

# Synthesis, Spectral and Antibacterial Studies of Binuclear Titanium(IV) / Zirconium(IV) Complexes of Piperazine Dithiosemicarbazones

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## ABSTRACT

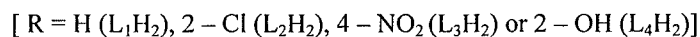
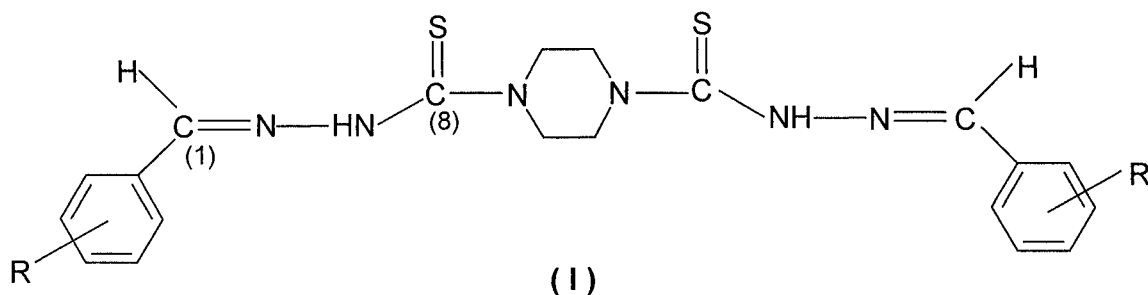
The reactions of mono(cyclopentadienyl)titanium(IV) trichloride and bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride with a new class of dithiosemicarbazone, derived by condensing piperazine dithiosemicarbazide with benzaldehyde ( $L_1H_2$ ), 2-chlorobenzaldehyde ( $L_2H_2$ ), 4-nitrobenzaldehyde ( $L_3H_2$ ) or salicylaldehyde ( $L_4H_4$ ) have been studied and different types of binuclear products, *viz.* [ $\{CpTiCl_2\}_2L$ ], [ $\{Cp_2MCl\}_2L$ ], ( $L=L_1, L_2$  or  $L_3$ ), [ $\{CpTiCl\}_2L_4$ ] and [ $\{Cp_2M\}_2L_4$ ] ( $M=Ti$  or  $Zr$ ), have been isolated. Tentative structures are proposed for these complexes based upon elemental analyses, electrical conductance, magnetic moment and spectral (electronic, IR,  $^1H$  and  $^{13}C$  NMR) data. Attempts have been made to establish a correlation between antibacterial activity and the structures of the products.

## INTRODUCTION

Thiosemicarbazones and their metal complexes are of considerable current interest because of their potentially beneficial pharmacological properties and a wide variation in their modes of bonding and stereochemistry /1-6/. Heterocyclic thiosemicarbazones exercise their beneficial therapeutic properties in mammalian cells by inhibiting ribonucleotide reductase, a key enzyme in the synthesis of DNA precursors /7/. Their ability to provide this inhibitory action is thought to be owing to coordination *via* their N – N – S tridentate ligating system. Recent developments in the structural nature of metal complexes of heterocyclic thiosemicarbazones are correlated with their biological activities. It has been suggested that the stereochemistries and activities of complexes often depend upon the nature of N(4) substituents and on groups attached to N(1). Recently, a number of papers have also appeared /4/ on bis(thiosemicarbazone) derivatives (derived from dialdehyde or diketons) in which two thiosemicarbazone moieties are connected by their imine nitrogens, to N(1) carbon skeleton. However, very few reports are available on

bis(thiosemicarbazones) in which two thiosemicarbazone moieties are connected by their amide nitrogens, N(4). West *et al.* named /8/ ligands of the second category as dithiosemicarbazones in order to differentiate it from the first category. They also reported /8/ Co(II), Ni(II) and Cu(II) complexes of such types of ligands, viz. N, N'-dimethylethylene diamine or piperazine dithiosemicarbazones.

The present paper describes the synthesis and characterization of titanium(IV) / zirconium(IV) derivatives with new ligands derived from piperazine dithiosemicarbazide with benzaldehyde, 2-chlorobenzaldehyde, 4-nitrobenzaldehyde or salicylaldehyde. The structure of ligands (I) is shown below.



