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Metal complexes of Schiff bases: Preparation, characterization and synthesis of Schiff base derived from salicylaldehyde and triazole and its transition metal complexes

Archana Saxena

Department of Chemistry, M.I.T., Moradabad, India

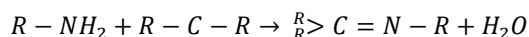
ABSTRACT

The Schiff bases and a series of transition metal complexes of Ti(III), V(III), Mn(III), Ru(III), CO(II), Ni(II), Zn(II), Cd(II) and Cu(II) with a tridentate ligand is derived from the inserted condensation of salicylaldehyde with 4-amino 5-mercapto 1,2,3 triazole in a 1:1 molar ratio. The synthesized complexes were characterized by several techniques using molar conductance, elemental and spectral analyses, magnetic measurements, Infra-red spectroscopy, NMR, electronic spectra, Mass spectra particle data. Based on these studies octahedral structures have been assigned to these complexes.

Keywords: Salicylaldehyde, Mercapto, Triazole and Octahedral.

INTRODUCTION

Schiff bases have a huge amount of synthetic uses in organic chemistry. Especially in ligand a metal surrounded by a cluster of ion or molecule, is used for preparation of complex compound named as Schiff bases[1]. Schiff bases are the compounds containing azimethine group ($-C = N -$). A Schiff base is a nitrogen analog of an aldehyde or ketone in which the $> C = O$ group is replaced by ($> C = N - R$) group between the (O) and (N) atoms which play an important role in the formation of metal complexes and that Schiff base compound show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the amine (N) atom [2]. They are condensation products of ketones or aldehydes with primary amine according to the following scheme.



Where R may be an alkyl or an aryl group.

The formation of a Schiff bases from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis or upon heating. The common Schiff bases are generally solids, which are lacking physical strength but at least some form insoluble salts with strong acids. Polydentate ligands, such as Schiff bases assisted by metal ions, provide highly organized supramolecular metal complexes. Such complexes possess binding sites and cavities for various cations, anion and organic molecules [3-4].

Today, Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures. During the past two decades considerable attention has been paid to the chemistry of the metal complexes of Schiff base containing nitrogen and other donors[5,6]. As the continuation interest of our study of transition metal complexes here we present the synthesis & characterization of new complex derivatives of 4-amino 5-mercapto 1, 2, 3 triazole.

MATERIALS AND METHODS

All other chemicals employed were of the highest grade available. Unless and solvents otherwise reagent grade reactants and solvents were used as received from chemical suppliers. Ethanol and ether were distilled before use.

Preparation of ligand: Figure 1 shows, Salicylaldehyde (.01mol) and 4-amino5-mercapto 1,2,4 triazole (1.29gm .01mol) were mixed in ethanol (20ml) and the mixture was refluxed for 30 minutes on a water bath when a brownish solution was obtained. Partial evaporation of the solvent under a fan gave crystals of the Schiff base which were filtered washed with ethanol and dried in vacuo and yield = 70%, M.P =170.

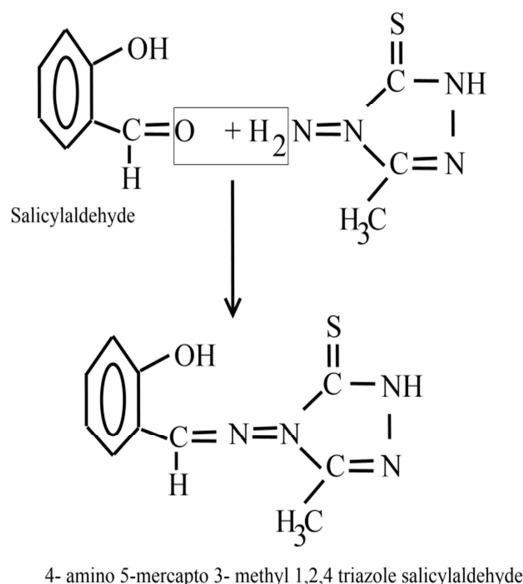


Figure 1: Preparation of ligand

Characterization of ligand:

The ligand was subjected to elemental analyses of C, H, N to ascertain its molecular composition the IR spectra of the ligand were recorded in KBr phase. The melting point of the ligand was determined by open capillary method & uncorrected.

