

## Synthesis, Characterization and Antimicrobial Activity of Zirconium (IV) Complexes

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**ABSTRACT.** Heteroleptic complexes of zirconium (IV) derived from bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones of the general formula  $ZrLL'$  (where  $LH_2 = RC(NH(C_6H_4))SC : C(OH)N(C_6H_5)N : CCH_3$ ,  $R = -C_6H_5$ ,  $-C_6H_4Cl(p)$  and  $L'H_2 = RC : (NOH)C : C(OH)N(C_6H_5)N : CCH_3$ ,  $R' = -CH_2CH_3$ ,  $-C_6H_5$ ,  $-C_6H_4Cl(p)$ ) were prepared by the reactions of zirconium tetrachloride with disodium salts of Schiff bases ( $L Na_2$ ) and oximes of heterocyclic  $\beta$ -diketones ( $L' Na_2$ ) in 1:1:1 molar ratio in dry refluxing THF. The structures of these monomeric zirconium (IV) complexes were elucidated with the help of elemental analysis, molecular weight measurements, spectroscopic (IR, NMR and mass) studies. A distorted trigonal bipyramidal geometry may be suggested for these heteroleptic zirconium (IV) complexes. The ligands (bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones) and their heteroleptic complexes of zirconium (IV) were screened against *A. flavus*, *P. aeruginosa* and *E. coli*.

**Key words:** Zirconium (IV) complexes, Antimicrobial activity

### INTRODUCTION

One of the important dimension of fascinating materials chemistry is the hybrid materials.<sup>1-5</sup> It has been realized early on that the hybrid materials can exhibit superior properties<sup>6-9</sup> as compared to their pure counterparts. The possibility to develop multifunctional materials<sup>10</sup> has provided further impetus in the field of hybrid materials. There are reports available in the literature concerning the synthetic and structural aspects of organic derivatives of zirconium (IV).<sup>11-15</sup> The metal-organic framework of zirconium (IV) complexes are generally developed by the interaction of zirconium alkoxides and zirconium tetrachloride with various potential organic ligands in different stoichiometric ratios in anhydrous media. The metal-organic framework of zirconium (IV) complexes possess various catalytic and technological applications.<sup>16-18</sup> The metal-organic framework of zirconium (IV) complexes act as a precursor for the development of  $ZrO_2$ .<sup>19,20</sup>  $ZrO_2$  displays special properties and put to use in various fields such as engineering ceramics,<sup>21</sup> chromatography<sup>22</sup> and pharmaceutical applications.<sup>23</sup> The reactivity of zirconium tetrachloride may be modified by organic modifiers like bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones which are potential organic ligands possessing interesting structural features. In view of the interesting results obtained in our

previous investigation<sup>3</sup> concerning the encapsulation of zirconium (IV) in sterically constrained sulphur containing Schiff bases derived from heterocyclic  $\beta$ -diketones, we now report the preparation and structural aspects of heteroleptic zirconium (IV) complexes of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones. It is interesting to study the comparative ligating capability of these two organic ligands towards zirconium (IV) in these heteroleptic complexes. The metal-organic framework of these zirconium (IV) complexes consists of zirconium surrounded by oxygen, nitrogen and sulphur. N, S-orthometallated zirconium (IV) chelates form a part of the heteroleptic zirconium (IV) complexes. Zirconium is surrounded by five, six and seven membered rings. The ligands and their newly synthesized heteroleptic complexes of zirconium (IV) were screened against *A. flavus*, *P. aeruginosa* and *E. coli*.

### EXPERIMENTAL SECTION

All experimental manipulations were carried out under strictly anhydrous conditions. The solvents were dried before use by standard methods. The bulky Schiff bases<sup>24</sup> ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones<sup>25</sup> were prepared by reported method.  $ZrCl_4$  is commercially available. Zirconium was estimated as  $ZrO_2$ .<sup>26</sup> Molecular weight measurements of hete-

roleptic complexes of zirconium (IV) were carried out cryscopically in benzene solution. IR (4000-400  $\text{cm}^{-1}$ ) spectra of the samples were recorded on SHIMADZU, FTIR-8400 spectrophotometer and samples were prepared as KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the samples were recorded in  $\text{CDCl}_3/\text{CDCl}_3$  and  $\text{DMSO}-d_6$  solutions on JEOL FTAL 300 NMR spectrometer operating at 300 and 75.45 MHz, respectively.

### Synthesis of Heteroleptic Zirconium (IV) Complex $[\text{ZrL}_1\text{L}'_1]$

To a methanolic solution of sodium (0.1115 g, 4.84 mmol), THF solution of the ligands, the bulky Schiff base ligand containing a sulphur atom  $[\text{L}_1\text{H}_2]$  (0.4680 g, 1.21 mmol) and oxime  $[\text{L}'_1\text{H}_2]$  of heterocyclic  $\beta$ -diketones (0.2969 g, 1.21 mmol) were added and the reaction mixture was heated for ~6 hours. After that, a THF solution of  $\text{ZrCl}_4$  (0.2824 g, 1.21 mmol) was added to the sodium salt of the two organic ligands and the reaction mixture was further heated for ~8 hours. The  $\text{NaCl}$  formed during the reaction was filtered off. After stripping off the excess solvent under reduced pressure, a brown coloured solid was isolated which was purified by recrystallization from dry chloroform and pet.-ether mixture. The reagents in g (mmols) are described in Table 1. The physical and analytical data of this complex,  $\text{ZrL}_1\text{L}'_1$  and other analogous complexes are summarized in Table 2.

