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Synthesis, Characterization and Antimicrobial Activity of Some Schiff Base Metal Chelates

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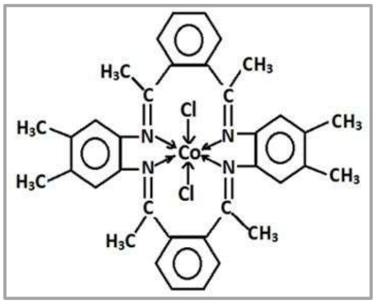
ABSTRACT

The aim of the study focuses on the synthesis of Schiff base metal complexes and their antimicrobial evaluation. A novel Schiff base was synthesized from 1,2-diacetylbenzene and 4,5-dimethyl-o-phenylenediamine, followed by complexation with Cu(II), Co(II), and Ni(II) ions. The resulting complexes were characterized using conductivity measurements, magnetic susceptibility, IR, and electronic spectroscopy. Their antibacterial activity was assessed using the disc diffusion method.

Graphical abstract:



Structure of the macrocyclic complex [Co(Mac)Cl_2]

Keywords: Coordination, Schiff base ligands, Infrared, UV-Vis, Antibacterial activity.

INTRODUCTION

Multidentate ligands and their metal complexes have played a crucial role in the advancement of coordination chemistry. Schiff bases, named after Hugo Schiff, are compounds containing a carbon-nitrogen double bond (C=N, azomethine group), with the nitrogen atom attached to an aryl or alkyl group rather than hydrogen. They follow the general formula R_1 R_2 C=N-R_3, where R_3 is an aryl or alkyl group, making Schiff bases stable imines [1-10].

Even after over a century of study, Schiff bases and their transition metal complexes remain of significant interest due to their chelating properties, ease of synthesis, and moderate electron-donating ability. These metal complexes have widespread applications, particularly in catalysis, where their roles continue to evolve. The chemistry of the carbon-nitrogen double bond is fundamental to the progress of chemical sciences, and Schiff-base compounds are extensively used in fine chemicals and pharmaceuticals.

Bioinorganic and medicinal chemists have devoted considerable attention to the relationship between metal ions and their complexes, particularly for their potential as antitumor and antibacterial agents. The interaction of metal ions with antibiotics can either enhance or suppress antimicrobial activity. However, in many cases, complexation with metals significantly improves the pharmacological activity of the ligand.

Several novel transition metal [Co(II), Ni(II), and Cu(II)] complexes of substituted pyridine Schiff bases have been synthesized and characterized using physical, spectral, and analytical techniques. The Schiff bases act as de-protonated tetradentate ligands in the complexation reaction with these metal ions [11-14]. Various transition and inner-transition metal complexes with bi-, tri-, and tetradentate Schiff bases containing nitrogen and oxygen donor atoms play essential roles in biological systems.
Certain metal elements, such as V, Cr, Mn, Fe, Co, Ni, Cu, and Zn, are indispensable for the normal functioning of living organisms. Present in trace and ultra-trace quantities, these transition elements play critical roles at the molecular level within biological systems and are known to form Schiff base complexes.

In this study, we report the synthesis, characterization, and antimicrobial activity of a series of MLX_2-type complexes, where M = Co(II), Ni(II), or Cu(II), and X = Cl^-, Br^-, NO_3^-, or ClO_4^-. The Schiff base ligands used are 16-membered macrocyclic compounds formed via a metal-catalyzed template condensation of 4,5-dimethyl-o-phenylenediamine and 1,2-diacetylbenzene.

MATERIALS AND METHODS

Chemicals: Most of the special chemicals used were of BDH, and Aldrich AnalR grade and were used without further purification. They are: 4,5-dimethyl O-phenylenediamine and 1,2-diacetylbenzene and metal(II) chlorides. Methanol was used as the medium in all preparations. The bacterial strains used are four Gram-negative bacterials: *Escherichia coli*. *Pseudomonas aeruginosa, Salmonella typhi* and *Shigella flexneri* and two Gram- positive bacteria’s *Bacillus subtilis* and *Staphylococcus aureus.*

Some representative preparation of macrocyclic complexes are described here. Analytical data for the complexes are given in table 1.