## EXPERIMENTAL

All reactions were carried out under strictly anhydrous conditions. THF was dried by heating under reflux over sodium wire. The Et<sub>3</sub>N was purified by published methods /9/. Mono(cyclopentadienyl)titanium(IV) trichloride was prepared from Cp<sub>2</sub>TiCl<sub>2</sub> and TiCl<sub>4</sub> in p-xylene /10/. Bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride were prepared /11/ by heating CpNa with appropriate metal chloride in a N<sub>2</sub> atmosphere. Elemental analyses and physical measurements were made as noted earlier /7/. Piperazine dithiosemicarbazide was prepared as reported by West *et al.* /8/.

### Preparation of dithiosemicarbazones

Piperazine dithiosemicarbazide (0.01 mol) and appropriate aldehyde (benzaldehyde, 2-chlorobenzaldehyde, 4-nitrobenzaldehyde or salicylaldehyde) (0.02 mol) were dissolved in ethanol (30 cm<sup>3</sup>) and to this 2-3 drops of glacial acetic acid was added. The mixture was refluxed for 7-8 hours. The solution was concentrated to *ca.* 15 cm<sup>3</sup> and light petroleum (b.p. 60-80<sup>o</sup>) (~10 cm<sup>3</sup>) was added. The resulting solid was filtered, washed with cold i-PrOH and dried under vacuum.

L<sub>1</sub>H<sub>1</sub>: Yield ~ 72% ; Anal. Found : C, 58.3%; H, 5.3%; N, 20.2%; S, 15.6%; Calcd. for C<sub>20</sub>H<sub>22</sub>N<sub>6</sub>S<sub>2</sub> : C, 58.5%; H, 5.4%; N, 20.5%; S, 15.6%. IR : 3150 cm<sup>-1</sup> (ν N-H), 1570 cm<sup>-1</sup> (ν C=N), 800 cm<sup>-1</sup> (ν C=S),  
<sup>1</sup>HNMR : δ 12.60 (N-H), δ 8.18 (-CH=N-), δ 3.35(C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>); <sup>13</sup>C NMR : δ 165.0 (C-1), δ 150.0 (C-8), δ 62.8 (C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>), δ 3.35 (C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>)

$L_2H_2$ : Yield ~ 68%; Anal. Found : C, 50.0%; H, 4.1%; N, 17.3%; S, 13.2%; Cl, 14.8%; Calcd. for  $C_{20}H_{20}N_6S_2Cl_2$  : C, 50.1%; H, 4.2%; N, 17.5%; S, 13.4%; Cl, 14.8%. IR :  $3165\text{ cm}^{-1}$  (v N-H),  $1565\text{ cm}^{-1}$  (v C=N),  $795\text{ cm}^{-1}$  (v C=S);  $^1\text{HNMR}$  :  $\delta$  12.95 (N-H),  $\delta$  8.20 (-CH=N-),  $\delta$  3.32 ( $C_4H_8N$ );  $^{13}\text{C}$  NMR :  $\delta$  164.5 (C-1),  $\delta$  148.2 (C-8),  $\delta$  61.5 ( $C_4H_8N_2$ ).

$L_3H_2$ : Yield ~ 70%; Anal. found : C, 47.8%; H, 3.9%; N, 22.2%; S, 12.6%; Calcd. for  $C_{20}H_{20}N_8S_2O_4$  : C, 48.0%; H, 4.0%; N, 22.4%; S, 12.8%. IR :  $3160\text{ cm}^{-1}$  (v N-H),  $1560\text{ cm}^{-1}$  (v C=N),  $790\text{ cm}^{-1}$  (v C=S);  $^1\text{HNMR}$  :  $\delta$  12.70 (N-H),  $\delta$  8.20 (-CH=N-),  $\delta$  3.30 ( $C_4H_8N$ );  $^{13}\text{C}$  NMR :  $\delta$  164.2 (C-1),  $\delta$  149.0 (C-8),  $\delta$  61.8 ( $C_4H_8N_2$ ).

$L_4H_4$ : Yield ~ 78%; Anal. found : C, 54.1%; H, 5.0%; N, 18.7%; S, 14.5%; Calcd. for  $C_{20}H_{22}N_6S_2O_2$  : C, 54.3%; H, 5.0%; N, 19.0%; S, 14.5%. IR :  $3150\text{ cm}^{-1}$  (v N-H),  $1565\text{ cm}^{-1}$  (v C=N),  $805\text{ cm}^{-1}$  (v C=S);  $^1\text{HNMR}$  :  $\delta$  12.85 (N-H),  $\delta$  8.21 (-CH=N-),  $\delta$  3.32 ( $C_4H_8N$ );  $^{13}\text{C}$  NMR :  $\delta$  164.8 (C-1),  $\delta$  149.2 (C-8),  $\delta$  62.0 ( $C_4H_8N_2$ ).

