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RESEARCH ARTICLE

Spectral and Biological studies of Manganese (II) and Cobalt (II) Complexes with Schiff Base Derived from 2-Thiophenecarboxylaldehyde and 2-nitrobenzoic Acid

A.V.G.S. Prasad*[1], P. Venkateswara Rao[1], P.S.S. Prasad[2]

[1]*Department of Chemistry, Nizam College (Autonomous), Hyderabad- A.P., India.*

[2]*Drug Control Administration, Hyderabad, India.*

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ABSTRACT

In the present study an intermolecular reductive Schiff base formation from nitro derivative and benzaldehydes is carried out in the presence of iron powder and dilute acid. Schiff base has been synthesized from 2-thiophenecarboxyldehyde and 2-nitro benzoic acid. Metal complexes of the Schiff base were also prepared from salts of Mn (II) and Co (II) in an alcoholic medium. The chemical structures of the Schiff-base ligand and its metal complexes were confirmed by various spectroscopic studies. The free Schiff base and its complexes have been tested for their antibacterial as well as antifungal activity by using disc diffusion method and the results discussed. The experimental results suggest that Schiff base derivatives are more potent in antibacterial and antifungal activities.

KEYWORDS

Schiff base, 2-thiophenecarboxyldehyde, 2-nitro benzoic acid, Metal complexes, Antibacterial activity, Antifungal activity

INTRODUCTION

Schiff bases are important intermediates for the synthesis of various bioactive compounds. Furthermore, they are reported to show a variety of biological activities including antibacterial, antifungal, anti-cancer and herbicidal activities.[1-5]

Schiff base (azomethine) derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities.[6]

Transition metal Schiff base complexes are used in various fields, such as medicine, agriculture, industries etc. For example, [Co(acac2-en)] in dimethylformamide, pyridine and substituted pyridines proved to be involved in oxygen metabolism.[7]

Oxovanadium Complexes have been found strongly active, against some type of Leukemia.[8] Transition metal complexes derived from a number of amino acids have been reported to have biological activity.[9]

Popova and Berova, reported that copper is good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis hepatitis, leprosy, anemia and Leukemia in children.[10]

In view of these facts we can clear about that Schiff base are important not only in medical chemistry, but also in organic synthetic chemistry. Schiff base perhaps are synthesized in various method. Traditional formation of Schiff bases from nitroarene starting materials requires a two-step process in which the

***Address for Correspondence:**
A.V.G.S. Prasad
Department of Chemistry, Nizam College (Autonomous)
Hyderabad- A.P (India)
E-Mail Id: avvasiva@gmail.com

nitroarene is first reduced to the aniline, then isolated, and subsequently condensed with the desired carbonyl. Recently, catalytic Schiff base formation from nitroarenes and carbonyls has been reported.[11-17]

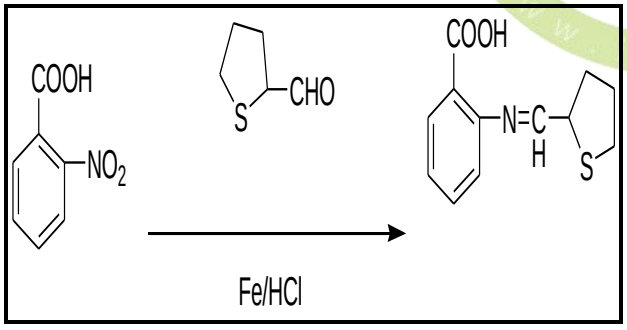
This paper reports the studies on manganese (II) and cobalt (II) complexes of the Schiff base derived from 2-nitrobennzoic acid and 2-thiophenecarboxylaldehyde.

MATERIALS AND METHOD

All glass wares used were well washed with detergent, rinsed with distilled water and dried in an oven. All chemicals and solvents used were of analytical grade (AnalaR or BDH) while 2-nitro benzoic acid, 2-thiophenecarboxyldehyde were obtained from Sigma-Aldrich and were used without further purification. Infrared spectral analysis were recorded using a Fourier transformed IR Genesis series model in Nujol in the range 400-4000cm^{-1}.

Synthesis of Schiff Base

The intermolecular reductive Schiff base formation of thiophene 2 carboxaldehyde and 2-nitro benzoic acid in ethanol/water yields a single product according to following reaction:



Hydrochloric Acid (0.13 mL, 4.5 mmol) was added to a mixture of 2 nitro benzoic acid (1.20 gr, 0.72 mmol), thiophene 2 carboxaldehyde (1.195r, 0.72 mmol), and iron powder (0.409 g, 7.32 mmol) in 24 mL of EtOH–H_2O (2:1 v/v) solution. The reaction was heated to 65°C for 1.5 h before being filtered while hot. The filtrate was extracted using CH_2Cl_2 (2 × 25 mL) after which the organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo to yield 1.69g (70%). The melting point of the resulting schiff base was found to be 142-144°C. The color of the product is yellow.

