

SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZONE CORE LIGAND**DURGESH KUMAR RAI^a AND ANKUSH SINGH^{b1}**^{ab}Department of Chemistry, Sam Higginbottom Institute of Technology and Sciences, Allahabad, U.P., India**ABSTRACT**

A series of metal complexes of Fe(II) and Zn(II) having the general composition $[M(L)X_2]$ with benzil bis(thiosemicarbazone) has been prepared and characterized by element chemical analysis, magnetic susceptibility measurements, and spectral (FTIR) studies. The IR spectral data suggest the involvement of sulphur and azomethane nitrogen in coordination to the central metal ion. On the basis of spectral studies, complexes of Zn(II) and Fe(II) show octahedral geometry. The aromatic benzaldehyde dissolved in aqueous acetic acid, were oxidized in quantitative to good yields by 30% H_2O_2 in presence of traces of $[M(L)X_2]$ (substrate : catalyst ratio 85 400 to 387 500 : 1). Conditions for highest yields, under most economical conditions were obtained. Higher catalyst concentrations decrease the yield. In this new, simple and economical method which is environmentally safe and requires less time, $[M(L)X_2]$ species of Fe and Zn (II) probably catalyze the oxidation.

KEYWORDS : Benzil, bis(thiosemicarbazone), Fe(II), Zn(II) FTIR, Benzaldehyde, Catalyst, Hydrogen Peroxide, Oxidation

Thiosemicarbazones are an important class of N,N,S,S donors which have pharmacological interest due to their significant antibacterial, antiviral, antimalarial, antileprotic, and anticancer activities. Thiosemicarbazones usually are chelating ligands with transition metal ions, bonding through sulfur and hydrazine nitrogen. The chemistry of iron and zinc receives attention primarily because of the fascinating electron transfer and energy-transfer properties displayed by the complexes of this metal. Transition metal complexes offer a wide range of oxidation states and reactivity of the iron and zinc complexes depend on the stability and inter convertibility of these oxidation states, which in turn depend on the nature of the ligand bound to the metal. Transition metal complexes are effective catalysts in cross-coupling reactions, but their use as catalysts for aryl-aryl coupling has not been much studied. Mild and efficient aromatic couplings have been reported. Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis. The development of new procedures that can use air or molecular oxygen as oxidant is environmentally attractive. The oxidation of organic compounds with an eco friendly oxidant, aqueous hydrogen peroxide is a challenging goal of catalytic chemistry. In recent years, a considerable amount of research was dedicated to the preparation of various transition metal complexes catalysts and their application for oxidations of various organic compounds.

Homogeneous catalysis by ruthenium and osmium

compounds has been reported by several workers but the use of $[Fe(II)BBTSC]$ and $[Zn(II)BBTSC]$ as homogeneous catalyst in acidic medium has not yet been reported. In the present system good yield is obtained with substrate catalyst ratio ranging from 85400 to 341250:1 and it oxidizes a wider range of organic compounds, and it is a more convenient, eco-friendly and economical compared to many other systems. To explore the potential of the present system for conversion of various other groups in aqueous acetic acid medium, here in the oxidation of benzaldehyde by 30% H_2O_2 in the presence of traces of $[Fe(II)BBTSC]$ and $[Zn(II)BBTSC]$ is reported (Dutta et al., 2011; Raja et al. 2008 and Tondon et al. 2005).

MATERIALS AND METHODS**Material**

All the chemicals used of analytical R grade and procured from Qualikem and Loba metal salts were purchased from Ranbaxy and used as received.

Methods**Synthesis of ligand (L)**

Hot ethanolic solution of thiosemicarbazide (1.82 g, 0.02 mol) and ethanolic solution of benzil (2.1 g, 0.01mol) were mixed in the presence of few drops of conc.HCl with constant stirring. This mixture was refluxed at 60-70°C for 3 hours. The completion of the reaction was confirmed by the TLC. The reaction mass was degassed on a rotator evaporator, over a water bath. The degassed reaction mass on cooling gives cream-colored crystals. It was

¹Corresponding author

filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10} , (yield (65%), mp $164^{\circ}C$). Element chemical analysis data are shown in Table, 1.

Synthesis of Complexes

Hot ethanolic solution (20 mL) of corresponding metal salts (0.01mol) was mixed with hot ethanolic solution of the respective ligand (0.01mol). The mixture was refluxed for 3-4 hours at $50-60^{\circ}C$. On cooling the contents, the colored complex separated out in each case. It was filtered and washed with 50% ethanol and dried under vacuum over P_4O_{10} . Purity of the complexes was checked by TLC.

