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Studies on Mixed Ligand Complexes of Oxovanadium(IV) with 2-(3′-Phenyl-5′-Chloro Indole-2′-Carboxamidyl) Iminomethyl Furan as Primary and 2-Carboxyphenyl-Azo-β-Naphthyl Amine as Secondary Ligand

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A polydentate Schiff base ligand, 2-(3′-phenyl-5′-chloro indole-2′-carboxamidyl) iminomethyl furan, has been prepared by the condensation of 3-phenyl-5-chloro indole-2-carboxyhydrazide and furfural. A number of oxovanadium(IV) complexes have been synthesised by the interaction of vanadyl salts with the Schiff base as primary and 2-carboxyphenyl-azo-β-naphthyl amine as secondary ligand. The isolated mixed ligand complexes are characterised by elemental alalysis, magnetic, spectral and thermogravimetric studies.

Analytical data suggest the formulae (VOLL′)X [where $L = C_{20}H_{14}N_3O_2Cl$, $L' = C_{17}H_{12}N_3O_2$ and X = Cl, Br, I, NO_3, NCS, ClO_4] for the isolated complexes. The Λ_m values of the complexes lie in the range 102.2–106.8 $ohm^{-1}\ cm^2\ mol^{-1}$ in DMSO at the concentration 10^{-3} M indicating that these are 1 : 1 electrolytes. IR spectra suggest that the Schiff base and azo compound serve as tridentate and bidentate ligands respectively in the formation of complexes. Magnetic and reflectance spectral studies show that the complexes possess distorted octahedral geometry. TGA shows the decomposition of the complexes in 300–570°C temperature range. V_2O_5 is obtained as the final product in each case. The screening of the complexes and ligands against organisms such as *E. coli* and *S. aureus* shows that the complexes are more active than the ligands.

Key Words: Mixed ligand complexes, Synthesis, Spectral, Magnetic and thermal characteristic.

INTRODUCTION

The coordination chemistry of vanadium has received considerable attention since the discovery of the presence of vanadium in enzymes[1]. Its biological importance has been further exemplified by its incorporation in natural product, in the blood of sessile marine organisms and in the enzymes of potent inhibitor of phosphoryl transfer[2]. Recent investigations also support the fact that vanadium is involved in biological system in more than one way[3–5].

The chemistry of Schiff base complexes continues to attract many researchers[6, 7]. Synthesis and spectral studies of some oxovanadium(IV) complexes have been carried out[8]. Here we report the mixed ligand complexes of VO(IV) with 2-(3′-phenyl-5′-chloro indole-2′-carboxamidyl) iminomethyl furan as primary and 2-carboxyphenyl -azo-β-naphthyl amine as secondary ligand with a view that the synthesised complexes may be of some biological significance as indole-2-car-

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boxy-hydrazides have shown good anti-inflammatory and antimicrobial activities[9].

EXPERIMENTAL

3-Phenyl-5-chloro indole-2-carboxyhydrazide was synthesised by the reported precedure[9]. 2-(3′-phenyl-5′-chloro indole-2′-carboxamidyl) iminomethyl furan (PCCIF) was prepared by refluxing a mixture of furfural (0.01 mol) and 3-phenyl-5-chloro indole-2-carboxyhydrazide (0.01 mol) in ethanol for 3 h on a water bath. A few drops of concentrated HCl were also added in the mixture. The orange yellow product was formed after cooling at room temperature. It was recrystallised from chloroform. 2-Carboxyphenyl-azo-β-naphthyl amine (CPANA) was synthesised following the standard procedure[10]. Oxovanadium(IV) chloride, perchlorate and bromide were prepared according to the literature procedure[11]. VO(IV) iodide was obtained by treating an alcoholic solution of $VOCl_2$ with KI[12]. VO(IV) thiocyanate was obtained by treating an aqueous solution of VO(IV) perchlorate with KCNS. $VO(NO_3)_2$ was prepared by treating a solution of $VOCl_2$ with silver nitrate. Conductivity measurements were carried out on Systronics conductivity bridge. IR spectra were recorded on Perkin-Elmer 783 spectrophotometer. Reflectance spectra were taken on Carl-Zeiss Jena VSU-2p spectrophotometer.

Preparation and isolation of the complexes

The respective vanadyl salt solution (10 mmol) in 30 mL ethanol-water mixture (1 : 1 v/v) was mixed with PCCIF solution (10 mmol) in 1 : 1 molar ratio. The separated solid compounds were filtered, washed with ethanol and dry ether and dried over anhydrous $CaCl_2$. Yield 58–60%.

The mixed ligand complexes were synthesised by the addition of ethanolic solution (10 mmol) of CPANA to the solution of the above compounds followed by the addition of sodium acetate in order to raise the pH to 7–7.5. The separated compounds were filtered off, washed with ethanol and dry ether and dried over anhydrous $CaCl_2$. Yield 48–49%.

RESULTS AND DISCUSSION

The complexes are insoluble in common organic solvents but dissolve in $PhNO_2$, DMF and DMSO. Analytical data reported in Table-1 suggested 1 : 1 : 1 (M-L-L′) stoichiometry for all the mixed ligand complexes. The electrolytic conductance values in DMSO (Table-1) at the concentration 10^{-3} M indicate 1 : 1 electrolytic nature of the complexes.

