

A STUDY OF DIVALENT AND TRIVALENT TRANSITION METAL CHELATES OF NITROGEN CONTAINING LIGANDS

Dr. Yogender Singh

Assist. Prof. Chemistry

M.K.R. Govt. Degree College, Saddik Nagar, Ghaziabad, U.P.

E.Mail- yschemistry1981@gmail.com

Abstract

The electronic structure of transition metal atoms can be written as $[]ns^2(n-1)d^m$, where the inner d orbital has more energy than the valence-shell s orbital. In divalent and trivalent ions of the transition metals, the situation is reversed such that the s electrons have higher energy. The magnetic measurements are of immense importance in determining the nature of bond and stereochemistry of the complexes. The present studies have been initiated in the direction of evaluating the bonding, structure, geometry and other characteristics of metal chelates. The research work deals with the synthesis of ligands, methods of preparation and isolation of complexes. The next part of the research work deals with the synthesis and characterization of trivalent metal chelates (Five and six coordinate complexes).

INTRODUCTION

The chemistry of coordination compounds has made colossal advances both from the theoretical and preparative aspects in the last fifty five years. Thanks to the stupendous efforts of chemists belonging to different disciplines that it has now been possible not only to unravel the mystery of a board of inorganic complexes, but also to synthesise and characterise them. In fact, the basic understanding about the coordination compounds has undergone such a drastic change since the time of Werner, that it shall be improper to consider coordination chemistry as an isolated branch for study and research, but to consider it in its totality, giving due importance to its various ramifications. There are several modern areas of interest on which a coordination chemist can focus his attention. These are:

- (i) synthesis of complexes using reactants which may be highly volatile or may undergo decomposition or hydrolysis,
- (ii) nucleophilic substitution reactions leading to a change in the geometry of the molecule, and
- (iii) structure of the resulting product as worked out on the basis of various bonding theories in connection with their quantum mechanical treatment. It is with the latter aspect in view that most of the investigations described in the present thesis are based.

Metal-ligand interactions involving a large pH range and non-aqueous solvents present many interesting point requiring further elucidation. In the former case it has been claimed that the reaction product undergoes dimerisation depending upon the pH of the medium. Attempt has been made in this thesis to investigate this aspect on the basis of magnetic and spectral data. Various physico-chemical techniques are employed for ascertaining the

structure and geometry of the compounds. These are colorimetry calorimetry. DTA, TGA, potentiometry, polarography, UV, IR, EPR, NMR, X-ray diffraction electron and neutron diffraction etc. Relevant to the present investigations are UV - Vis, IR, magnetic susceptibility and elemental analysis.

The magnetic measurements are of immense importance in determining the nature of bond and stereochemistry of the complexes. The theories advanced by Van Vleck and Pauling provided a satisfactory explanation to account for the moments of spin-free and spin-paired compounds of first row transition metals. The advent of computer science in conjunction with vector coupling techniques has made calculations of considerable complexity, possible. However, there has not been a parallel development in the definition of Hamiltonians. The recently developed Normalized Spherical Harmonic Hamiltonian Theory, firmly based on group theoretical arguments of general validity fills this vacuum. This theory provides a number of advantages including standardization for interpreting the electronic spectra of coordination compounds.

