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Spectrophotometric Study of a new Complexation between Zn(II) and 5-Bromosalicylaldehde Thiosemicarbazone and Its Application

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Abstract

A new complex of Zn(II) and 5-Bromosalicylaldehyde thiosemicarbazone (5-BSAT) has been studied. In solution, the 5-BSAT reacts with Zn(II) to form a complex with the maximum absorbance at 381 nm. Zn(II) ion forms a 1:1 stoichiometric complex. The stability constant is $4.21x10^5$. The formation of the complex was completed within 20 min at pH 6.8 and V_{DMF} = 2 mL. Beer's law is obeyed over the range from 0.13 mg. L^{-1} to 0.39 mg. L^{-1} Zn (II) and the apparent molar absorptivity (ε) is 1.08×10^4 $L.mol^{-1}.cm^{-1}$. The complex has been formulated and characterized by mass spectrometry, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopies and IQmol program. The molecular formula of the complex is $C_8H_8O_2N_3SBrZn$. The ligand coordinated as an ONS tridentate dianion through the oxygen atom of the deprotonated phenolic OH-group, the azomethine nitrogen atom and the sulfur atom after deprotonation of the thiosemicarbazide residue in its thiol form. Based on these results, the 5-BSAT reagent was applied to determine zinc in waste water samples and the complex showed an effective antimicrobial activity.

Keywords: Zinc; complex; 5-bromosalicylaldehyde thiosemicarbazone; ONS donors.

1. Introduction

Thiosemicarbazones and their metal complexes present a wide range of applications that stretch from their use in analytical chemistry, through pharmacology to nuclear medicine [1,2]. These reagents function as good chelating agents and form complexes with metal ions by bonding through thionate sulfur atom, hydrazine nitrogen atom and oxygen atom in ortho hydroxyl group [3-8]. Their derivatives are of considerable interest due to their versatility as ligands bearing suitable donor atoms for coordination to metals with a strong coordinating ability [9]. They show a wide range of chemical properties depending on the parent aldehyde or ketone [10-12]. Zn(II) forms a chelate complex with many reagents such as thiosemicarbazones. Some representative examples are benzildithiosemicarbazone [13], di-2-pyridyl ketone salicyloylhydrazone [14], 2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone [15], pyridoxal-4- phenyl-3-thiosemicarbazone [16], N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone [17], di-2-pyridyl ketone benzoylhydrazone [18], bis-[2,6-(2′-hydroxy-4′-sulpho-1′-napthylazo)]pyridine disodium salt [19], and 5,7-dibromo-8-hydroxyquinoline [20], salicylaldehyde thiosemicarcbazone [21]. In recent years, the complexation of 5-bromosalicylaldehyde thiosemicarbazone (5-BSAT) reagent with some metallic ions has been reported. The reagent forms complexes with Fe(II), Fe(III), Cu(II), Ni(II), Ru(III), Ag(I), Pt(II), Pd(II), Mn(II) which were studied in structure and magnetic properties [22-26]. Ramanjaneyulu and coworkers have studied complexation of 5-BSAT with Fe(II), Co(II) and Cu(II) ions in solution and applied in individual analysis of these ions [27-29]. According to our knowledge, there have not been any reports and research on structures of Zn(II)-5BSAT complex. The present study deals with the synthesis, characterization, elucidation of the structure and its application of new Zn(II) complex with 5-BSAT.

2. Experimental

Chemicals and Instruments

All chemicals were commercially available with analytical grade of purity and used without further

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purification. 10^{-2} M reagent solution was prepared by dissolving 0.0685g of 5-BSAT in 25 ml DMF. Stock solutions of Zn(II) 10^{-2} M were prepared from a suitable mass of the compound and made up to the mark in a 100-ml volumetric flask.

Infrared spectra were recorded in a Shimadzu spectrum FTIR System in region 4000 – 400 cm^{-1} using KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature on a Bruker DRX 500 spectrometer in DMSO-d6, using TMS as the internal standard. Shimadzu LC/MS system was used for recording of mass spectra and the confirmation of molecular formulas of compounds. A Perkin – Elmer Lambda 25 QA – Certificate spectrophotometer was used to record the absorbance spectra with a 1-cm path length quartz cell. Mettler Toledo digital pH meter with a combined glass electrode was used for pH measurements.