### Antimicrobial Activity

The ligands (bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones) and their heteroleptic complexes of zirconium (IV) have been screened for their growth inhibitory activity in vitro against bacteria (*E. coli* and *P. aeruginosa*) and fungus (*A. flavus*). In order to evaluate the antimicrobial activity in vitro, of the ligands and zirconium (IV) complexes, well diffusion method was adopted. The different test organisms were proceeded separately using a sterile swab over previously sterilized culture medium plates and the zone

of inhibition were measured around well. Different concentrations (10 ppm, 50 ppm, 100 ppm and 200 ppm) of the test compounds dissolved in DMSO were present in the well. Ampicillin and Flucanazol were used as reference separately. Initially, these plates were placed at low temperature for one hour, to allow the maximum diffusion of the compounds from the test well into the surrounding areas. Then, later on, these plates were incubated at 37 °C for 24 hours in case of bacteria and 48 hours for fungi. After this process, inhibition zones were observed clearly and measured. Five replicates of each test extract were examined and the mean values were referred.

## RESULTS AND DISCUSSION

Heteroleptic complexes of zirconium (IV) of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones having the general formula  $\text{ZrLL}'$  (where  $\text{LH}_2 = \text{RCNH}(\text{C}_6\text{H}_4)\text{SC} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3$ ,  $\text{R} = -\text{C}_6\text{H}_5$ ,  $-\text{C}_6\text{H}_4\text{Cl}(\text{p})$  and  $\text{L}'\text{H}_2 = \text{R}'\text{C} : (\text{NOH})\text{C} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3$ ,  $\text{R}' = -\text{CH}_2\text{CH}_3$ ,  $-\text{C}_6\text{H}_5$ ,  $-\text{C}_6\text{H}_4\text{Cl}(\text{p})$ ) were prepared by the reaction of zirconium tetrachloride with disodium salt of Schiff bases ( $\text{LNa}_2$ ) and oximes of heterocyclic  $\beta$ -diketones ( $\text{L}'\text{Na}_2$ ) in 1:1:1 molar ratio in dry THF. It is outlined in the following Scheme 1.

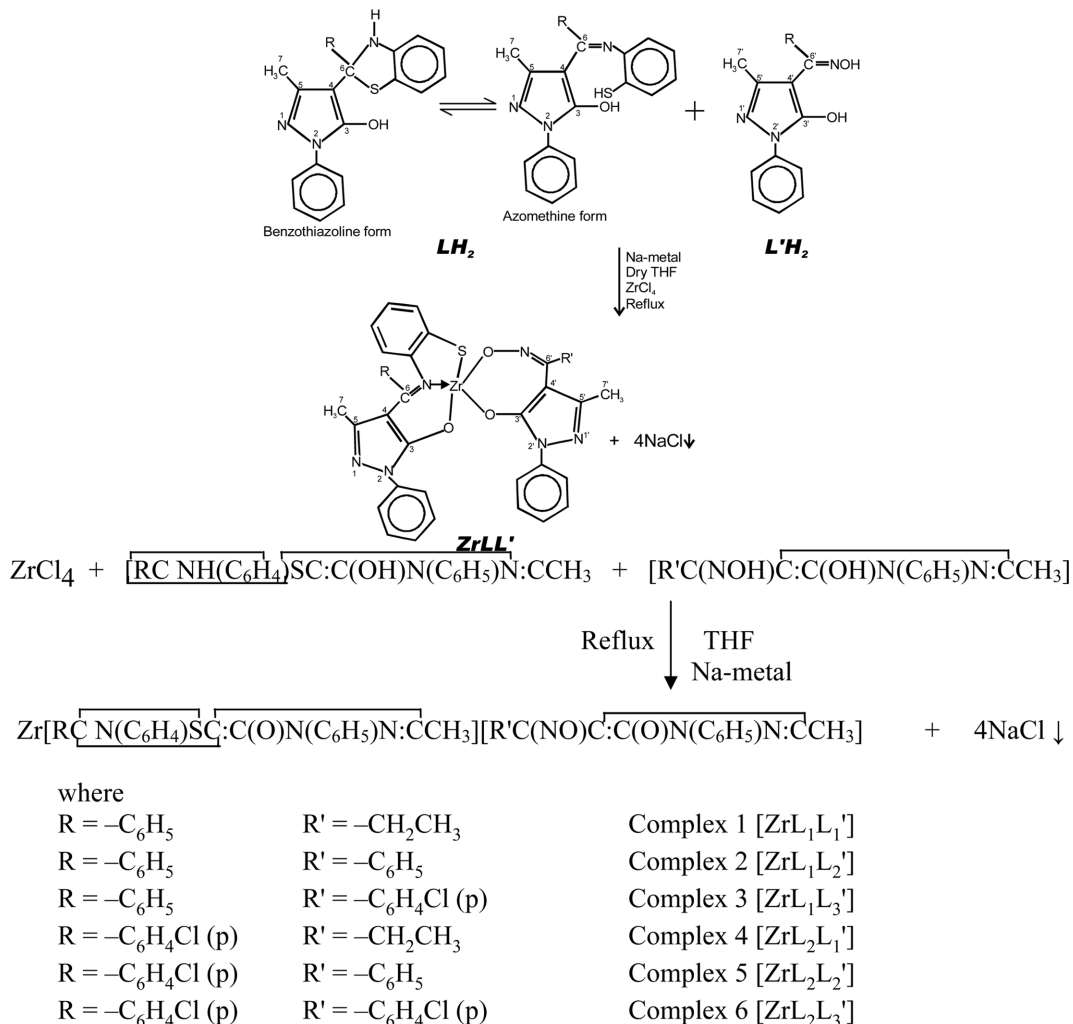
These reactions were completed in ~ 12 hours of refluxing. The  $\text{NaCl}$  formed in these reactions was filtered off. After stripping off the excess solvent under reduced pressure, coloured solid products were isolated. These coloured solid products were purified by recrystallization from chloroform and pet.-ether mixture. These coloured solid products were found to be powdery in nature. These heteroleptic complexes of zirconium (IV) were monomers as revealed by molecular weight measurements.

