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RESEARCH ARTICLE

MICROWAVE SYNTHESIS, SPECTRAL AND ANTIMICROBIAL STUDIES OF SOME SCHIFF BASE METAL COMPLEXES

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Abstract

Eco-friendly synthesis and green applications are continuously being explored by researchers all over the world. The numerous research pieces of evidence that microwave technology is a sophisticated tool for both synthesis and leading applications of Schiff base compounds. The greener approach is prioritized over the conventional synthesis because of its environment friendly less energy consuming, less time consuming, less hazardous compounds synthesis with low cost. Some new Schiff base complexes of VO(IV) and Co(II) derived from 4-dimethyl aminobenzaldehyde with 3, 4-dichloroaniline (DCA) have been synthesized by conventional as well as microwave methods and characterized by elemental analysis, FT-IR, ESR and molar conductance. The complexes are colored and stable in air at room temperature. The Schiff base and metal complexes show a good activity against the bacteria; E. coli, S. aureus, S. fecalis and fungi A. niger, T. polysporum. The antimicrobial results also indicate that the metal complexes are better antimicrobial agents as compared to the Schiff base. These observations show that the majority of the complexes are more active than their Schiff base ligand. The higher inhibition zone of metal complexes than that of the ligand can be explained on the basis of Overtone's concept and Chelation theory. The findings of the bactericidal and fungicidal investigation of the compounds against the opportunistic pathogens reveal that the synthesized compounds have antipathogenic activity.

Introduction:-

Schiff bases and their bio-active complexes have been studied extensively over the past decade. Schiff bases provide potential sites for bio-chemically active compounds. Because of increasing biological and catalytic significance of vanadium, intense attention has been focused on it, over the past two decades. Vanadium constitutes 0.015% of earth's crust which is nearer to abundance of zinc. Biochemical role of vanadium has now become a widely chosen topic of bioinorganic chemistry. The Schiff base ligands widely vary in their structure flexibility, electronic nature and the presence of additional donor atoms besides imino nitrogen. The central metal in these complexes act as active sites and thereby successfully catalyze chemical reactions. The Schiff base transition metal complexes are a

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family of attractive oxidation catalysts for a variety of organic substrates because of their cheap and easy synthesis & their chemical and thermal stability [1-6].

Microwave irradiated synthesis is a branch of green and pollution free chemistry. Microwave assisted reactions are offering low cost, reduced pollution and offer high yield together with simplicity in processing and handling. The basis of this technique of synthesis is much faster with high yields compared to conventional methods. The salient features of microwave approach are simple reaction conditions, shorter reaction times and enhancements in yields [7-13].

In this study we report on the synthesis, spectral and physicochemical characterization of Co(II) and VO(IV) complexes with ligand derived from 4-dimethyl aminobenzylidine-3,4-dichloroaniline (DCA) (Figure 1).the metal complexes formed with new ligand may be used as precursor for the synthesis of new compounds. Some of them show interesting chemical physical and biological character.

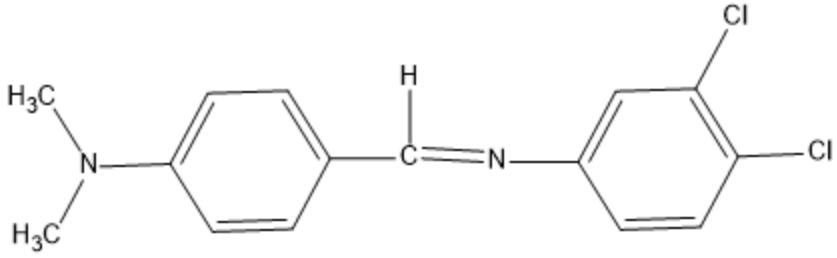

Figure 1:- Structure of Schiff base Ligand.

