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Spectroscopic and Antimicrobial Studies of Some 2-hydroxybenzilidene-3-aminophenol Complexes

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ABSTRACT

The Schiff base 2-hydroxybenzilidene-3-aminophenol was synthesized and used for the preparation of coordination complexes with some transition and inner transition metals. All the compounds were characterized by elemental analysis, IR and UV spectral studies, and molar conductivity studies. The antimicrobial activities were checked against four different bacterial species *E.coli*, *B.subtills*, *S.auereus* and *P.aeruginosa* and also screened for activity against the fungus *Rhizopus*, the common bread mould.

Key words: Schiff base, ligand, complex, transition metal, lanthanides, antibacterial and antifungal studies

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INTRODUCTION

Schiff bases and their transition and inner transition metal complexes, containing nitrogen and oxygen donor atoms play important role in biologic and inorganic research and have been studied extensively due to their unique coordination and biological properties [1-2]. They have also been employed as anticancer, antihypertensive and anti-inflammatory agents. As a continuation of our earlier works [3] on the complexes containing hydroxyl groups, we report herein the synthesis of some novel Schiff base complexes containing bivalent and trivalent metals. Also the possible structures have been characterized by conventional physico-chemical methods. Finally the compounds were screened for antibacterial activity against *E.coli*, *B.subtilis*, *S.aureus* and *P.aeruginosa* and antifungal activity against the common bread mould, *Rhizopus*.

MATERIALS AND METHODS

All chemicals and solvents were of analytical reagent grade. 2-hydroxybenzaldehyde was distilled before use. The transition metal salts were prepared from the corresponding metal carbonates by standard method [4]. Similarly the lanthanide nitrates were prepared from the metal oxides, Ln_2O_3 (>99.95%).

Experimental

The melting points were determined on a Thosniwal melting point apparatus. The Schiff base and the complexes were analyzed for carbon, hydrogen and nitrogen content on a Heracus CHN rapid analyzer. The metal content in the complexes were determined gravimetrically as oxides. Molar conductance in DMF and acetonitrile in 10^{-3}M solutions were measured at room temperature using an Elico CM-180 conductivity meter with a dip type cell of platinum electrodes. (Cell constant = 0.986 cm^{-1}). The IR spectra of the complexes and ligand were recorded in the range $400\text{-}4000\text{ cm}^{-1}$ on a Shimadzu IR-470 spectrophotometer in KBr disc. The electronic spectra in ethanol solution (10^{-3}M) were recorded in the range $200\text{-}900\text{ nm}$ on a Shimadzu UV-160A spectrometer.

Synthesis of 2-hydroxybenzilidene-3-aminophenol (H_2L)

3-Aminophenol (0.109g,) in 20 mL ethanol was mixed with 2-hydroxybenzaldehyde (0.122g,) in 20 mL ethanol. The mixture was refluxed for 2 hours on boiling water bath and evaporated to dryness at room temperature. The orange solid was filtered, washed with 50% ethanol and ether and dried in a desiccator over anhydrous CaCl_2 . The ligand is recrystallised from ethanol.

Synthesis of Transition Metal Complexes $[\text{M}(\text{HL})(\text{H}_2\text{O})_3]\text{X}$: (Ia)

To the refluxing solution of the Schiff base (L) (0.11g,0.5mmol) in 30 ml acetonitrile, added 0.5mmol aqueous solution of the transition metal salt $\text{MX}_n \cdot m\text{H}_2\text{O}$ (where $\text{M}=\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ and $\text{X} = -\text{ClO}_4$, $-\text{NO}_3$ and Cl) drop wise and refluxed for 2 hours and concentrated. The precipitate formed was washed with 50% ethanol and then ether. It is dried over anhydrous CaCl_2 and recrystallized from ethanol.

Synthesis of Lanthanide Complexes $[\text{ML}_2(\text{H}_2\text{O})_3](\text{NO}_3)_3$: (Ib)

The Schiff base (0.213g, 1mmol) in 20 mL ethyl acetate was refluxed on a water bath. To the boiling solution, 0.5 mmol solution of the lanthanide nitrate, $\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ where $\text{Ln} = \text{Ce}(\text{III})$ and $\text{Er}(\text{III})$ in ethanol was added drop by drop. The mixture was refluxed for 3 hours, concentrated by evaporation and kept overnight. The precipitate was washed with 50% ethanol and ether and dried in a desiccator over anhydrous CaCl_2 . The complexes are purified by recrystallisation using ethanol.