### IR Spectra

A comparative study of the IR spectra of these heteroleptic zirconium (IV) complexes of bulky Schiff base ligands containing a sulphur atom and oximes of hetero-

**Table 1.** The reagents in g (mmols) of heteroleptic zirconium (IV) complexes of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones

Complex no.	Complex Formula	Na	LH <sub>2</sub>	L'H <sub>2</sub>	ZrCl <sub>4</sub>
1	ZrL <sub>1</sub> L' <sub>1</sub> [C <sub>36</sub> H <sub>30</sub> N <sub>6</sub> O <sub>3</sub> SZr]	0.1115 (4.84)	0.4680 (1.21)	0.2969 (1.21)	0.2824 (1.21)
2	ZrL <sub>1</sub> L' <sub>2</sub> [C <sub>40</sub> H <sub>30</sub> N <sub>6</sub> O <sub>3</sub> SZr]	0.1150 (5.00)	0.4827 (1.24)	0.3674 (1.24)	0.2912 (1.24)
3	ZrL <sub>1</sub> L' <sub>3</sub> [C <sub>40</sub> H <sub>29</sub> N <sub>6</sub> O <sub>3</sub> SZrCl]	0.1154 (5.01)	0.4843 (1.25)	0.4109 (1.25)	0.2922 (1.25)
4	ZrL <sub>2</sub> L' <sub>1</sub> [C <sub>36</sub> H <sub>29</sub> N <sub>6</sub> O <sub>3</sub> SZrCl]	0.1160 (5.04)	0.5291 (1.26)	0.3089 (1.26)	0.2939 (1.26)
5	ZrL <sub>2</sub> L' <sub>2</sub> [C <sub>40</sub> H <sub>29</sub> N <sub>6</sub> O <sub>3</sub> SZrCl]	0.1142 (4.96)	0.5209 (1.24)	0.3649 (1.24)	0.2892 (1.24)
6	ZrL <sub>2</sub> L' <sub>3</sub> [C <sub>40</sub> H <sub>28</sub> N <sub>6</sub> O <sub>3</sub> SZrCl <sub>2</sub> ]	0.1165 (5.06)	0.5314 (1.26)	0.4149 (1.26)	0.2950 (1.26)



Scheme 1.

cyclic  $\beta$ -diketones with their parent ligands furnished useful and relevant information about bonding patterns. The formation of Zr-O bond<sup>15</sup> is supported by the appearance of a medium intensity band in the region 545-560  $\text{cm}^{-1}$  in the IR spectra of these heteroleptic complexes of zirconium (IV) of the type ZrLL'. A medium intensity band present in the region 425-430  $\text{cm}^{-1}$  may be due to the formation of Zr←N bond<sup>15</sup> (through Schiff base nitrogen). In the IR spectra of the bulky Schiff base ligands containing a sulphur atom, two broad bands present in the region 3400  $\text{cm}^{-1}$  and 3300  $\text{cm}^{-1}$  may be assigned to  $\nu\text{OH}$  and  $\nu\text{NH}$ , respectively.<sup>24,27</sup> These  $\nu\text{OH}$  and  $\nu\text{NH}$  bands were absent in the IR spectra of the corresponding zirconium (IV) complexes. The appearance of a band at 1605  $\text{cm}^{-1}$  in the IR spectra of these heteroleptic zirconium (IV) complexes may be attributed to  $>\text{C}=\text{N}$ - which indicates that the bulky Schiff base ligand containing a sulphur atom of

heterocyclic  $\beta$ -diketones are existing in benzothiazoline form in the free state and rearrange to azomethine form during complex formation.

