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MICROWAVE SYNTHESIS AND PHYSICOCHEMICAL CHARACTERIZATION OF VO(IV) AND Co(II)SCHIFF BASE METAL COMPLEXES

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ABSTRACT

The Sustainable/Greener approach is prioritized over the conventional approach because of its environment-friendly, less time-consuming, less energy-consuming, less hazardous compounds synthesis, and low expenditure. New Schiff base and their VO(IV) and Co(II) complexes formed by the condensation of 4-dimethyl aminobenzaldehyde and 3-chloro-4-fluoroaniline have been synthesized by conventional as well as microwave methods. These compounds have been synthesized by conventional as well as microwave methods. These compounds have been characterized by elemental analysis, FT-IR, FAB-mass, molar conductance, electronic spectra, magnetic susceptibility, thermal and XRD analysis. The complexes are coloured and stable in air. Analytical data revealed that all the complexes exhibited 1:2 (metal:ligand) ratio with the coordination 4. FAB-mass and thermal data show degradation pattern of the complexes. XRD patterns indicate crystalline nature for the complexes.

INTRODUCTION

Designing of novel coordination complexes by condensing the novel Schiff base ligand and transition metal ions creates a challenging and interesting field for the researchers. The Schiff base ligands are the "Versatile actors" in the field of biomedical science and technology. Metal complexes have been receiving considerable attention for many years, due to their interesting characteristics in the field of material science and biological systems. A large number of Schiff bases and their complexes have possess important properties e.g. their ability to reversibly bind oxygen, transfer of an amino group and complexing ability towards some toxic metals. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Metal complexes of Schiff bases are becoming increasingly important as biochemical, analytical homogenous and heterogenous catalysis, magnetism and antimicrobial agents, in the design of molecular modeling and industrial fields [1-4].

Microwave-assisted synthesis is a branch of green chemistry. Microwave irradiated reactions are offering reduced pollution, low cost 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 shorter reaction times, simple reaction conditions and enhancements in yields[5-9].

In this study we report the synthesisand physicochemical characterization of Co(II) and VO(IV) complexes with ligands derived from 4-dimethyl aminobenzylidine-3-chloro-4-fluoroaniline (DFA)(Figure 1). The metal complexes formed with new ligand may be used as precursors for the synthesis of new compounds. Some of them may exhibit interesting physical chemical and biological properties.

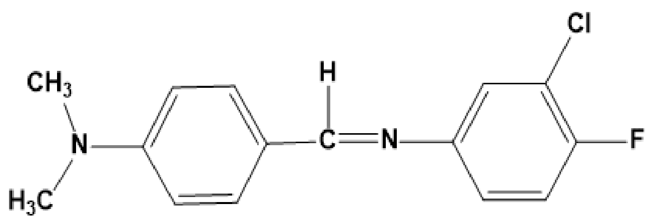

Figure 1.4-Dimethyl aminobenzylidine-3-chloro-4-fluoroaniline (DFA) ligand

EXPERIMENTAL

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. The FAB mass

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spectra were recorded at room temperature on a JEOL SX 102/ DA-6000 mass spectrometry/data system using argon/xenon (6 kV, 10mA) as the FAB gas (accelerating voltage 10 kV) at SAIF. CDRI, Lucknow. 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.). 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, CDRILucknow and SAIF Panjab University, Chandigarh in wave number region 4000-400 cm^{-1}. Thermogravimetric analysis was carried out under atmospheric condition with a heating rate 10°C min^{-1} on TGA Q500 universal V4.5A TA instrument. Powder X-ray diffraction (XRD) patterns were recorded on a RINT2000 wide angle goniometer. X-ray diffractometer, operated at 40 kV and 30 mA generator using the CuKα line at 1.54056 Å as the radiation sources. Sample was scanned between 5° to 70° (2θ) at 25 °C. Microwave 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.

Conventional synthesis of the Ligand

DFA Schiff base was synthesized by the condensation of 1:1 ratio of 4-dimethyl aminobenzaldehyde with 3-chloro 4-fluoroaniline dissolved in methanol. The resulting reaction mixture was refluxed for 4hrs 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: 67.8%).

Microwave method for the Synthesis of Schiff base

The equimolar (1:1) ratio of 4-dimethylaminobenzaldehyde with 3-chloro-4-fluoroaniline (DFA) was mixed thoroughly in a grinder. The reaction mixture was then irradiated by the microwave oven using 3-4 mL solvent. The reaction was completed in a short time (4.5min). 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 and purity of the product was monitored by TLC using silica gel G (yield: 90%).

Conventional synthesis of the metal complexes

The metal complexes have been prepared by mixing the methanolic solution of $VOSO_4.5H_2O/CoCl_2.6H_2O$ to the methanolic solution of Schiff base DFA in 1:2 molar ratios. The resulting mixture was then refluxed on water bath for about 6-7 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 50-70°C (yield: 69.2-72.7%).