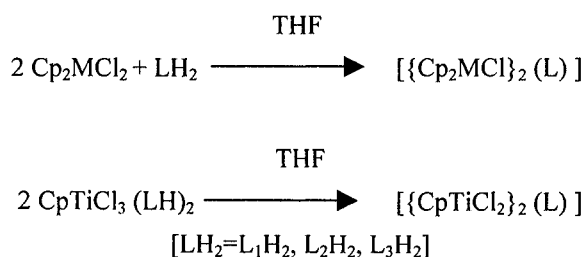
### Reactions of $Cp_2MCl_2$ and $CpTiCl_3$ with dithiosemicarbazones

To a solution of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride or mono(cyclopentadienyl)titanium(IV) trichloride (20 mmol) in dry THF (*ca.*  $40\text{ cm}^3$ ) was added the appropriate dithiosemicarbazone (10 mmol). To the resulting clear solution,  $Et_3N$  (20 mmol) was added and the mixture was stirred for *ca.* 12-22 h at room temperature. Precipitated  $Et_3NHCl$  was removed by filtration and the volume of the solution was reduced to *ca.*  $15\text{ cm}^3$  under reduced pressure. Light petroleum (b.p.  $60-80\text{ }^\circ\text{C}$ ) ( $10\text{ cm}^3$ ) was then added. The colored precipitate thus obtained was thoroughly washed with  $Et_2O$  and recrystallized from 1:1 THF:  $Et_2O$ .

The details and important physical characteristics of new compounds are recorded in Table 1. The nuclear magnetic resonance spectra of ligands and the complexes were recorded on a Bruker 400 spectrometer. Chemical shifts are expressed relative to an internal reference TMS (1% by volume).

## RESULTS AND DISCUSSION

A systematic study of the reactions of bis(cyclopentadienyl)titanium(IV)/ zirconium(IV) dichloride and mono(cyclopentadienyl)titanium(IV) trichloride with piperazine dithiosemicarbazones (molar ratio 2:1, respectively) in anhydrous THF in the presence of triethylamine may be represented by the following equations:



**Table 1.** Reactions of mono(cyclopentadienyl)titanium(IV) trichloride and bis(cyclopentadienyl)titanium(IV)/ zirconium(IV) dichloride with piperazine dithiosemicarbazones