In the IR spectra of the sterically hindered oximes of heterocyclic  $\beta$ -diketones, broad bands appearing in the region 3129-2356  $\text{cm}^{-1}$  may be assigned to  $\nu\text{OH}$  and  $\nu\text{NOH}$ , respectively.<sup>25</sup> These bands were found to be absent in the IR spectra of the corresponding zirconium (IV) complexes which indicates the formation of Zr-O bond. The formation of Zr-O bond is further corroborated by the presence of a medium intensity band in the region 545-560  $\text{cm}^{-1}$  in the IR spectra of these heteroleptic zirconium (IV) complexes. In the IR spectra of the bulky oximes of heterocyclic  $\beta$ -diketones, band appearing at 1520  $\text{cm}^{-1}$  may be due to  $\nu>\text{C}=\text{N}$ - ( $>\text{C}=\text{NOH}$  group). This band shifts to a lower wave number in the corresponding heteroleptic zirconium (IV) complexes (1500-1505  $\text{cm}^{-1}$ ) which further

supports the involvement of iminoxy ( $>C=NOH$ ) group of oximes in bonding with zirconium atom. In the IR spectra of the bulky oximes of heterocyclic  $\beta$ -diketones, other bands present at  $1610\text{ cm}^{-1}$  and at  $1560\text{ cm}^{-1}$  may be attributed to  $\nu>N-Ph$  and  $\nu>C=C</>C=N-$ , respectively. No appreciable shift was observed in the position of these bands in the corresponding zirconium (IV) complexes.

### $^1H$ NMR Spectra

The  $^1H$  NMR spectra of heteroleptic zirconium (IV) complexes of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones and their parent ligands were recorded in the suitable deuterated solvent using TMS as an internal standard and are summarized in Table 3. The  $^1H$  NMR spectra of these heteroleptic zirconium (IV) complexes showed expected multiplicity of peaks. In the  $^1H$  NMR spectra of the bulky sulphur containing Schiff bases, the broad singlets observed in the region  $\delta$  5.20-6.42 ppm may be due to  $>NH/-SH$  protons which disappeared in the  $^1H$  NMR spectra of the corresponding zirconium (IV) complexes, indicating deprotonation of  $>NH/-SH$  protons and formation of Zr-O bond through Schiff base. In the  $^1H$  NMR spectra of the sterically hindered oximes of heterocyclic  $\beta$ -diketones, the proton signals for  $-OH$  and  $>C=NOH$  are observed in the region  $\delta$  10.20-10.50 ppm which were found to be absent in the corresponding zirconium (IV) complexes of the

type  $ZrLL'$  indicating deprotonation and formation of Zr-O bond through oxime. The aromatic protons of the bulky Schiff base ligand containing a sulphur atom of heterocyclic  $\beta$ -diketones and the corresponding zirconium (IV) complexes are present as a complex pattern in the region  $\delta$  6.54-8.05 ppm and are overlapping with the aromatic protons of the oximes of heterocyclic  $\beta$ -diketones.

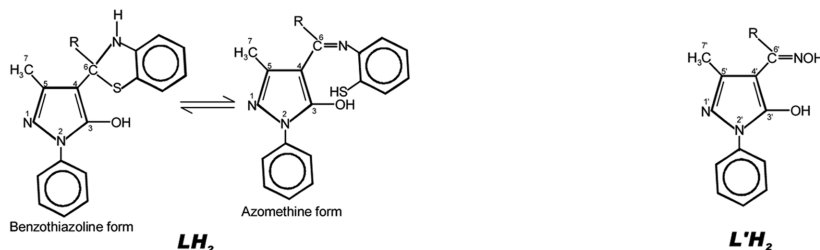
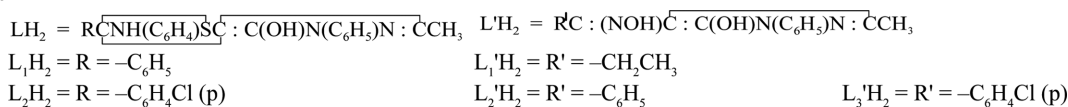
### $^{13}C$ NMR Spectra

The  $^{13}C$  NMR spectra of the heteroleptic zirconium (IV) complexes of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones and their parent ligands were recorded in the suitable deuterated solvent and are summarized in Table 4. The  $^{13}C$  NMR spectral study of the heteroleptic zirconium (IV) complexes and their parent ligands provided useful and relevant information which was used in establishing the coordination behaviour of the two organic ligands and the structures of these heteroleptic zirconium (IV) complexes. In the  $^{13}C$  NMR spectra of the bulky Schiff base ligands containing a sulphur atom, the  $C_6$  carbon signal was observed in the region  $\delta$  190.13-191.80 ppm. The  $C_6$  carbon signal shows some upfield shift (Table 4) in its position in the corresponding heteroleptic zirconium (IV) complexes which indicates the participation of  $>C_6=N-$  in bonding. In the  $^{13}C$  NMR spectra of the oximes of heterocyclic  $\beta$ -diketones, the  $C_6'$  carbon signal was observed

**Table 2.** Physical and analytical data of heteroleptic complexes of zirconium (IV) of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones

Complex no.	Complex Formula (Colour)	NaCl Found (Calc.)	% Zr Found (Calc.)	m.p (in $^{\circ}C$ )	Mol. Wt. Found (Calc.)	Yield (in %)
1	$ZrL_1L'_1 [C_{36}H_{30}N_6O_3SZr]$ (light brown)	0.26 (0.28)	12.74 (12.73)	220	740.15 (716.55)	86
2	$ZrL_1L'_2 [C_{40}H_{30}N_6O_3SZr]$ (brown)	0.28 (0.29)	11.92 (11.91)	260	780.04 (765.59)	89
3	$ZrL_1L'_3 [C_{40}H_{29}N_6O_3SZrCl]$ (yellow)	0.27 (0.29)	11.41 (11.40)	230	820.87 (800.09)	85
4	$ZrL_2L'_1 [C_{36}H_{29}N_6O_3SZrCl]$ (light green)	0.28 (0.29)	12.14 (12.12)	250	755.87 (752.05)	87
5	$ZrL_2L'_2 [C_{40}H_{29}N_6O_3SZrCl]$ (brown)	0.28 (0.29)	11.41 (11.40)	200	820.10 (800.09)	88
6	$ZrL_2L'_3 [C_{40}H_{28}N_6O_3SZrCl_2]$ (yellowish brown)	0.28 (0.29)	10.93 (10.94)	210	849.00 (833.59)	84

where



**Table 3.**  $^1\text{H}$  NMR data of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones and their heteroleptic complexes of zirconium (IV)

