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A Study of “Spectral and magnetic studies of four, five and six coordinated complexes of substituted hydrazides and hydrazones with Ni(II), Co(II), Mn(II) and Cr(III) metals”

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Abstract

The paper takes an in-depth look at the work of Metal-ligand interactions involving a large pH range and non-aqueous solvents which present many interesting points requiring further elucidation. In the former case, it has been claimed that the reaction product undergoes dimerization 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 calorimetry, DTA, TGA, potentiometry, polarography, UV, IR, EPR, NMR, X-ray diffraction, electron and neutron diffraction etc. Relevant to the present investigations are UV and Vis, IR, magnetic susceptibility and elemental analysis.

The role of metal ions in the biological system is seen in connection with enzymes polypeptides and amino acids. These acts as energy reacting catalyst by coordinating through certain ligand atom.

In view of the importance of Schiff's base complexes in biological reaction, it was through worthwhile to carry out investigations with metal complexes of pyridine based hydrazides and hydrazones. This is because they are versatile and interesting ligands, for several reasons, viz. (a) these can function as tri-,tetra- or pentadentate ligands, (b) coordination can occur through dianionic, monoanionic or neutral forms of these ligands and (c) these can sometime bridge two metal ions through nitrogen to oxygen atoms. The antibacterial and antifungal activities of Co(II) complexes are well known. Therefore, the following ligands were synthesized and their complexes with Ni(II), Co(II), Cr(III) and Mn(II) were isolated both at low and high pH.

Keywords: Introduction, object, scope, hypothesis, summary, spectral and magnetic studies, isolation and qualitative analysis.

Introduction

The chemistry of coordination compounds has made colossal advances both from the theoretical and preparative aspects in the last fifty years.

There are several modern areas of interest on which attention has been paid in this research. These are:

- Synthesis of complexes using reactants which may be highly volatile or may undergo decomposition or hydrolysis,
- Nucleophilic substitution reaction leading to a change in the geometry of the molecule, and
- 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.

The magnetic measurements are of immense importance in determining the nature of bond and stereochemistry of the complexes. The theories advanced by Van Vleck [1] and Pauling [2] provided a satisfactory explanation to account for the moments of spin-free and spin-paired compounds of first row transition metals. Kotani's theory [3] appears to provide a reasonable explanation for low moments in terms of increased orbital coupling in compounds of heavy metals. Recently, Konig et al. [4] have presented the complete theory of paramagnetism in transition metal ions for various electronic configurations in cubic and lower symmetry fields. It has been found that high spin entities are obtained with ligands containing hard donor atoms such as nitrogen and oxygen, while the low spin complexes are formed by soft donors, e.g. arsenic and phosphorous. However, Coleman and Taylor [5] have reported that five-coordinate complexes of ligands having even hard donors exhibit sub-normal magnetic moments. The anti-ferromagnetic interactions between the adjacent metal atoms seem to lower the magnetic moments, a phenomenon best known for polymeric compounds [6,7,8,9].

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 is of immense use in conforming 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 [10,11,12,13]. Therefore, it is evident that a clear picture can be deduced regarding the coordination number, 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.

Materials and Methods

Role of metal ions

The role of metal ions in the biological systems [14] is usually perceived in connection with enzymes, polypeptides and amino acids. These act as energy reacting catalysts by coordinating through certain ligand atom. For example, Na+, K+, Mg and Ca coordinate through oxygen and carry out biological function such as charge transfer, trigger reactions, hydrolysis etc. On the contrary, heavy metal ions like Zn, Cd, Co, Cu, Fe, Mo and Mn coordinate with nitrogen and sulphur ligands to help pH control, hydrolysis, redox reactions, there is yet another aspect of coordination compounds, which recognizes electron transport in living matter through a number of steps involving some very complicated structured oxidation-reduction enzymes in conjunction with metal-sulphur proteins.

Intermediate formation

Furthermore, it is believed that the intermediate formed in the trans amination reaction is a metal-Schiff's base complex formed through inner sphere bridge mechanism and is known since the mid nineteenth century [15, 16]. The importance of coordination sphere can be realized from the fact that substances capable of being attached to a single metal atom through three, four, five, six and even higher donor atoms can exist [17], which can serve as models for energy transfer in naturally occurring systems.