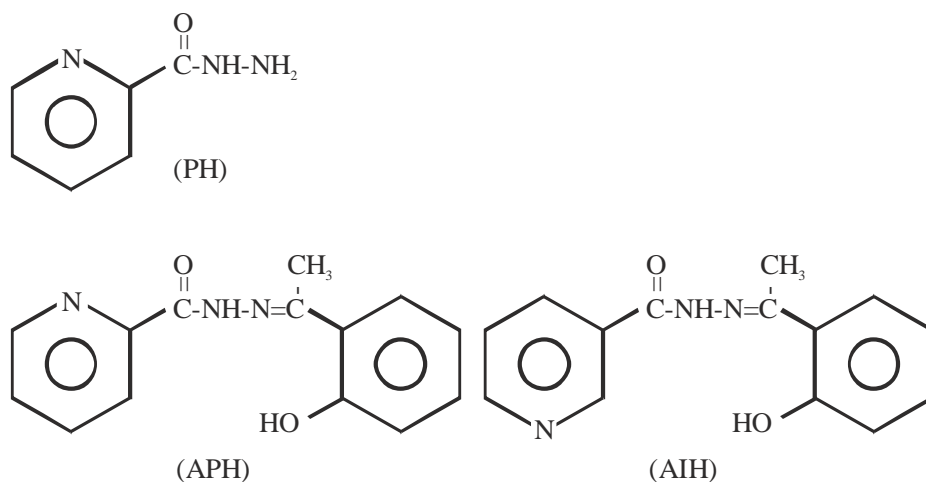
The conclusions arrived at by correlating the electronic spectra and magnetic properties have been fully supported by the vibrational spectral studies. These studies have been of specific importance in determining the bonding sites of a ligand and are of immense use in confirming the mono-, di- or polymeric nature of the compounds. The far i.r. region has been particularly utilized in differentiating the stereo chemistry of the molecules, since the magnitudes of shifts and regions of metal-ligand vibrations are dependent on configuration and geometries of the molecules (1). Therefore, it is evident that a oxidation state, spin configurations, stereochemistry of the complex molecule and the nature of metal donor link by correlating the magnetic, electronic and vibrational spectral characteristics of transition metal complexes.

The present studies have, therefore, been initiated in the direction of evaluating the bonding, structure, geometry and other characteristics of metal chelates. The present ligands have potential donor sites, viz., pyridine nitrogen, ketonic or enolic amide oxygen, hydrazinic or azomethine nitrogen and phenolic oxygen, which are suitably placed for coordination. The interesting feature is the presence of two oxygen atoms and either of them may act as a bridge between the two metal atoms.

In view of what has been said in the preceding paragraphs of the importance of Schiff's base complexes in biological reactions (5). It was though worthwhile to carry out investigations with metal complexes of pyridine based hydrazides and hydrazones. This is because they are versatile and interesting ligands (7,10,22) for several reasons viz., (a) these can function as tri-, tetra or pent dentate ligands, (b) coordination can occur through dianionic, monoanionic or neutral forms of these ligands (3,14,26). and (c) these can sometime bridge two metal ions through nitrogen or oxygen atoms.

In spite of the fact that much work has been reported on pyridine based acid hydrazides, relatively a few studies have been made with metal complexes of hydrazones derived from aldehydes and ketones (2,5,21). It has been observed that Schiff's bases derived from o-hydroxy aromaticaldehydes and ketones give rise to condensed bi- or polynuclear complexes involving phenoxide bridging and conform to varied stereo chemistries (10) While a large number of binuclear complexes of Cu (II) have been extensively studied (12,14,16). relatively a few such complexes or other transition metal ions are known (17,25,28,29). With this aim in view the following ligands were synthesized, and their

complexes with Ni(II), Co (II), Cr(III), Mn. (III), Co(III), VO(II), Pd(II), Pt (II) and Cu (II) were isolated both at low and high pH.



The complexes have been characterised to be four, five or six- coordinate with the help of analysis, conductance. molecular weight, magnetic. electronic and infrared spectral studies.

Besides studying the stereochemical aspects of the complexes, the present work can be faithfully extended on the following lines:

- (i) Synthesising the metal chelates both in their low and high valency states.
- (ii) X- ray absorption spectral studies (K-edge) for elucidating the symmetry of the coordination sphere, nature and length or metal- ligand bonds.
- (iii) X- ray diffraction studies for amorphous compounds and X-ray crystallographic for absolute structure determination.
- (iv) ESR measurements for elucidating the spin and ground states of the metal ions in different stereo chemistries.
- (v) Measurements of magnetic anisotropy to understand and deduce the electronic structure of metal complexes.
- (vi) Low temperature spectral studies which provide a comprehensive quantitative analysis of the absolute amount of distortion.