Complex No.	Ligands and complexes	$\text{RCNH}(\text{C}_6\text{H}_4)\text{SC} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3, [\text{LH}_2]$			$\text{R}'\text{C} : (\text{NOH})\text{C} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3, [\text{L}'\text{H}_2]$				
		>NH/-SH	Ring methyl	Ring phenyl, terminal -C <sub>6</sub> H <sub>5</sub> /-C <sub>6</sub> H <sub>4</sub> Cl(p), thiophenol ring	>NOH OH	Ring methyl	Ring phenyl, terminal -C <sub>6</sub> H <sub>5</sub> /C <sub>6</sub> H <sub>4</sub> Cl(p)	CH <sub>2</sub>	CH <sub>3</sub>
1	L <sub>1</sub> H <sub>2</sub>	5.20 (bs)	1.92(s)	6.55-8.05 (m)					
	L <sub>1</sub> 'H <sub>2</sub>				10.20 (bs)	2.48(s)	7.20-7.83 (m)	2.73 (q)	1.18 (t)
2	ZrL <sub>1</sub> L <sub>1</sub> '	-	1.79 (bs)	6.61-7.84 (m)	-	*	**	2.45 (q) <sub>unr.</sub>	1.19 (t) <sub>unr.</sub>
	L <sub>2</sub> H <sub>2</sub>				10.50 (bs)	2.09(s)	7.12-7.99 (m)		
3	ZrL <sub>1</sub> L <sub>2</sub> '	-	1.70 (s)	6.61-8.00 (m)	-	1.78(s)	**		
	L <sub>3</sub> H <sub>2</sub>				10.50 (bs)	2.16(s)	7.21-7.98 (m)		
4	ZrL <sub>1</sub> L <sub>3</sub> '	-	1.84 (s)	7.05-7.91 (m)	-	1.81 (s)	**		
	L <sub>2</sub> H <sub>2</sub>	6.42 (bs)	2.10 (s)	6.54-7.86 (m)					
5	ZrL <sub>2</sub> L <sub>1</sub> '	-	1.88 (s)	6.62-7.90 (m)	-	*	**	2.34 (q) <sub>unr.</sub>	1.13 (t) <sub>unr.</sub>
	L <sub>2</sub> H <sub>2</sub>								
6	ZrL <sub>2</sub> L <sub>2</sub> '	-	1.93 (s)	6.63-7.90 (m)	-	1.79 (s)	**		
	ZrL <sub>2</sub> L <sub>3</sub> '	-	1.86 (s)	6.95-7.55 (m)	-	1.92 (s)	**		

Note: where (bs) = broad singlet, (s) singlet, (t) triplet, (q) quartet, (m) = multiplet, unr. = unresolved

\*Merge with ring methyl protons of Schiff base of heterocyclic  $\beta$ -diketone

\*\*Merge with phenyl region of Schiff base of heterocyclic  $\beta$ -diketone

LH<sub>2</sub> =  $\text{RCNH}(\text{C}_6\text{H}_4)\text{SC} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3$ , L'H<sub>2</sub> =  $\text{R}'\text{C} : (\text{NOH})\text{C} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3$

L<sub>1</sub>H<sub>2</sub> = R = -C<sub>6</sub>H<sub>5</sub>, L<sub>1</sub>'H<sub>2</sub> = R' = -CH<sub>2</sub>CH<sub>3</sub>

L<sub>2</sub>H<sub>2</sub> = R = -C<sub>6</sub>H<sub>4</sub>Cl (p), L<sub>2</sub>'H<sub>2</sub> = R' = -C<sub>6</sub>H<sub>5</sub>, L<sub>3</sub>'H<sub>2</sub> = R' = -C<sub>6</sub>H<sub>4</sub>Cl (p)

**Table 4.**  $^{13}\text{C}$  NMR data of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones and their heteroleptic complexes of zirconium (IV)