Antibacterial Studies

The bacterial subcultures of *E.coli*, *B.subtilis*, *S.aureus* and *P.aeruginosa* were obtained from School of Environmental Sciences, Cochin University of Science and Technology, Kochi. The test of antibacterial activity adopted disc diffusion method [5], using DMSO as solvent. Nutrient agar was used as the culture medium which consists of beef extract, albumins and agars. The culture medium, experiment ware and the paper discs were sterilized for 30 minutes at 120°C; the culture medium was transferred to petry dishes and frozen at about 37°C. The medium was inoculated with the bacteria using a platinum wire loop. The blotting paper discs were prepared by dipping in the sample solution (0.0003g Schiff base/ complex in 1mL DMSO) and then dried in an incubator. These discs were applied on the bacteria grown in agar plates. They were allowed to incubate at 37°C and the inhibition zone around the discs was measured as zone diameter in millimeters. Blank tests showed that DMSO solvent did not affect the antimicrobial activity of the compounds.

Antifungal Studies

Antifungal activities were checked against the fungus *Rhizopus*, the common bread mould. It was grown on soaked bread in petry dishes. The sample solution (1mg in 1ml DMSO) was applied over it. Kept for one week in open air and growth of the fungus was assessed.

RESULT AND DISCUSSION

The elemental analysis and some physical data of the compounds are given in Table 1. All compounds are non hygroscopic solids, insoluble in water but soluble in all common organic solvents like ethanol, acetonitrile, DMF and DMSO. The molar conductivity data (Table 2) suggests 1:1 electrolytic nature for the transition metal complexes and 1:3 nature for inner transition complexes [6].

IR Spectra

The characteristic bands of the Schiff base and the complexes are given in Table3. The ligand shows a strong band at 1589.3 cm^{-1} characteristic of ν (C=N) stretching vibration[7]. But in complexes, the azomethine frequency shows a marked downfield shift indicating coordination through N atom. The coordination through phenolic oxygen after deprotonation is evidenced by the disappearance of ν (OH) broad band near 3300 cm^{-1} and appearance of ν (C-O) phenolic band at 1200-1295 cm^{-1} . This is further supported by ν (M-O) around 450 cm^{-1} . In nitrate complexes, presence of uncoordinated nitrate ion is confirmed by a very strong band at 1380 cm^{-1} and a medium band at 824 cm^{-1} due to ν_2 and ν_3 vibrations of nitrate group of D_{3h} symmetry [8]. The characteristic strong band at 1110 cm^{-1} in perchlorate complexes is assigned to the ν_3 vibration of ionic perchlorate group[9].

UV-Visible Spectra

The electronic spectra of all the compounds show two maxima at 33900 and 39200 cm^{-1} corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions[9]. In the complexes, $n \rightarrow \pi^*$ band is found to be red shifted in the region 33300-33500 cm^{-1} and the $\pi \rightarrow \pi^*$ band is blue shifted in the region 39800-42000 cm^{-1} . The f-f band is observed in Er(III) and Ce(III) complexes near 20000 cm^{-1} . The d-d transitions in Co(II) complexes are observed at 9000, 18000 and 19000 cm^{-1} . The Ni(II) complexes exhibited transitions at 11000, 18000 and 23500 cm^{-1} . The Cu(II) complexes displayed a broad band centered at 16500 cm^{-1} .

Antimicrobial Activities

The results of antibacterial activities are displayed in Table 4. The ligand and all the complexes showed prominent activity against all the bacteria *E.coli*, *B.subtilis*, *S.aureus* and *P.aeruginosa*. All the complexes are