Microwave method for the Synthesis of metal complexes

The ligand and the metal salt were mixed in 1:2 (metal:ligand) ratio in a grinder. The reaction mixture was then irradiated in the microwave oven using 3-4 mL solvent. The reaction was completed in a short time (5-7 min). 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: 80.4-84.6%).

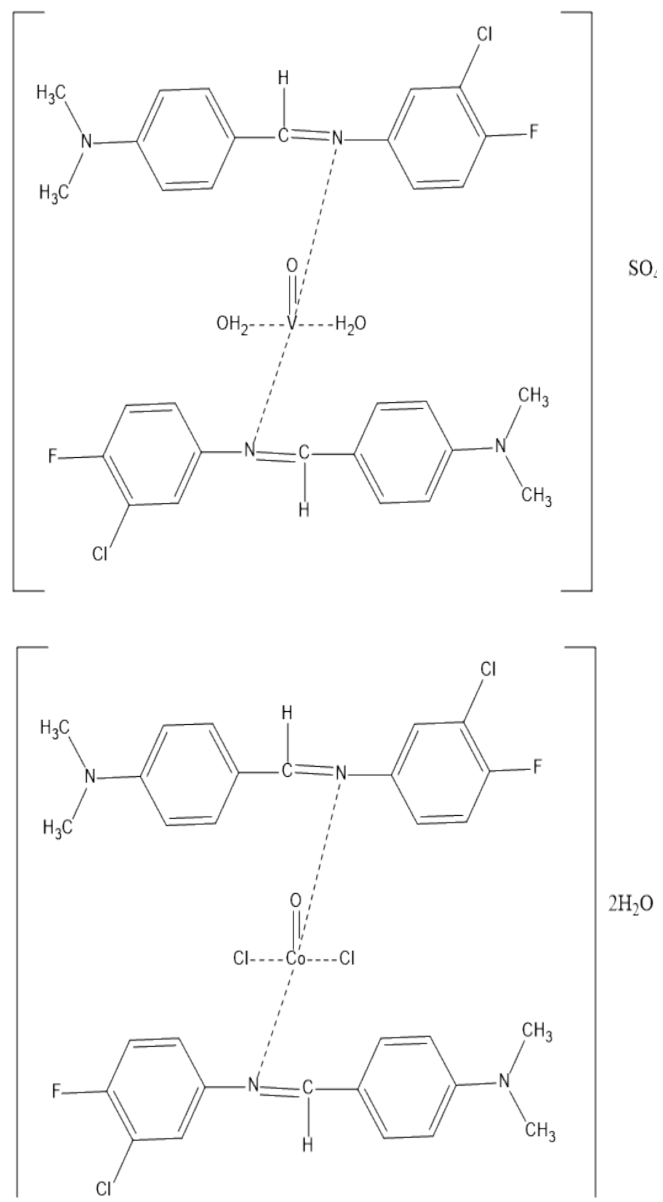

Figure 2:DFA with Oxo vanadium (IV) and Cobalt(II) complexes

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 rotating of 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 and more or less soluble in common organic solvents. Comparative study results obtained by microwave assisted synthesis; versus conventional heating method is that some reactions which required 5-8 h. by conventional method, was completed within 5-8 min. by the microwave irradiation technique and yields have been improved from 69.3-72.7% to 80.4-90.5%. The comparison study data of microwave and conventional methods, with analytical and physical data of the compounds are given in the Table 1. Analytical date show that metal complex have 1:2 (metal: ligand) stoichiometry. The molar conductance in methanol(10-3 M solutions),of the complexes is 41.9 and 90.2 Scm^2 mol-1 this suggest the non-electrolytic nature of Co(II) complex and electrolytic nature of VO(IV)complex [10,11].

FAB Mass spectra

The FAB mass spectrum gives additional information about the analysed species. The FAB mass spectrum of $[VO(DFA)_2(H_2O)_2].SO_4$ shows a molecular ion peak (M^+) at m/z 754 which suggest the monomeric nature of the complex and confirm the proposed formula. The spectrum of complex also shows a series of peaks (754, 651, 391, 277and 107) corresponding to various fragments. Their intensity gives an idea of the stability of the fragments. The value 107 corresponds to VO with chelated O and N donors as ligand moiety [12,13].

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
	CM (h.)	MM (min.)	CM	MM	C	H	N	
$C_{15}H_{14}N_2ClF$ (DFA) 276.5 Dirty Green	4.0	4.2	67.8	90.5	65.3 (65.0)	5.1 (5.0)	10.5 (10.0) -	-
$[VO(C_{15}H_{14}N_2ClF)_2(H2O)_2].SO_4$ 751.6 Turmeric	7.3	8.0	69.3	80.4	47.9	4.4	9.1	90.2
$[Co(C_{15}H_{14}N_2ClF)_2Cl_2].2H_2O$ 716.9 (Leaf Green)	6.3	6.9	72.7	84.6	50.2 (50.0)	4.0 (4.4)	9.1 (7.8)	41.9
Conductance (Λm) = Scm^{2}mol^{-1}								

Infrared 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.

