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## Zinc (II) Complexes of Symmetrical bis-hydrazide ligands: Synthesis, Characterization and Properties

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### ABSTRACT

The Zinc(II) complexes of acetoacetic acid hydrazide (AAAH), butyrylacetic acid hydrazide (BUTAH) and benzoylacetic acid hydrazide (BENZA) were prepared and characterized by elemental analysis, infrared spectroscopy and electronic reflectance spectra. The comparison of infrared spectra of the ligands and complexes allowed the establishment of the coordination mode of the ligand to the metal in the complexes, while the reflectance spectra gave an indication of the stereochemistry of the complexes. The bases coordinate in a bifunctional manner using both the oxygen atom of the carbonyl group and the nitrogen of the -NH<sub>2</sub> group. The stability of the bis-complexes was confirmed by the formation of the compounds in appreciable yields.

**Keywords:** Zinc complexes, infrared, reflectance, bifunctional, bases

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## INTRODUCTION

The coordination chemistry of transition metals with ligands from the hydrazide family based on  $-\text{CONHNH}_2$  and their derivatives has been of interest. This is due to the different bonding modes shown by these ligands with metals of varied electropositivity [1,2]. Hydrazides possessing an azomethine- $\text{NHN}=\text{CH}-$  constitute an important class of compounds for new drug development [3]. This class of compounds have been studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal properties and find applications in biomimetic catalytic reactions [1-3, 5]. The hydrazides based on  $-\text{CONHNH}_2$  and their derivatives contain trigonal N- and O-donors making them potential chelating ligands [4]. Hydrazide derivatives and complexes have supramolecular interactions because they include the hydrogen-bonding donors (amino group) and acceptors (carbonyl), and as a result hydrogen bonding plays an important role in extending and stabilizing the structures of the resultant complexes [4]. The mode of coordination of benzoic acid hydrazide to  $\text{Li}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Mg}^{2+}$  were reported [6]. The luminescence properties of Zn(II) and Cd(II) complexes of N'-(2-hydroxybenzoyl)isonicotinohydrazide and N'-(2-hydroxybenzoyl)nicotinohydrazide had been investigated [4]. Also, the mode of coordination and the biological activity of some Zn(II) complexes with acetic acid(3-chloro- 4-hydroxyl benzylidene)-hydrazide and acetic acid(2-nitro-benzylidene) hydrazide have been found out to have interesting biological applications [3]. Hence, our interest in the syntheses, physicochemical properties, mode of coordination and the stability of some zinc(II) complexes of acetoacetic acid hydrazide, butyrylacetic acid hydrazide and benzoylacetic acid hydrazides.

## MATERIALS AND METHOD

### Reagents

Reagent grade ethylacetoacetate, ethylbutyrylacetate, ethylbenzoylacetate, hydrazine hydrate, methanol, ethanol, ammonia and the metal salts; zinc(II) acetate dihydrate and zinc(II) sulphate heptahydrate were purchased from the British Drug House Chemicals Ltd (BDH) and Aldrich Chemicals Co., and were used without further purification.

### Preparation of the ligands

The ligands, acetoacetic acid hydrazide, butyrylacetic acid hydrazide and benzoylacetic acid hydrazide were prepared according to our earlier report [7].

### Preparation of the compounds

#### Preparation of $\text{Zn}(\text{AAAH})_2\text{SO}_4$

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (1.73g, 6.0mmole) dissolved in 5mL 40% methanol was stirred while 2.00g (12.0mmole) acetoacetic acid hydrazide suspension in 10mL methanol was added dropwisely.

Precipitation was observed after pH was raised to 9 while stirring continued for additional 1hr. The white compound formed was filtered by suction, washed with 40% methanol, and deionised water before it was dried over calcium chloride in a dessicator (1.76g, 75%). The  $\text{Zn(AAAH)}_2(\text{OAc})_2$  complex was prepared employing the same procedure.

#### **Preparation of $\text{Zn(BUTAH)}_2(\text{OAc})_2$**

1.51g (6.9mmole)  $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 13mL 40% methanol and stirred in a 250mL beaker while butyrylacetic acid hydrazide (2g, 14.0mmole) in 10mL methanol was added dropwisely. White precipitates were observed immediately, and the mixture was stirred for 1hr before it was filtered by suction, washed with 40% methanol, deionised water and dried over calcium chloride (2.01g, 62%).  $\text{Zn(BUTAH)}_2\text{SO}_4$  was prepared using similar method but precipitation occurred after the pH was raised to 9.