Table 1 Analytical Data of the Ligand and the Complexes

Molecular formula	Mol Wt	Colour	MP °C	Yield	% found / (calculated)			Metal %
					C	H	N	
H ₂ L	213.0	Yellowish orange	261	71%	60.67 (61.97)	5.56 (5.16)	6.19 (6.57)	--
[Co(HL)(H ₂ O) ₃]ClO ₄	423.0	Reddish brown	>300	75	29.29 (29.68)	3.85 (3.10)	10.51 (9.80)	11.23 (12.02)
[Co(HL)(H ₂ O) ₃]NO ₃	385.0	Brown	260	80	33.79 (33.21)	4.99 (4.25)	3.75 (3.71)	14.70 (14.13)
[Co(HL)(H ₂ O) ₃]Cl	358.5	Brown	245	80	35.15 (34.62)	5.12 (5.39)	3.93 (3.32)	115.10 (14.75)
[Ni(HL)(H ₂ O) ₃]ClO ₄	424.7	Red	>300	65	30.12 (29.40)	3.20 (3.93)	9.89 (9.22)	12.86 (12.40)
[Ni(HL)(H ₂ O) ₃]NO ₃	386.7	Yellowish red	240	85	45.26 (45.93)	3.80 (4.12)	10.2 (10.21)	13.25 (13.91)
[Ni(HL)(H ₂ O) ₃]Cl	360.2	Yellowish red	253	80	49.95 (49.26)	4.15 (4.65)	10.9 (11.2)	13.98 (14.22)
[Cu(HL)(H ₂ O) ₃]ClO ₄	429.5	Black	>300	75	29.71 (29.09)	5.03 (5.71)	9.82 (10.25)	16.22 (16.59)
[Cu(HL)(H ₂ O) ₃]NO ₃	391.5	Brownish black	265	82	45.71 (45.23)	6.71 (6.22)	11.21 (11.75)	18.21 (18.95)
[Cu(HL)(H ₂ O) ₃]Cl	365.0	Brownish black	278	79	48.22 (48.39)	7.32 (7.17)	12.01 (11.89)	19.75 (19.31)
[Ce(H ₂ L) ₂ H ₂ O](NO ₃) ₃	771.2	Brown	280	80	33.57 (33.10)	3.07 (3.17)	6.72 (6.98)	18.24 (18.88)
[Er(H ₂ L) ₂ H ₂ O](NO ₃) ₃	798.0	Brown	265	75	31.39 (31.92)	2.87 (3.02)	6.28 (6.02)	20.27 (20.79)

Table 2 Conductance Data

Empirical formula/ Molecular formula	λ_m $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	
	DMF	Acetonitrile
H ₂ L	–	–
[Co(HL)(H ₂ O) ₃]ClO ₄	82	135
[Co(HL)(H ₂ O) ₃]NO ₃	79	141
[Co(HL)(H ₂ O) ₃]Cl	82	133
[Ni(HL)(H ₂ O) ₃]ClO ₄	82	162
[Ni(HL)(H ₂ O) ₃]NO ₃	83	159
[Ni(HL)(H ₂ O) ₃]Cl	80	155
[Cu(HL)(H ₂ O) ₃]ClO ₄	75	127
[Cu(HL)(H ₂ O) ₃]NO ₃	76	129
[Cu(HL)(H ₂ O) ₃]Cl	80	132
[Ce(H ₂ L) ₂ H ₂ O](NO ₃) ₃	239	377
[Er(H ₂ L) ₂ H ₂ O](NO ₃) ₃	220	382

Table 3 IR Spectral Data of the Ligand and the Complexes

	$\nu(\text{OH})$ (cm ⁻¹)	$\nu(\text{CH=N})$ (cm ⁻¹)	$\nu(\text{C-O})$ (cm ⁻¹)	$\nu(\text{M-N})$ (cm ⁻¹)	$\nu(\text{M-O})$ (cm ⁻¹)	$\nu(\text{NO}_3)$ (cm ⁻¹)	$\nu(\text{ClO}_4)$ (cm ⁻¹)
H ₂ L	3319b	1589.3s	1232.4m	-	-	-	-
[Co(HL)(H ₂ O) ₃]ClO ₄	3292b	1563s	1210m	612w	456w	-	1119s
[Co(HL)(H ₂ O) ₃]NO ₃	3265b	1561s	1211m	615w	455w	1380s	-
[Co(HL)(H ₂ O) ₃]Cl	3190b	1569s	1210m	609w	455w	-	-
[Ni(HL)(H ₂ O) ₃]ClO ₄	3200b	1566s	1202m	602w	469w	-	1112s
[Ni(HL)(H ₂ O) ₃]NO ₃	3275b	1560s	1201m	596w	472w	1385s	-
[Ni(HL)(H ₂ O) ₃]Cl	3282b	1552s	1216m	596w	470w	-	-
[Cu(HL)(H ₂ O) ₃]ClO ₄	3222b	1562s	1220m	605w	459w	-	1125s
[Cu(HL)(H ₂ O) ₃]NO ₃	3230b	1555s	1220m	609w	460w	1382s	-
[Cu(HL)(H ₂ O) ₃]Cl	3252b	1561s	1219m	609w	460w	-	-
[Ce(H ₂ L) ₂ H ₂ O](NO ₃) ₃	3200b	1567s	1206m	592w	423w	1382s	-
[Er(H ₂ L) ₂ H ₂ O](NO ₃) ₃	3258b	1563s	1203m	585w	423w	1382s	-