In view of what has been said in the preceding paragraphs of the importance of Schiff's base complexes in biological reactions [17,18], it was thought worthwhile to carry out investigations with metal complexes of pyridine based hydrazides and hydrazones.

SCOPE

It has been found [19,20,21] that amides can coordinate through oxygen or deprotonated nitrogen atom and it depends upon the experimental conditions as to which one of them will coordinate to the metal atom - a fact which has also been confirmed by X-ray analysis [22].

Polynuclear complexes result from the formation of bridges by atoms, ions or molecules which are coordinatively unsaturated, i.e., which after forming one bond still contain at least one unshared pair of electrons and are thus able to form an additional bond. The most widely studied of such bridging groups include O-2, O2-, OH-, NH-2, SO2-4, HCOO- and CH3COO- [23,24]. Bridges may be formed singly (by joining corners of two octahedra), doubly (by joining the edges of two octahedra) a triply (by joining the faces of two octahedra), which is an obvious parallel to the formation of single, double and triple bonds formed by carbon. It should be clear that the number of bridges connecting the two metal atoms cannot exceed three. It is also evident that for binuclear complexes containing one, two or three bridges, each of the metal atoms can still be bonded to five, four or three groups, respectively.

HYPOTHESIS

Besides studying the stereo chemical aspects of the complexes, the present work can be fruitfully extended on the following lines:

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

Results & Conclusion

As we can clearly see the importance of metal ions in the biological system in connection with enzymes polypeptides and amino acids. These acts as energy reacting catalyst by coordinating through certain ligand atom.

This study deals with the isolation of cobalt (II) and nickel(II) complexes of picolinic acid hydrazide, o-hydroxyacetophenone picolinoyl hydrazone and o-hydroxyacetophenone iso-nicotinoyl hydrazone at both low and high pH and are characterised to be four-,five- or six- coordinate with the help of analyses, molecular weight, conductance, magnetic, electronic and infrared spectral studies.

The Co(II) complexes at low pH are stable upto 300⍰. They are soluble in H_2O and ethanol but are insoluble in other solvents. The analyses of the complexes conform to the formulae $Co(C_6H_7N_3O)_2Cl_2$, $Co(C_{14}H_{12}N_3O_2)Cl$ and $Co(C_{14}H_{12}N_{3}0_{2})_2$, respectively.

- The I.R. spectra of Ni (II) and Co(II) helps us in drawing the following conclusions:
- In the PH and APH complexes, pyridine nitrogen coordinates, while it does not do so in AIH complexes, perhaps due to steric effects.
- The hydrazinic nitrogen in PH and azomethine nitrogen in APH and AIH participate in coordination.
- The phenolic oxygen coordinates through deprotonation at both low and high pH in APH and AIH complexes, but does not bridge the two metal atoms.
- At low pH, amide oxygen coordinates to the metal atom in the keto form, while at high pH, it does so in the enol form and forms a bridge between the two metal atoms.
- The magnetic and electronic spectral studies of Ni (II) and Co (II) complexes reveals the following informations:
- Ligands PH and AIH act as tridentate, while APH is tetradentate. All form two types of complexes, depending upon pH of the reaction mixture.
- Complexes synthesised at low and high pH are monomeric and dimeric, respectively.
- In complexes synthesised at high pH, the dimerisation is initiated by enolic oxygen, which acts as a bridge between the two metal atoms.
- In PH and APH complexes, besides phenolic oxygen, ketonic or enolic oxygen and hydrazinic or azomethine nitrogen, pyridine nitrogen also takes part in coordination, while it is not so in AIH complexes.
- (5.2.5) At low pH, PH and AIH complexes are six coordinate while those of APH are five-coordinate. At high pH, except AIH complexes which are four-coordinate all other complexes are five-coordinate.
- The I.R. spectra, magnetic and electronic spectral studies of Cr(III) have been discussed. Based on these studies, the following conclusions are drawn:
- Ligand APH acts as tetradentate, while PH and AIH behave as terdentates.
- All ligands from monomeric complexes at low pH, At high pH, dimeric complexes are formed in which enolic oxygen acts as a bridge.
- PH and APH form tetragonally distorted octahedral complexes, both at low and high pH.
- AIH forms five-coordinate complexes. At low pH, they are trigonal bipyramidal, while at high pH, they conform to square pyramidal structure.

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