Magnetic and reflectance spectral studies

The observed higher μ_{eff} values (1.84–1.89 B.M.) in comparison to spin only value (1.73 B.M.) suggest the presence of some spin orbit interaction of vanadium ion in VO(IV) complexes.

The spectra of the complexes showed low energy band at 12,850–13,500 cm^{-1} corresponding to $^2B_2 \rightarrow {}^2E$ transition. The second band at 16,400–15,600 cm^{-1} was assigned to $^2B_2 \rightarrow {}^2B_1$ transition (10 Dq)[13]. The high energy band at

25,200–24,700 cm^{-1} was assigned to $^2B_2 \rightarrow {}^2A_1$ transition plus CT absorption. The observed spectral bands suggested distorted octahedral geometry to the complexes. The calculated values of parameters: Dq and Ds (axial parameter), Dt (equatorial parameter), DQ, DS and DT (NSH Hamiltonian parameters) are in the range 1,640–1,580, 3,270–3,200, 790–720, 32,534–31,070, 22,894–21,700 and 10,842–9,758 cm^{-1} respectively. The values of the parameters are in agreement with the distorted octahedral geometry.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF VO(IV) COMPLEXES

S.No.	Complex	C % Calcd. (Found)	H % Calcd. (Found)	N % Calcd. (Found)	Metal % Calcd. (Found)	Halogen/ NCS/ClO_4 % Calcd. (Found)	Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
1.	[VOLL′]Cl	58.74 (58.39)	3.44 (3.42)	11.11 (11.07)	6.74 (6.70)	9.38 (9.32)	102.6	1.86
2.	[VOLL′]Br	55.47 (55.18)	3.25 (3.28)	10.49 (10.43)	6.36 (6.32)	4.43, 9,99 (4.40, 9.94)	102.2	1.89
3.	[VOLL′]I	52.39 (52.70)	3.07 (3.04)	9.91 (9.97)	6.01 (6.03)	4.18, 14.99 (4.22, 14.89)	104.6	1.84
4.	[VOLL′]NO_3	56.74 (56.22)	3.32 (3.34)	12.53 (12.47)	6.51 (6.54)	4.53 (4.56)	106.8	1.87
5.	[VOLL′]NCS	57.04 (56.81)	3.34 (3.31)	10.79 (10.75)	6.54 (6.58)	4.55, 7.45 (4.52, 7.48)	105.9	1.89
6.	[VOLL′]ClO_4	54.16 (54.44)	3.17 (3.15)	10.25 (10.29)	6.21 (6.18)	4.32, 12.13 (4.29, 12.06)	106.2	1.87

where L = $C_{20}H_{14}N_3O_2Cl$ and L′ = $C_{17}H_{12}N_3O_2$

IR spectra

The band, characteristic of ν(C═N) observed at 1,625 cm^{-1} in the Schiff base ligand (PCCIF), gets shifted to a lower frequency band (1,610–1,600 cm^{-1}) in the spectra of complexes which shows that azomethine nitrogen takes part in coordination. The Schiff base shows intense absorptions at 1,675, 1,500 and 1,280 cm^{-1} which may be respectively assigned to amide I, amide II and amide III bands. These bands appear in the regions 1,655– 1,645, 1,530–1,525 and 1,325– 1,315 cm^{-1} in the spectra of complexes suggesting the coordination[14] of carbonyl oxygen. ν(N—H) band remains unperturbed in the complexes showing non-involvement of this group in bond formation with the metal ion. The Schiff base shows strong bands at 610 and 590 cm^{-1}, assigned to furan ring-deformation modes[15]. These bands show a red shift of 30–20 cm^{-1} on complexation, indicating metal-ligand bonding through the furfuryl oxygen atom.

In the mixed ligand complexes, the asymmetric and symmetric vibrations of the carboxylate group, ν_{asym}(COO) and ν_{sym}(COO), occur at 1,617–1,612 and 1,445–1,440 cm^{-1} respectively. The observed difference [Δν(COO) 180–150 cm^{-1}] indicates the presence of monodentate carboxylate group in the present compounds[16–18]. A bathochromic shift of the —N═N band[19], located at 1,400

cm^{-1} in CPANA, is observed (1,385–1,380 cm^{-1}) in the mixed ligand complexes which shows the link of metal with the azo nitrogen. Thus the azo compound serves as bidentate ligand in the complexation. However, conclusive evidence regarding the bonding of oxygen and nitrogen atoms has been provided by far infrared spectral data. The ν(M—O) and ν(M—N) vibrations are observed in the regions 5,10–500 and 440–430 cm^{-1} respectively. ν(V=O) stretch is observed in the range 980–970 cm^{-1} in these complexes.

Thermal Characteristic

The decomposition of mixed ligand complexes, under study, started at 300°C. The initial weight loss was observed in 300–420°C temperature range. The azo ligand was eliminated at this temperature. Further decomposition occurred in the 420–570°C temperature range and organic ligands were completely lost. V_2O_5 was obtained as the final product in each case.

Biological Studies

The ligands and the isolated VO(IV) complexes have been screened for antimicrobial activity against *E. coli* and *S. aureus*. The results show that the mixed ligand complexes are more active in comparison to the ligands.

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