Materials and Methods:-

All the used chemicals and solvents were of Anal R grade. All the reagents used for the preparation of the Schiff base were obtained from HI media. Metal salts were purchased from CDH Chemie. Elemental analyses were performed on Heroes elemental analyser SAIF, CDRI, Lucknow. Molar conductance measurements were conducted using 10^{-3} M solutions of the complexes in methanol on Elico-CM 82 Conductivity Bridge at room temperature. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using $CuSO_4.5H_2O$ as the calibrant. Diamagnetic corrections were applied in compliance with Pascal's constant. FT-IR spectra were recorded in KBR medium on a Perkin Elmer RX1 spectrophotometer SAIF, CDRI Lucknow and SAIF Panjab University Chandigarh in ware number region 4000-400 cm^{-1}. Electronic Spectra (in MeOH) were recorded on Perkin Elmer Lambda- 2B Spectrophotometer (range 200-700 nm) at Department of Chemistry, Dr. HarisinghGour University, Sagar (M.P.). Microware assisted synthesis were carried out in open glass vessel on a modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, microwave energy output 800W and microwave frequency 2450 MHz. A thermocouple device was used to monitor the temperature inside the vessel of the microwave. The Microwave reactions were performed using on/off cycling to control the temperature. X-band EPR spectra were recorded on a Varian E-112 Spectrometer at room temperature operating at the X-band region with 100 kHz modulation frequency, 5 mw microwave power and 1 G modulation amplitude using TCNE as the internal standard.

Conventional synthesis of the Ligand:

DCA Schiff base was synthesized by the condensation of 1:1 ratio of 4-dimethyl aminobenzaldehyde with 3, 4-dichloroaniline dissolved in methanol. The resulting reaction mixture was refluxed for 4.5 hrs and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol and finally recrystallized from ethanol and ether and dried in air at room temperature and preserved in a $CaCl_2$ desiccator. The purity of synthesized compounds was checked by TLC using silica gel G (yield: 76.7%).

Microwave method for the synthesis of Schiff base:

The equimolar (1:1) ratio of 4-dimethyl aminobenzaldehyde and 3, 4-dichloroaniline with methanolic solution were mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4 mL of dry ethanol as a solvent. The reaction was completed in a short time (5 min) with higher yields. The resulting product was then recrystallized with ethanol, finally dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The progress of the reaction, purity of the product was monitored by TLC using silica gel G (yield: 87%).

Conventional method for the synthesis of metal complexes:
The metal complexes have been prepared by mixing the methanolic solution of $VOSO_4.5H_2O/CoCl_2.6H_2O$ (0.003 mole) to the methanolic solution of Schiff base (DCA) (0.006 mole) in 1:2 molar ratio. The resulting mixture was then refluxed on water bath for about 8-10 hours. A coloured product appeared on standing and cooling the above solution. The complex was filtered, washed with ether and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. It was further dried in an electric oven at 30-70°C.

Microwave method for the synthesis of metal complexes:
The ligand and the metal salts were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated by the microwave oven by taking 3-4 mL of dry ethanol as a solvent. The reaction was completed in a short time (6-9 min) with higher yields. The resulting product was then recrystallized with ethanol and ether and finally dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 80-82%).

Biological activity:
The in-vitro biological activity of the Schiff base and its complexes was tested against the bacteria Escherichia coli, Staphylococcus aureus and S. feacalis by disc diffusion method using nutrient agar as medium and gentamycin as control. The antifungal activities of the compounds were also tested by the Well diffusion method against the fungi Aspergillusniger, and Trichodermapolysporum, cultured on potato dextrose agar as medium. In a typical procedure, a well was created on the agar medium and nystatin as the control was inoculated with the fungi. Each of the compounds was dissolved in DMSO and solutions of the concentrations (25, 50 and 100 ppm) were prepared separately. In a typical procedure, a well was made on agar medium inoculated with microorganism. The well was filled with the test solution using a micropipette and the plate was incubated 24 hrs for bacteria at 37°C and 72 hs for fungi at 30°C. During this period, the test solution diffused and the growth of the inoculated microorganism was affected.