#### **Preparation of $\text{Zn(BENZA H)}_2(\text{OAc})_2$**

$\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$  (1.85g, 8.4mmole) dissolved in 40mL 40% methanol was stirred while 3g (17.0mmole) benzoylacetic acid hydrazide in 10mL methanol was added dropwisely. Precipitation was observed immediately while stirring continued for additional 1hr. The white precipitate formed was filtered by suction, washed with 40% methanol, and deionised water before it was dried over calcium chloride in a dessicator (3.40g, 74%). The  $\text{Zn(BENZA H)}_2\text{SO}_4$  complex was prepared employing the same procedure except that precipitation occurred after the pH was raised to 9.

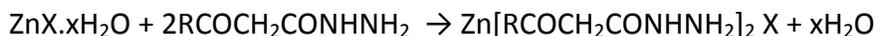
#### **Physical measurements**

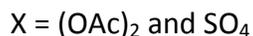
Elemental analyses were performed using a Perkin-Elmer 240C elemental analyser. The percentage metal was determined by the employment of complexometric titration using EDTA [8]. The infrared spectra were recorded on a Nicolet Avater 330FT- IR spectrophotometer using KBr discs. Genesys 10 scanning spectrophotometer (Thermo Electron Corporation) was used to record the electronic reflectance spectra of the ligand and complexes.

### **RESULTS AND DISCUSSION**

#### **Preparation of the compounds**

The acetoacetic acid hydrazide, butyrylacetic acid hydrazide and benzoylacetic acid hydrazide were prepared from the ethyl ester according to literature procedure [7]. The zinc(II) complexes were prepared in good yield by reacting the respective zinc(II) salts with their hydrazide ligands as shown below:





The Zn(II) acetoacetic acid hydrazide were not soluble in acetone, DMSO, water, ethanol,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{NO}_3$  and methanol. The butyrylacetic acid hydrazide complexes and benzoylacetic acid hydrazide complexes were sparingly soluble in the solvents used but very soluble in coordinating solvent like DMSO while being insoluble in water. The complexes are white, non-hygroscopic and some of them are non-melting solids. The results of the analytical data are summarized in Table 1.

**Table 1: Analytical data of ligands and complexes**

Compound	Molecular formula	Formula weight	Colour	%Yield	M.pt	% Observed (Calculated)			
						Metal	C	H	N
AAAH	$\text{C}_4\text{H}_8\text{N}_2\text{O}_2$	116.12	White	61	217 – 219	- -	41.22 (41.37)	6.86 (6.94)	23.68 (24.13)
Zn(AAAH) <sub>2</sub> (OAc) <sub>2</sub>	$\text{C}_{12}\text{H}_{22}\text{N}_4\text{O}_8\text{Zn}$	415.71	white	42	168	15.56 (15.73)	34.73 (34.67)	5.23 (5.33)	13.44 (13.48)
Zn(AAAH) <sub>2</sub> SO <sub>4</sub>	$\text{C}_8\text{H}_{16}\text{N}_4\text{O}_8\text{SZn}$	393.68	White	75	164	16.22 (16.60)	40.72 (24.41)	4.52 (4.10)	18.11 (14.23)
BUTAH	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2$	144.18	White	62	218 – 220	- -	49.66 (49.99)	8.32 (8.39)	19.31 (19.43)
Zn(BUTAH) <sub>2</sub> (OAc) <sub>2</sub>	$\text{C}_{16}\text{H}_{30}\text{N}_4\text{O}_8\text{Zn}$	471.81	White	62	238	13.73 (13.86)	40.89 (40.73)	6.02 (6.41)	11.62 (11.88)
Zn(BUTAH) <sub>2</sub> SO <sub>4</sub>	$\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_8\text{SZn}$	449.79	White	78	294	(14.98) (14.53)	(32.31) (32.04)	5.42 (5.38)	12.15 (12.46)
BENZAHA	$\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$	178.19	White	70	156 – 158	- -	60.44 (60.66)	5.62 (5.66)	15.66 (15.72)
Zn(BENZAHA) <sub>2</sub> (OAc) <sub>2</sub>	$\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_8\text{Zn}$	539.85	White	74	158 – 160	12.61 (12.11)	48.62 (48.95)	4.85 (4.90)	10.44 (10.38)
Zn(BENZAHA) <sub>2</sub> SO <sub>4</sub>	$\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_8\text{SZn}$	517.83	White	84	180	12.63 (12.62)	42.04 (41.75)	3.91 (3.89)	10.94 (10.82)