Preparation of Macrocyclic Coordination Compound [3,4:11,12dibenzo7,8:15,16di (3’4’di methylebenzo) Dichlorido-2,5,10,13tetramethyl1,6,9,14 tetraazacycl ohexadeca-1,5,9,13, tetra enatocohalt (II) represented by [Co (Mac)Cl$_2$]: Cobalt (II) chloride hexahydrate (2.3 g, 0.01 mol), 1,2-diacetylbenzene (2.3 g, 0.02 mol) and 4,5- dimethyl ortho phenylenediamine (2.7, 0.02 mol) were refluxed together in the molar ratio 1:2:2 in ethanolic solution medium for 6 hours. The reaction mixture was cooled to room temperature and brown colored solution was first formed, was concentrated by evaporation gradually. The brown product was filtered and washed with ethanol and dried over anhydrous $CaCl_2$ in a desiccator.

Table1. Microanalytical data of the ligands and their Metal(II) complexes

Compound	%Found Calculated			
	C	H	N	M
[Co(mac)Cl$_2$]	65.9	5.32	8.48	8.9
[Ni(mac)Cl$_2$]	64.15	4.45	9.21	9.67
[Cu(mac)Cl$_2$]	58.43	4.21	8.45	9.31

[3,4:11,12-dibenzo-7,8:15,16-di(3’4’-dimethylebenzo)]Dichloro-2,5,10,13-tetramethyl-1,6,9,14-

tetra-aza cyclo-hexadeca 1,5,9,13, tetraenato Nickel(II) represented by [Ni(Mac)Cl_2]: Nickel (II) chloride hexahydrate (2.3 g, 0.01 mol), 1,2-diacetylbenzene (2.3 g, 0.02 mol) and 4,5- dimethyl-ortho-phenylene-diamine (2.7 g, 0.02 mol) were refluxed together in the molar ratio 1:2:2 in ethanolic solution medium for 6 hours. The reaction mixture was cooled to room temperature and green coloured solution was first formed, was concentrated by evaporation gradually. The green product was filtered and washed with ethanol and dried over anhydrous $CaCl_2$ in a dessicator.

[3,4:11,12-dibenzo-7,8:15,16-di(3'4'-dimethylbenzo)] Dichlorido-2,5,10,13-tetramethyl-1,6,9,14 tetraazacyclo hexadeca-1,5,9,13-tetraenatocopper (II)represented by [Cu(Mac)Cl_2]: Copper (II) chloride hexahydrate (2.3 g, 0.01 mol), 1,2-diacetylbenzene (2.3 g, 0.02 mol) and 4,5- dimethyle-ortho-phenylene-diamine (2.7 g, 0.02 mol) were refluxed together in the molar ratio 1:2:2 in ethanolic solution medium for 6 hours. The reaction mixture was cooled to room temperature and blue coloured solution was first formed, was concentrated by evaporation gradually. The blue product was filtered and washed with ethanol and dried over anhydrous $CaCl_2$ in a dessicator.

Physical Measurements: The Elemental analysis for C, H, and N were determined using a Perkin Elmer model 2400 series 11 CHNS/O elemental analyzer. The percentage metals were determined by EDTA complexometric [15] titration.The molar conductivity measurements were done using a Conductivity Meter model 160 Orion with a cell constant of 0.82 ata concentration of dimethyl formamide (DMF) 10^{-3}M at room temperature were measured using direct reading conductivity meter, Systronics conductivity bridge type 305. Infrared spectra were recorded on FTIR-84005 Model Spectrophotometer using Nujol mull techniques in the range 200-4000cm^{-1}. Spectra were recorded for both the ligands and the complexes. Electronic spectra of the ligands and complexes were recorded using UV/Vis 2500 Series Spectrophotometer in the range 200-1100 nm using chloroform and DMF as the solvent. *Magnetic susceptibility data were recorded using Guoy method at room temperature using Hg[Co(NCS)4] as Calibrate.*

Anti-microbial Activity of Complexes: Antibacterial studies were made using the agar-well diffusion method [16]. The wells (6 mm in diameter) were dug in the media with the help of a sterile metallic borer with centers at least 24 mm apart (NCCLS, 1990). The recommended concentration of the test sample (1 mg mL^{-1} in DMSO) was introduced in the respective wells. The plates were incubated immediately at 37°C for 24 h. Activity was determined by measuring the diameter of the zones (mm) showing complete inhibition.

