Studies of Co(II) and Mn(II) Complexes of Schiff Base Derived From 2-Chlorobenzaldehyde and Thiosemicarbazide

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Abstract: *This research is to investigate the condensation of 2-chlorobenzaldehyde and thiosemicarbazide in acetic acid medium leads to the formation of 2-chlorobenzaldenethiosemicarbazone. The 2-chlorobenzaldenethiosemicarbazone ligand acts as a bidendate ligand and co-ordinates with metals like Manganese and Cobalt. The shift to lower frequency of C=N as well as C=S vibrations in the FT-IR spectrum of the complexes compared to that of the ligand indicates that the metal co-ordination occurs at both N and S. Further, the ^{1}H-NMR spectrum of the complex [$CoBr_2$(Cl-btsc)] shows that the tautomerism between thione and thiol has occured during the co-ordination. The TGA thermogram of the complex [CoBr2(Cl-btsc)] is observed among the all complexes strong peak at temperature 358°C. The complex have higher thermal stability and decomposes almost completely at this temperature.*

Keywords: Schiff base complexes; Non-Linear optical properties; Cobalt and Manganese halid, 2-chlorobenzaldene thiosemicarbazone;

1. INTRODUCTION

A crystal may be defined as a solid composed of atoms arranged in a periodic pattern in three dimensions. Crystals differ from gases, liquids and solids because the atomic or molecular or ionic arrangement in the liquids do not posses the essential requirement for periodicity. In the biological and medical point of view, transition metal Schiff base complexes show antifungal, antimalarial and antiviral activities [1-3]. Schiff base ligands have been particularly valuable for designing complexes of widely different structural type.

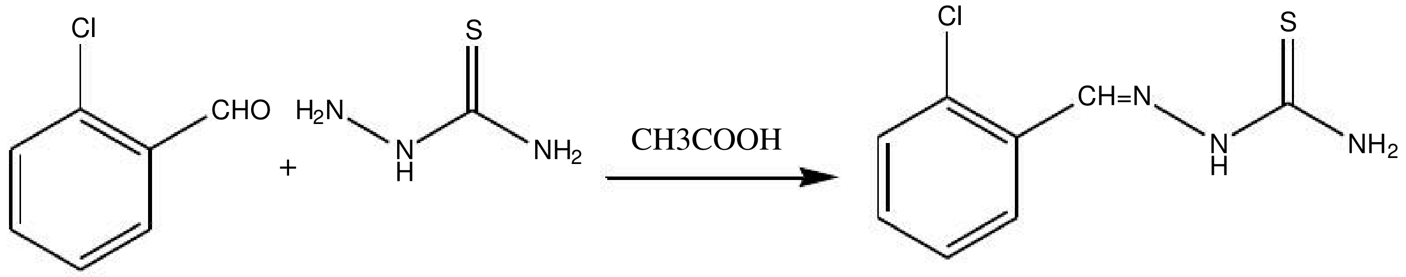
Thiosemicarbazones and substituted thiosemicarbozones are important organic analytical reagents. They contain azomethine nitrogen atom[4-7]. These reagents act as good chelating agents and form complexes with various metal ions by bonding through thio keto sulphur atom and hydazino nitrogen atom [8-10]. They are obtained by condensing thiosemicarbazide with suitable carbonyl compound.

Xiao-Zeng You et. el has reported the synthesis, characterization and non-linear optical properties of cadmium halide complexes with 2-chlorobenzaldehyde thiosemicarbazone[11]. Based on various characterization techniques, they concluded that in cadmium iodide and bromide, the co-ordination geometry of Cd(II) confirms a tetrahedral configuration with two sulphur atoms from two unequivalent neutral ligands and two bromide atoms. Also the above complexes were found to exhibit powder SHG (NLO) efficiencies approximately 20 times that of urea. Further, they suggested that intermolecular contacts play a major role in controlling the SHG efficiencies of compounds. Based on the literature, transition metal complexes containing schiff base ligands are expected to be a good non-linear optical material. Hence, in the present study, it is proposed to prepare Schiff base ligand 2-chlorobenzaldehyde thiosemicarbazone and its complexes using halides of Manganese and Cobalt. The ligand and complexes were characterized by various instrumental techniques in order to establish the bonding mode between metal and ligand Non-linear optical activities of the complexes and thermal stability also have been tested.

2.MATERIALS AND METHOD

All chemicals were of reagent grade and were used without further purification.

2.1 Synthesis of 2-Chlorobenzaldene thiosemicarbazone ligand (Cl-btsc)



Melting point : 178°C Colour : Pale yellow

Five drops of acetic acid were added to a mixture of thiosemicarbazide (0.91g, 10 mmol) and 2-Chlorobezaldehyde (1.40g; 10 mmol) in refluxing ethanol. The solution was further refluxed over water bath for 2 hr and a pale yellow solid was formed. The solid was filtered off by suction and dried over silica gel in a desiccator.

