired electron in a t_{2g} orbital which is directed towards π orbitals of the bridging ligand, thus facilitating the interaction. Alternatively quenching of the orbital contribution may also be partly responsible for the observed magnetic moments. The experimentally observed room temperature magnetic moments for the Ni(II) lie in the range 2.9- 3.2 B.M and are within the limits usually observed for the hexa coordinated complexes of the metal ion.

The electronic spectra of the , Ni(II) complexes show charge transfer transition band in the range 23180-27770cm⁻¹ .They do not show d-d transition because of their poor solubility in suitable organic solvents.ref The diffuse reflectance

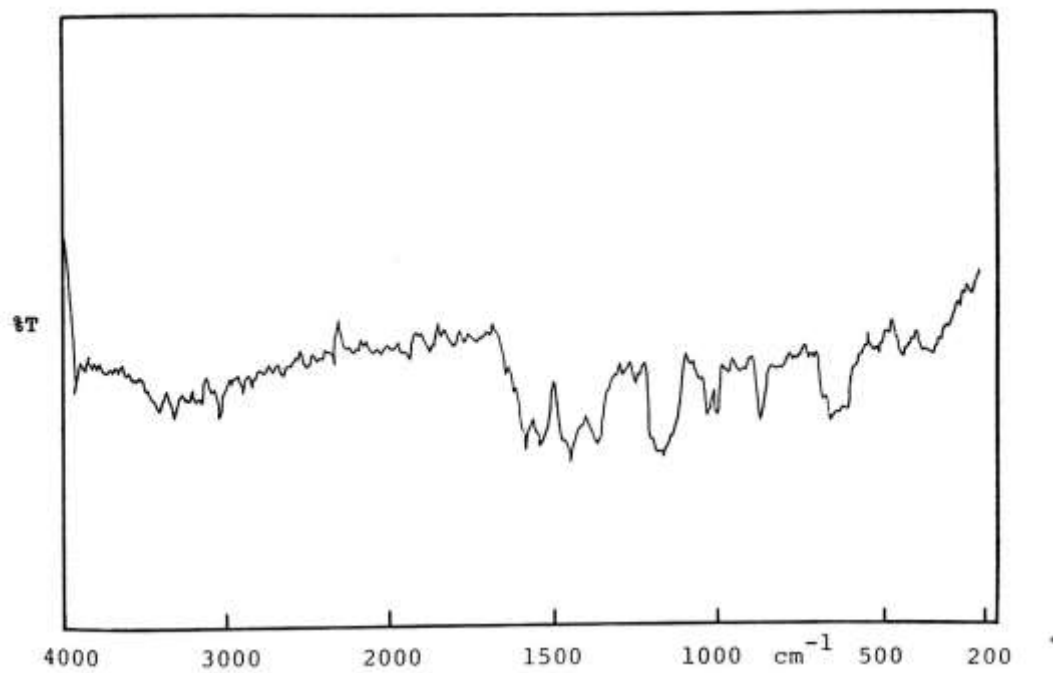
Ni₂(HPEIBSA)₂Cl₂.4H₂O

The complex Ni₂(HPEIBSA)₂Cl₂.4H₂O loses four coordinated water molecules in the temperature range 120°C-180°C. This loss is accompanied by an exothermic hump in the corresponding DTA curve. The order of reaction and the energy of activation for the dehydration reaction have been calculated by the method of Freeman and Carroll and are found to be unity and 3.661 kcal/mole, while the heat of dehydration is calculated to be 28.91 kcal/mole.

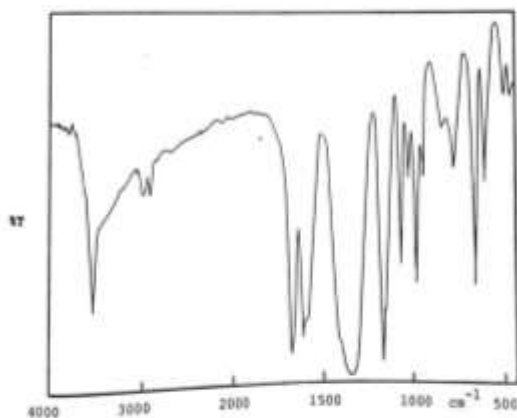
As shown in Table, the probable pattern of decomposition of the complex indicates further loss of a part of the ligand including four phenyl groups during the second stage of decomposition. The remaining portion of the organic moiety is lost during the next two steps of decomposition until the temperature of 700°C is reached. Above this temperature, the residue left corresponds to nickel oxide as indicated by its percentage weight which agrees well with the value calculated on the basis of the composition of the complex.