Acetoacetic acid hydrazide (AAAH), butyrylacetic acid hydrazide (BUTAH) and benzoylacetic acid hydrazides (BENZAHA) have three possible centres for coordination, viz. oxygen of the carbonyl of the amide group and nitrogen of the  $-\text{NH}_2$  group [6] and the isolated carbonyl group. If these ligands act as monofunctional bases, coordination should preferably take place through oxygen due to greater electron density at the oxygen atom [6]. Coordination through nitrogen alone is unlikely because the basic nature of nitrogen is reduced by carbonyl group [6]. If the ligands act as bifunctional bases, then both the donor atoms would be involved in coordination [6]. When oxygen to metal and /or nitrogen to metal bonds are present in the complex, the spectrum of the complex should differ significantly from that of the free AAAH, BUTAH and BENZAHA molecules. Coordination of the hydrazides to the metal through their oxygen atom should tend to increase the single bond character of the carbonyl group and thus shift the carbonyl stretching band to the lower frequencies [6]. Simultaneously, the double bond character of the C-N group would be increased with consequent shifting of its stretching band to the higher frequencies [6]. There should be either no appreciable change in

$\nu(\text{N-H})$  or it should be slightly shifted to a higher region [6]. On the other hand, if coordination occurs through nitrogen atom, the frequency shift would just be the reverse of the above. Similarly, coordination through both oxygen and nitrogen is expected to result in a decrease in both  $\nu(\text{C=O})$  and  $\nu(\text{N-H})$  [6].

The benzoylacetic acid hydrazide has the highest value for the “amide I” and “amide II” bands due to the electron withdrawing inductive effect of the aryl group on the adjacent carbonyl group which is also electron withdrawing. The withdrawal of electrons from the group led to the reduction of the electrons density available to the  $-\text{CONHNH}_2$  group thereby leading to the shortening of bonds which resulted in a blue shift in the “amide I” and “amide II” bands of the ligand relative to that of AAAH and BUTAH. The red shift in the “amide I” and “amide II”

**TABLE 2: KEY INFRARED FREQUENCIES AND ELECTRONIC SPECTRA TRANSITIONS FOR THE COMPOUNDS ( $\text{cm}^{-1}$ )**

Compounds	Amide I	Amide II	$\nu(\text{NH}_2)$	$\nu(\text{C=O})$	Electronic bands ( $\times 10^3$ )
AAAH	1612(m)	1544(w)	3539(w)	1782(m)	51,282, 37,175
$\text{Zn}(\text{AAAH})_2(\text{OAc})_2$	1582(s)	1530(w)	3211(m)	1734(m)	50,505, 41,494
$\text{Zn}(\text{AAAH})_2\text{SO}_4$	1575(s)	1505(s)	3204(w)	1724(w)	50,505, 43,668, 41,494
BUTAH	1618(m)	1592(w)	3460(m)	1727(w)	45,045
$\text{Zn}(\text{BUTAH})_2(\text{OAc})_2$	1572(m)	1514(m)	3200(m)	-	41,494
$\text{Zn}(\text{BUTAH})_2\text{SO}_4$	1572(m)	1514(m)	3217(w)	-	42,017
BENZAHA	1626(m)	1600(s)	3452(w)	1740(m)	49,751, 41,494
$\text{Zn}(\text{BENZAHA})_2(\text{OAc})_2$	1600(m)	1553(m)	3223(w)	1737(m)	40,000, 38,610
$\text{Zn}(\text{BENZAHA})_2\text{SO}_4$	1606(m)	1521(m)	3447(m)	-	46,083, 39,063

bands of the butyrylacetic acid hydrazide at  $1618 \text{ cm}^{-1}$  and  $1592 \text{ cm}^{-1}$  respectively, relative to that of the benzoylacetic acid hydrazide was attributed to the electron donating effect of the propyl group on the adjacent carbonyl group to the  $-\text{CONHNH}_2$ . In the “amide I” and amide II” of the acetoacetic acid hydrazide at  $1612 \text{ cm}^{-1}$  and  $1544 \text{ cm}^{-1}$  respectively, the red shift observed was higher than that of the butyrylacetic acid hydrazide. This may be due to the presence of the two methylene groups between  $\text{CH}_3-$  and  $-\text{CO}-$  groups of the butyrylacetic acid hydrazide which reduces the electron donating effect of the  $\text{CH}_3-$  on the adjacent carbonyl group which now led to the carbonyl group reducing the availability of electrons to the  $-\text{CONHNH}_2$  group. This consequently, resulted in the blue shift observed relative to the red shift in the acetoacetic acid hydrazide.

The  $\nu(\text{C=O})$ , “amide I” of the AAAH hydrazide ligand at  $1612 \text{ cm}^{-1}$  shifted significantly to  $1582 \text{ cm}^{-1}$  for the  $\text{Zn}(\text{AAAH})_2(\text{OAc})_2$  and  $1575 \text{ cm}^{-1}$  for the  $\text{Zn}(\text{AAAH})_2\text{SO}_4$  complex which strongly suggest the coordination through oxygen. A significant negative shift in the  $\nu(\text{N-H})$  of the  $-\text{NH}_2$  group to  $3211 \text{ cm}^{-1}$  and  $3204 \text{ cm}^{-1}$  respectively for the isolated complexes indicate the that nitrogen is also involved in coordination besides oxygen.