General procedure

Synthesis of complex

Ethanolic solution (30 mL) of the 5-bromosalicylaldehyde thiosemicarbazone ligand (shown in Figure 1; 1 mmol; 0.2742 g) was added to 20 mL solution of $ZnCl_2$ (1 mmol; 0.1363 g) and the reaction mixture was refluxed for 4 hours. Volume of the resulting solution was reduced to 20 mL in a rotary vacuum evaporator and the solution was left overnight. The resulting crystalline compound was filtered, washed with ethanol-dioxane mixture, and dried in vacuum. The yellow white crystalline product was the air which was stable, soluble in most common polar organic solvents and insoluble in a polar organic solvents and water.

Studying of complexation in solution

Appropriate volumes of Zn(II) standard solutions, 5.0 mL of 0.1M KNO_3, 2.0 mL of DMF, 5.0 mL of buffer solution (pH 6.8) and 1.0 mL of 0.01 M 5-BSAT solution were added into a 25.0 mL standard flask and the volume was made up to the mark with double distilled water. A portion of the solution was transferred into a quartz cell and variations of absorbance were recorded for each sample. The same procedure was carried out with other ions at suitable buffer solutions.

Evaluation of antimicrobial activity

The spectrophotometric determination of bacteria number method (Harley-Prescott, 2002 [30]) was used to determine the minimum inhibition concentration (MIC) of Zn-5BSAT complex. The MIC was considered to be the lowest concentration that completely inhibits bacteria comparing with the control.

3. Results and Discussion

Spectral data of complex

UV vis spectra

The absorption spectra for a new Zn(II) complex with 5-BSAT and reagent against blank solution at pH 6.8 in wavelength range 365–500 nm are shown in Figure 1. The maximum wavelength of the complex is 381 nm. It indicates that the band is shifted to lower energies (bathochromic shift) after complexation.

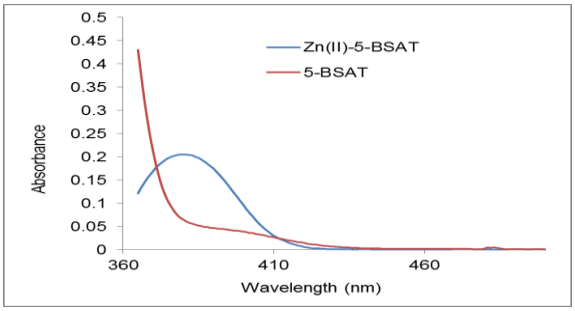


Fig. 1. UV vis spectra of 5-BSAT reagent and Zn(II) – 5-BSAT complex at pH 6.8.

FT-IR spectra of complex

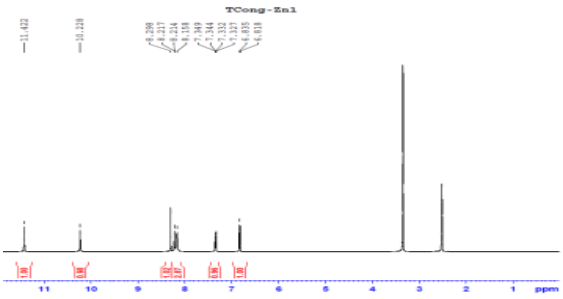
In FT-IR, 5-BSAT exhibits a sharp band at 1612 cm^{-1} due to azomethine linkage (C=N). From Table 1, in the complex, this band appears at a frequency lower (approximately 12 cm^{-1}) than that on the free ligand. This clearly indicates the involvement of nitrogen atom in coordination due to a reduction in the electron density in the azomethine linkage. In the complex, thiosemicarbazones behave as double deprotonated tridentate ligands, coordinating with the central ion through phenolic oxygen atom, azomethinic nitrogen atom and sulfur atom forming two five- and six-membered heterocycles. The medium intensity band in the region 488 cm^{-1} is attributed to Zn–O and in the region 472 cm^{-1} is attributed to Zn–S bonds.