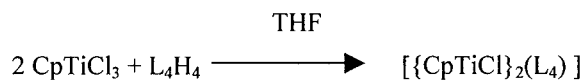
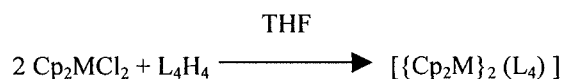
Reactants	Molar ratio	Reflux time(h)	Product/ Colour	Yield (%)	C	H	N	S	M	Cl
$\text{CpTiCl}_3 + \text{L}_1\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	15	$[\{\text{CpTiCl}_2\}_2(\text{L}_1)]$ yellowish brown	62	46.2 (46.4)	3.7 (3.9)	10.7 (10.8)	8.1 (8.2)	12.2 (12.3)	18.2 (18.3)
$\text{CpTiCl}_3 + \text{L}_2\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	18	$[\{\text{CpTiCl}_2\}_2(\text{L}_2)]$ yellowish brown	60	42.3 (42.5)	3.1 (3.3)	9.7 (9.9)	7.5 (7.6)	11.2 (11.3)	25.0 (25.1)
$\text{CpTiCl}_3 + \text{L}_3\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	15	$[\{\text{CpTiCl}_2\}_2(\text{L}_3)]$ yellow	58	41.2 (41.5)	3.1 (3.2)	12.7 (12.9)	7.4 (7.4)	11.0 (11.0)	16.2 (16.3)
$\text{CpTiCl}_3 + \text{L}_4\text{H}_4 + \text{Et}_3\text{N}$	2:1:4	12	$[\{\text{CpTiCl}\}_2(\text{L}_4)]$ brown	68	48.6 (48.9)	3.7 (3.8)	11.2 (11.4)	8.6 (8.7)	13.0 (13.0)	9.5 (9.6)
$\text{Cp}_2\text{TiCl}_2 + \text{L}_1\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	15	$[\{\text{Cp}_2\text{TiCl}\}_2(\text{L}_1)]$ brown	65	57.3 (57.5)	4.7 (4.8)	9.8 (10.0)	7.5 (7.6)	11.4 (11.5)	8.5 (8.5)
$\text{Cp}_2\text{TiCl}_2 + \text{L}_2\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	18	$[\{\text{Cp}_2\text{TiCl}\}_2(\text{L}_2)]$ yellowish brown	62	53.0 (53.1)	4.1 (4.2)	9.2 (9.3)	7.0 (7.1)	10.5 (10.6)	15.5 (15.7)
$\text{Cp}_2\text{TiCl}_2 + \text{L}_3\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	16	$[\{\text{Cp}_2\text{TiCl}\}_2(\text{L}_3)]$ reddish brown	64	51.8 (51.9)	4.0 (4.1)	12.0 (12.1)	6.6 (6.9)	10.2 (10.3)	7.5 (7.7)
$\text{Cp}_2\text{TiCl}_2 + \text{L}_4\text{H}_4 + \text{Et}_3\text{N}$	2:1:4	12	$[\{\text{Cp}_2\text{Ti}\}_2(\text{L}_4)]$ brown	70	60.2 (60.4)	4.7 (4.8)	10.5 (10.6)	8.0 (8.1)	12.0 (12.0)	—
$\text{Cp}_2\text{ZrCl}_2 + \text{L}_1\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	18	$[\{\text{Cp}_2\text{ZrCl}\}_2(\text{L}_1)]$ brown	62	52.0 (52.1)	4.2 (4.4)	9.0 (9.1)	6.7 (6.9)	19.7 (19.8)	7.6 (7.7)
$\text{Cp}_2\text{ZrCl}_2 + \text{L}_2\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	22	$[\{\text{Cp}_2\text{ZrCl}\}_2(\text{L}_2)]$ light brown	58	48.3 (48.5)	3.7 (3.9)	8.4 (8.5)	6.3 (6.5)	18.3 (18.4)	14.3 (14.3)
$\text{Cp}_2\text{ZrCl}_2 + \text{L}_3\text{H}_2 + \text{Et}_3\text{N}$	2:1:2	22	$[\{\text{Cp}_2\text{ZrCl}\}_2(\text{L}_3)]$ yellowish brown	60	47.2 (47.5)	3.7 (3.8)	11.0 (11.0)	6.1 (6.3)	17.9 (18.0)	6.9 (7.0)
$\text{Cp}_2\text{ZrCl}_2 + \text{L}_4\text{H}_4 + \text{Et}_3\text{N}$	2:1:4	16	$[\{\text{Cp}_2\text{Zr}\}_2(\text{L}_4)]$ brown	68	54.3 (54.5)	4.2 (4.3)	9.3 (9.5)	7.2 (7.3)	20.6 (20.7)	—

$\text{L}_1\text{H}_1$  = Dithiosemicarbazone derived from piperazine dithiosemicarbazide and benzaldehyde

$\text{L}_2\text{H}_2$  = Dithiosemicarbazone derived from piperazine dithiosemicarbazide and 2-chlorobenzaldehyde

$\text{L}_3\text{H}_3$  = Dithiosemicarbazone derived from piperazine dithiosemicarbazide and 4-nitrobenzaldehyde

$\text{L}_4\text{H}_4$  = Dithiosemicarbazone derived from piperazine dithiosemicarbazide and salicylaldehyde



In formulas for the complexes, L is the symbol for the dianion when both of the thiosemicarbazone moieties have lost their amide proton N(2)H in the piperazine dithiosemicarbazone ligands derived from benzaldehyde, 2-chlorobenzaldehyde and 4-nitrobenzaldehyde. L<sub>4</sub> represents the loss of both amide protons and phenolic protons from the salicylaldehyde piperazine dithiosemicarbazone.

