



SPECTRAL STUDIES OF ZINC (II) COMPLEX OF 2-ACETYLBNZOTHIOPHENE 3-THIOSEMICARBAZONE.

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ABSTRACT

Transition metal complexes of thiosemicarbazones have generated considerable interest due to their wide ranging biological activities. Zinc II complexes with thiosemicarbazone ligands were reported to possess antiproliferative, antitumor and antimicrobial activities. In this work, zinc (II) complex of 2-acetylbenzothioephene 3-thiosemicarbazone [Zn(BTTS)₂] has been prepared by condensation of zinc acetate dihydrate with 2-acetylbenzothioephene 3-thiosemicarbazone in ethanol. The complex has been characterized by elemental analysis (C, H, N and S) and spectroscopic methods (infrared, ¹H and ¹³C NMR). The spectroscopic results obtained for the zinc (II) complex of 2-acetylbenzothioephene 3-thiosemicarbazone clearly indicated that the ligand in the zinc complex is found to coordinate in the thiole form. Spectroscopic results suggested that the ligand coordinated to the metal centre as a bidentate N, S-donor forming a five-membered chelate ring and the geometry surrounding the zinc centre is close to a tetrahedron.

Keywords: *Thiosemicarbazone, Zinc (II) complex, Spectral studies.*

INTRODUCTION

Thiosemicarbazones are one of the most important nitrogen sulfur donor ligands. Thiosemicarbazones and their metal complexes are of considerable current interest because of their potentially beneficial biological activity, such as antiviral, antitumor, antifungal,

antibacterial and antimalarial activity (Altun et al. 2000; Cukurovali et al. 2006; Kasuga et al. 2003; Sharma et al. 2006). Several zinc (II) complexes with thiosemicarbazones were prepared and their antiproliferative, antitumor and antimicrobial activities were investigated (Ferrari et al. 2000; Kasuga et al. 2003; Kovala-Demertzi et al. 2006). This paper will describe the preparation and characterization of zinc (II) complex of 2-acetylbenzothiophene 3-thiosemicarbazone.

MATERIALS AND METHODS

All chemicals were of reagent grade and used as commercially purchased without further purification. The elemental analysis were carried out on an a Fison EA 1108 CHN-S analyzer. Infrared spectra were recorded on a Perkin-Elmer FT-IR model GX infrared spectrophotometer as KBr and polyethylene discs. The ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a JEOL ECP 400 MHz spectrometer in deuterated DMSO, relative to the internal standard tetramethylsilane (TMS). Melting points were determined on an Electrothermal 9300 instrument.

The 2-acetylbenzothiophene 3-thiosemicarbazone HBTTS ligand (fig. 1) was produced by condensation of 2-acetylbenzothiophene with thiosemicarbazide and few drops of concentration H_2SO_4 . The x-ray structure of this ligand was reported in our previous work (Kayed et al. 2009). Zinc II complex of the ligand was prepared by condensation of zinc acetate dihydrate with 2-acetylbenzothiophene 3-thiosemicarbazone in ethanol for three hours. The yellow crystals which separated were isolated by filtration and washed with ethanol.

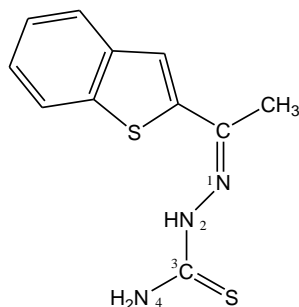


Fig. 1 2-acetylbenzothiophene 3-thiosemicarbazone ligand.

RESULT AND DISCUSSION

Elemental analysis and physical properties of the ligand HBTTS and zinc complex are given in Table 1. The complex is stable in air. It is soluble in DMSO and DMF, but insoluble in water and common organic solvents. The molar conductivity of the complex which has been recorded in DMSO (10^{-3} M) at room temperature show that the complex is non electrolyte.

Table 1 Analytical data and physical properties of the ligand and complex.

| Compound | Color | Yield | M.p.(°C) | Found (Calcd) % | | | | Zn | Λ_M (μ S/cm) |
|-----------------------------|--------|-------|----------|------------------|----------------|------------------|------------------|------------------|---------------------------------|
| | | | | C | H | N | S | | |
| HBTTTS | Yellow | 68.00 | 210-212 | 52.98 (52.32) | 4.45 (4.71) | 16.85 (16.59) | 25.72 (24.95) | - | - |
| [Zn(BTTS) ₂] | Yellow | 65.58 | 240-242 | 46.42 (47.00) | 3.27 (3.58) | 15.05 (14.95) | 22.87 (22.82) | 10.84 (11.63) | 0.36 |

