

NOTES

Synthesis and Characterization of Mixed Ligand Complexes of Oxovanadium (IV)

SURESH K. AGARWAL* and DINESH KUMAR

Department of Chemistry,
L.R. (P. G.), College
Sahibabad-201 005, India

Mixed ligand complexes of oxovanadium (IV) with indole-3-thiohydrazide as primary and 3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridine carboxylic acid as co-ligand have been synthesized and characterised on the basis of analytical, conductance, magnetic and spectral studies.

The chemistry of N & S containing ligands make them interesting in several biological systems. Acid hydrazides and hydrazones are quite extensively studied as typical examples of nitrogen and sulphur containing systems. Oxovanadium (IV) complexes with thiohydrazide derivatives have been reported in the literature¹. Here, we report the mixed ligand complexes of oxovanadium (IV) with indole-3-thiohydrazide as primary and 3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridine carboxylic acid as co-ligand.

Indole-3-thiohydrazide (ithH) was synthesised according to literature procedure² and 3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridine carboxylic acid (hhmpcaH₂) (Aldrich Chemical Co.) and used as such.

Preparation of the Complexes :

[VOL₂X]X (where L = ithH and X = Cl, Br, NO₃, NCS)

The chloro complex was prepared by adopting the procedure described earlier¹. According to the method, a methanolic solution of the salt was treated with 1 : 2 molar ratio of thiohydrazide solution. The separated complex was filtered, washed with methanol and ether and dried over CaCl₂. The bromo, nitrate and thiocyanato complexes were prepared by adding lithium bromide, lithium nitrate and potassium thiocyanate to the reaction mixture. (Yield ca 65.0-67.5%).

Mixed Ligand Complexes :

[VOLL'X] (where L = ithH, L' = hhmpcaH and X = Cl, Br, NO₃, NCS)

The mixed ligand complexes were synthesised by the addition of ethanolic solution (10 mmole) of 3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridine carboxylic acid to the solution of the complexes [VOL₂X]X followed by the addition of sodium acetate in order to raise pH to 7-7.6. The separated complexes were filtered, washed with ethanol and dry ether and dried over anhydrous CaCl₂ (yield, ca 48.0 - 50.0%).

Analytical data are within $\pm 1\%$ error and favour 1 : 1 : 1 (M—L—L') stereochemistry for the complexes having general composition [VOLL'X] (X=Cl, Br, NO₃ or NCS). The mixed complexes are non-hygroscopic & stable. The complexes are insoluble in water and common organic solvents but they dissolve appreciably in DMF and DMSO. Conductance data (4.2–6.5 ohm⁻¹ cm² mol⁻¹) at the concentration 10⁻³ M in DMF show their non-ionic nature. The magnetic moments of the complexes lie in the range 1.84–1.88 B.M. These values correspond to one unpaired spin. Due to the insolubility of complexes in most of organic solvents, their molecular weights could not be determined.

A band observed at *ca* 935 cm⁻¹ in the spectrum of thiohydrazide is assigned as $\nu_{C=S}$. This band gets shifted in low frequency region *ca* 910 cm⁻¹ in the spectra of mixed complexes which suggests that the thiocarboxyl sulphur is involved in complexation. The replacement of NH₂ bending mode (1600 cm⁻¹) of thiohydrazide by a higher energy band (1615–1625 cm⁻¹) is suggestive of coordination of hydrazino terminal nitrogen³. Sharp vibrations seen in the region 3290–3240 cm⁻¹ in the spectrum of thiohydrazide are shifted to a medium broad band existing at *ca* 3220 cm⁻¹ in the complexes which further supports the coordination of hydrazino terminal nitrogen. The bands, characteristic of indole ring remain unaltered. In the spectra of the mixed complexes, the changes in the symmetric and asymmetric stretching vibrations due to $\nu_{C=C} + \nu_{C=N}$ and decrease in pyridine-ring-breathing modes clearly show the involvement of ring nitrogen in the coordination of oxovanadium. The frequency bands characteristic of $\nu_{sym} COO$ and $\nu_{asym} COO$ and alcoholic group present in hmpcaH₂ remain unchanged in the spectra of complexes while the band characteristic of phenolic —OH is not traceable showing its deprotonation and involvement of the oxygen atom in bond formation. Some non-ligand bands in the lower frequency region (340–350, 400–460 cm⁻¹) exist which may be due to M—S, M—O and M—N vibrations. The bands observed at *ca* 220 cm⁻¹ in halo complexes are assigned as ν_{M-Cl} or ν_{M-Br} . In the thiocyanato complex, $\nu(C-S)$ observed at 825 cm⁻¹ and δ NCS at 470 cm⁻¹ showed N-bonded to metal atom. In the nitrate complex, the observed bands indicate the monodentate nature of —NO₃.

Financial assistance from CSIR, New Delhi is gratefully acknowledged.

REFERENCES

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