Results and Discussion:-

As a result of microwave-assisted synthesis, it was observed that the reaction was completed in a short time with higher yields compared to the conventional method.In the microwave method homogeneity of reaction mixture was increased by the rotation of the reaction platform tray. The confirming of the results was also checked by the repeating of the synthesis process.

All the metal complexes are coloured, solid and stable towards air and moisture at room temperature. They decompose on heating at high temperature, more or less soluble in common organic solvents.Comparative studies between the microwave-assisted synthesis and conventional heating method indicate that while the conventional method required 5-9 h to complete, microwave-assisted syntheses completed within 4-10 min with improved yields from 68-77% to 80-87%. The comparison study data of microwave and conventional methods, with analytical and physical data of the compounds are given in the **Table 1**. Elemental analysis of the complexes indicates the stoichiometry to be l:2metal:ligand (Schiff base). The molar conductance in methanol, of the complexes is 31.5 and 81.3 S cm^2 $mole^{-1}$ this suggest the non-electrolytic nature of Co(II) complex and uni-bivalent electrolytic nature of VO(IV) complex [14,15].

Table 1:- The comparative results of conventional and microwave methods, analytical, physical data and magnetic moment values of the compounds.

Compound Mol. Wt. (Colour)	Reaction period		Yield (%)		Elemental analysis, found (calcd.) %			*Λ_m	#μ_{eff}
	CM (hs)	MM (min.)	CM	MM	C	H	N		
$C_{15}H_{14}N_2CI_2$ (DCA) 293 (Light Yellow)	4.0	5.0	76.7	87.0	61.6 (61.4)	4.2 (4.7)	9.7 (9.5)	-	-
$[VO(C_{15}H_{14}N_2CI_2)_2(H_2O)_2].SO_4.H_2O$ 802.9 (Turmeric)	8.9	6.9	71.2	82.1	45.3 (45.8)	4.1 (4.0)	6.9 (6.9)	81.3	1.77
$[Co(C_{15}H_{14}N_2CI_2)_2Cl_2].4H_2O$	9.2	8.2	68.5	80.5	45.8	4.3	6.9	31.5	4.39

787.9 (45.6) (4.5) (7.1)
(Tobacco Green)

CM = Conventional method, time in hours; MM = Microwave method, time in minutes
*Λ_m= ($\Omega^{-1}cm^2mol^{-1}$); #μ_{eff}= B.M.

IR Spectra:
The IR spectra of the complexes were compared with those of the free ligand in order to determine the involvement of coordination sites in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared.

In the IR spectrum of the DCA ligand medium intensity band at 1578 cm^{-1}due to ν(C=N) azomethine group has shifted to lower wave numbers by 20-25 cm^{-1} in the complexes. It indicates that coordination takes place through the azomethine nitrogen. The appearance of broad bands at 3340 and 3380 cm^{-1} in the spectra of both the complexes have been assigned to associated water molecules. However, a medium intensity band at 669 cm^{-1} in VO(IV) complex is assignable to rocking mode of coordinated water molecule. The new bands at 461±17 cm^{-1} in both the complexes and a band at 562 cm^{-1} in VO(IV) complex have been assigned to (M-N) and (M-O) bonding respectively. A new band appears at 977 cm^{-1} has been assigned to ν(V=O) vibration [16-18].

Magnetic Moments and Electronic Spectra:
The electronic spectral data of the metal complexes in MeOH solution are given in Table 2. The nature of the ligand field around the metal ion has been deduced from the electronic spectra. The electronic spectrum of Co-DCA complex shows two bands of appreciable intensity at 12388 cm^{-1} and 20325. These transitions have tentatively been assigned to $^4A_2$-$^4T_1$ (F) (ν_2) and $^4A_2$-$^4T_1$ (P) (ν_3) respectively. The magnetic moment is 4.30 B.M. Thus the tetrahedral geometry has been suggested for this complex. Oxovanadium(IV)- DCA complex exhibit two bands at 12471 cm^{-1} and 21341 cm^{-1} which have tentatively been assigned to $^2B_2$-^2E (ν_1) and $^2B_2$-$^2B_1$(ν_2) transition. The magnetic moment is 1.77 B. M. This data suggest the trigonalbipyramidal/square pyramidal geometry for VO(IV) complex [19-24].