Table 1: Ligand Characterization detail

| S. No. | Name & Molecular formula of the ligands | Colours | M.P /D.T. | Elemental Analyses | | | | | Molor Conductance |
|--------|--|------------|-----------|--------------------|-------------|---------------|-------------|---------------|-------------------|
| | | | | % of C | % of H | % of N | % of S | % of Cl | |
| 1. | 4- amino 5-mercapto 3- methyl 1,2,4 triazole salicylaldehyde | Colourless | 170 | 51.20 (50.20) | 4.20 (4.08) | 23.90 (22.80) | 6.83 (5.80) | 13.67 (12.57) | DMSO |

Synthesis of Metal Complexes:

General method has been used for the preparation of all the complexes. The Schiff base was prepared as follows; a solution of 4- amino 5-mercapto 3- methyl 1,2,4 triazole (1.29gm,.01mol) was added to a solution of salicylaldehyde (.01mol) were mixed in ethanol (20mol). The resulting mixture was refluxed for 30 minutes on a water bath. In the next step, the metal salt (20ml ethanol) were added to the ligand solution under continuous stirring when the

complex was precipitate. The obtained coloured product was separated by filtration washed with distilled water and ethanol and dried under vacuum. Recrystallization from hot methanol gave the metal complexes [7, 8].

CHARATERIZATION OF METAL COMPLEXES OR ANALYSES AND INSTRUMENTATION:

The complexes were subjected to elemental analyses. The metal was estimated gravimetrically. The molar conductance of the complexes was measured at 10^{-3} dilution in DMSO/ methanol or both dilutions at 25°C indicate its 1:2 electrolytic nature. The magnetic properties of the complexes were studied & infrared and visible spectra were recorded. The complexes also subjected to the thermo gravimetric analyses. The colours of complexes were noted and their melting point was determined [9,10].

Elemental analyses:

Elemental analyses were performed on a Perkin-Elmer-24⁰C model at the central drug research Institute (CDRI), LUCKNOW.

Infra-Red studies:

The Infra red studies of the complexes were recorded with Perkin Elmer spectrophotometer model 651 in KBr or Nujol Phase from 4000cm^{-1} to 250cm^{-1} at R.S.I.C, CRDI, LUCKNOW.

Conductivity measurements:

Conductivity measurements were carried out by Philips at department of chemistry, Bareilly college, Bareilly. The conductance of the complex was measured in methanol & DMSO.

Magnetic Susceptibility:

The magnetic susceptibility was determined by Gouy's method using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant.

Electronic Spectra:

The electronic spectra of the complexes were recorded by Beckmann-DU spectrometer.

Table-2: Characterization of metal complex

| | | | | | |
|---------------------------------------|--|-------------|------------------|------------------|------------------|
| Name & Molecular formula of complexes | 4-amino 5-mercapto-3-methyl 1,2,4 triazole salicylaldehyde Titanium (III) Chloride [$\text{C}_{10}\text{H}_9\text{N}_4\text{O}$]. $3\text{H}_2\text{O}$.TiCl | | | | |
| Colour | Brownish | | | | |
| M.P/D.T | 250 | | | | |
| Elemental Analyses | % of C | % of H | % of N | % of M | % of O |
| | 35.79 (34.69) | 4.39 (3.69) | 16.42 (15.70) | 13.78 (12.28) | 20.82 (19.32) |
| Molar Conductance | Methanol | | DMF | | DMSO |
| | 105 | | 80 | | 40 |
| Magnetic Moments in B.M. | 171 | | | | |

RESULTS AND DISCUSSION

The Schiff bases are subjected to elemental analyses. The results of elemental analyses (C, H, N, S) with molecular formula and the melting points are presented in Table 2. The analytical data for the complexes suggested 1:2 stiochiometry for all the synthesized complexes. [11,12]

The elemental analyses for C,H,N & S and gravimetric estimation of the metal & chloride indicated 1:1 metal ligand molar ratio in the complex. The melting point of the ligand was 190°C and that of the complex was 250°C . This vast difference in melting points of the ligand and the complex indicate that the complex has been formed. This is also supported by other physio chemical studies. On this basis comes out to be $[\text{C}_{10}\text{H}_9\text{N}_4\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{TiCl}]$.