EXPERIMENT

Firstly, the synthesis of ligands is carried out. Three ligands viz, Picolinic acid hydrazid (PH), Ortho hydroxyl acetophenone picolinoyl hydrozone (APH) and ortho hydroxyl- acetophenone iso-nicotiyl hydrazone (ATH) were prepared.

Synthesis of Picolinic Acid Hydrazide (pH)

It was synthesised by refluxing ethyl 1-2 picolinate and hydrazine hydrate (99%) in 1:1 molar ratio on a water bath for five hours On cooling white crystalline product was obtained. It was filtered and recrystallised from ethanol when colourless needle shaped crystals (m.pt.101⁰) were obtained Yield ~85% . Similarly, the synthesis of Ortho Hydroxy

Acetophenone Picolinoyl Hydrazone (APH) was done. It was prepared by refluxing ethanolic solutions of picolinic acid hydrazide (0.1M) and o-hydroxyacetophenone (0.1M) for about three hours. On cooling a white product was obtained which was filtered. It was recrystallised from ethanol, when shining colourless crystals (m.pt. 214°) were obtained Yield ~ 75%. Post synthesis of ligands, complexes were prepared and isolated.

Methods of preparation and isolation of complexes

Two of nickel (II) and cobalt (II) complexes with PH. APH and AIH were synthesised at low and high pH as follows: Nickel (II) Complexes

Low pH complexes

Ethanolic solutions of PH (100ml; 0.01 mole) and nickel (II) chloride (100ml:0.005 mole) were mixed with constant stirring. The mixture (pH~2.3) was refluxed for about 4 hours. The solution was concentrated on a sand bath to half its volume and kept overnight. The light blue crystals thus obtained were filtered and recrystallised from ethanol and dried under vacuum. Yield~50%. Nickel hydrazones were obtained by first refluxing ethanolic solutions of PH or INH (100ml;0.01 mole) and o- hydroxyacetophenone (25ml;0.01 mole) followed by adding an ethanolic solution of nickel (II) chloride (50ml; 0.005 mole) dropwise with constant shaking. The reaction mixture (pH~2.2-2.7) was refluxed for about 3 hrs. concentrated and kept overnight . Light bluish or greenish crystals were obtained. They were filtered, washed acetone, recrystallised form ethanol and dried under vacuum. Yield~50-55%. The analytical data of the complexes reveal their formulae to be $Ni(C_6H_7N_3O)Cl_2$, $Ni(C_{14}H_{12}N_3O_2)$ and $Ni(C_{14}H_{12}N_3O_2)Cl$, respectively and their results are given. The complexes do not undergo decomposition on keeping in air and are stable upto $275^{\circ}C$. They are soluble in water, ethanol and dimethylformamide.

