

Short communication

Synthesis and antifungal potential
of Co(II) complexes of 1-(2'-hydroxyphenyl) ethylideneanilinesH.S. Hothi^a, Anju Makkar^{a,*}, J.R. Sharma^b, M.R. Manrao^a^a Department of Biochemistry and Chemistry, Punjab Agricultural University, Ludhiana 141 004, India^b Department of Plant Pathology, Punjab Agricultural University, Ludhiana 141 004, India

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Abstract

Synthesis of Co(II) complexes from 1-(2'-hydroxyphenyl)-ethylideneaniline and its N-phenyl derivatives has been described and their structures have been established on the basis of elemental analysis and IR studies. The complexes have been screened for their antifungal potential against *Alternaria alternata*, *Fusarium oxysporum* and *Myrothecium roridum* by spore germination inhibition method and the results are discussed.

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1. Introduction

Schiff bases in general have been shown to be biological active [1]. The effect of presence of various substituents in the phenyl rings of aromatic Schiff bases [2–7] on their antifungal activity has been reported. It has been found that in general the complexation of Schiff bases with iron, copper, zinc and other metals influences their antifungal activity [8–12]. With this view and in continuation of work on the study of Schiff bases and their metal complexes, it was proposed to synthesise cobalt complexes from 1-(2'-hydroxyphenyl) ethylideneaniline and its N-phenyl derivatives and to study their antifungal potential and the results of this work are being communicated in this paper.

1-(2'-Hydroxyphenyl)-ethylideneaniline and its N-phenyl derivatives (Ia–Va), synthesised by condensing 2'-hydroxyacetophenone with aniline, 4-anisidine, 4-phenetidine, 4-hydroxyaniline and 4-chloroaniline, respectively, in equimolar ratio [13], on refluxing with cobalt acetate tetrahydrate in ethanol yielded cobalt complexes Ib–Vb, respectively. On the basis of elemental analysis, the metal to ligand stoichiometry of 1:2 has

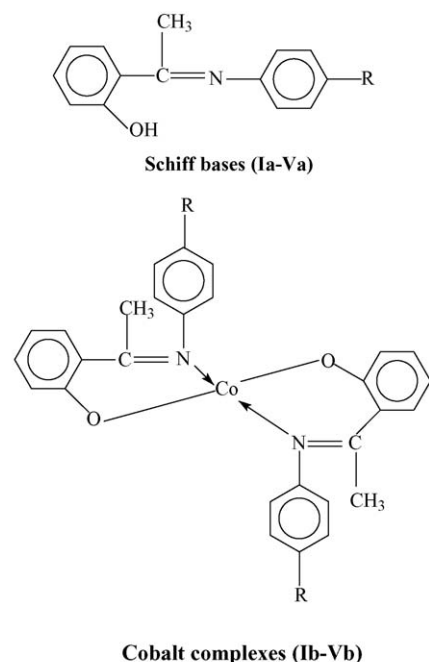
been proposed for Co(II) complexes. The proposed structure (Fig. 1) for these complexes has the support of IR spectra.

The IR spectra of the ligands showed a weak band in the region 3000–3100 cm⁻¹ instead of a strong band around 3300–3400 cm⁻¹ due to phenolic group, perhaps due to intramolecular hydrogen bonding between phenolic hydrogen and nitrogen of azomethine linkage. The band disappeared in the IR spectra of cobalt complexes indicating the deprotonation of phenolic group by the cobalt ion suggesting that –OH group of the ligand has been utilised in the formation of metal–oxygen bond. The high intensity band at 1300–1355 cm⁻¹ assigned to phenolic C–O linkage shifted towards higher wave number of 1335–1400 cm⁻¹ confirming the involvement of OH group in bond formation with metal ion. These observations are in accordance with the already reported results [14].

A strong band in the Schiff bases at 1645–1608 cm⁻¹ region underwent a negative shift of 30–40 cm⁻¹ in cobalt complexes confirming the formation of co-ordinate bond from azomethine nitrogen to metal ion. From the analytical data and infrared studies, it has been concluded that the ligand has linked through phenolic oxygen and co-ordinated through azomethine nitrogen behaving as a bidentate ligand (Fig. 1). The complexes along with their characteristics are recorded in Table 1 and their IR spectra in Table 2.

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Compound	R
Ia, Ib	H
IIa, IIb	OCH ₃
IIIa, IIIb	OC ₂ H ₅
IVa, IVb	OH
Va, Vb	Cl

Fig. 1. Structures of Schiff bases and their cobalt complexes.