b= broad; s= strong; m= medium; w= weak

Table 4 Antibacterial Activity Results

	E. coli	B. subtilis	S. aureus	P. aeruginosa
H ₂ L	++	+	+	+
[Co(HL)(H ₂ O) ₃]ClO ₄	+++	+	++	+
[Co(HL)(H ₂ O) ₃]NO ₃	+++	++	+++	+++
[Co(HL)(H ₂ O) ₃]Cl	++	+	++	++
[Ni(HL)(H ₂ O) ₃]ClO ₄	+++	++	+	+
[Ni(HL)(H ₂ O) ₃]NO ₃	+++	+++	++	++
[Ni(HL)(H ₂ O) ₃]Cl	++	+	++	+
[Cu(HL)(H ₂ O) ₃]ClO ₄	+++	+++	++	++
[Cu(HL)(H ₂ O) ₃]NO ₃	+++	+++	+++	+++
[Cu(HL)(H ₂ O) ₃]Cl	+++	++	++	++
[Ce(H ₂ L) ₂ H ₂ O](NO ₃) ₃	++	++	+	++
[Er(H ₂ L) ₂ H ₂ O](NO ₃) ₃	+	+	+	+
DMSO	-	-	-	-

Percentage of Inhibition: Below 5mm = (-), 5mm-10mm = (+), 10mm-15mm = (++) , 15mm-20mm = (+++)

Fig:1 Structure of Transition metal Complexes [M(HL)(H₂O)₃]X where M=Co(II), Ni(II) and Cu(II) and X = -ClO₄, -NO₃ and -Cl

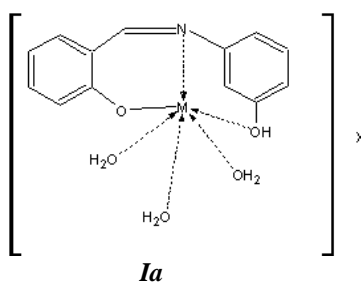
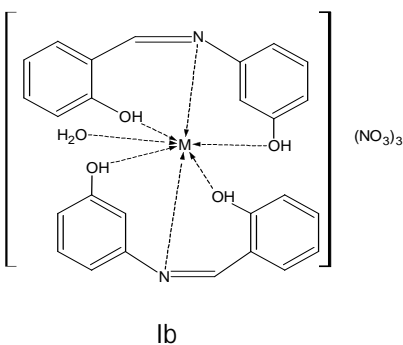


Fig:2 Structure of Lanthanide Complexes [M(H₂L)₂(H₂O)](NO₃)₃ where M = Ce(III) and Er(III)



found to be more active compared to the parent Schiff base. This is because on chelation [11], the charge on the metal ion is reduced to a minimum increasing the lipophilicity of the complexes. This leads to the break down of the permeability barrier of the bacterial cell and thus retards the normal cell processes. Among the complexes formed from different metals, Cu(II) complexes showed maximum inhibition. Also comparing the anionic species, nitrate complexes were found to inhibit bacterial growth most effectively. Antifungal studies against the fungus, Rhizopus on soaked bread showed that both ligand and all the complexes exhibited almost hundred percent inhibitions.

In summary, we have synthesized some transition and inner transition metal complexes from the Schiff base 2-hydroxybenzylidene-3-aminophenol with Co(II), Ni(II), Cu(II), Ce(III) and Er(III) and characterized by conventional methods. The possible structures are given in Fig: 1-3. Promising results are obtained when screened for antibacterial and antifungal activities.

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