Catalytic Activity

Benzaldehyde 10.00 mmole was taken in a single necked round bottom flask. In the flask, glacial acetic acid 87.50 mmole was added and the contents of the flask were shaken, so that aromatic aldehyde dissolved completely in acetic acid. Adding the catalyst [Fe(II)BBTSC] and [Zn(II)BBTSC] 2.40 the flask was kept in a water bath (Metrex C.No.-MSB-40,S.No.-408/546) at a desired temperature. A water cooled reflux condenser was fitted on a flask. When the temperature of a reaction mixture has attained the desired temperature, H_2O_2 159.00 mmole was added and the mixture was kept at the temperature $80^{\circ}C$ for desired time 150 minute. After this, the flask was taken out and the content was poured on crushed ice. Immediately benzoic acid precipitated out as a curdy mass. Precipitate was filtered out and the filtrate was extracted with 10.00 ml ether. The ether content of the extract was evaporated on a water bath. The residue was purified by dissolving it in minimum amount of hot water.

The precipitate obtained on cooling was again filtered off. The processes was repeated till no more precipitate was obtained on cooling the solution. The

precipitate obtained each time was mixed and weighted after proper drying. After re-crystallization with hexane, we obtained a white solid.

Characterization

The C, H, and N were analyzed on Perkin elemental analyzer 2400II. elemental analyzer. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $Hg[Co(SCN)_4]$ as callibrant. Diamagnetic corrections were made by using Pascal's constants. spectrometer. FTIR spectra (KBr) were recorded Perkin 2989 in $400-4000\text{ cm}^{-1}$ range (Raja et al. 2010; Singh et al. 2012).

RESULTS AND DISCUSSION

Magnetic Susceptibility

The observed magnetic moments of Fe(II) and Zn (II) complexes are given in Table 1. The best summary of the results on the magnetic behavior of Fe(II) and Zn (II) compounds was given by (Figgis and Nyholm). The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. The magnetic moment observed for the Fe(II) complexes lies in the range (4.2-5.95 BM) of which is consistent with the octahedral stereochemistry of the complexes. The magnetic moment observed for the Zn(II) complexes lies in the range of (2.89-2.95 BM) which is consistent with the octahedral stereochemistry of the complexes.

Infrared Spectra

The assignments of the significant IR spectral bands of ligand and its metal complexes are presented in Table, 2. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide $-NH-C=S$ functional group. The $\nu(S-H)$ band at 2565 cm^{-1} is absent in

Table 1: Physical measurements and elemental analysis Magnetic susceptibilities

Compounds	Yield (%)	Color	Mp(C)	C %	H %	N %	μ_{eff} (BM)
Ligand (L)	65	Cream	164 C	53.92	4.41	23.58	-----
[Fe(L)Cl ₂]	66	Brown	282 C	34.43	3.12	23.43	5.94
[Zn(L)Cl ₂]	62	Off-white	286 C	34.50	3.29	22.89	2.95

Table 2: Infrared spectral bands (cm⁻¹)

Compounds	ν (N-H)	ν (N-N)	N(C=N)	ν (C=S)	ν (M-N)
Ligand (L)	3230	1178	1536	832	-
[Fe(L)Cl ₂]	3232	1133	1588	829	424
[Zn(L)Cl ₂]	3231	1132	1599	830	425

the IR spectrum of ligand but ν (N-H) band at 3230 cm⁻¹ is present, indicating that in the solid state, the ligand remains as the thione tautomer. The position of ν (C=N) band of the thiosemicarbazone appeared at 1536 cm⁻¹ is shifted towards lower wave number in the complexes indicating coordination via the azomethane Nitrogen. This is also confirmed by the appearance of bands in the range of 424-425 cm⁻¹, this has been assigned to the ν (M-N). A strong band found at 1178 cm⁻¹ is due to the ν (N-N) group of the thiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bond strength, which again confirms the coordination via the azomethane nitrogen. The band appearing at 832 cm⁻¹ ν (C=S) in the IR spectrum of ligand is shifted towards lower wave number. It indicates that thione sulphur coordinates to the metal ion. Thus, it may be concluded that the ligand behaves as tetradentate chelating agent coordinating through azomethane nitrogen and thiolate sulphur.

Catalytic activity

Benzaldehyde 10.00 mmole was taken in a single necked round bottom flask. In the flask, glacial acetic acid 87.50 mmole was added and the contents of the flask were shaken, so that aromatic aldehyde dissolved completely in acetic acid. Adding the catalyst [Fe(II)BBTSC] and [Zn(II)BBTSC] 2.40 mmole the flask was kept in a water bath (Metrex C.No.-MSB-40,S.No.-408/546) at a desired temperature. A water cooled reflux condenser was fitted on a flask. When the temperature of a reaction mixture has attained the desired temperature, H₂O₂ 159.00 mmole was added and the mixture was kept at the temperature 80°C for desired time 150 minute. After this, the flask was taken out and the content was poured on crushed ice. Immediately benzoic acid precipitated out as a curdy mass. Precipitate

Table 3 : Variation in The Concentration Of Acetic Acid on Yield of Benzoic Acid

Acetic acid : Water	% yield
1 : 0	-
1 : 1	65
1 : 2	85

was filtered out and the filtrate was extracted with 10.00 ml ether. The ether content of the extract was evaporated on a water bath. The residue was purified by dissolving it in minimum amount of hot water.