High pH complexes

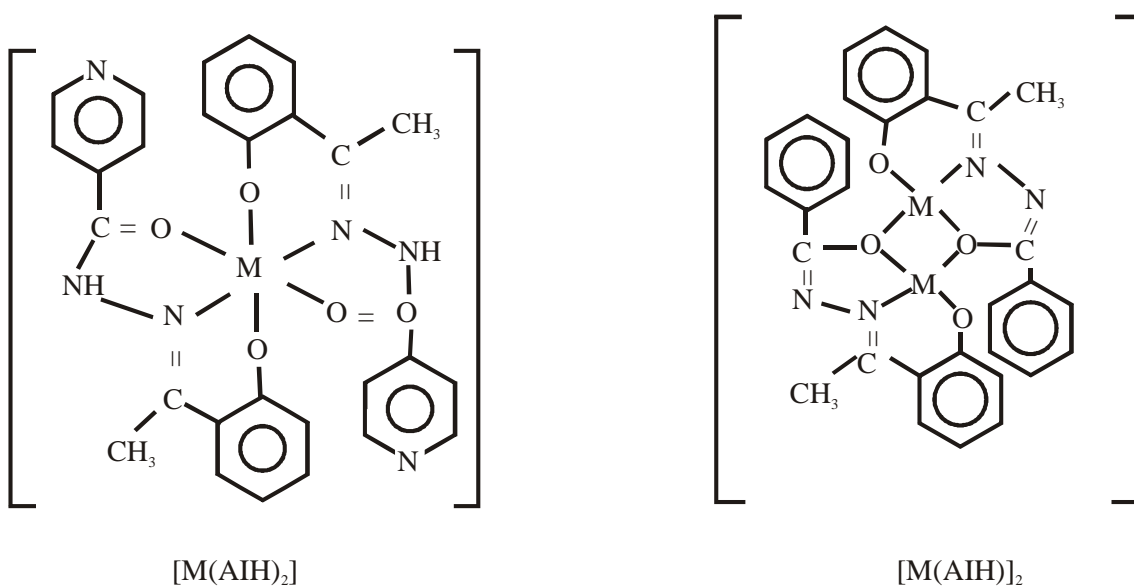
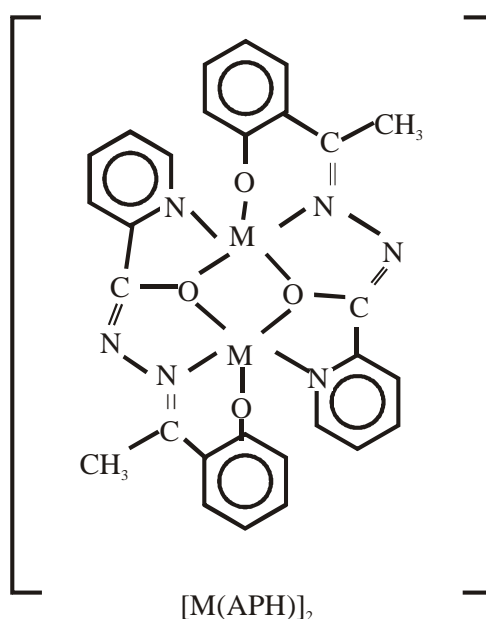
To warm ethanolic solution of nickel (II) chloride (50ml;0.01ml) and PH (50ml;0.02 mole) an ethanolic solution of potassium hydroxide was added dropwise with constant stirring, till pH became 4.9. The reaction mixture was refluxed for 1 hr, when a green precipitate was obtained. It was cooled, filtered, washed with ethanol, ether and dried under vacuum. yield~70%. The ethanolic solution of PH (50ml; 0.02 mole) was refluxed with o-hydroxyacetophenone (25ml;0.021 mole) for 1hr. To the hot solution warm ethanolic solution of nickel (II) chloride (100ml; 0.01 mole) was added gradually. The pH was then raised to ~5.0 by dropwise addition of ethanolic solution of potassium hydroxide, when the blue solution changed to olive green. On refluxing it for 1hr, a precipitate was filtered, washed with ethanol, ether and dried under vacuum. Yield~50%.

DISCUSSION

The first and second part of the research caters to synthesis of ligands and methods of preparation and isolation of complexes. It is followed by the characterization of complexes of divalent metals with the help of magnetic, electronic and infra red spectral studies - the complex investigated together with their analytical data and colours. The next part of the research work deals with the synthesis and characterization of trivalent metal chelates (Five and six coordinate complexes) PH, APH and AIH are chosen to synthesis the complexes of trivalent chromium, manganese and cobalt(30,31). These are characterized by analyses, molecular weight, conductance, magnetic and spectral studies. The important feature of the compounds is displayed by their being dimeric where enolic oxygen acts as a

bridge. A positive test for the chloride ion could only be seen on decomposition of these complexes, which is indicative of atoms being inside the coordination sphere ligand. Subsequently, the research work deals with the magnetic and spectral properties of dimeric five and six coordinate complexes of oxovanadium (IV) with PH, APH and AIH the analytical data reveal 1:1 metal to ligand to stoichiometry. Next, the synthesis and characterization of dimeric four and five coordinate complexes of the palladium, platinum and copper metals by analysis, conductance molecular weight determination, magnetic resonance, i.r. and electronic spectral studies is carried out.

The following structure may be proposed for the complexes.



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