TABLE
Thermal Decomposition Data for
Ni₂ (HBEIBSA)₂ Cl₂.4H₂O

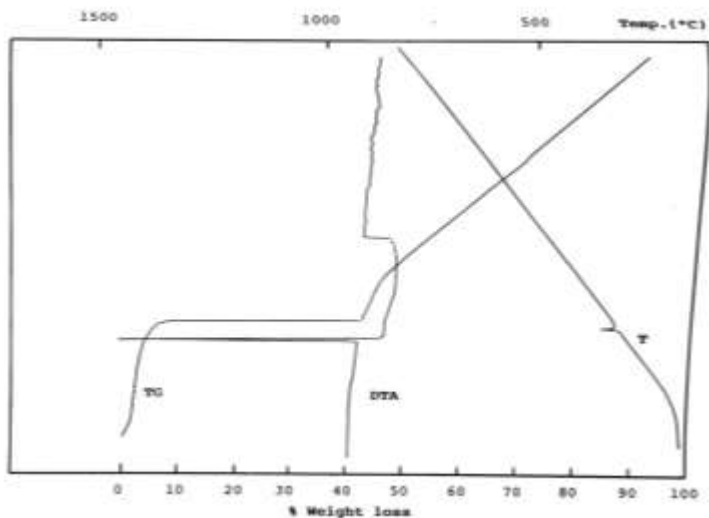
	Loss of Group	Temperature range (°C)	% Weight loss	
			Observed	Calculated
(I)	4H ₂ O N = 1.0 E = 36.61 k cal mol ⁻¹ ▲H = 28.91 k cal mol ⁻¹	~ 180	6.5	7.09
(ii)	4H ₂ O + 4(C ₆ H ₅) + 2(C=NOH)	~ 220	45.5	45.90
(iii)	4H ₂ O + 4(C ₆ H ₅) + 2(C=NOH) + 2(CN-C ₆ H ₄) + 2SO ₂	~ 440	80.0	81.40



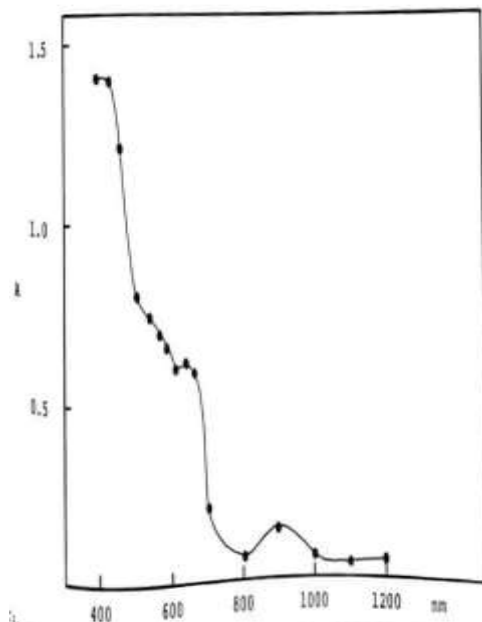
FTIR spectrum of $\text{Ni}_2(\text{HPEIBSA})_2 \cdot \text{Cl}_2 \cdot 4\text{H}_2\text{O}$.



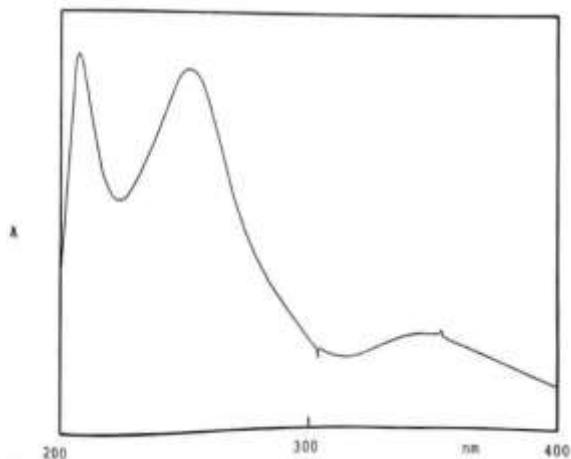
FTIR Spectrum of $\text{Ni}_2(\text{HAMEIBSA})_2 \cdot \text{Cl}_2 \cdot 4\text{H}_2\text{O}$



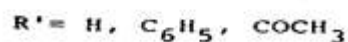
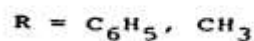
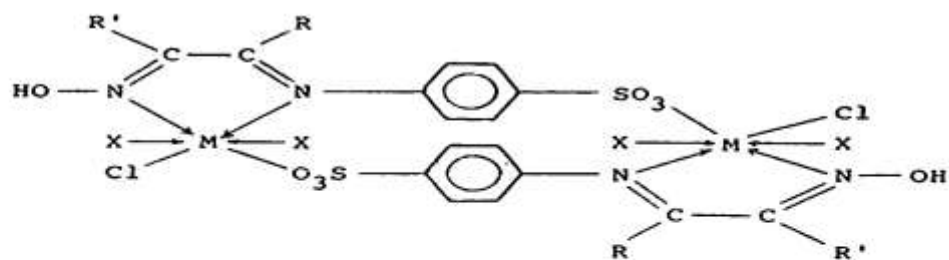
Thermogram of $Ni_2(HPEIBSA)_2.Cl_2.4H_2O$.



Diffuse reflectance spectrum of $Ni_2(HBEISA)_2.Cl_2.4H_2O$.



electronic absorption spectrum of $Ni_2(HBEIBSA)_2.Cl_2.4H_2O$.



Acknowledgement

The author is thankful to Dr. N.V. Thakkar, Department of Chemistry, The Institute of Science for his invaluable guidance for this work.

5. References

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