Preparation of the Metal (II) Schiff Base Complexes

The metal (II) Schiff base complexes were prepared by mixing hot ethanol-water mixture (1:1) of the respective metal (II) chloride (1mmol) and hot ethanolic solution of the Schiff base (0.231g, 2mmol). The resulting mixture was refluxed for 1 hour and allowed to cool in an ice bath to precipitate the product, which was separated, washed with a 1:1 ethanol-water mixture and then diethyl ether.

RESULTS AND DISCUSSION

The prepared Schiff base is yellow, has melting point of 143^{o}C and percentage yield of 70%. The manganese (II) and cobalt (II) Schiff base complexes are light yellow, have decomposition temperature of 300 and 320^{o}C and percentage yield of 55 and 78%, respectively. These high values of decomposition temperature revealed that the complex compounds are quite stable.

The Schiff base is soluble in most organic solvents but insoluble in water, however, the manganese (II) and cobalt (II) Schiff base complexes are slightly soluble in most organic solvents except DMSO.

The molar conductance measurements of the complexes in 10^{-3} M DMSO determined are 16.73 and 16.95 ohm^{-1}cm^{2}mol^{-1}, for manganese (II) and cobalt (II) complexes, respectively, indicating their non-electrolytic nature. The IR spectral data of the Schiff base showed a band at 1600cm^{-1}, which is assigned to ν(C=N) stretching vibration, a feature found in Schiff bases.

This band is also observable in the complex compounds, suggesting that the Schiff base has coordinated to the respective metal (II) ions. The strong band observed in the free Schiff base at 3460cm^{-1}, is absent in the complex compounds, which suggests deprotonation of the Schiff base on coordination to the respective metal ion. The bands in the regions 515 – 516 cm^{-1} and 490 – 495 cm^{-1} are attributed to ν(M-O) and ν(M-N) stretching vibrations

respectively, confirming the coordination of the Schiff base to the respective metal ions. The broad band in the region 3390-3550cm^{-1} is accorded to *ν*(O—H) stretching vibrations, a feature indicating the presence of water.

Antimicrobial and Antifungal Screening

Antimicrobial activity of the synthesized compounds was screened using the disc diffusion method against selected pathogens. The compounds were dissolved in DMSO and sterilized by filtering through 0.45 µm millipore filter. Nutrient agar (antibacterial activity) and sabouraud dextrose agar medium (antifungal activity) was prepared and sterilized by an autoclave and transferred to previously sterilized petridishes.

After solidification, petriplates were inoculated with bacterial organisms in sterile nutrient agar medium at 45^{o}C, and fungal organism in sterile sabouraud's dextrose agar medium at 45^{o}C in aseptic condition. Sterile whatmann filter paper discs were impregnated with synthesized compounds at a concentration of 25,100 mg/disc was placed in the organism-impregnated petri plates under sterile condition. Antibiotic discs of gentamycin (100 µg/disc) and fluconazole (100 µg/disc) were used as positive control, while DMSO used as negative control. Then the plates were incubated for 24 h at 37 ± 1^{o}C for antibacterial activity and 48 h at 37 ± 1^{o}C for antifungal activity. The zone of inhibition was calculated by measuring the minimum dimension of the zone of no microbial growth around the each disc.

Schiff bases and their derivatives have been prepared by a simple and environmentally friendly reductive imination procedure.

This methodology uses only Fe powder in acidic EtOH/H_2O as a reducing agent which upon reduction spontaneously condenses with an aldehyde in situ. The structures of the synthesized compounds were supported by physical data and following spectral analysis.

The synthesized compounds therefore, present a new scaffold that can be used to yield potent antimicrobial compounds. It can be concluded that these compounds certainly holds great promise towards good active leads in medicinal chemistry.

CONCLUSION

Schiff bases and their derivatives have been prepared by a simple and environmentally friendly reductive imination procedure. This methodology uses only Fe powder in acidic EtOH/H_2O as a reducing agent which upon reduction spontaneously condenses with an aldehyde in situ. The structures of the synthesized compounds were supported by physical data and following spectral analysis.

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Table 1: Antimicrobial Activities of synthesized Schiff base and Derivatives Azetidinones

Compound	Bacteria and fungal along with zone of inhibition(mm)								
	S.Aureaus (µ/ml)			E.Coli(µ/ml)			A.Niger (µ/ml)		
	50	100	200	50	100	200	50	100	200
SB	---	---	10	15	05	10	---	10	15
SB Mn	10	20	05	5	10	15	10	15	15
SB Co	15	15	15	15	--	10	--	10	10
gentamycin	15	20	20	15	20	25	---	----	----
fluconazole	--	---	---	---	---	---	10	15	15

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