Table 1. Selected FT-IR data of 5-BSAT and its complex with Zn(II)

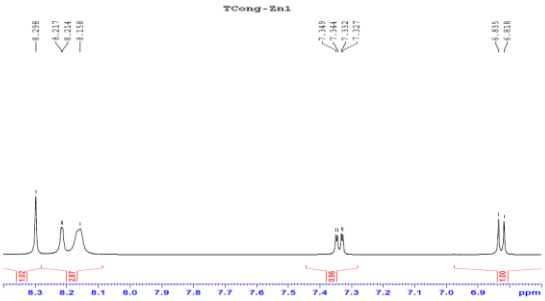
(ν_{max}, cm^{-1})	–OH, –NH	–NH	CH, aromatic	CH=N, azomethine	C=S
5-BSAT	3454	3250	3161	1612	1060
Zn(II)–5-BSAT	3454	3244	3159	1600	1064

The ^{1}H-NMR and ^{13}C-NMR spectra

The ^{1}H-NMR and ^{13}C-NMR spectra of the complex were recorded in DMSO-d6 (Figure 2 and Figure 3). The ^{1}H-NMR spectral data are reported along with the possible assignments. All the protons were found to be in the expected regions. ^{13}C-NMR spectrum of Zn(II) – 5-BSAT have also been taken. The spectrum showed bands attributed to C-N at δ 156, aromatic carbon between δ 138 and 118, carbonyl carbon attached to N at δ 178.



a/ full ^{1}H-NMR spectrum



b/ expended ^{1}H-NMR spectrum

Fig. 2. ^{1}H-NMR spectrum of Zn(II) – 5-BSAT complex

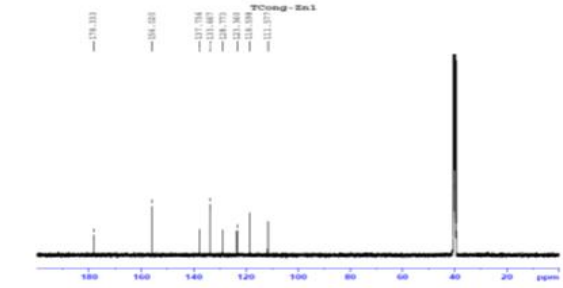


Fig. 3. ^{13}C-NMR spectrum of Zn(II) – 5-BSAT complex

Mass spectra

In mass spectrum of the Zn(II) – 5-BSAT complex (Figure 4), the molecular ion peak is observed at 353 m/z. Since the compound contains three nitrogen atoms (odd number), it gives a molecular ion peak with an odd mass number (nitrogen rule). The $[M-H]^-$ and $[M+H]^+$ ion peaks also appear/ are also found. Therefore, the molar ratio of the complex (1:1) is also assigned again. The molecular formula of the complex is $C_8H_{10}O_2N_3SBrZn$.

From FT-IR, ^{1}H-NMR, ^{13}C-NMR and MS spectroscopies, the structure of the new Zn(II)–5-BSAT complex is proposed in Figure 5.

The molecular structure of Zn(II) – 5-BSAT complex was simulated by using IQmol program as shown in Figure 6 [31-32]. An attempt to gain a better insight on the molecular structure of these complexes, geometric optimization has performed using DFT/B3LYP method as implemented in Q-Chem 4.4 [33-34]. Convergence criteria were set to 0.01 kcal/mol.Å for B3LYP calculations with 6-31G* basis set.