Table 2:-Electronic spectral and magnetic moment values of complexes.

S.No.	Complexes	Transitions	Bands(cm^{-1})	Magnetic Moment (B.M.)
1.	VO(IV)-DCA	$^2B_2$-^2E(ν_1)	12471	1.77
		$^2B_2$-$^2B_1$(ν_2)	22341	
		$^2B_2$-$^2A_1$(ν_3)		
2.	Co(II)-DCA	^{4}A2-$^4T_1$(F)(ν_2)	12388	4.30
		$^4A_2$-$^4T_1$(P)(ν_3)	20325	

ESR Spectra:
The spectrum of VO(IV) complex have been recorded on X-band EPR spectra were recorded on a Varian E-112 spectrometer at room temperature operating at the X-band region with 100 kHz modulation frequency, 5 mw microwave power and 1 G modulation amplitude using TCNE as the internal standard. The values of ESR parameters of VO(IV) complex of DCA viz. g^{11}, $g^{\perp}$, g_{av}, and Δg are as 1.9198, 1.9604, 1.9468 and 0.0406 respectively. The parameter $g_{av}$was obtained by equation [(g_{av}) = 1/3($2g^{\perp}$+ g^{11})] [25, 26].

Antimicrobial activities:
The in-vitro Antimicrobial activity of the synthesized Schiff base ligand and its corresponding metal complexes on selected bacteria E. coll, S. aureus and S. feacalis and two fungi A. niger and T. Polysporum was carried out. All of the tested compounds showed good biological activity against microorganism. On comparing the biological activity of the Schiff base and its metal complexes with the standard bactericide and fungicide, it is show that the some metal complexes have good activity as compared to the standard but all the complexes are more active than ligand. The higher inhibition zone of metal complexes than those of ligand can be explained on the basis of Overtone's concept and chelation theory. On chelation, the polarity of the metal ion will be reduced to greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π-electrons over the whole chelating ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. There

are other factors which also increases the activity are solubility, conductivity and bond length between the metal and ligand [27-31].

The bactericidal and fungicidal investigation data of the compounds are summarized in Tables 3 and 4. The results of the investigations account for the antipathogenic behavior of the compounds and this efficacy is positively modified on complexation.

Table 3:- Antibacterial screening data for the ligand and its complexes.

Comp.	Diameter of inhibition zone (mm)								
	E.Coli			**S.aureus**			**S. feacalis**		
	25	**50**	**100**	**25**	**50**	**100**	**25**	**50**	**100**
DCA	11	13	15	11	12	18	10	14	20
Co(II)	20	24	27	13	14	16	12	14	18
VO(IV)	14	16	18	12	12	15	12	13	17
Gentamycin (Standard)	22	24	28	100	100	100	18	22	24

Table 4:- Antifungal screening data for the ligand and its complexes.

Compound	Diameter of inhibition zone (mm);Concentration in ppm					
	A. niger			**T. Polysporum**		
	25	**50**	**100**	**25**	**50**	**100**
DCA	10	14	22	11	15	20
Co(II)	17	19	22	19	22	24
VO(IV)	16	18	20	18	20	22
Nystatin	20	22	24	23	25	27

Conclusion:-

In summary, the present research work illustrates the syntheses of some Schiff base derived transition metal complexes using both conventional approach as well as microwave-assisted method. These synthesized compounds characterized by various physicochemical and spectral analyses. In the result of microwave assisted synthesis, it has been observed that the reaction time decreased from hours to minutes and availability of the product within better yields compared to the conventional method. The antimicrobial data show that the metal complexes to be more biological active compared to their parent Schiff base ligand against all pathogenic species. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased. The Schiff base ligand was found to be biologically active and their metal complexes displayed enhanced antimicrobial activity against one or two strains. Chelation tends to make the ligand act as more powerful and potent bactericidal agent. Further chelation can help in MDR problems.

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