Complex No.	Ligands and Complexes	$\text{RCNH}(\text{C}_6\text{H}_4)\text{SC} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3, [\text{LH}_2]$						$\text{R}'\text{C} : (\text{NOH})\text{C} : \text{C}(\text{OH})\text{N}(\text{C}_6\text{H}_5)\text{N} : \text{CCH}_3, [\text{L}'\text{H}_2]$							
		C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	Phenyl region	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	CH <sub>2</sub>	CH <sub>3</sub>	Phenyl region
1	L <sub>1</sub> H <sub>2</sub>	161.15	104.18	137.28	191.80	15.75	115.21-148.58								
	L <sub>1</sub> 'H <sub>2</sub>							161.79	94.43	138.71	191.07	15.94	24.16	13.46	119.34-146.58
2	ZrL <sub>1</sub> L <sub>1</sub> '	166.40	110.88	137.40	189.80	14.07	122.80-139.27	166.76	*	*	*	*	30.91	11.05	**
	L <sub>2</sub> H <sub>2</sub>							160.77	105.01	138.91	196.96	15.11			120.81-148.92
3	ZrL <sub>1</sub> L <sub>2</sub> '	163.41	107.28	137.98	187.62	16.04	120.11-148.17	*	*	*	*	*			**
	L <sub>3</sub> H <sub>2</sub>							160.08	104.08	137.31	189.62	15.23			120.13-148.96
4	ZrL <sub>1</sub> L <sub>3</sub> '	163.38	107.30	137.86	185.98	14.12	120.03-148.15	163.47	*	*	187.62	16.07			**
	L <sub>2</sub> H <sub>2</sub>	160.48	103.92	137.64	190.13	15.43	115.16-148.99								
5	ZrL <sub>2</sub> L <sub>1</sub> '	165.30	105.60	136.98	189.11	14.12	115.22-148.92	*	*	*	*	16.85	32.47	10.89	**
	L <sub>2</sub> H <sub>2</sub>	162.05	105.94	137.75	184.62	14.70	118.66-147.50	*	*	*	*	15.47			**
6	ZrL <sub>2</sub> L <sub>2</sub> '	162.05	105.94	137.75	184.62	14.70	118.66-147.50	*	*	*	*	15.47			**
	***ZrL <sub>2</sub> L <sub>3</sub> '	165.06	106.10	136.78	186.88	14.13	115.23-148.92	*	*	*	*	16.11			**

Note: \*indicates carbon signals of the Schiff bases are overlapping with the corresponding carbon signals of the oximes of heterocyclic  $\beta$ -diketones.

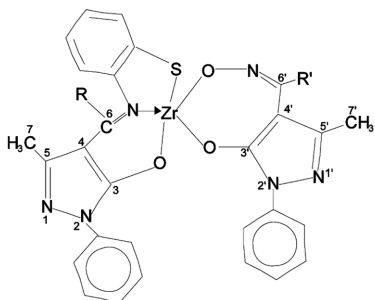
\*\*merge with phenyl region of Schiff base of heterocyclic  $\beta$ -diketones.

\*\*\*MS : m/z 834.1 [M]<sup>+</sup>, 472.0, 450.1, 354.1, 260.1, 220.2

in the region  $\delta$  189.62-191.07 ppm. The C<sub>6</sub>' carbon signal experiences some upfield shifts in its position in the corresponding heteroleptic zirconium (IV) complexes. The C<sub>6</sub> carbon signal is overlapping with the C<sub>6</sub>' carbon signal in heteroleptic zirconium (IV) complexes. The C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> and C<sub>7</sub> carbon signals of bulky Schiff base ligand con-

taining a sulphur atom and the corresponding carbon signals in the of the heterocyclic  $\beta$ -diketones are summarized in Table 4.

Heteroleptic zirconium (IV) complexes of bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones were found to be monomers



where		
R = -C <sub>6</sub> H <sub>5</sub>	R' = -CH <sub>2</sub> CH <sub>3</sub>	Complex 1 [ZrL <sub>1</sub> L <sub>1</sub> ']
R = -C <sub>6</sub> H <sub>5</sub>	R' = -C <sub>6</sub> H <sub>5</sub>	Complex 2 [ZrL <sub>1</sub> L <sub>2</sub> ']
R = -C <sub>6</sub> H <sub>5</sub>	R' = -C <sub>6</sub> H <sub>4</sub> Cl (p)	Complex 3 [ZrL <sub>1</sub> L <sub>3</sub> ']
R = -C <sub>6</sub> H <sub>4</sub> Cl (p)	R' = -CH <sub>2</sub> CH <sub>3</sub>	Complex 4 [ZrL <sub>2</sub> L <sub>1</sub> ']
R = -C <sub>6</sub> H <sub>4</sub> Cl (p)	R' = -C <sub>6</sub> H <sub>5</sub>	Complex 5 [ZrL <sub>2</sub> L <sub>2</sub> ']
R = -C <sub>6</sub> H <sub>4</sub> Cl (p)	R' = -C <sub>6</sub> H <sub>4</sub> Cl (p)	Complex 6 [ZrL <sub>2</sub> L <sub>3</sub> ']

Fig. 1. Structure of complex ZrLL'.

as revealed by molecular weight measurements. On the basis of physico-chemical and spectroscopic studies, the following plausible structure may be proposed for these heteroleptic zirconium (IV) complexes of the type ZrLL' (Fig. 1).

The heteroleptic zirconium (IV) complexes of the type ZrLL' contain five coordinated zirconium centres and a distorted trigonal bipyramidal geometry may be proposed for these complexes. Zirconium is encapsulated in the bulky Schiff base ligands containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones which afforded the metallacyclic systems in which zirconium is surrounded by O, N and S atoms. A part of metal-organic framework of these heteroleptic zirconium (IV) complexes consists of N, S-orthometallated zirconium (IV) chelates. These heteroleptic zirconium (IV) complexes possess Zr←N bond. These heteroleptic zirconium (IV) complexes contain a five, a six and a seven membered ring.