Colours, elemental analyses and molar conductivities are listed in Table 1. Complexes are soluble in dimethylformamide, dimethylsulphoxide, nitrobenzene, tetrahydrofuran. The molar conductances of the complexes in DMF are in the range 6.0-10.0 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, which are well below the range observed for uni-univalent electrolytes in this solvent. Magnetic susceptibility measurements show that they are diamagnetic. The electronic spectra of the complexes show a broad band in the 22200-23800 cm<sup>-1</sup>, region which can be assigned /12/ to charge-transfer, a result in accord with their (n-1)d<sup>0</sup>ns<sup>0</sup> electronic configuration. The ligands show bands at ca. 35000 cm<sup>-1</sup> and 28000 cm<sup>-1</sup>, which are assigned to n → π\* transitions associated with imine and thioamide functions of the thiosemicarbazone moieties, respectively. In their respective complexes, these bands shift slightly to higher frequencies.

### I.R.Spectra

Absorption bands occurring at ca. 3000 cm<sup>-1</sup> for ν (C-H), ca. 1420 cm<sup>-1</sup> for ν (C-C) and ca. 1020 cm<sup>-1</sup> for ν (C-H) in all the complexes are assigned to the cyclopentadienyl group and indicate that these groups are π-bonded to the metal /13/.

The i.r. spectral bands most useful for determining the coordination mode for the dithiosemicarbazones are listed in Table 2. These ligands can exist either as a thione or the thiol tautomeric forms or as an equilibrium mixture of both forms, since they have a thioamide, -NH-C(=S) function. The i.r. spectra in the solid state do not show any ν(S-H) band but exhibit a medium ν(N-H) band at ca. 3150 cm<sup>-1</sup>, indicating that in the solid state, they remain mainly in the thione form. However in solution they readily convert to the thiol tautomeric form with the concomitant formation of titanium(IV) / zirconium(IV) complexes of the protonated mercapto form of the ligands. This is indicated by the absence of -NH band in the complexes. The i.r. spectra of the complexes also show a new band at ca. 600-620 cm<sup>-1</sup> owing to conversion /4/ of C=S to C-S<sup>-</sup>. The new band in the complexes at ca. 380-400 cm<sup>-1</sup> is assigned /13/ to ν(M-S) and shows that sulfur is bonded to titanium/zirconium atom. The ν(C=N) shift of the dithiosemicarbazones from 1570-1560 cm<sup>-1</sup> to lower energy in the spectra of complexes indicates coordination of the imine nitrogens N(1). However, the loss of N(2)H's from the two dithiosemicarbazone moieties, by thione – thiol tautomerism produces additional carbon-nitrogen double bonds, N(2)=C(S) which is indicated by the appearance of a band at ca. 1590 cm<sup>-1</sup> in the complexes. Bands in the 460-475 cm<sup>-1</sup> region are assigned /13/ to ν(M-N) and support coordination of the imine nitrogens. The ν(M-Cl) bands have been assigned in the 330-315 cm<sup>-1</sup> region.

Table 2

IR spectral data of titanium(iv)/zirconium(iv) derivatives with piperazine dithiosemicarbazones

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S}^-)$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$	$\text{C}_5\text{H}_5$
$\{[\text{CpTiCl}_2]_2(\text{L}_1)\}$	1580s, 1550m	620m	475m	400m	3000s, 1425m, 1015m
$\{[\text{CpTiCl}_2]_2(\text{L}_2)\}$	1590s, 1545m	615m	470m	395m	3010s, 1420m, 1020m
$\{[\text{CpTiCl}_2]_2(\text{L}_3)\}$	1585s, 1545m	625m	472m	390m	3000m, 1420m, 1025m
$\{[\text{CpTiCl}_2]_2(\text{L}_4)\}$	1590s, 1545m	610m	470m	400m	2990s, 1415m, 1020m
$\{[\text{Cp}_2\text{TiCl}]_2(\text{L}_1)\}$	1585s, 1550m	615m	468m	390m	3000m, 1425m, 1020m
$\{[\text{Cp}_2\text{TiCl}]_2(\text{L}_2)\}$	1580s, 1545m	618m	465m	395m	3010s, 1420m, 1010w
$\{[\text{Cp}_2\text{TiCl}]_2(\text{L}_3)\}$	1595s, 1540m	620m	475m	385m	3000m, 1415m, 1015m
$\{[\text{Cp}_2\text{Ti}]_2(\text{L}_4)\}$	1590s, 1550m	625m	470m	395m	3010s, 1425m, 1020m
$\{[\text{Cp}_2\text{ZrCl}]_2(\text{L}_1)\}$	1590s, 1545m	620m	460m	380m	3010s, 1420m, 1020m
$\{[\text{Cp}_2\text{ZrCl}]_2(\text{L}_2)\}$	1585s, 1540m	615m	460m	385m	2990m, 1425w, 1025m
$\{[\text{Cp}_2\text{ZrCl}]_2(\text{L}_3)\}$	1595s, 1540m	620m	465m	380m	3000m, 1420m, 1020m
$\{[\text{Cp}_2\text{Zr}]_2(\text{L}_4)\}$	1590s, 1540m	610m	468m	385m	3005m, 1410m, 1015w

