

NOTE

Synthesis, Characterisation and Biocidal Study of Transition Metal Complexes of Schiff Base Derived from 2-Hydroxynaphthaldehyde

BHARTI SAXENA and V.M. SAHAI*

Department of Applied Chemistry, Madhav Institute of Technology and Science (Jiwaji University), Gwalior, India

In the present work, we have synthesised some transition metal complexes of a Schiff base derived from 2-hydroxynaphthaldehyde. The structures of the new chelates were established by analytical and spectral data. Some of the metal chelates were found active against selected bacteria and fungi.

Key Words: Transition metal chelates, Schiff base.

Many Schiff bases are known to have various biological activities. Recently many Schiff bases and their metal complexes are reported to have antimicrobial activity.^{1,2} The Schiff bases synthesized by the interaction of naphthaldehyde derivatives with various amines are found to have significant biocidal activity. These observations lead to the synthesis of new *o*-hydroxynaphthaldehyde derivatives containing one naphthalene ring substituted with one amino group and a functional group. In the present work we describe the synthesis of a Schiff base of 2-hydroxynaphthaldehyde and its Ni(II), Co(II), Cu(II), Zn(II) complexes.

2-Hydroxynaphthaldehyde-2-anthranilic Acid (HNAA): 0.05 M ethanolic solution of 2-anthranilic acid was mixed with 0.05 M solution of 2-hydroxynaphthaldehyde, and the mixture was refluxed over a water bath for 2 h. The separated solid was recrystallised from proper solvent to give the desired compound (m.p. 254°C).

Synthesis of metal complexes

All the metal complexes were synthesized by the following general method. A reaction mixture containing 0.0025 M ethanolic solution of the respective metal acetate and 0.0025 M ethanolic solution of the ligand was subjected to reflux for 1-2 h. On cooling, the coloured complex was separated out and recrystallized in ethanol (yield 61-68%).

The melting points recorded are uncorrected; the ligands and their corresponding metal complexes were analysed for C, H and N in U.D.C.T., Bombay. Metals were estimated by their standard methods after decomposing the complexes with 1 : 1 mixture of concentrated H₂SO₄ and HNO₃. Infrared spectra were recorded in the range 4000-400 cm⁻¹ in KBr pellets employing Perkin-Elmer 157 IR spectrophotometer.

A broad band in the region of 3560-3480 cm⁻¹ in the IR spectra of free ligand is

due to —OH stretching vibrations, which has disappeared in the spectra of their metal complexes, concluding that the coordination of the ligand to the metal ion has taken place through the deprotonation of phenolic group. The $>C=N$ stretching frequency in the region of $1640\text{--}1545\text{ cm}^{-1}$ in the ligand shifts to lower frequency ($1630\text{--}1570\text{ cm}^{-1}$) in their metal complexes. This shift in the frequency shows the involvement of azomethine nitrogen ($>C=N$) in coordination. In metal complexes, the coordinated water molecules are indicated by a sharp band in the region of $3350\text{--}3300\text{ cm}^{-1}$ followed by another band at coordinated water molecules. Some new bands developed in the IR spectra of metal complexes in the region of $635\text{--}625\text{ cm}^{-1}$ and $435\text{--}420\text{ cm}^{-1}$ are probably due to vibration of $\nu(M-O)$ and $\nu(M-N)$ bands respectively.³ These bands are further evidences in favour of the coordination of ligands to metal through azomethine, phenolic and carboxylate groups.

The possibility of complexation can be predicted by the comparative study of IR spectrum of a free ligand and its metal chelates⁴. In the metal chelate the water molecule exists as a ligand and not as water of crystallization. Results of elemental analysis are in agreement with the calculated value and thus molecular weight of the compound could be calculated.

