

**METAL COMPLEXES OF TRI AND TETRA DENTTATE
AZOMETHINES DERIVED FROM 2-HYDRAZINO BENZOIC ACID**

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ABSTRACT

Synthesis and characterization of metal complexes derived from azomethine compounds viz., H-PMCPH and H₂-PECPH have been discussed. Schiff bases H-PMCPH and H₂-PECPH have been prepared by the condensation of 2-hydrazinobenzoic acid with pyridine 2-carboxaldehyde and 3-acetyl-4-hydroxy-6-methyl-2-pyrone.

Key words: Metal Complexes; Tri and tetradentate; Azomethines; 2-Hydrazino Benzoic Acid

Introduction

In this chapter the synthesis and characterization of metal complexes derived from azomethine compounds viz., H-PMCPH and H₂-PECPH have been discussed in two sections. Both the Schiff bases H-PMCPH and H₂-PECPH have been prepared by the condensation of 2-hydrazinobenzoic acid with pyridine 2-carboxaldehyde and 3-acetyl-4-hydroxy-6-methyl-2-pyrone (dehydroacetic acid) respectively. The former Schiff base is a nitrogen heterocyclic and monobasic in character. It provides NNO donor sequence to the metal ions hence tridentate⁽¹⁻³⁾. The latter Schiff base is a dibasic oxygen heterocyclic compound and exhibits multidenticity character, it being a tri and tetradentate towards metal ions. The ligand provides ONO and O, ONO donor sequence during metal chelation process.

Experimental

The following general procedure was adopted to synthesize the metal complexes.

To the hot ethanolic suspension of [0.120g, (0.0005 mol) in 50 ml ethanol] of the Schiff base H-PMCPH ethanolic solution of divalent / trivalent metal chloride (0.00025mol) [Cr(III) 0.067g;

Mn(II) 0.049 g; Fe(III) 0.041g; Co(II) 0.059g; Ni(II) 0.059g; Cu(II) 0.043g; Zn(II) 0.034g] was added in small increments. 0.041g (0.00025 mol) vanadyl sulphate was used in case of oxovanadium (IV) complex. It was observed that the ligand has dissolved completely after slow heating in presence of metal ion. The reaction contents were refluxed for 10-20 h periodically checking the pH of the solution and adjusting to ~5-6 with ethanolic ammonia. The coloured products so obtained were filtered in hot condition, washed with hot ethanol and ether successively and dried in vacuum. The purity of the complexes was tested by TLC using different solvent mixtures. Yields: 50-60%.

Result and Discussion

The complexes were found to be stable to atmospheric conditions. They are soluble in DMF and DMSO. They decompose around 165⁰C but the complete decomposition takes place beyond 300⁰C where they form metal oxides⁽⁴⁾.

Elemental Analysis

The analytical data of the complexes is given in Table-4A.1. the analysis of carbon, hydrogen, nitrogen, chloride, sulphur (wherever present) and metal reveals the following formulae (VO C₁₃H₁₂N₂O₃)₂SO₄; CrC₁₃H₁₂N₃O₃C₁₂; MnC₁₃H₁₆N₃O₅Cl; FeC₁₃H₁₂N₃O₃C₁₂; CoC₁₃H₁₆N₃O₅Cl; NiC₁₃H₁₀N₃O₂Cl; ZnC₁₃H₁₄N₃O₄Cl.

Analytical data reveals metal to ligand ratio is 1:1 in all the complexes. The data suggests presence of one chloride per divalent metal ions and two chlorides per trivalent ions⁽⁵⁾.

Thermogravimetric Analysis

Thermogravimetric analysis was carried out for all the complexes except Ni(II), IR spectrum of which did not show any broad trough indicating the absence of coordinated water molecules.