Blending of the two components, organic components, the bulky Schiff base ligands containing a sulphur atom and oxime of heterocyclic  $\beta$ -diketones and the inorganic component, ZrCl<sub>4</sub> afforded heteroleptic zirconium (IV) complexes of the type ZrLL'. The interaction of ZrCl<sub>4</sub> with the Schiff bases and oximes of heterocyclic  $\beta$ -diketone in 1:1:1 molar ratio in dry THF yielded heteroleptic zirconium (IV) complexes, ZrLL'. There is a formation of a five membered and a six membered ring in the Schiff base component whereas a seven membered ring is formed in the oxime component of these heteroleptic zirconium (IV) complexes.

#### Antimicrobial Activity

The organic ligands (bulky Schiff base ligands contain-

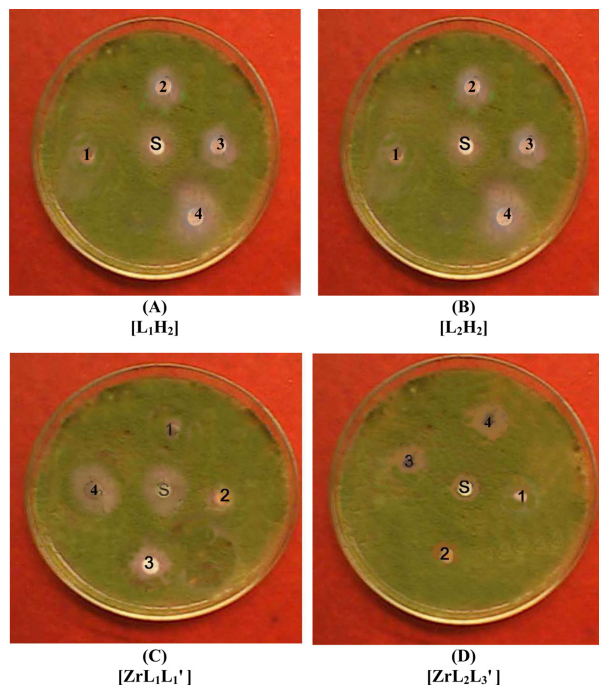


Fig. 2. Inhibition zones of ligands [L<sub>1</sub>H<sub>2</sub>]=A, [L<sub>2</sub>H<sub>2</sub>]=B and their heteroleptic complexes of zirconium(IV), [ZrL<sub>1</sub>L<sub>1</sub>']=C and [ZrL<sub>2</sub>L<sub>3</sub>']=D against *A. flavus*. [L<sub>1</sub>H<sub>2</sub>, L<sub>2</sub>H<sub>2</sub> and L<sub>3</sub>H<sub>2</sub> were found to be inactive=Ia].

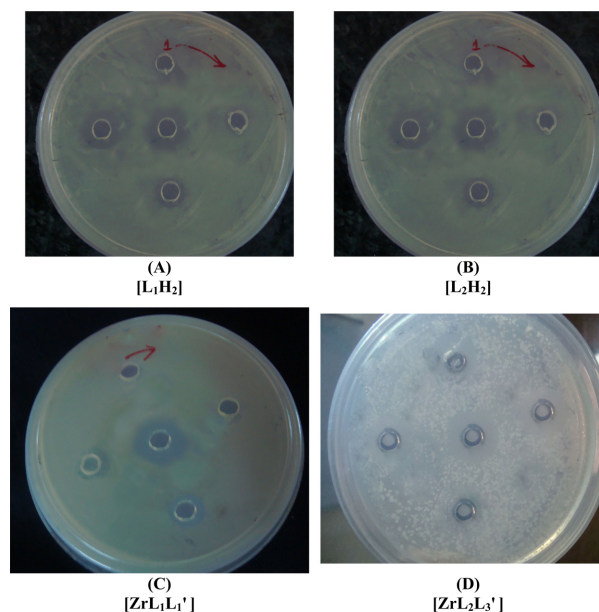
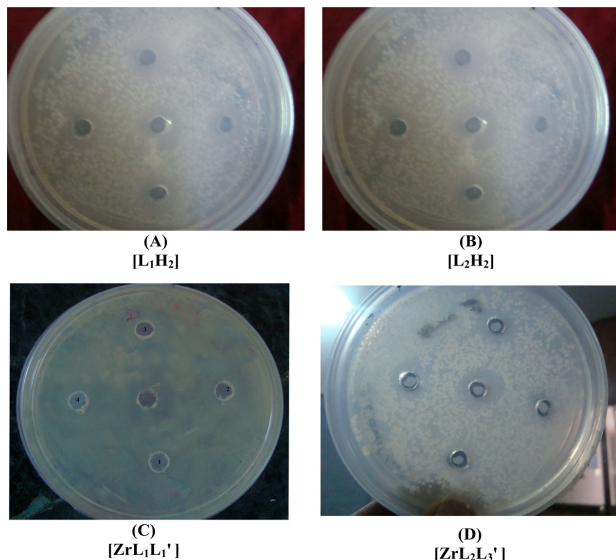