The precipitate obtained on cooling was again filtered off. The processes was repeated till no more precipitate was obtained on cooling the solution. The precipitate obtained each time was mixed and weighted after proper drying. After re-crystallization with hexane, we obtained a white solid.

Benzaldehyde was taken for determining the catalytic activity (yield) of the transition metal complexes [Fe(II)BBTSC] and [Zn(II)BBTSC] maximum yield of the product i.e. (84% 102.48 mg and 82% 100.04 mg) was obtained when reaction conditions have Hydrogen peroxide (30%) 159.00 mmole, Acetic acid(glacial) 87.50 mmole, benzaldehyde 10.00 mmole, temperature 80°C, duration of experiment 150 minutes Fe(II)BBTSC and Zn(II)BBTSC 2.40×10^{-5} mmole.

The amount of Hydrogen peroxide 159.00 mmole (30%), Fe(II)BBTSC and Zn(II)BBTSC (2.40×10^{-5} mmole), benzaldehyde 10.00 mmole, temperature 80°C and duration of experiment 150 minutes was fixed and now we change the concentration of acetic acid was changed. The observed variable yield of product is mentioned in

Table 4 : Variation in the catalyst concentration Fe(II)BBTSC on yield of benzoic acid

Amount of catalyst [Fe(II)BBTSC] x10 ⁻⁵ mole	% yield
2.40	84
4.80	81
9.60	55
19.20	48

(Table,3). When the ratio of acetic acid and water is 1:2 then we obtained 85% maximum yield. On decreasing the concentration of acetic acid the yield of the product (benzoic acid) increasing.

The amount of hydrogen peroxide 159.00 mmole (30%), acetic acid (glacial) 87.50 mmole, benzaldehyde 10.00 mmole, temperature 80°C and duration of experiment 150 minutes was fixed and then the concentration of catalyst was changed. The observed variable yield of product is mentioned in Table, 4. We observed at 2.40 x10⁻⁵ mmole concentration of catalyst the yield of the product was maximum 84%. On increasing the concentration of catalyst [Fe(II)BBTSC] the yield of the product (benzoic acid) decreases. This may be due to the unproductive decomposition of oxidant at higher concentrations of the catalyst.

The amount of Hydrogen peroxide 159.00 m mole (30%), acetic acid(glacial) 87.50 mmole, Benzaldehyde 10.00 mmole, temperature 80°C and duration of experiment 150 minutes was fixed and then the concentration of catalyst was changed. The observed variable yield of product is mentioned in Table,5.

We observed at 2.40 x10⁻⁵ mmole concentration of

Table 5: Variation of catalyst concentration Zn(II)BBTSC on yield of benzoic acid

Amount of catalyst [Zn(II)BBTSC] x10 ⁻⁵ mole	% yield
2.40	82
4.80	74
9.60	52
19.20	45

catalyst the yield of the product was 82% . On increasing the concentration of catalyst [Zn(II)BBTSC] the yield of the product (benzoic acid) decreases. This may be due to the unproductive decomposition of oxidant at higher concentrations of the catalyst.

Identification of Product

The product was identified for the presence of (-COOH) functional group test. It was confirmed by the appearance of effervescence in the presence of sodium bicarbonate i.e. removal of CO₂ gas.

The melting point of product (benzoic acid) was observed by Capillary melting point method.

The melting point of pure benzoic acid is 122°C and observed melting point of the product was 121.4°C (Singh and Ramesh, 2010)

CONCLUSION

It may be concluded that the ligand behaves as tetradentate chelating agent coordinating through azomethane nitrogen and thiolate sulphur. The magnetic moment observed for the Fe(II) and Zn(II) complexes lies in the range of 2.89-5.95BM which is consistent with the octahedral stereochemistry of the complexes. This study was performed mainly to determine the efficiency and economy of the simple and novel [Fe(II)BBTSC] and [Zn(II)BBTSC] hydrogen peroxide system to oxidize the organic compounds. Some amount of benzoic acid could not be separated under laboratory condition and there are some factor which effect the yield of the products as like the solubility of acetic acid and concentration of hydrogen peroxide. Due to variable oxidation state and vacant d-orbital, transition metal complexes show catalytic activity. The main aim of the study was to find out catalytic activity of transition metal complexes by a method which should be cheap, easy to set up and above all it should be eco-friendly, as no hazardous by-products are formed, which are otherwise obtained in most of the traditional methods. It is maintained here that the only by-products of the present systems are water and oxygen which are good from the environmental point of view. The present system is

expected to be of immense importance from the industrial point of view as well as on the laboratory scale.

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