### <sup>1</sup>H N.M.R. spectra

The <sup>1</sup>H n.m.r. spectra of the complexes (Table 3) have been recorded in deuterated dimethylsulphoxide. The line intensities were determined by planimetric integration. A comparison of the ligands with the complexes leads to the following conclusions:

- The  $\delta$  6.65-6.80 signal may be assigned to the cyclopentadienyl ring protons and indicate the rapid rotation of the ring about the metal-ring axis.
- The signal of N(2)H is seen at *ca.*  $\delta$  12.60-12.95 in the ligands. In the complexes neither this signal nor a thiol SH signal is visible.
- The chemical shifts at *ca.*  $\delta$  3.35 ppm can be due to piperazine ring protons which shifted slightly downfield in the complexes.

### <sup>13</sup>C N.M.R. spectra

The <sup>13</sup>C n.m.r spectra of ligands and the corresponding complexes were recorded in DMSO (Table 3). The <sup>13</sup>C resonance signals are assigned according to chemical shift theory. The compounds show cyclopentadienyl peak at *ca.*  $\delta$  117 (relative to TMS). A considerable shift takes place in the position of -C-S (*ca.* 165 ppm, ligands) and C = N (*ca.* 150 ppm, ligands) indicating coordination through the azomethine nitrogen and the thiol group. The signal for piperazine group appears at *ca.*  $\delta$  62.8 in the ligands, which shift, slightly downfield in the complexes.

**Table 3**  
NMR data ( $\delta$ , ppm) of titanium(IV) / zirconium(IV) derivatives with piperazine dithiosemicarbazones

Compound	$^{13}\text{C}$ -							
	$^1\text{H}$ - $\eta^5 - \text{C}_3\text{H}_5$	$\text{C}_4\text{H}_4\text{N}_2$	Phenyl group	$-\text{CH}=\text{N}$	$\eta^5 - \text{C}_5\text{H}_5$	C(8)	C(1)	
$[\{\text{CpTiCl}_2\}_2(\text{L}_1)]$	6.80s	3.45s	7.30s	8.20s	117.8	155.65	168.20	
$[\{\text{CpTiCl}_2\}_2(\text{L}_2)]$	6.75s	3.48s	7.60-7.75m	8.25s	117.5	158.20	167.20	
$[\{\text{CpTiCl}_2\}_2(\text{L}_3)]$	6.70s	3.46s	7.70-7.82m	8.22s	117.0	156.32	167.60	
$[\{\text{CpTiCl}_2\}_2(\text{L}_4)]$	6.78s	3.45s	7.72-7.85m	8.26s	117.2	155.20	168.15	
$[\{\text{Cp}_2\text{TiCl}\}_2(\text{L}_1)]$	6.72s	3.50s	7.40s	8.18s	117.8	157.50	167.85	
$[\{\text{Cp}_2\text{TiCl}\}_2(\text{L}_2)]$	6.74s	3.46s	7.48-7.65m	8.25s	117.4	158.10	168.00	
$[\{\text{Cp}_2\text{TiCl}\}_2(\text{L}_3)]$	6.78s	3.48s	7.45-7.70m	8.20s	117.5	128.50	168.25	
$[\{\text{Cp}_2\text{Ti}\}_2(\text{L}_4)]$	6.80s	3.42s	7.50-7.72m	8.28s	117.2	155.70	168.10	
$[\{\text{Cp}_2\text{ZrCl}\}_2(\text{L}_1)]$	6.65s	3.45s	7.32m	8.16s	116.2	155.25	168.12	
$[\{\text{Cp}_2\text{ZrCl}\}_2(\text{L}_2)]$	6.68s	3.42s	7.42-7.65m	8.20s	116.5	156.80	168.25	
$[\{\text{Cp}_2\text{ZrCl}\}_2(\text{L}_3)]$	6.65s	3.45s	7.40-7.70m	8.18s	116.8	156.70	168.10	
$[\{\text{Cp}_2\text{Zr}\}_2(\text{L}_4)]$	6.70s	3.40s	7.48-7.75m	8.22s	116.0	157.35	168.0	

