



Synthetic, Structural and Biochemical Investigations of Titanium (IV) Complexes with Nitrogen–Oxygen and Nitrogen–Sulphur Donor Ligands

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ABSTRACT

Some new titanium (IV) complexes from semicarbazone and thiosemicarbazone ligands have been synthesized. These semicarbazone and thiosemicarbazone ligands have been prepared by condensing carbonyl compounds with semicarbazide hydrochloride and thiosemicarbazide in 1:2 molar ratio in ethanolic medium. The monomeric nature of these complexes has been decided by their molecular weight determination. The bonding pattern and probable geometry of these complexes have been investigated on the basis of elemental analysis, UV, IR, and (¹H, ¹³C) NMR spectral studies. The ligands and their metal complexes have been screened for antibacterial and antifungal activities and are found quite active in this respect. Titanium (IV) complexes have been found to be more active than their uncomplexed ligands.

Keywords: Semicarbazone, Thiosemicarbazone, Spectral studies, Antibacterial activities, Antifungal activities, Titanium (IV) complexes.

INTRODUCTION

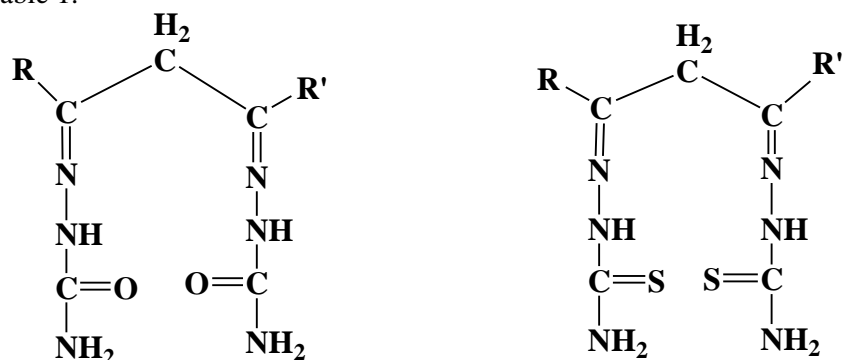
Schiff bases (also termed as imine or azomethine) generally are bi-, tri- or tetra- dentate chelate ligands and easily react with almost all transition metal ions and form very stable complexes with them. They show interesting properties, e.g. their ability to reversibly bind oxygen, complexing ability towards toxic metals, catalytic activity [1-2] in reactions such as oxidation, hydroxylation, aldol condensation and photochromic properties. Schiff bases and their metal complexes exhibit a broad spectrum of biological activity which includes bactericidal, fungicidal and acaricides [3-5]. They also find varied applications in medicine, agriculture and industry. These include their uses as pigments and dye for cotton, wool, synthetic fibres and plastics, high temperature stabilizers, inhibitors against corrosion [6] of metals and alloys, anti-knocking agents, photographic emulsions and liquid display composition. Semicarbazones and thio semicarbazones are also known as azomethines, both the ligands can exist in tautomeric forms are capable of acting as a neutral or charged ligand. Semicarbazones and thiosemicarbazones usually act as chelating ligands with metal ions by bonding oxygen/sulphur and azomethine nitrogen. In recent years there has been considerable interest in semicarbazones and thiosemicarbazones due to their wide range of biological applications. Titanium and Ti alloys which have good mechanical properties, high corrosion resistance, excellent biocompatibility[7] are commonly found in orthopaedic prostheses, orthodontics, joint replacements and so on[8]. The interest in titanium (IV) complexes is due to their different mode of

coordination and applicability in different area of science. Due to the introducing of ($>C=N$) azomethine linkage with the titanium (IV) metal, the biological activity [9-10] and efficiency of complexes have affected. Coordination number four is the lowest coordination state for titanium compounds [11]. Higher coordination numbers also exist for titanium having pentagonal bipyramidal, capped octahedral and capped trigonal prism [12-13] geometries.

MATERIALS AND METHODS

Analytical methods and physical measurements: The entire chemicals used were of the AR grade and the solvents were dried by standard method. All the reactions were carried out under strictly anhydrous condition. The electronic spectra were recorded in methanol on a Toshniwal spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer RX1 FTIR spectrophotometer in the region $4000-400\text{ cm}^{-1}$. ^1H NMR was recorded on a Joel (model FX 90Q) using DMSO-d_6 as solvent. ^{13}C NMR was recorded on a 90MHz Joel (FX 90Q) NMR spectrometer using dry DMSO as the solvent at 84.25 MHz TMS was used as internal reference for ^1H NMR and ^{13}C NMR. Titanium was estimated by gravimetrically. Nitrogen was estimated by the Kjeldal's method [14]. Molecular weights were determined by the Rast's method.

Synthesis of ligands: Semicarbazones and thiosemicarbazones were synthesized by the condensation of diketones viz. acetyl acetone, benzoyl acetone and glyoxal with semicarbazide hydrochloride and thiosemicarbazide in 1:2 molar ratio using absolute alcohol as the reaction medium. The mixture was heated on a water bath for about half an hour and then allowed to cool at room temperature. The crystals that separated out were recrystallized from the same solvent. Their physical properties and analysis have been recorded in table 1.