RESULTS AND DISCUSSION

The prepared ligands and their metal (II) complexes gave (%) yield ranging from 63 - 94. The complexes gave various shades of colours ranging from dark brown to dark green. This indicates that the ligands or complexes are probably pure. The conductivity values (Tables 2-6) of the ligands and the complexes in DMF at the concentration 10^{-3} mol. dm^{-3} are in the range 16-17 S cm^2 mol^{-1}. This indicates that they are non-electrolytes. The microanalysis data of the ligands and the metal (II) complexes are presented in table 1. In general, the complexes analyzed as [MCl_2 (Mac)], where M = Co(II), Ni(II) or Cu(II). This shows that the complexes are anhydrous.

Table 2. Band positions of electronic transitions (cm^{-1}) of the Co(II)complexes[Co(Mac)X_2]

Compounds	υ1	υ2	υ3	C.T.Band
[Co(Mac)Cl_2]	8760	17600	22300	34600
[Ni(Mac)Cl_2]	9400	18000	24900	34700
[Cu(Mac)Cl_2]	17600	-	-	26500

Table 3. Infrared spectral bands(cm^{-1}) of cobalt(II), nickel(II)

and copper(II), Complexes [M(Mac)X_2]

Complex	ν(C=N)	ν(M−N)	ν(M−X)
[Co(Mac)Cl_2]	1604	453	508
[Ni(Mac)Cl_2]	1609	457	577
[Cu(Mac)Cl_2]	1606	458	574

Table 4. Data of electrical conductance for the Co(II)complexes[Co(Mac)X_2]

Compounds	Scm^{2}mole^{-1}	solvent
[Co(Mac)Cl_2]	16	DMF
[Ni(Mac)Cl_2]	17	DMF
[Cu(Mac)Cl_2]	16	DMF

Table 5. Data of magnetic moment of the Co(ll)complexes[Co(Mac)X_2]

Complexes	Colour	μ_{eff}(B.M.)	Magneticnature
[Co(Mac)Cl_2]	Brown	4.7	Paramagnetic
[Ni(Mac)Cl_2]	Green	2.5	Paramagnetic
[Cu(Mac)Cl_2]	Blue	2.1	Paramagnetic

Table 6. Antimicrobial properties (primary screening) of Schiff bases and Metal(II) complexes

Compound	Inhibition zone diameter (mm)					
	Gram-negative				Gram-positive	
	Escherichia coli	*Pseudomonas aeruginosa*	*Salmonella typhi*	*Shigella flexneri*	*Bacillus subtilis*	*Staphylococcus aureus*
[Cu(Mac)Cl_2	22	16	21	14	21	16
[Co(Mac)Cl_2]	20	18	19	19	16	18
[Ni(Mac)Cl_2]	21	20	22	21	19	18

The IR spectra (Table 3) of the Schiff base ligand, showed bands resulting from the bands corresponding to (C=N), (M-N) and (M-X) stretchings were observed in the 1604-1616, 453-478 and 508-577 cm^{-1} regions respectively in both the ligands. The comparison of the IR spectra of the ligand and their metal (II) complexes indicated that the ligand is coordinated to the metal ions in different ways. The band appearing at(C=O) 1714- 1725 cm-^{1} (N-H) 3430 due to 1,2-diacetyl benzene and dimethyl 0-phenylenediamine in the ligand is shifted to lower frequency by 2-10 cm^{-1} in the complexes, indicating the participation of the azomethine nitrogen in coordination with the metal ion. Further evidence of the coordination of this Schiff-base ligand with the metal ions was shown by the appearance of weak frequency new bands at 453-478 and 508-577 cm^{-1}. These were assigned [**17-24**] to the metal-nitrogen (M-N) and metal-chlorine (M-Cl) vibrations, respectively.