**Table 4**  
Antibacterial activity of piperazine dithiosemicarbazones and their corresponding  
titanium(IV) / zirconium(IV) complexes

Compound	Diameter of inhibition zone (mm)	
	<i>B. subtilis</i>	<i>E. Coli</i>
L <sub>1</sub> H <sub>2</sub>	8	9
[{CpTiCl <sub>2</sub> } <sub>2</sub> (L <sub>1</sub> )]	20	18
[{CpTiCl} <sub>2</sub> (L <sub>1</sub> )]	15	12
[{Cp <sub>2</sub> ZrCl} <sub>2</sub> (L <sub>1</sub> )]	12	10
L <sub>2</sub> H <sub>2</sub>	12	12
[{CpTiCl <sub>2</sub> } <sub>2</sub> (L <sub>2</sub> )]	22	20
[{Cp <sub>2</sub> TiCl} <sub>2</sub> (L <sub>2</sub> )]	18	16
[{Cp <sub>2</sub> ZrCl} <sub>2</sub> (L <sub>2</sub> )]	14	15
L <sub>3</sub> H <sub>2</sub>	10	12
[{CpTiCl <sub>2</sub> } <sub>2</sub> (L <sub>3</sub> )]	20	18
[{Cp <sub>2</sub> TiCl} <sub>2</sub> (L <sub>3</sub> )]	16	14
[{Cp <sub>2</sub> ZrCl} <sub>2</sub> (L <sub>3</sub> )]	14	14
L <sub>4</sub> H <sub>4</sub>	12	11
[{CpTiCl} <sub>2</sub> (L <sub>4</sub> )]	20	19
[{Cp <sub>2</sub> Ti} <sub>2</sub> (L <sub>4</sub> )]	16	16
[{Cp <sub>2</sub> Zr} <sub>2</sub> (L <sub>4</sub> )]	13	12
Ampicillin	35	35

