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SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE DERIVED FROM 4-BENZOYL-3-METHYL-1-PHENYLPYRAZOL-5-ONE AND P-ANISIDINE

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ABSTRACT

Schiff base derived from condensation of (4-benzoyl-3-methyl-1-phenylpyrazol-5-one and p-anisidine). This Schiff base ligand was then complexed with Ni(II), Co(II), Cr(III), Mn(II) metal salts. The resultant complexes were characterized by elemental analysis, IR Spectroscopy, UV-Vis. Spectroscopy, thermal stability, and magnetic susceptibility. The anti-microbial activity was analysed by ditch plate method.

Key words: Benzoyl derivative, Schiff base, Ni(II), Co(II), Cr(III), Mn(II), Characterization, Structures, Anti-microbial activity.

INTRODUCTION

Schiff bases are the compounds having (>C=N-) linkage. The transition metal complexes have a variety of applications in chemical world. The complexes have many anti-microbial activity over some gram positive and gram negative bacteria (*Bacillus subtilis*, *Staphylococcus aureus*, *Salmonella typhi* and *Eschirichia coli*). Many metal complexes of Schiff bases have medicinal and biological importance. Schiff bases and their metal complexes have paramount applications in the field of food[1] and dyes industry, agriculture, analytical chemistry, catalysis, and polymer science. They play a vital role in metabolic and toxicological functions in biological system[2,3]. The present paper describes synthesis, characterization and bacterial studies of Ni(II), Co(II), Cr(III), Mn(II) complexes of Schiff base derived from 4-benzoyl-3-methyl-1-phenylpyrazol-5-one and p-anisidine .

EXPERIMENTAL

All the chemicals used for synthesis were of AR grade. Solvents were double distilled before use. Classical method was used for the preparation of Schiff's bases i.e. by refluxing amines like p-anisidine.

Preparation of 4-benzoyl-3-methyl-1-phenylpyarazol-5-one

It is a benzoyl derivative of 3-methyl-1-phenylpyrazol-5-one ($C_{10}H_{10}N_2O$).

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Preparation of 3-methyl-1-phenylpyrazol-5-one

In an evaporating dish 50 g (49 mL, 0.384 mol) of redistilled ethylacetoacetate and 40 g (36.5 mL, 0.37 mol) of phenyl hydrazine were mixed together. The mixture was heated on a boiling water bath/sand bath for about 2 hrs with constant stirring. The heavy reddish syrupy liquid obtained was allowed to cool and about 100 mL of ether as added with constant stirring (vigorously), when a yellowish solid was obtained within 15 min. This solid is washed with ether to remove colour impurities. It was recrystallized from hot water.

Benzoyl derivative

The solid obtained (3-methyl-1-phenylpyrazol-5-one) was taken in a round bottom flask (5.22 g, 0.029 mol) and calcium hydroxide (3.87 g, 0.05 mol) and 1,4-dioxane (55 mL) were added. It was stirred at 70°C on a magnetic stirrer. To this hot mixture, benzoyl chloride (3.32 mL, 0.029 mol) was added drop wise with constant stirring. After completion of addition of benzoyl chloride, the mixture was kept at 70°C for 30 min. It was then refluxed for 3 hr at 110-115°C. The resulting mixture was added to a beaker containing crushed ice and HCl (5.4). The solid obtained was 4-benzoyl-3-methyl-1-phenylpyrazol-5-one. It was filtered, washed several times with water and dried at room temperature and recrystallized from 50% alcohol.

Preparation of Schiff's bases

1:1 mol of p-anisidine and Benzoyl derivative were mixed in a R. B. F with a few drops of HCl. Absolute alcohol was used as a solvent. Then this mixture was refluxed on a boiling water bath for about 2 hr and it was monitored by TLC. The hot solution was then poured in crushed ice, a greenish powdered precipitate was obtained.

Preparation of metal complexes

The ligand and metal salt were taken in the 2:1 stoichiometric ratio. The ligand was dissolved in minimum quantity of alcohol and the salt was dissolved in minimum quantity of water. Both the solutions were mixed with constant stirring. The pH was adjusted with 0.1 M NaOH (pH: 7.5-8.5). A coloured complex was formed. It was kept on boiling water bath on magnetic stirrer for 1 hr.