Molar conductance:

The determination of molar conductance of the in DMSO & methanol 10^{-3}M dilution at 25°C indicate its 1:2 electrolytic natures.

Magnetic Moments:

The complex was found to be possessing magnetic moments of 1.78 B.M., which is slightly higher than the expected value of 1.73 B.M. for d^1 system like Titanium (III).

Infra-Red Spectra:

In order to study the binding mode of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with spectra of the metal complexes. The I. R. spectrum of the schiff base shows a medium intensity band at 3200cm^{-1} , which may be assigned to $\nu(\text{O-H})$ & $\nu(\text{NH})$ modes[13,14]. The absence of this band in the IR spectrum of the complex indicated the deprotonation and consequent co-ordination of the phenolic $-\text{OH}$ group. This also indicates the presence of deprotonated thiol form of the ligand in the complex.[15,16] The ligand does not exhibit any band around 2500cm^{-1} due to $\nu(\text{S-H})$ and this indicates the presence of thione form of the ligand in the solid state. The free ligand shows a band at 1140cm^{-1} due to $\nu(\text{C=S})$. This band disappears in the I.R. spectrum of the complex, and a new band appears at 617cm^{-1} in the I.R. spectra of the complex due to $\nu(\text{C=S})$ mode. Thus the I.R. spectrum is indicative of sulphur co-ordination. The I.R. spectrum of the ligand exhibits a band at 1610cm^{-1} , which may be assigned to $\nu(\text{C=N})$. This band shifts to lower side in the I.R. spectra of the complex. This indicates co-ordination through nitrogen atom of the azomethine group. It appear, therefore the ligand is acting as dibasic tridentate ONS donor[17,18].

Co-ordination Water:

The presence of co-ordinated water molecules in the complex may be infra red by the appearance of band at 3300 & 800cm^{-1} in their spectra of the complex. This is also supported by thermo gravimetric analyses, which shows the loss of water molecules around 140°C .

Electronic Spectra:

The electronic spectra absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used for assigning the stereochemistry of metal ions in the complexes based on the position and no. of d-d transition peaks.

The Electronic spectra of the complex show a band at 18300Cm^{-1} , which may be assigned to d-d transition. The value of d-d transition corresponds to crystal field splitting energy. The spectrum of the complex also shows a weak band at 22629Cm^{-1} with shoulder in the region of 17460cm^{-1} . These bands have been assigning to $2\text{B}_{1g} \rightarrow 2\text{B}_{2g}$ and $2\text{A}_{1g} \leftarrow 2\text{B}_{2g}$ transition respectively [19]

CONCLUSION

On the basis of above mentioned facts the complex appears to have octahedral geometry, three co-ordination sites are occupied by tridentate ligand molecule and the remaining three by water molecules. The structure of the complex may therefore, be represented as.

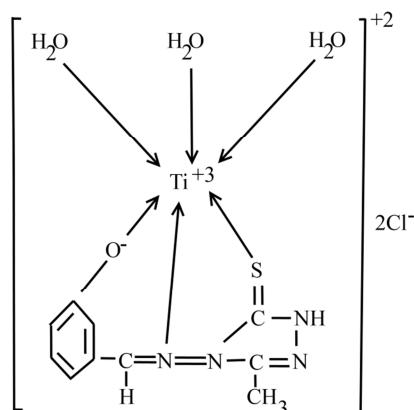


Figure 2: structure for 4-amino 5-mercapto-3-methyl 1, 2, 4 triazole salicylaldehyde Titanium (III) Chloride

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