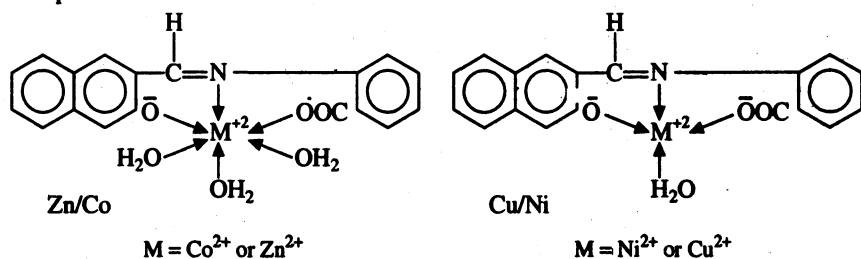


TABLE-1

KEY IR SPECTRAL DATA (cm^{-1}) OF HYDROXYNAPHTHALDEHYDE ANTHRANILIC ACID LIGAND AND ITS METAL(II) COMPLEXES

	Metal complexes				Probable assignments
	Co(II)	Ni(II)	Cu(II)	Zn(II)	
3550 (b)	-	-	-	-	—OH (phenolic) stretching
3480 (b)	-	-	-	-	—OH str. vib. of free COOH gp
-	3300 (b)	3320 (b)	3310 (b)	3300 (b)	Coord. water molecule
1680 (s)	1660 (b)	1670 (s)	1670 (s)	1660 (s)	$>C=O$ stretching
1600 (s)	1570 (s)	1570 (s)	1570 (s)	1565 (s)	$>C=N$ Stretching
1545 (m)	1530 (m)	1535 (m)	1530 (m)	1530 (m)	Asymm. str. of COO^-
1350 (m)	1340 (m)	1335 (m)	1335 (m)	1330 (m)	Symm. str. of COO^-
1450 (s)	1440 (s)	1440 (s)	1450 (m)	1460 (m)	Aromatic $C=C$ stretching
950 (m)	-	-	-	-	OH bending (acid)
-	875 (s)	870 (s)	880 (m)	875 (s)	Coord. water molecule
-	625 (s)	630 (s)	635 (s)	625 (s)	$\nu(M-N)$
-	425 (m)	425 (m)	435 (m)	420 (m)	$\nu(M-O)$

TABLE-2
PHYSICAL AND ANALYTICAL DATA OF HYDROXYNAPHTHALDEHYDE-
ANTHRANILIC ACID AND ITS METAL COMPLEXES

S.No.	Compd.	m.f. (m.w.)	Colour	Analysis, Found (Calculated)		
				C	H	N
1.	HNAA	C ₁₈ H ₁₃ O ₃ N (291)	Yellow	73.6 (74.22)	4.3 (4.66)	4.6 (4.81)
2.	HNAA-Co(II)	C ₁₈ H ₁₇ O ₆ N-Co (402)	Brown	54.2 (53.73)	3.9 (4.22)	3.6 (3.48)
3.	HNAA-Ni(II)	C ₁₈ H ₁₃ O ₄ N-Ni (366)	Light green	57.0 (59.01)	4.0 (3.55)	4.1 (3.82)
4.	HNAA-Cu(II)	C ₁₈ H ₁₃ O ₄ N-Cu (371)	Yellow	57.5 (58.29)	3.8 (3.55)	3.6 (3.83)
5.	HNAA-Zn(II)	C ₁₈ H ₁₇ O ₆ N-Zn (408)	Yellow	50.2 (52.94)	3.8 (4.16)	3.6 (3.43)

Biocidal activity of a potentially active molecule is altered on its complexation with a suitable metal ion⁵ because metals function as enzyme activators. The antibacterial and antifungal activity of these compounds on selected bacteria *S. aureus* (Gram +ve) and *E. coli* (Gram -ve) and some fungi *A. niger* and *C. albicans* was carried out. Serial dilution method was used for testing anti-microbial activity of Schiff base as well as its metal complexes.

Culture media for growing bacteria consist of peptone, yeast extract, beef extract, Dextrose and Agar. pH is maintained about 6.5. Culture media for growing fungi consist of peptone, dextrose and agar. pH adjusted to 5.4 with suitable buffer.

The culture media used for slant and broth was sterilized by moist heat sterilization in an autoclave at 121°C using 15 lbs pressure for 15 min. Solutions of all the test compounds were prepared by dissolving 1 mg/mL of the substance in ethanol. All the solutions were sterilized by passing through G-5 sintered glass crucible.

The observed results of MIC(s) of Schiff base and its metal chelates are presented in Table-3. MIC values reveal an enhancement of the antimicrobial activity of Schiff base in the form of its metal chelates.

TABLE-3
MINIMUM INHIBITORY CONCENTRATION (MIC) IN µg/mL OF HNAA AND ITS
METAL COMPLEXES

S.No.	Compound	Bacteria		Fungi	
		<i>S. Aureus</i>	<i>E. Coli</i>	<i>A. Niger</i>	<i>C. Albicans</i>
1.	HNAA	100	100	50	50
2.	HNAA-Co(II)	50	25	25	25
3.	HNAA-Ni(II)	25	25	50	50
4.	HNAA-Cu(II)	25	25	25	25
5.	HNAA-Zn(II)	30	50	50	50

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