Fig. 3. Inhibition zones of ligands [L<sub>1</sub>H<sub>2</sub>]=A, [L<sub>2</sub>H<sub>2</sub>]=B and their heteroleptic complexes of zirconium (IV), [ZrL<sub>1</sub>L<sub>1</sub>']=C and [ZrL<sub>2</sub>L<sub>3</sub>']=D against *P. aeruginosa*. [L<sub>1</sub>H<sub>2</sub>, L<sub>2</sub>H<sub>2</sub> and L<sub>3</sub>H<sub>2</sub> were found to be inactive=Ia].

ing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones) and their heteroleptic complexes of zirconium (IV) were screened against *A. flavus* (Fig. 2), *P. aeruginosa*



**Fig. 4.** Inhibition zones of ligands  $[L_1H_2]=A$ ,  $[L_2H_2]=B$  and their heteroleptic complexes of zirconium (IV),  $[ZrL_1L_1']=C$  and  $[ZrL_2L_3']=D$  against *E. coli*.  $[L_1H_2, L_2H_2$  and  $L_3H_2$  were found to be inactive= $I_a$ ].

(Fig. 3) and *E. coli*. (Fig. 4). During the present investigation, the growth inhibitory potential of these ligands and their complexes of zirconium (IV) towards the test organisms has been studied and summarized in Table 5.

A comparative study of the results of this investigation reveals that these newly synthesized heteroleptic complexes of zirconium (IV) were more growth inhibitory

than their corresponding organic ligands. The growth inhibition was found to increase with the concentration of the compounds/zirconium (IV) complexes.

The structure-activity relationship of these newly synthesized heteroleptic complexes of zirconium (IV) was discussed in terms of the following factors

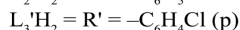
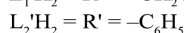
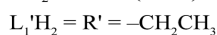
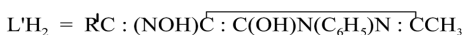
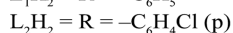
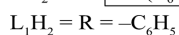
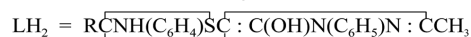
1. The presence of N, S-orthometallated<sup>28</sup> zirconium (IV) chelates which form a part of these heteroleptic zirconium (IV) complexes.
2. The coordination number<sup>29</sup> and geometry<sup>29</sup> of zirconium (IV) complexes.
3. The effect of substitution on the ligands.
4. The presence or absence of halogen atom<sup>30</sup> in zirconium (IV) complexes.
5. Nature of metal.

These heteroleptic complexes of zirconium (IV) possess five coordinated zirconium centres<sup>31</sup> and a distorted trigonal bipyramidal geometry<sup>32</sup> may be suggested for these complexes. The heteroleptic complexes 4,5 and 6  $[R = -C_6H_4Cl(p)]$  were found to be more active than complexes 1,2 and 3 ( $R = -C_6H_5$ ). Some substitutions were carried out on the oxime ligand. The complexes where  $R' = -C_6H_4Cl(p)$  were found to be more active than the complexes where  $R' = -C_6H_5$ . The complexes where  $R' = -CH_2CH_3$  were having lowest activity. The most active complex was 6 while the least active complex was 1. It is pertinent to note that the presence of chlorine atom has some effect on the activity of these complexes.

**Table 5.** Antimicrobial activities of bulky Schiff base ligand containing a sulphur atom and oximes of heterocyclic  $\beta$ -diketones and their heteroleptic complexes of zirconium (IV)

Complex No.	Ligands and Complexes	<i>A. flavus</i>				<i>P. aeruginosa</i>				<i>E. coli</i>			
		10 ppm	50 ppm	100 ppm	200 ppm	10 ppm	50 ppm	100 ppm	200 ppm	10 ppm	50 ppm	100 ppm	200 ppm
	$L_1H_2$	-	0.3	0.5	0.7	-	0.2	0.5	0.6	-	0.4	0.4	0.7
	$L_1'H_2$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$
1	$ZrL_1L_1'$	0.3	0.5	0.8	1.1	0.4	0.5	0.7	1.2	0.4	0.6	0.9	1.2
	$L_2H_2$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$
2	$ZrL_1L_2'$	0.6	0.8	1.1	1.5	0.7	0.9	1.2	1.5	0.7	0.9	1.3	1.6
	$L_3H_2$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$	$I_a$
3	$ZrL_1L_3'$	0.7	1.0	1.3	1.7	0.8	1.0	1.4	1.7	0.8	1.1	1.5	1.7
	$L_2H_2$	-	0.4	0.6	0.8	-	0.3	0.6	0.9	-	0.4	0.7	0.9
4	$ZrL_2L_1'$	0.5	0.6	0.9	1.4	0.5	0.7	1.0	1.3	0.6	0.8	1.1	1.4
5	$ZrL_2L_2'$	0.7	1.1	1.4	1.7	0.9	1.0	1.4	1.8	0.8	1.2	1.6	1.7
6	$ZrL_2L_3'$	0.9	1.3	1.7	2.0	1.0	1.3	1.7	2.1	0.9	1.5	1.8	2.2

Where  $I_a$  = Inactive and (-) = No growth



These complexes contain a five, a six and a seven membered rings<sup>28,33</sup> and a part of metal-organic framework of these complexes consists of N, S-orthometallated zirconium (IV) chelates. In these metallacyclic systems, zirconium is surrounded by three heteroatoms O, N and S. Further, these complexes contain Zr←N bonds. These structural features of these complexes may contribute to the activity of these complexes.

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