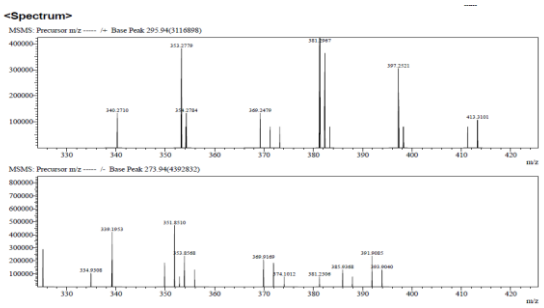


Fig. 4. High resolution mass spectrum of Zn(II) – 5-BSAT complex

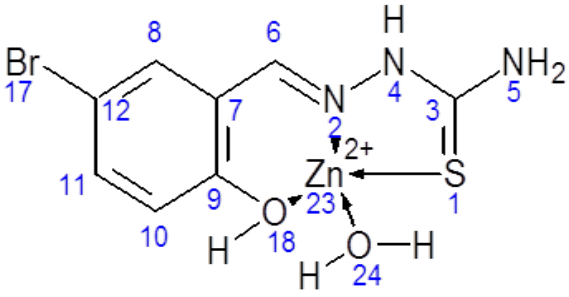


Fig. 5. Structure of Zn(II) – 5-BSAT complex

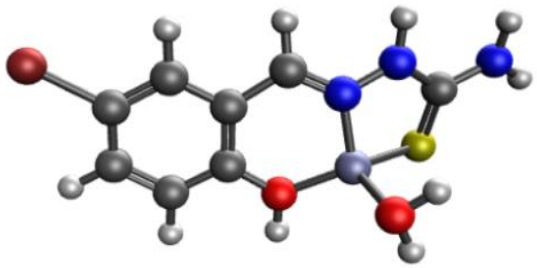


Fig.6. Molecular Modelling of the complex by IQmol program

Table 2 showed binding length values of 5-BSAT and Zn (II) –5-BSAT complex. The C-O bond length increased from 1.341 Å in the 5-BSAT ligand to 1.416 Å in the Zn (II) –5-BSAT complex. The C-S bond length increased from 1.663 Å in the 5-BSAT ligand to 1.736 Å in the Zn (II) –5-BSAT complex. Similarly, N-C (S) bond length decreased from 1.378 Å in ligands to 1.361 Å. These changes, along with the change in charge, show the coordinated involvement of oxygen and sulfur atoms. Similarly, the change in charge of N2 atom and N2-N4, N2-C6 bond length also showed the formation of Zn-N2 coordination link. The bonding angles around the Zn(II) central ion is in the range of 87-113°. These angles are close to the 109.5° value, suggesting that the suitability of the geometric proposition of the forming complex is the tetrahedron.

Table 2. Selected bond distance for 5-BSAT and Zn(II)–5-BSAT complex

No.	Bond	Length (Å)	
		5-BSAT	Zn(II)–5-BSAT
1	O18-C9	1.34141	1.41566
2	S1-C3	1.66333	1.73636
3	N5-C3	1.37384	1.32637
4	C3-N4	1.37829	1.36080
5	N4-N2	1.35334	1.37777
6	C6-N2	1.28870	1.29850
7	N2-Zn23	-	2.01235
8	S1-Zn23	-	2.27174
9	Zn23-O24	-	1.99970
10	Zn23-O18	-	2.02416

Analytical studies

There are many parameters affecting the absorption intensity of the formed products which were studied and the reaction conditions were optimized.

Effect of pH

The effect of pH on the absorbance of the Zn(II)-5BSATcomplex was investigated over a range (5-8), the results from Figure 7 showed that complex of Zn(II) exhibited maximum absorbance in the pH range 6.5 – 7.0. So, further investigations were carried out on pH 6.8.

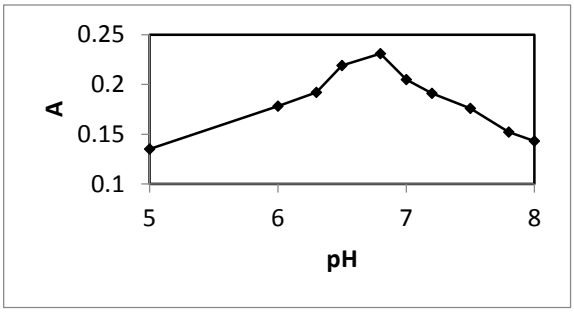


Fig. 7: Effect of pH on the formation of complex

Effect of reaction time

To measure the completeness of complex formation reaction, the absorbance values of complex were monitored at different intervals of time. The complex formation was completed after 5 min and stable for 1 hour. Therefore, absorption measurements were performed at the range 5 – 30 min after mixing of 5-BSAT reagent.

Effect of 5 BSAT concentration

The effect of different amounts of 5-BSAT on the absorbance of complex was studied. It was expected that increasing 5-BSAT concentration causes an increase in absorbance because an increase in 5-BSAT concentration caused an increase in complex concentration. At higher concentrations of reagent, the concentration of complex did not change significantly but the concentration of uncomplexed 5-BSAT increased significantly. When the amount of reagent is a 5-8 fold excess over the maximum concentration of Zn(II), the formation of complex got its maximum. The results showed that, when increasing the amount of DMF, the absorbance of the solution increased and stabilized when V_{DMF} = 2 ml.

Effect of foreign ions

The effect of various diverse ions on the absorbance of a solution containing 2×10^{-5} M Zn(II) was studied. Table 3 summarizes the interference concentration of foreign ions in the Zn(II) – 5-BSAT complex. Among the cations, alkaline, alkaline earth ions and most of anions (concentration ions higher 60 fold) did not interfere in Zn-5BSAT complex. On the contrary, Ce(IV), Mo(VI), Sb(III), V(V), Cu(II), Cr(III), Fe(III), Co(II), Cd(II) ions interfered in Zn-5BSAT.