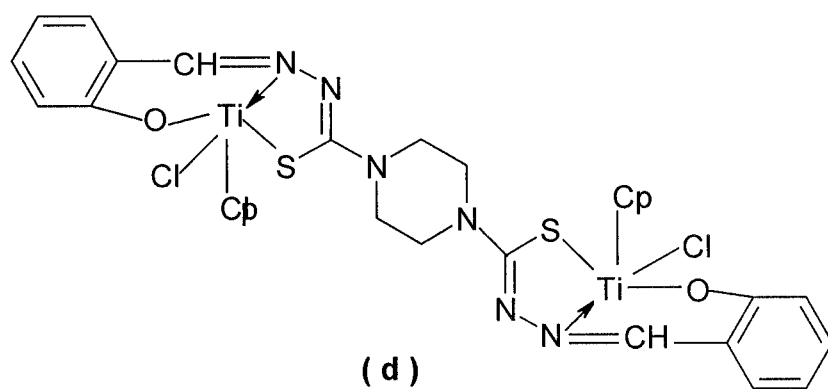
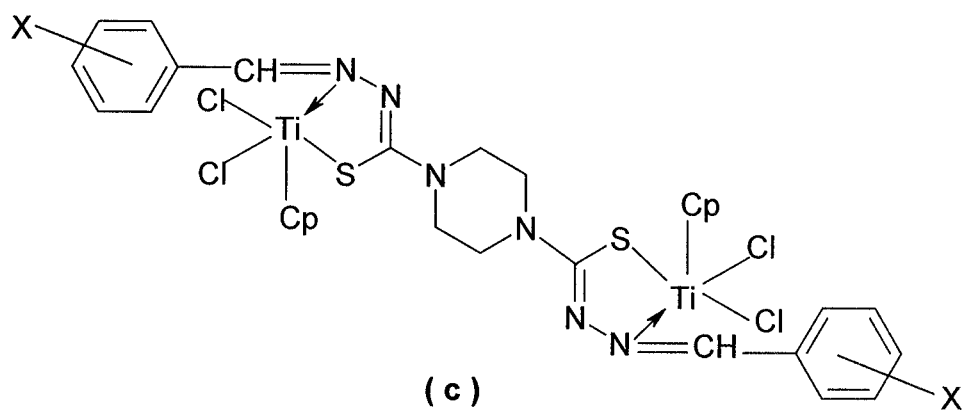
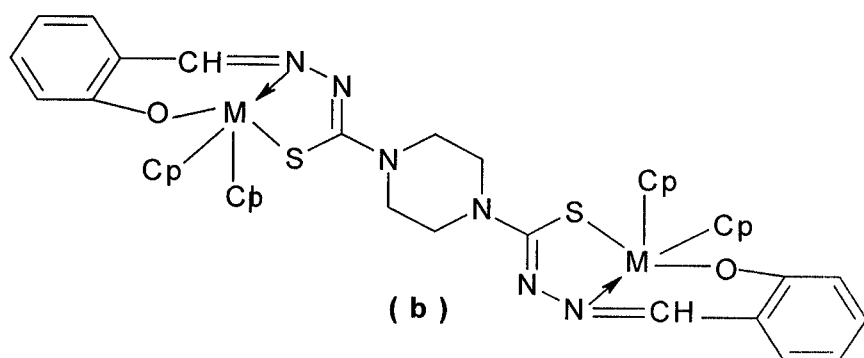
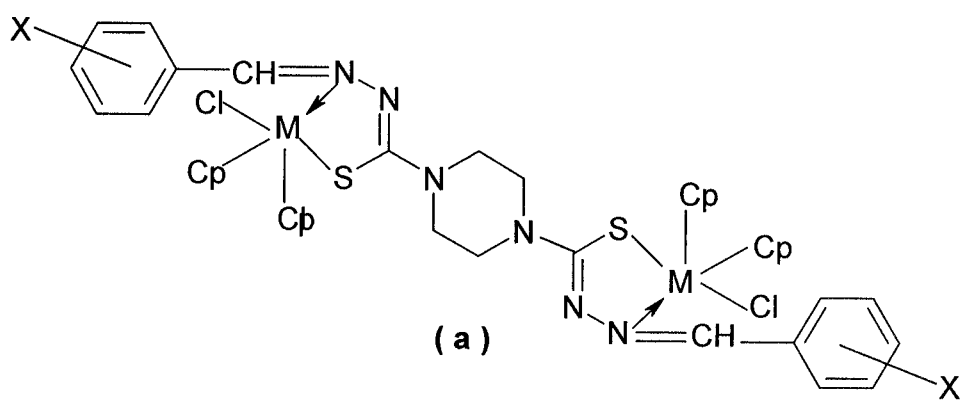
### Antibacterial Activity

The antibacterial activity of the complexes together with the parent ligands has been screened /14/ against Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli* by the paper disk plate method at 1000 ppm conc. The inhibition zone (mm) around each disk was measured after 24 h and the results of these studies are listed in Table 4. The results lead to the following conclusions:

- The complexes are slightly more toxic than the parent ligands.
- The titanium complexes show better activity than zirconium complexes.
- Mono(cyclopentadienyl)titanium(IV) derivatives possess better activity than bis(cyclopentadienyl)titanium(IV) derivatives .
- The best activity was recorded with mono(cyclopentadienyl)titanium(IV) derivatives with ligand L<sub>2</sub>H<sub>2</sub> *i.e.* containing –Cl group at phenyl ring of the thiosemicarbazone moieties.

On the basis of elemental analysis, electrical conductance and spectral data, the following structures for the complexes are proposed.



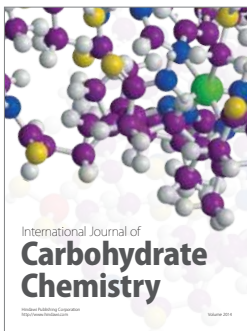
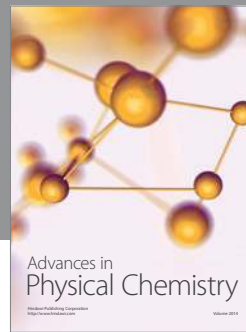
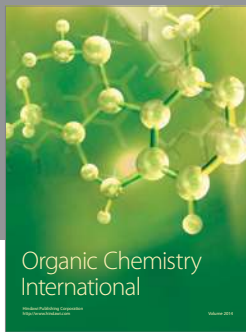


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