The electronic spectra of the ligands and the metal complexes were determined in DMF in the range 200–700 nm. On the basis of previous assignments of related complexes [**13, 25-28**] band I,II and III represent transitions around 8760–17600, 16500 –18000 and 22100–24900 cm^{-1} respectively. The broad band at 22100–24900 cm-^{1} is assigned to d-d transition of the metal ions. The positions of the seb and sin the spectra of the metal complexes are consistent with the expected octahedral or tetrahedral geometry. Antibacterial activity of the Schiff base and its corresponding metal(II) complexes were determined against four Gram-negative (*Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi* and Schigella flexineri and two other Gram Positive *Bacillus subtilis and Staphylococcus aureus bacterial stains.*

The Schiff base compound exhibited varying degrees of inhibitory effects (low to moderate) on the growth of different tested strains (Table 5 and Figure 1).

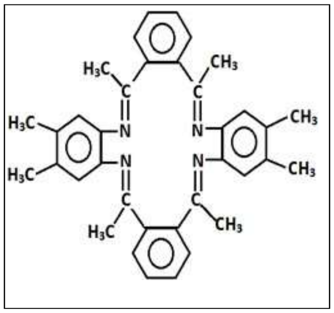


Figure 1. Structure of ligand (Mac).

The Schiff base, L1 showed no inhibitory action against the Gram-negative species, *Salmollella typhi* and *Shigella flexneri*, and the Gram-positive species, *Bacillus subtilis*. In contrast, the growth of all the Gram- negative and Gram-positive species was inhibited by all the metal complexes under investigation. These results are similar to other reports in the literature [27, 29], which stated that biologically inactive compounds become active and less biologically active compounds become more active upon coordination. In comparison, the uncomplexed ligand in present work has been shown to be less active than the metal complexes.

The preliminary screening showed that the compounds $NiCl_2$ (Mac) and $CuCl_2$ (Mac), are the most active against both Gram-negative and Gram-positive organisms. The MIC of all the three active compounds varies from 10-100 µg mL^{-1}. The compound [$CuCl_2$(Mac)] proved to be the most active one. It inhibited the growth of *Salmonella typhi, Shigella flexneri* and *Bacillus subtilis* at 10 µg mL^{-1} concentration. This study may serve as a basis for the chemical modifications directed towards the development of a new class of antibacterial agents. The complexes are multi-colored, the ratio of metal to ligand are 1:2 in all the metal complexes as confirmed by their microanalysis. The complexes are non-electrolytes as confirmed from their conductivity measurements. The electronic spectral data suggest a plausible octahedral or tetrahedral geometry around the metal ions as shown in the proposed structures (Figure 2).

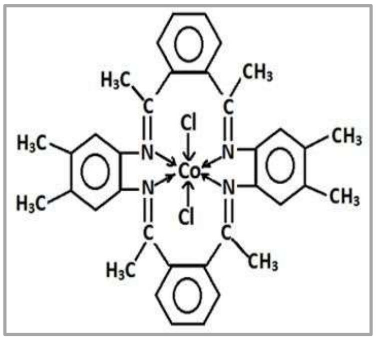


Figure 2. Structure of the macrocyclic complex [$Co(Mac)Cl_2$]

APPLICATION

Schiff base metal chelates have diverse applications spanning biological, analytical, and industrial fields, including acting as catalysts, antimicrobial, antifungal, antitumor, antioxidant, antiviral agents in biological fields, and in metal ion analysis and removal.

CONCLUSION

The Stereo chemical environment of the metal ions in each case is octahedral. The 16 membered ligand behaves in a tetradentate manner utilizing all of its nitrogen donor atoms. The anions are also coordinated to the metal ions in a unidentate manner. The broad nature of electronic spectral bands suggests tetragonal distortion in the complexes. The proposed structures of the ligand and metal (II) complexes (taking Co as representative metal) are shown in figures 1 and 2. The *in vitro* antimicrobial screening of the complexes confirmed their potency against most of the microorganisms used in this study.

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