Table 3. Interference concentration of foreign ions in the Zn(II)–5-BSAT complex

M^{n+}	Fold
Cr(III)	3.5
Cu(II)	18
Ce(IV)	22
Mo(VI)	15
Ni(II)	3
Fe(III)	30
V(V), Cd(II), Sb(III), Mn(II)	>60
Other metal, ions and anion	>200

Calibration curves

A set of sample solutions with different metal ions concentrations was prepared and measurements were carried out under the optimum conditions. The calibration curve of four complexes was shown in Figure 8. The calibration curve of the Zn^{2+} ions measured at different ranges was linear in the ranges 2.0×10^{-6} – 6.0×10^{-5} mol.L^{-1}. The calibration plot followed the equation A = 0.011C + 0.0527 (R^2 = 0.9984). The molar absorptivity, ε of the complex was 1.08×10^{4} L.mol^{-1}.cm^{-1}.

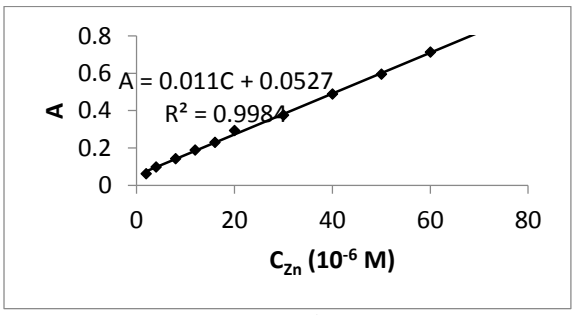


Fig. 8: The calibration curve of Zn(II)-5BSAT complex

The composition of the complex

The composition of complex was determined by molar ratio method. From Figure 9, we could conclude that Zn(II) ion forms a 1:1 stoichiometric complex. The constant stability calculated by this method is 4.21×10^5.

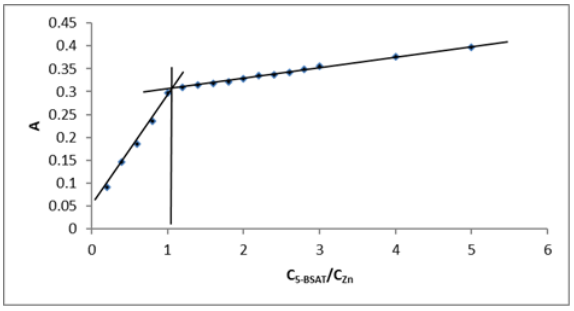


Fig. 9: Molar ratio method for Zn(II)–5-BSAT complex

The proposed method was applied to zinc determination in a plating plant water (A) and waste water from ceramics and glass factories (B) without any other pretreatment. The zinc concentration of the diluted sample was determined to (A): 1.30 mg/l by AAS and to 1.23 mg/l by the proposed method with a relative error of -5.38%; (B): 1.42 mg/l by AAS and to 1.48 mg/l by the proposed method with a relative error of +4.05%. The proposed method could be applied in analytical chemistry.

Antimicrobial activity studies

On the other hand, based on the research methods, after 20 hours of incubation, the optics density (OD) data of culture media with bacteria and substrate (Zn-5BSAT complex) were obtained. The data showed that the OD of samples had a relation between grown bacteria density and Zn-5BSAT concentration in medium. The data showed that the Zn-5BSAT complex had a wide effect on bacteria. Evaluation of the resistance of Zn-5BSAT on 3 types of bacteria resulted in the following: MIC concentrations of S. aureus, E. coli and Pseudomonas aeruginosa were 30 ppm, 50 ppm and 60 ppm respectively. This means that the ability of S. aureus to Zn-5BSAT is the lowest. It requires a concentration of only 30ppm to affect the growth of S. aureus while this concentration is approximately 2 times greater to be able to influence the development of E. coli and Pseudomonas aeruginosa. Zn-5BSAT has better antimicrobial activity against S. aureus than E. coli and Pseudomonas aeruginosa.

4. Conclusion

In this report, we concluded that the new complex (Zn-5BSAT) was investigated. The structure of the complex was described. The analytical properties were studied and applied to analyze zinc samples. The Zn-5BSAT complex showed effective antimicrobial activities.

Conflicts of interest

There are no conflicts to declare.

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