

Synthesis and Characterization of Mixed Ligand Complexes of VO(IV) and ZrO(IV) with 3-Phenyl-5-methoxy indole-2-carboxymidyl Furoinimine as Primary and 3'-(2-Carboxyphenylazo)-2'-amino Pyridine as Co-Ligand

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Mixed ligand complexes of VO(IV) and ZrO(IV) with 3-phenyl-5-methoxy indole-2-carboxymidyl furoinimine (PMICF) as primary and 3'-(2-carboxyphenylazo)-2'-amino pyridine (CPAP) as co-ligand have been synthesized and characterized on the basis of analytical, conductance, spectral and thermal data. Analytical data suggested 1 : 1 : 1 (MO-L-L') stoichiometric composition for all the complexes [where M = V(IV)/Zr(IV), L = PMICF and L' = CPAP]. Electrolytic conductance data ($\Delta M = 72.3\text{--}78.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of all the complexes of VO(IV) revealed their 1 : 1 electrolytic nature except VO(IV) complex prepared by taking vanadyl sulphate and the above ligands which is non-electrolyte. On the other hand, ZrO(IV) complexes are non-electrolytes. Electronic spectra of VO(IV) complexes showed that they exhibit distorted octahedral configuration. IR spectra showed that the primary ligand (PMICF) acts as a tridentate ligand and the azo compound (CPAP) serves as bidentate ligand. Thermal stabilities of these complexes have also been investigated.

Key Words: Mixed ligand complexes, Synthesis, Analytical, Spectral and thermal studies.

INTRODUCTION

Hydrazone derivatives containing additional donor sites such as $>C=O$, heterocyclic nitrogen or sulphur systems have interesting ligational features and several earlier workers have reported a large number of coordination compounds with such ligands¹⁻³. Recently, heterocyclic azo compounds have received much attention⁴⁻⁷. Here, the mixed ligand complexes of VO(IV) and ZrO(IV) with 3-phenyl-5-methoxy indole-2-carboxymidyl furoinimine (PMICF) as primary and 3'-(2-carboxyphenylazo)-2'-aminopyridine (CPAP) as co-ligand are reported.

EXPERIMENTAL

3-Phenyl-5-methoxy indole-2-carboxymidyl furoinimine was synthesized by the reported procedure using furoin and 3-phenyl-5-methoxy indole-2-carboxyhydrazide. For the synthesis of 3'-(2-carboxyphenylazo)-2-amino pyridine, 2-carboxy benzene diazonium chloride was obtained from anthranilic acid by the adopted method⁹ and it was coupled with 2-amino pyridine at 0–5°C. The ligands were purified by recrystallization from chloroform. All chemicals used were of

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AnalaR grade. Conductivity measurements were carried on Systronics conductivity bridge. IR spectra were recorded on Perkin-Elmer 783 spectrophotometer.

Preparation and isolation of the complexes

The hydrazone (PMICF) dissolved in ethanol (40 mL, 0.01 mol) was mixed with the azo ligand (CPAP) in ethanol (40 mL, 0.01 mol) and solution of oxovanadium/zirconyl salt (0.01 mol) was added dropwise with constant stirring by a magnetic stirrer. A dehydrating agent, 2,2-dimethoxy propane was added and the pH of the mixture was adjusted to 5.6–6.9 by adding acetate buffer. The solid complexes separated out on heating the reaction mixture at about 80°C for 1 h over a water bath. The compounds were filtered off and washed with a little of ethanol, acetone and dry ether and dried *in vacuo* over P₂O₅; yield 49–51%.

RESULTS AND DISCUSSION

Analytical data reported in the table suggested 1 : 1 : 1 stoichiometric composition for the mixed ligand complexes. The complexes are soluble in common organic solvents, DMF and DMSO. The molar conductance data (Table) in acetone at the concentration 10⁻³ M indicate 1 : 1 electrolytic nature of all the complexes of VO(IV) except that prepared from VOSO₄, which is non-electrolyte. However, ZrO(IV) complexes show non-electrolytic behaviour ($\Delta M = 5.7\text{--}6.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

The room temperature magnetic moments of the vanadyl complexes lie in the range 1.85–1.92 BM, a value close to the spin only value expected for VO(IV) complexes with normal magnetic properties¹⁰. ZrO(IV) complexes, on the other hand, are diamagnetic.

Electronic spectra of acetonic solution of VO(IV) complexes showed low energy band at 13,450–12,900 cm⁻¹ corresponding to ²B₂ → ²E transition. The second band at 15,900–15,650 cm⁻¹ was assigned to ²B₂ → ²B₁ transition¹¹. The high energy band at 25,100–24,800 cm⁻¹ was assigned to ²B₂ → ¹A₁ transition plus CT absorption. These spectral data suggested distorted octahedral configuration¹² for the present VO(IV) complexes.