Oxovanadium (IV), Cr(III), Fe(III) complexes show thermograms where deauration occurs at 180-200⁰C in a single step supported by a broad endothermic peak at the same temperature in DTA curve. The weight loss (4.31-4.70%) is in conformity with the loss of one water molecule per mole of complex in each of these complexes. Hence, it may be concluded that water molecule occupies the coordination sphere in these complexes. From the endotherms of Cu(II), Zn(II), Mn(II) and Co(II) complexes it may be concluded that two coordinated water molecules per mole of complex are present in the first two complexes (weight loss, 9.6H %) and three coordinated molecules per mole in the remaining two complexes as the deauration occurs around 165⁰C in the first two complexes and near 235⁰C in the latter two complexes (weight loss, 12.35%) in a single step. Simultaneous elimination of coordinated water suggests that they are in the same chemical environment⁽⁷⁾.

Infrared Spectra

The IR spectral data of the complexes is given in Table-4A.2 and representative spectra of the complexes are given in fig. IVA.1 to IVA.4

The comparison of IR spectra of the ligand with the metal complexes shows characteristic changes in frequencies which are attributed to NNO sequence in the ligand for metal binding interactions towards bivalent/ trivalent metal ions used during complexation studies.

The two bands assignable for ν_{NH} and ν_{OH} at 3377 and 3213 cm^{-1} respectively in free ligand undergo changes in the band structure and appear as a broad band in the range of 3448-3070 cm^{-1} in spectra of all the complexes except that of Ni(II). This band may represent features due to u of coordinated water⁽⁸⁾. The strong band observed at 1677 cm^{-1} due to $\nu_{\text{C=O}}$ (carboxylic acid) disappears on complexation indicating the preference of carboxylate mode in chelation. The non-ligand bands appearing in the range of 1610-1670 cm^{-1} and 1370-1420 cm^{-1} assignable to ν_{COO} (asy) and ν_{COO} (sy) in the spectra of complexes confirm the carboxylate binding to metal ions. Further, the band position clearly indicates positive shift in ν_{COO} (asy) and negative shift in ν_{COO} (sy) in comparison with the corresponding bands recorded in the IR spectrum of sodium salt of H-PMCPH. These values clearly indicate that the $\Delta\nu(\nu_{\text{asy}} - \nu_{\text{sy}})$ is $> 200 \text{ cm}^{-1}$ further confirming unidentate coordination of carboxylate group⁽⁹⁾. This becomes possible due to deprotonation of -COOH function and subsequent binding through carboxylate oxygen. Another notable feature is the change in the position and band structure observed in the region of 1603-1570 cm^{-1} assigned to $\nu_{\text{C=C}}$, $\nu_{\text{C=N}}$ (free and pyridine ring) and δ_{NH} of the free ligand. This multiple band exhibits at least two distinct structures. Instead, the complex spectra indicates change of this band into one band or two band system with a negative shift down to the region of 1590-1560 cm^{-1} assignable to $\nu_{\text{C=N}}$ with consequential changes in $\nu_{\text{C=C}}$ and δ_{NH} confirming involvement of azomethine nitrogen and pyridyl nitrogen during complexation⁽¹⁰⁾.

The spectra of metal complexes provide ample evidence in support of involvement of pyridyl nitrogen. The absorption bands at 620 and 405 cm^{-1} which are due to pyridine in plane and out of plane ring deformations in free ligand respectively, show positive shifts subsequent to coordination and are observed around 640-656 cm^{-1} and 425-460 cm^{-1} respectively.

A band of medium intensity located in the range of 1038-1059 cm^{-1} assignable to $\nu_{\text{N-N}}$ in all the complexes has been observed compared to the corresponding band at 1013 cm^{-1} in the free ligand. The positive shift of this band clearly establishes involvement of one of the nitrogen of hydrazine moiety in dictation, preferably the azomethine nitrogen.

A strong non-ligand band appears at 972 cm^{-1} in oxovanadium (IV) complex is attributed to $\nu_{\text{V=O}}$. The bands at 520, 980, 1138 cm^{-1} are assignable to bidentate sulphate bridging in oxovanadium (IV) complex. The non-ligand bands observed in the range of 820-908 cm^{-1} are due to rocking

modes of coordinated water. The new bands observed in all the complexes in the range of 620-240cm⁻¹ have been assigned to M-O, M-N, M-Cl and M-Py stretching frequencies.

On the basis of IR spectral data of the metal complexes compared to those observed in free ligand, it is concluded that the ligand is monobasic and exhibits NNO donor sequence in tridentate fashion.

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