Table 1
Characteristics of Co(II) complexes

Compound	Yield (%)	M.p. (°C)	Colour	Molecular formula
Ib	64	> 250	Light pink	Co(C ₁₄ H ₁₂ NO) ₂
IIb	72	238	Greyish brown	Co(C ₁₅ H ₁₄ NO ₂) ₂
IIIb	68	> 250	Light pink	Co(C ₁₆ H ₁₆ NO ₂) ₂
IVb	70	> 250	Dark brown	Co(C ₁₄ H ₁₂ NO ₂) ₂
Vb	65	243	Light pink	Co(C ₁₄ H ₁₁ NOCl) ₂

Table 2
IR spectral data (cm⁻¹) of ligands and cobalt complexes

Compound	ν _{C=N}		ν _{C=O}	
	a	b	A	B
I	1644	1615	1302	1349
II	1608	1582	1308	1352
III	1609	1584	1307	1346
IV	1645	1604	1355	1399
V	1610	1589	1311	1346

a Ligands (Ketimines), b Cobalt complexes.

The Co(II) complexes (Ib–Vb) were screened in vitro for their antifungal potential against *Alternaria alternata*, *Fusarium oxysporum* and *Myrothecium roridum* by spore germination inhibition technique [15] at various concentrations. The results have been expressed in terms of ED₅₀ values in Table 3. The complexes have been found to be very effective against *A.*

Table 3
Antifungal potential of ligands and cobalt complexes

Compound	ED ₅₀ values (ppm) against					
	<i>A. alternata</i>		<i>F. oxysporum</i>		<i>M. roridum</i>	
	A	b	a	b	a	b
I	*	17	*	78	*	85
II	*	18	936	132	350	92
III	*	20	680	150	330	70
IV	*	170	*	373	*	360
V	*	18	770	155	*	62
Cobalt acetate tetrahydrate	–	40	–	16	–	65
Indofil M-45	28	28	–	–	32	32
Bavistin	–	–	8	8	–	–

*: More than 1000 ppm; a: ligands (Ketimines); b: Cobalt complexes.

alternata, less against *M. roridum* and least against *F. oxysporum*. Four of the test complexes (Ib, IIb, IIIb and Vb) have ED₅₀ values less than 20 ppm against *A. alternata* that is lower than the ED₅₀ value (28 ppm) shown by Indofil M-45. Four of the test complexes (Ib, IIb, IIIb and Vb) have ED₅₀ values less than 100 ppm against *M. roridum*. The ED₅₀ values of the test complexes against *F. oxysporum* varies from 78 to 373 ppm. A comparison of antifungal potential of the Co(II) complexes (Ib–Vb) with the parent Schiff bases (Ia–Va) has shown that the complexation of Schiff bases with cobalt enhances their antifungal potential manifold in general and this enhancement is much more pronounced against *A. alternata* and *M. roridum*.

2. Experimental

The melting points reported are uncorrected. The compounds gave satisfactory elemental analyses. The IR spectra were recorded on a Perkin–Elemer FTIR in KBr.

3. General procedure for the preparation of Schiff bases

2'-Hydroxyacetophenone (0.1 mol) was taken in methanol (60 ml) in a beaker (250 ml). To this was added aniline/substituted aniline (0.1 mol). The mixture was warmed for a few minutes to get a clear solution and allowed to stand at room temperature for 4–5 hours. The crude solid that separated out, was filtered and recrystallised from methanol to get pure crystals of 1-(2'-hydroxyphenyl)-ethylideneaniline (Ia) or its N-phenyl derivatives (IIa–Va).

4. Synthesis of Co(II) complexes

Cobalt acetate tetrahydrate (0.002 mol) taken in ethanol (5 ml) was added to solution of 1-(2'-hydroxyphenyl)-ethylideneaniline/its N-phenyl derivative (0.004 mol) dissolved in ethanol (10 ml). The colour of the solution was changed to yellowish green. The mixture was refluxed for 2–3 hours on a water bath. A coloured solid separated out which was filtered, washed with ethanol and dried under reduced pressure over fused calcium chloride to get the respective cobalt complex (Ib–Vb).

5. In vitro screening for antifungal potential

The stock solution of each compound Ib–Vb was prepared by dissolving each chemical (20 mg) in absolute alcohol (0.5 ml) and the volume was made to 10 ml with sterilised distilled water. The resultant solution of 2000 ppm concentration was diluted serially to 1000, 500, 250, 100, 50, 25 and 10 ppm concentrations by sterilised distilled water.

Ten-day-old cultures of the fungi were taken from PDA slants and sterilised distilled water was added to form the suspension of the spores. After shaking the tube thoroughly, the suspensions were filtered through three layers of sterilised cheese cloth under aseptic conditions to remove mycelial and agar bits. Standardised spore suspension (1×10^6 spores per ml) was made with the help of haemocytometer.

The cavity slides were used to study the spore germination inhibition by the compounds. Small droplet (0.02 ml) of the spore suspension and the compound solution in equal quantity were seeded in the cavities of the slides. These slides were placed in petriplates lined with moist filter paper and incubated at 24 ± 1 °C for 20 hours. The germination of the spores was recorded and the per cent spore germination inhibition was calculated.

The antifungal potential has been expressed as ED_{50} values calculated by log probability method.

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