RESULTS AND DISCUSSION

Elemental analysis data (Table 1) confirms the molecular formula of Schiff base and its metal complexes. All these complexes are coloured and quite stable having melting point in the range of 140-203°C. As per the analytical data, the Schiff base derived from 4-benzoyl-3-methyl-1-phenylpyrazol-5-one and p-anisidine forms ML_2 type of metal complexes. All these complexes are soluble in organic (non-polar) solvents.

In the electronic spectrum of the Schiff Base in alcohol, an intense absorption was observed at 205 nm in the ultra-violet region, which can be assigned to $n \longrightarrow \sigma^*$ transitions which are mainly the intraligand transitions. In the spectra of complexes, this absorption shows some shift towards the longer wavelengths due to complex formation.

The light green Ni(II) complex shows bands at 15,625 cm^{-1} (640 nm), 16,949 cm^{-1} (590 nm) and 23,809 cm^{-1} (420 nm) in the visible region due to the transitions[4],

$$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F) \quad \nu_1$$

$$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F) \quad \nu_2$$

$$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P) \quad \nu_3$$

respectively, which indicates an octahedral environment for Ni(II) ion.

The dark brown Co(II) complex shows two d-d transition bands at 18,867 cm^{-1} (530 nm) and 10,869 cm^{-1} (920 nm), which correspond to the following transitions,

$$4T_1g(F) \longrightarrow 4T_{1g}(P)\ \nu_3$$

$$4T_{1g}(F) \longrightarrow 4T_{2g}(F)\ \nu_1$$

The ν_2 band was not observed here. It has been frequently found in high spin octahedral complexes that ν_3 band involving one electron transfer is stronger than ν_2 band involving two electron transition. The ν_2 band appears as a shoulder or often does not appear at all[5].

Mn (II) complex shows absorption at 20,833 cm^{-1} (480 nm) and the transition was assigned to as

$$^6A_{1g}(S) \longrightarrow {}^4T_{2g}(G)$$

which corresponds to octahedral geometry around Mn(II) ion.

The six coordinated Cr(III) complex belongs to $3d^3$ system. It showed only two transitions at 16,949 cm^{-1} (590 nm) and 29,940 cm^{-1} (334 nm). The possible transitions are

$$^4A_{2g} \longrightarrow {}^4T_{2g}\quad \nu_1$$

$$^4A_{2g} \longrightarrow {}^4T_{1g}(F)\ \nu_2$$

$$^4A_{2g} \longrightarrow {}^4T_{1g}(P)\ \nu_3$$

This shows the octahedral geometry around Cr(III) ion

In the infrared spectrum of Schiff Base, a strong band was observed at 1620 cm^{-1}, which is due to the presence of azomethine group (>C=N-). However, in the metal complexes, this band is observed with some shift in the frequency range of 1610-1625 cm^{-1}, which confirms the coordination is through nitrogen atom of azomethine group. There are two additional bands found in all the metal complexes in the range of 540-670 cm^{-1} and 510-530 cm^{-1}, which were assigned as bending frequency of metal-nitrogen bond and metal-oxygen bond, which is absent in the Schiff Base.

The ligand showed a broad band centred near 3150-3450 cm^{-1}, which is assigned to ν_{OH} mode of pyrazolones nucleus at fifth position, It is absent in metal complexes, which further confirms the bond between metal and oxygen at fifth position. Neutral complexes of Ni(II), Co(II), Cr(III) and Mn(II) of the ligand show a broad band in the range of 3380-3150 cm^{-1}, which have significantly different characteristics from those bands due to ν_{OH} stretching vibration of the ligand, which is assigned as stretching frequency of water molecule. There is also a medium intensity band in the range of 625-750 cm^{-1} due to coordinated water molecule. Also the band attributed to δ_{OH} in the Schiff Base is absent in the metal complexes. This indicates involvement of oxygen in coordination to metal ion[6]. These values are given in Table 2.

The presence of coordinated water molecule is further confirmed by the results of thermal studies. From TGA-DTA analysis, it was shown that there is a weight loss in the range of 120-200°C corresponds to the number of water molecule.