The IR spectrum of DFA ligand (Schiff base) exhibits a strong band at 1579 cm^{-1} due to azomethineν(C=N) group. This has shifted towards lower frequency. It shifts down by 21-30 cm^{-1} in the metal complexes. This suggests the coordination through the azomethine nitrogen. This is further supported by the new bands at 458±12 cm^{-1}for ν(M-N).

The appearance of broad band at 3390±16 cm-1in the spectra of both the complexes have been assigned to associated water molecules and a medium intensity band at 670cm-1in VO(IV) complex suggests the coordinated water molecules. A new band at 576 cm^{-1}in VO(IV)complex has been assigned to M-O bonding[14-17].

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-DFA complex shows a band of appreciable intensity at 12531 cm^{-1}which have tentatively been assigned to $^4A_2$-$^4T_1$ (F) (ν_2) transition. The magnetic moment is 4.30 B.M. Thus the tetrahedral geometry has been suggested for this complex. Oxovanadium(IV)- DFA complex exhibit two bands at 12285 cm^{-1} and 21232 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 B. M. This data suggest the trigonalbipyramidal/square pyramidal geometry for VO(IV) complex [18-21].

Table 2. Electronic spectral and magnetic moment values of complexes

S.No.	Complexes	Transitions	Bands(cm^{-1})	Magnetic Moment (B.M.)
1.	VO(IV)-DFA	$^2B_2$-^2E(ν_1)	12285	1.80
		$^2B_2$-$^2B_1$(ν_2)	21232	
		$^2B_2$-$^2A_1$(ν_3)		

2.	Co(II)-DFA	$^4A2$-$^4T_1$(F) (ν_2)	12531	4.30
		$^4A_2$-$^4T_1$(P) (ν_3)		

X- RayDiffraction (XRD)

X-ray diffraction was performed of metal complexes. The XRD patterns indicate crystalline nature for the complexes. X-ray powder diffractogram of the complexes were recorded using CuKα as source in the range 5°-100° (2θ). X-ray crystal system has been worked out by trial, error methods for finding the best fit between observed and calculated $\sin^2\theta$. The X-ray diffractogram of VO(IV) complex of CFA, shows 21 reflections with maximum of reflection which corresponds to d= 15.910 Å. A comparison of the value reveals that there is a good agreement between calculated and observed value of $\sin^2\theta$. The observed values fit well in the orthorhombic system and gives a unit cell with lattice constant a =b=22.67 Å, c = 48.72 Å, and cell volume V = 24895.87 Å^3, Z=22, (number of molecule per unit cell). The observed value of density is 1.1032g/cm^3 while the calculated value has been found to be 1.1193 g/cm^3[22-24].

Thermal analyses

The thermal behaviour of metal complexes shows that the hydrated complexes lose molecules of hydration first; followed by decomposition of ligand molecules in the subsequent steps. Non-isothermal kinetic parameters of the [Co(DFA)$_2$Cl$_2$].2H$_2$O Complex given Table 3.

Table 3. Non-isothermal kinetic parameters of the [Co(DFA)$_2$Cl$_2$].2H$_2$OComplex

S. No.	Complexes	Methods	Dec. stage/ temp. (K)	E (J mol^{-1})	Z (S^{-1})	ΔS* (J mol^{-1})
1	[Co(DFA)$_2$Cl$_2$].2H$_2$O	P-N	Ist/453	64.90	1.54×10^{1}	-225.59
		C-R		75.43	5.68×10^{4}	-157.36
		P-N	IInd/573	21.63	2.69×10^{-12}	-471.77
		C-R		41.47	1.63×10^{-8}	-399.26

The TG curve of [Co(DFA)$_2$Cl$_2$].2H$_2$Othe complex shows a weight loss between 80-160° C. indicating the presence of two water molecules (lattice water) (Remaining wt%/ obs./ cal. 96/94). Above this temperature a gradual weight loss has been observed in general upto 420°C indicating decomposition of the coordinated part of the ligand in two steps. The weight loss observed between 180-290°C may be due to partially decomposed ligand moiety in the complex (Remaining wt.% obs./cal. 29/33). Above 290°Can inflection occurs in the curve and loss in the curve and loss in weight progresses upto 420°C. This indicates the elimination of the remaining thermally degradable part of the ligand. After this temperature, a horizontal region showing no weight change is due to cobalt oxide as a final pyrolysis product has been recorded (Remaining Wt.% obs./cal. 15/12.7)[25-29].

CONCLUSION

In the present research studies, our efforts are synthesized of some newly compounds from the conventional as well as microwave methods. 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 classical method. FAB-mass and thermal data show degradation pattern of the complexes. Thermogravimetric studied of the complexes also helped to characterize the complexes. The XRD patterns indicate crystalline nature of the complexes.

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