

Synthesis of new ligands having O,N and S sites

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ABSTRACT

Study of metal complexes has been of great importance. Versatile chelating ability of the biological active neutral bases is the latest aspect in the development of co-ordination chemistry. With this view in this study some mixed ligand complexes of attired biological activity were prepared.

Key words: New Ligands, O,N and S sites.

INTRODUCTION

The formation of mixed ligand complexes depend on all the factors which influence both the metal ion and ligand molecules individually. In the case of metal ions, the formation of mixed ligand depends mainly on its electronic structure and ionic potential (charge/ionic radii ratio). In terms of ligands, the mixed ligands depends on the basicity of ligands, its dentateness, the nature of donor atoms present in it, types of low ring formed (5 or 6 membered ring) and also on the number of fused rings formed during complexation. Beside the above, the nature of metal-ligand bond whether, it is σ or π , mutual polarisability of the metal ion and ligands are the additional factors which play a vital role in the mixed ligand complex formation. In addition to the above, the soft-soft or hard-hard acid-base interactions favour the greater stability of the resulting complex.

The metal chelates of nitrogen containing ligands have been found more biologically active. There are references on transition metal complexes with biologically active ligands such as 2,2'-bipyridyl, o-phenanthroline, 2-picolonic acid, 8-hydroxy quinoline, α -alanine and histidine etc. Some of them have also been reported as potential drugs 2,2'-bipyridyl, o-phenanthroline, from stable complexes with metal ions at pH which also remain stable even

at higher buffer region. Both these compounds have therefore been used widely as primary ligand in the study of variety of mixed-ligand complexes. It is found that the metal chelates of these two ligands are very active against the Gram positive and Gram negative bacteria and different fungi.

MATERIAL AND METHODS

All the chemical used were of either Analar or G.R. grades. Freshly prepared double distilled water was used for preparation of solutions and kept in well stoppered neutral glass ligands were synthesized and isolated using method of Sharma²⁰.

Synthesis of ligands

Following ligands were synthesized and isolated using methods of sharma²⁰.

Synthesis of N-(2-pyridine)-anthranilic acid (C₁₂H₁₀N₂O₂)

9.94 m.mol of 2-amino-pyridine suspended in 50ml water was added to 100ml water solution of 15.85 mol chlorobenzoic acid and mixed well. With the help of dilute sodium bicarbonate solution, its pH was maintained almost neutral (7-8). All the contents of the mixture were refluxed for about 6h using water condenser on an oil bath. On cooling, the resultant filtrate was acidified with dil hydrochloric acid. The obtained precipitate was filtered, washed

with cold water and dried under vacuum in a desiccator. The crude product was recrystallized from alcohol.

Crude yield 18.65 gms.
Recrystallized 10.00 gms

Synthesis of diphenylamine-2-hydroxy-2'-carboxylic acid

6.50 gms of 2-amino phenol was dissolved in 40ml of water and 7.8 gms of the ortho chlorobenzoic was dissolved in 50ml of water separately. Both the solutions were mixed and pH of mixture was adjusted to 7-8 with sodium bicarbonate solution using the Universal indicator paper. The mixture thus formed was refluxed over an oil bath for about 5h. The solution was decolourised with the help of charcoal and filtered white hot. It was then acidified with A.R. hydrochloric acid to get a precipitate. The resultant precipitate was filtered, washed with cold water and dried as usual. It was recrystallised with alcohol to get crystals.

Crude yield 10.00 report in %
Recrystallized 5.7 report in %
Product

Synthesis of 2-hydroxy-benzalidine-anthranilic acid

2.74gms of 2-amino benzoic acid and 2.09 ml salicylaldehyde were dissolved in 10ml ethanol separately. Both these solutions were mixed together and refluxed over water bath for about 5h. The mixture was left at room temperature for over night and then orange red crystals were formed. The obtained crystals were filtered, washed with cold distilled water followed by ethanol and ether. Product was recrystallised with ethanol. Orange yellow crystals obtained were dried under reduced pressure over anhydrous calcium carbonate.

Crude yield 4.10 %
Recrystallized 2.78%

Synthesis of 2-hydroxybenzalidine-o-aminopyridine

2.09 ml salicylaldehyde was dissolved in minimum quantity of absolute ethanol. Similarly, 1.88 gm of 2-amino pyridine was also dissolved in minimum quantity of dry ethanol. Both the solutions were mixed and the mixture was refluxed for about 6h and then concentrated to reduce its volume to one third and cooled. On cooling, a crude product was obtained which was again recrystallized from alcohol. The yellow crystals were formed.

Crude yield 3.00 %
Recrystallized 1.82%

2-hydroxybenzalidine-2-aminothiophenol

An equal volume of ethanolic solution of 2.50 m.mol of 2-amino thiophenol and ethanolic solution of 2.02gm of salicylaldehyde were mixed and stirred well. The mixture thus obtained was refluxed over a water bath for about 6h and solution was cooled in a refrigerator. The obtained crystals were filtered, washed first with alcohol and then with ether. The crude product was recrystallised from ethanol finally to get orange crystals.

Crude yield 3.00 %
Recrystallized 1.82%

RESULTS AND DISCUSSION

Mixed-ligand complexes having ligands with N,S and O as donor atoms are quite common in biological and analytical systems. Thus an understanding of the significance of the ligand in biological system may reveal the mysterious surrounding of the protein-substrate interaction and the controlled mechanism that determines the coordination tendency of metal ions bound at the active sites of many enzymes in enzyme-metal ion-substrate reaction. The interaction of enzymes with substrates or inhibitors in biological system leads to the formation of enzyme-metal ion substrate ternary complex. The considerable importance of mixed complexes in biological fluids have been established.

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