Table 1: Elemental analysis of ligand and metal complexes

Samples	Molecular weight	Percentage of elements found (calc.)					Colour	Melting point
		%C	%H	%N	%O	%M		
Schiff Base	383	73 (75.19)	5.5 (5.48)	9.8 (10.96)	8.0 (8.35)		Green	
[(SB)$_2$Ni.2H$_2$O]	860.6	64.2 (67.08)	5.24 (5.12)	8.9 (9.78)	11.0 (11.18)	6.4 (6.82)	Dark green	163.7
[(SB)$_2$Co.2H$_2$O]	858.9	65 (67.22)	5.3 (5.13)	8.1 (9.80)	8.15 (8.05)	6.6 (6.64)	Green	142
[(SB)□Cr.2H□O]	853.9	66.2 (67.6)	5.1 (5.16)	8.1 (9.86)	12.1 (11.27)	6.0 (6.09)	Dark brown	203
[(SB)□Mn.2H□O]	856.9	67 (67.37)	5.3 (5.14)	8.8 (9.82)	12.2 (11.23)	6.2 (6.42)	Mud brown	140

Table 2: IR spectra of Schiff base and its metal complexes

Samples	ν_{OH}	$\nu_{C=N}$ (azo)	$\nu_{C=N}$ (pyro)	ν_{C-O} (phenolic)	ν_{C-H} (arom)	ν_{C-H} (aliph.)	δ_{OH}	δ_{H2O}	δ_{M-N}	δ_{M-O}	ν_{H2O}
Schiff Base	3495	1620	1490	1375	2980	2880	1250	-	-	-	
[(SB)$_2$Ni.2H$_2$O]	-	1625	1590	1430	3010	2895	1255	720	660	515	3350
[(SB)$_2$Co.2H$_2$O]	-	1625	1590	1440	3000	2890	1260	750	670	530	3150
[(SB)$_2$Cr.2H$_2$O]	-	1610	1580	1410	3000	2910	1250	625	610	510	3290
[(SB)$_2$Mn.2H$_2$O]	-	1620	1590	1375	3005	2920	1250	720	540	520	3380

The Schiff bases have slightly inhibited only gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*). Ni(II) and Co(II) complexes of Schiff Base also inhibited the growth of only gram positive bacteria. Therefore, it is highly active complex. Mn(II) complex inhibited only a single gram positive bacteria (*S. Aureus)*. The lest activity was shown by Cr(III) complex as no bacteria was inhibited. All these values are given in Table 3.

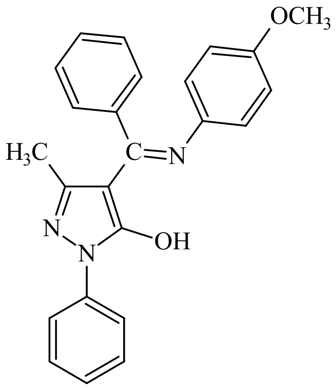
Table 3: Antibacterial activity of Schiff base of benzoyl derivative and p-anisidine

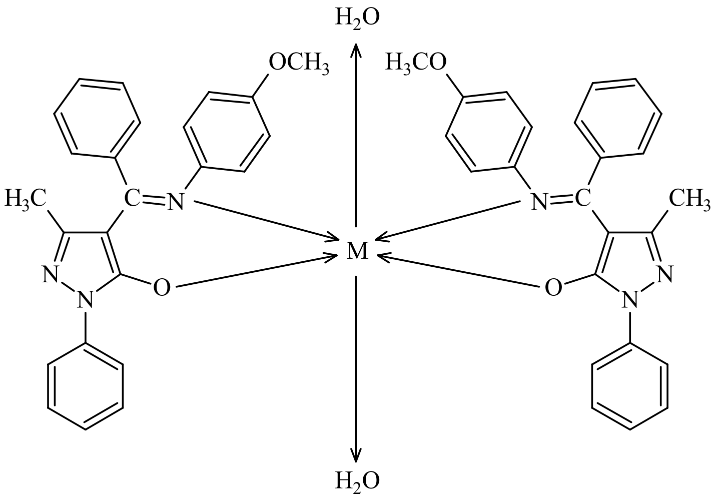
Compounds	Test organisms			
	B.subtilis	***S.aureus***	***E.coli***	***SPB***
Benzoyl derivative	-	-	+	+
Schiff base 1	-	-	+	+
Metal complexes of Schiff base				
Ni(II)	-	-	+	+
Co(II)	-	-	+	+
Cr(III)	+	+	+	+
Mn(II)	+	-	+	+

Note: "+" indicates inhibition of growth while "-" indicates no inhibition of growth

The antimicrobial activity of these complexes were tested using well established ditch plate method[7].

From the above studies, the following structure was proposed for Schiff base and its metal complexes, respectively.





M = Ni(II), Co(II), Cr(III) and Mn(II)

Note 1: For Cr(III) complex it is a cationic structure which is neutralised by chloride ions

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