The hydrazone (PMICF) shows intense absorptions at 1,630, 1,675, 1,505, 1,285 cm⁻¹ which may be respectively assigned to $\nu(\text{C}=\text{N})$, amide I, amide II and amide III bands¹³. The band due to $\nu(\text{C}=\text{N})$ shows a negative shift of 15–20 cm⁻¹ in the spectra of mixed ligand complexes showing that nitrogen of (C=N) group is involved in complexation. Further, a weak band occurring at 975 cm⁻¹ characteristic of $\nu(\text{N}-\text{N})$, in the spectrum of hydrazone, undergoes a +ve shift of about 20–25 cm⁻¹ in the spectra of complexes, thus confirming monodentate coordination of N–N moiety¹⁴. A negative shift of about 30–35 cm⁻¹ in the amide I and a +ve shift of ca. 25 cm⁻¹ in amide II and III bands in the spectra of complexes (except complex at serial no. 2 in the table) indicates the bonding of C=O group to the oxometal ions through oxygen. A medium intensity broad band observed around 3,250 cm⁻¹ assignable to $\nu(\text{NH})$, in the spectrum of hydrazone appears at 3,280–3,270 cm⁻¹ in the complexes suggesting the involvement of nitrogen of NH group of indole moiety of PMICF in coordination. However, the bands due to furyl oxygen, methoxy and hydroxyl groups seen in the spectrum of ligand (PMICF) remain unperturbed in the complexes showing their non-participation in complexation. Further, in the spectrum of complex at serial no. 2 in table, the amide I, amide II and

amide III bands of PMICF disappear which clearly suggest the destruction of C=O group presumably *via* the amide \rightleftharpoons imidol tautomerism. However, two new bands characteristic of $\nu(\text{NCO}^-)$ are observed in the 1,555 and 1,350 cm^{-1} region in the spectrum of this complex showing the enolisation of keto group and its subsequent deprotonation during complexation.

A band observed at 1,610 cm^{-1} in the spectrum of CPAP assignable to $\nu(\text{N}=\text{N})$ gets shifted to 1,590–1,580 cm^{-1} in all the complexes showing the coordination through N-atom of azo group¹⁵. In the spectra of complexes, appearance of bands at *ca.* 1,620 cm^{-1} and *ca.* 1,425 cm^{-1} instead of 1,590 cm^{-1} and 1,400 cm^{-1} (in the spectrum of azo ligand) corresponding to $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ vibrations confirms the chelation through the O-atom of the deprotonated carboxyl group of CPAP. The observed difference ($\Delta\nu(\text{COO}^-)$ *ca.* 190 cm^{-1}) further supports the fact. However, pyridine ring vibrations remain unaltered in the complexes.

Two non-ligand bands appearing at *ca.* 500 and 460–450 cm^{-1} in the spectra of all the complexes may tentatively be assigned as $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$. A strong band at $965 \pm 10 \text{ cm}^{-1}$ observed in the spectra of complexes may be assigned to $\nu(\text{M}=\text{O})$. In the spectrum of complex at serial no. 3, the bands at 2,050, 750 and 485 cm^{-1} are present which shows the presence of uncoordinated NCS while the bands existing at *ca.* 2,056, 850 and 478 cm^{-1} assigned to $\nu(\text{C}\equiv\text{N})$, $\nu(\text{C}-\text{S})$ and ENCS respectively in complex at serial no. 6 (Table-1) are expected to be due to the terminal N-bonded isothiocyanato group. In the complex 7th, OCIO_3 is unidentately coordinated (C_{3v} , symmetry) as $\nu_{\text{sym}}(\text{Cl}-\text{O})$, $\nu_{\text{sym}}(\text{ClO}_3)$, $\delta_{\text{asym}}(\text{Cl}-\text{O})$, $\delta_{\text{sym}}(\text{ClO}_3)$ and $\delta_{\text{asym}}(\text{ClO}_3)$ are located at 910, 1,040, 1,130, 690 and 620 cm^{-1} respectively. A band is seen at 220 cm^{-1} in the spectrum of complex 5th which may be assigned to $\nu(\text{M}-\text{Cl})$.

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA OF MIXED LIGAND COMPLEXES OF
VO(IV) AND ZrO(IV)

| Compounds | % Analysis: Calcd. (Found) | | | | | ΔM ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) |
|---------------------------|----------------------------|----------------|------------------|------------------|------------------|-----------------------------------------------------------------|
| | C | H | N | Anion | M | |
| [VOLL']Cl | 57.11 (57.44) | 3.75 (3.77) | 12.27 (12.16) | 4.44 (4.41) | 6.39 (6.34) | 72.3 |
| VOLL' | 59.84 (59.48) | 3.80 (3.83) | 12.86 (12.95) | — | 5.68 (6.73) | 4.8 |
| [VOLL']NCS | 55.54 (55.92) | 3.65 (3.63) | 11.93 (11.85) | 7.06 (7.01) | 6.21 (6.17) | 76.8 |
| [VOLL']ClO ₄ | 52.87 (52.59) | 3.47 (3.44) | 11.36 (11.30) | 11.53 (11.44) | 5.90 (5.85) | 78.6 |
| [ZrOLL' Cl] | 54.37 (54.01) | 3.57 (3.55) | 11.68 (11.75) | 4.22 (4.26) | 10.87 (10.81) | 5.9 |
| [ZrOLL'NCS] | 52.94 (53.31) | 3.48 (3.51) | 11.37 (11.29) | 5.73 (6.69) | 10.59 (10.66) | 5.7 |
| [ZrOLL'ClO ₄] | 50.51 (50.26) | 3.32 (3.30) | 10.85 (10.80) | 11.01 (10.95) | 10.11 (10.03) | 6.8 |

L = $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_5$ and L' = $\text{C}_{12}\text{H}_9\text{N}_4\text{O}_2$

The thermo-oxidative degradation of the complexes was studied by thermogravimetry. The endothermic weight loss in 430–470°C temperature range corresponds to the elimination of azo ligand. Thereafter, a continuous mass loss was observed in 580–610°C range and organic ligands were completely lost forming the corresponding metal oxides.

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