2.2 Synthesis of the metal complexes

2.2.1 2–Chlorobenzaldene thiosemicarbazone Cobalt Bromide [$CoBr_2$(Cl-btsc)]

An ethanolic solution of 2-chlorobenzaldene thiosemicarbazone (0.43g, 2 mmol) and Cobalt bromide (0.37g 2 mmol) were mixed. The colourless crystalline solid formed after refluxing over water bath for 5 hr was isolated, washed with ethanol and dried over silica gel in a desiccator.

2.2.2 2–Chlorobenzaldene thiosemicarbazone Cobalt Chloride[$CoCl_2$(Cl-btsc)]

An ethanolic solution of 2-chlorobenzaldene thiosemicarbazone (0.43g, 2 mmol) and Cobalt chloride (0.20g, 2 mmol) were mixed. The colourless crystalline solid formed after refluxing over water bath for 5 hr was isolated, washed with ethanol, and dried over silica gel in a desiccator.

2.2.3 2 – Chlorobenzaldene thiosemicarbazone Manganese Bromide[$MnBr_2$(Cl-btsc)]

An ethanolic solution of 2-chlorobenzaldene thiosemicarbazone (0.43g, 2 mmol) and Manganese bromide (0.72 g, 2 mmol) were mixed. The colourless crystalline solid formed after refluxing over water bath for 5 hr was isolated, washed with ethanol and dried over silica gel in a desiccator.

2.2.4 2 – Chlorobenzaldene thiosemicarbazone Manganese Chloride[$MnCl_2$(Cl-btsc)]

An ethanolic solution of 2-chlorobenzaldene thiosemicarbazone (0.43g, 2 mmol) and Manganese chloride (0.45g, 2 mmol) were mixed. The colourless crystalline solid formed after refluxing over water bath for 5 hr was isolated with ethanol and dried over silica gel in a desiccator.

2.3 Characterization of Ligand and Complexes

IR spectrum of the ligand and complexes 1,2,3 and 4 were recorded on a Perkin-Elmer 597 spectrophotometer in the range 4000-500 cm^{-1}, using KBr pellets. The ^1H-NMR spectrum of complexes has been recorded in chloroform using Bruker Cryospec WM 250 Spectrometer with tetra methyl silane (TMS) as the internal standard and TGA thermogravimetric analytical studies were carried out using TA 4000 METTLER SYSTEM and STA 1500 (version:V4.30) for the Cobalt bromide Schiff base complex. The TGA study was carried out up to 600°C at a heating rate of 15°C/min. were used to characterize the transition metal complexes.

2.4 Measurement of Non-linear optical activity

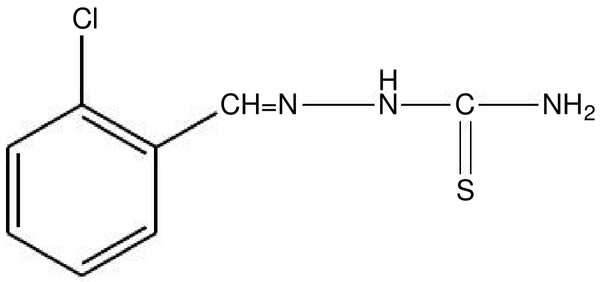
The second-order nonlinear optical intensities are estimated using powder of 76-154 µm diameter in the form of a pellet. The thickness of the pellet is about 0.8 mm. The pressure in compacting the pellet is 300

MPa. The experimental arrangement for the non-linear optical properties utilizes a M200 high-power mode-locked Nd:YAG laser with 200 ps, pulse at a repetition rate of 5Hz. The selected wavelength is 1064 nm. After the selection of the wavelength, the laser beam is split into two parts, one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference urea pellet.

3. RESULTS AND DISCUSSION

3.1 Characterization of Ligand by FT-IR Spectroscopy

The FT-IR spectrum of 2- chlorobenzaldene thiosemicarbazone ligand is shown a sharp peak at 750 cm^{-1} is assigned due to –C-Cl stretching vibration. The presence of aromatic ring system in the ligand is evidenced by the C-C stretchings of the benzene ring at 1619 cm^{-1} and 1511 cm^{-1}. Further, the C-H out of plane bending vibrations of benzene ring is indicated by a peak at 818 cm^{-1}. A strong band at 1611 cm^{-1} appeared due to C=N vibrations. The appearance of peak due to C=N vibrations indicates the formation of azomethine linkage in the ligand due to condensation of 2- chlorobenzaldehyde and thiosemicarbazide. The medium N-H vibrations are indicated by the peaks at 3415 and 3154 cm^{-1}. The presence of C=S (thione) group in the ligand is indicated by a sharp peak at 1089 cm^{-1}. All the above data from FT-IR spectroscopy reflect the structure of Schiff base ligand.