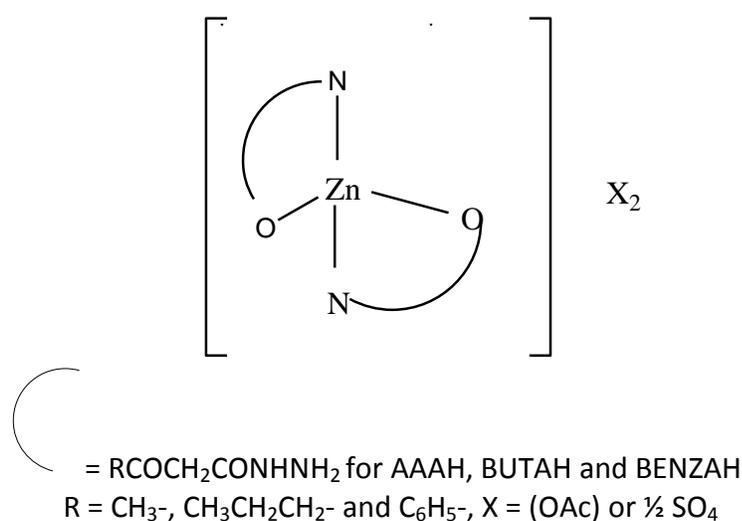
In the spectra of the butyrylacetic acid hydrazide, a considerable negative shift in the  $\nu(\text{C=O})$  are observed in the complexes indicating a decrease in the stretching force constant of  $\text{C=O}$  as a consequence of coordination through the carbonyl oxygen of the free ligand. Also, the negative shift observed in the  $\nu(\text{N-H})$  of the  $-\text{NH}_2$  group from  $3460 \text{ cm}^{-1}$  to  $3200 \text{ cm}^{-1}$  and  $3217$

$\text{cm}^{-1}$  respectively can be taken as an evidence of the participation of this group in bonding. This result is confirmed by the presence of new bands at  $519 \text{ cm}^{-1}$  for the two complexes, these bands can be assigned to  $\nu(\text{M} - \text{N})$  vibrations[1].

The benzoylacetic acetic acid hydrazide ligand spectra revealed the  $\nu(\text{C}=\text{O})$ , "amide I" band at  $1626 \text{ cm}^{-1}$  this experienced a negative shift to  $1600 \text{ cm}^{-1}$  and  $1606 \text{ cm}^{-1}$  respectively in the spectra of the complexes Table 2. Moreover, the  $\nu(\text{N-H})$  of the  $\nu(\text{NH}_2)$  group at  $3452 \text{ cm}^{-1}$  shifted slightly to  $3223 \text{ cm}^{-1}$  and  $3447 \text{ cm}^{-1}$  respectively for the benzoylacetic acid hydrazide complexes. The formation of the zinc(II) complexes was also confirmed by electronic reflectance spectra. The absorption spectra of the diamagnetic zinc(II) complexes were compared with the free ligands values with the presence of negative shifts. The absorption band of the zinc(II) complexes observed at  $50,505 \text{ cm}^{-1}$  attributed to  $n \rightarrow \sigma^*$  electronic transition of the excitation of the nitrogen lone pair electron to the antibonding  $\sigma$  - orbital of the amino group [9,10,11]. The  $\pi \rightarrow \pi^*$  transitions of the of the carbonyl group appeared in the range  $40,000 \text{ cm}^{-1} - 49,751 \text{ cm}^{-1}$  in all the complexes [9,10,11, 12]. Also, the  $\pi \rightarrow n$  transition of the carbonyl at  $38,610 \text{ cm}^{-1}$  to  $39,063 \text{ cm}^{-1}$  was observed in the zinc(II) complexes of the benzoylacetic acid hydrazide only.

## CONCLUSION

The synthesis of Zn(II) complexes of AAAH, BUTAH and BENZAH are reported for the first time. The vibrational spectroscopy showed that the ligands act as neutral bidentate ligands through the  $\nu(\text{C}=\text{O})$  of the carbonyl group and the  $\nu(\text{N-H})$  of the amino group. The stability of the bis- zinc(II) complexes of the hydrazides is demonstrated by the fact that these ligands yield only the bis-complexes as compared to our earlier reports on the analogues of cobalt(II) and nickel(II) complexes [7, 13, 14, 15]. From the results of the data obtained for the Zn(II) complexes, the suggested structure for the compounds is as shown in Fig. 1.



**Fig 1: Suggested structures for the complexes**

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