The principal IR bands of HL and zinc II complex are listed in Table 2. ν (C=N) in the ligand shifts to higher frequency in the spectra of complex indicates the coordination of azomethine group to the central metal atoms (Sreekanth et al. 2003). This can be attributed to the stabilization of the C=N azomethine bond in the complex for the presence of an important metal-to-ligand π back donation (Al-Kubaisi 2002). A small shift in the absorption band due to the ν (N-N) stretching vibration from 1102 cm^{-1} to a high region is due to the increase in the in the double bond character offsetting the loss of electron density via donation to the metal and is a confirmation of the coordination of the ligand through the azomethine nitrogen atom (Latheef et al. 2007). Coordination of azomethine nitrogen is consistent with presence of a band at 444 cm^{-1} assignable to ν (Zn-N) (Castin~eirasa et al. 1999; Kovala-Demertzi et al. 2006). In the complex, ν (CS) stretching vibration shifts to 1046 cm^{-1} as a result of enolization and consequent coordination to the zinc through the deprotonated thiolate (Kovala-Demertzi et al. 2008; Jouad et al. 2001). The coordination of the sulphur form C-S is confirmed by the presence of a new band at 353 cm^{-1} that can be assigned to ν (Zn-S) (Kovala-Demertzi et al. 2006; Kovala-Demertzi et al. 2008). The change in ν [N(4)H] in the spectra of the complex is a consequence of the coordination of the sulphur form C-S(NH₂) (Jouad et al. 2001). ν [N(2)H]

disappear in the spectra of the complex due to the deprotonation in the presence of Zn II and coordinates via thiolate sulfur (Bal-Demirci 2008).

Table 2 Principal IR bands of the ligand and complex (cm⁻¹).

| Compound | ν [N(2)H] | ν [N(4)H] | ν (C=N) | ν (C=S) | ν (N- N) | ν (M- N) | ν (M- S) |
|--------------------------|------------------|---------------|----------------|----------------|-----------------|-----------------|-----------------|
| | | 3436 | | | | | |
| HBTTs | 3153 | sym. | 1531 | 1074 | 1102 | - | - |
| | | 3328 | | | | | |
| | | 3448 | | | | | |
| [Zn(BTTs) ₂] | - | sym. | 1561 | 1046 | 1109 | 444 | 353 |
| | | 3330 | | | | | |
| | | asym | | | | | |

The ¹H NMR spectra of the ligand and zinc complex are tabulated in the Table 3. In the ¹H NMR spectrum of the complex, The absence of signals assigned N(2)H of the free ligand at 10.59 ppm confirms that N2 deprotonate and thiosemicarbazone coordinate to zinc atom via thiolate sulfur atom (Latheef et al. 2007). Table 4 shows the ¹³C NMR spectra of the ligand and complex. The shielding of C=S by about 6 ppm is due to thione-to-thiol evolution followed by sulfur metal coordination (Casas et al. 2002). The coordination through azomethine nitrogen effects the chemical shift of C=N to higher field (Labisbal et al. 2000).

Based on the above discussion a tetrahedral geometry for the complex is proposed (Fig. 2).

Table 3 ¹H NMR spectral data (δ , ppm) of the ligand and complex.

| Compound | N(2)H | N(4)H | C- CH ₃ | C-H Aromatic |
|--------------------------|-----------------|--------------|--------------------|------------------------------|
| HBTTs | 10.59 (1H,s) | 7.35 (2H, s) | 2.41 (3H,s) | 8.47, 7.86, 7.37, 7.88, 7.36 |
| [Zn(BTTs) ₂] | - | 7.42 (2H, s) | 2.49 (3H,s) | 8.04, 7.86, 7.37, 7.88, 7.36 |

Table 4 ^{13}C NMR spectral data (δ , ppm) of the ligand and complex.

| Compound | C=S | C=N | -CH ₃ | Aromatic |
|--------------------------|--------|--------|------------------|---|
| HBTTs | 178.80 | 144.61 | 14.27 | 143.26, 139.66, 139.60, 125.78, 124.93, 124.61, 124.26, 122.28 |
| [Zn(BTTs) ₂] | 172.21 | 149.18 | 14.36 | 143.88, 137.04, 134.75, 128.65, 126.27, 124.81, 124.62, 121.96 |

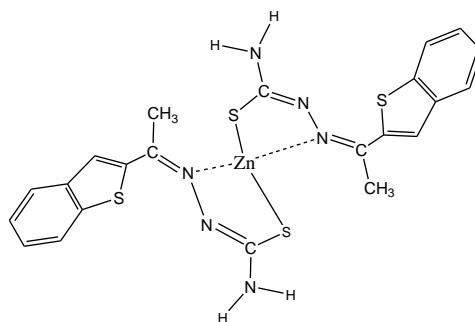


Fig. 2 proposed structure of Zinc II complex.

CONCLUSION

It may be concluded that the 2-acetylbenzothioephene 3-thiosemicarbazone HBTTs ligand coordinated to the zinc atom as a bidentate N, S-donor leading to the formation of five-membered chelate ring. The chelate are proposed to have tetrahedral geometry.

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