3.2 Characterisation of Schiff base Metal Complexes

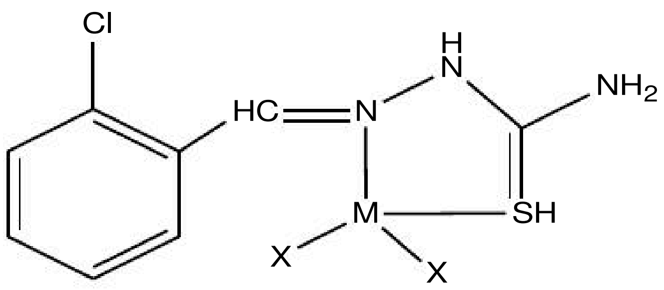
3.3 FT-IR Spectroscopy

The FT-IR Spectra of complexes 1,2,3 and 4 are show a broad bond around 795- 735 Cm^{-1} due to the strong C-Cl stretching vibration in the ring. The C-Cl stretching frequency is indicated by band at 754, 767, 769 and 776 cm^{-1} in complexes 1,2,3 and 4 respectively. There is no significant change in the absorption frequency of C-Cl stretching vibration ligand and complexes indicating C-Cl group is not affected by metal co-ordination. Also, no significant change is observed in N-H vibrations in the ligand and complexes. But in the case of C=N and C=S vibrations, a shift to lower frequency is observed in all the metal complexes when compared to pure ligand. The band due to C=N vibration in ligand at 1619 cm^{-1} is shifted to 1543-1570 cm^{-1} in complexes. The band due to C=S vibration in ligand appearing at 1071 cm^{-1} is shifted to 1029-1055 cm^{-1} in complexes. The shift to lower frequency of C=N and C=S vibrations in metal complexes compred to ligand can be accounted in terms of co-ordination of the transition metal at N and S atoms of the C=N and C=S group respectively. Due to co-ordination, at N and S, the electron density as well as bond order in C=N and C=S is decreased and hence the absorption frequency of the above linkages decrease to lower frequency.

3.4 ^{1}H-NMR Spectra

The bonding of ligand to metal is further supported by ^{1}H-NMR spectral studies. The ^{1}H-NMR Spectrum of the complex $[CoCl_2(Cl\text{-}btsc)]$ the NH proton signal around δ 10.7 ppm disappears in the spectrum of the complex showing deprotonation due to thioenolisation and co-ordination through the nitrogen atom of the ligand. The multiplet peak observed at δ 7.4 ppm has been assigned to the protons from phenyl group. The singlet observed at δ 1.8 ppm has been assigned to the proton from the NH_2 group of the thiosemicarbazide ligand.

Showed a shift in absorption frequency of C=S and C=N bands to lower frequency indicating that the lone pair of electrons present in both S and N is used for co-ordination with metal. i.e., the 2-chlorobenzaldenethiosemicarbazone ligand is acting as a neutral bidendate ligand. Based on the above studies, the possible co-ordination of the ligand with metal, and hence the probable structure of the prepared metal complexes is as given below[11].



Where M = Co, Mn X = Cl, Br

3.5 Non-linear optical property and Thermal Analysis

The Manganese complexe [$MnBr_2$(Cl-btsc)] were tested for NLO activity and found to be active. The efficiencies have been found to be better than the urea pellet reference material. The TGA thermogram of the complex [$CoBr_2$(Cl-btsc)] is observed among the all complexes strong peak at temperature 358°C. The complexe have higher thermal stability and decomposes almost completely at this temperature.

4. CONCLUSION

The condensation of 2-chlorobenzaldehyde and thiosemicarbazide in acetic acid medium leads to the formation of 2-chlorobenzaldenethiosemicarbazone. The 2-chlorobenzaldenethiosemicarbazone ligand acts as a neutral bidendate ligand and co-ordinates with Manganese and Cobalt. The shift to lower frequency of C=N as well as C=S vibrations in the FT-IR spectrum of complexes compared to that of ligand indicates that the metal co-ordination occurs at both N and S. The TGA thermogram of the complex [$CoBr_2$(Cl-btsc)] is observed among the all complexes strong peak at temperature 358°C. The complex have higher thermal stability and decomposes almost completely at this temperature. The Manganese complexe [MnBr2(Cl-btsc)] were tested for NLO activity and found to be active. The efficiencies have been found to be better than the urea pellet reference material.

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