Where $R = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$

$R' = \text{H}, \text{CH}_3$

Fig 1: Structure of Ligands

Table 1: Analytical and physical data of ligands

Ligands	Colour & State	M.P (°C)	Analysis (%)			M.Wt Found (Calcd.)
			C Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	
Acetyl acetone semicarbazone (L^1H_2)	Milky white Solid	275	38.14 (39.24)	38.11 (33.42)	-	213.16 (214.24)
Acetyl acetone thiosemicarbazone (L^2H_2)	Shiny Yellow Solid	230	33.24 (34.12)	33.39 (34.10)	25.68 (26.03)	245.18 (246.38)

Benzoyl acetone semicarbazone (L ³ H ₂)	White Solid	260	51.22 (52.16)	29.07 (30.42)	-	275.36 (276.30)
Benzoyl acetone thiosemicarbazone (L ⁴ H ₂)	Light Yellow Solid	210	45.22 (46.73)	26.07 (27.25)	19.67 (20.79)	307.38 (308.44)
Glyoxal semicarbazone (L ⁵ H ₂)	Light Yellow Powder	280	26.02 (27.91)	47.88 (48.82)	-	171.02 (172.15)
Glyoxal thiosemicarbazone (L ⁶ H ₂)	Yellow Powder	235	22.02 (23.52)	40.28 (41.14)	30.44 (31.39)	203.28 (204.29)

Synthesis of titanium (IV) complexes: Titanocene dichloride ($\eta^5\text{-C}_5\text{H}_5$)₂TiCl₂ reacts with semicarbazone/thiosemicarbazone and triethylamine in 1:1:2 molar ratio to form complexes. Et₃N was used as HCl recovering agent. The precipitate of Et₃N.HCl was removed by filtration. After the completion of the reaction, the products were dried under reduced pressure and analysed. All the newly synthesized titanium complexes are soluble in most common organic solvents viz., THF, acetone, chloroform, dichloromethane etc. The monomeric nature of these complexes is confirmed by molecular weights. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent. Their physical properties and analysis have been recorded in table 2.

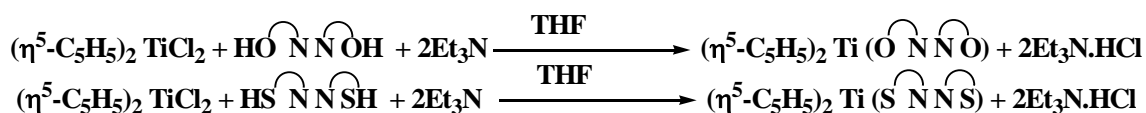


Table 2: Analytical and physical data of titanium (IV) complexes with semicarbazones and thiosemicarbazones

S. No	Reactants		Molar ratio	Product and Characteristics (Colour & state)	M.P. (°C)	Analysis: Found (Calcd.)%			Molecular Wt. Found (Calcd.)
	Titanium Compound	Ligand				N Found (Calcd.)	S Found (Calcd.)	Ti Found (Calcd.)	
1.	($\eta^5\text{-C}_5\text{H}_5$) ₂ TiCl ₂	C ₇ H ₁₄ N ₆ O ₂	1:1	TiC ₁₇ H ₂₂ N ₆ O ₂ Pale red solid	284	21.40 (21.53)	-	12.03 (12.27)	389.78 (390.26)
2.	($\eta^5\text{-C}_5\text{H}_5$) ₂ TiCl ₂	C ₇ H ₁₄ N ₆ S ₂	1:1	TiC ₁₇ H ₂₂ N ₆ S ₂ Brown solid	245	19.65 (19.90)	14.78 (15.18)	10.97 (11.33)	422.15 (422.39)
3.	($\eta^5\text{-C}_5\text{H}_5$) ₂ TiCl ₂	C ₁₂ H ₁₆ N ₆ O ₂	1:1	TiC ₂₂ H ₂₄ N ₆ O ₂ Red solid	272	18.36 (18.58)	-	10.42 (10.58)	451.91 (452.33)
4.	($\eta^5\text{-C}_5\text{H}_5$) ₂ TiCl ₂	C ₁₂ H ₁₆ N ₆ S ₂	1:1	TiC ₂₂ H ₂₄ N ₆ S ₂ Brown powdery	236	17.14 (17.35)	12.69 (13.24)	9.76 (9.88)	484.25 (484.46)
5.	($\eta^5\text{-C}_5\text{H}_5$) ₂ TiCl ₂	C ₄ H ₈ N ₆ O ₂	1:1	TiC ₁₄ H ₁₆ N ₆ O ₂ Reddish brown solid	283	23.85 (24.14)	-	13.59 (13.75)	347.68 (348.18)
6.	($\eta^5\text{-C}_5\text{H}_5$) ₂ TiCl ₂	C ₄ H ₈ N ₆ S ₂	1:1	TiC ₁₄ H ₁₆ N ₆ S ₂ Dark brown solid	239	21.93 (22.10)	16.72 (16.86)	12.32 (12.59)	379.83 (380.31)

RESULTS AND DISCUSSION

Electronic spectra: The electronic spectra of the ligands and their metal complexes were recorded in methanol. The K band at 290 nm due to π - π^* transitions of the ligand is observed, which remains unchanged in the corresponding complexes. A broad band at 410 nm in the spectra of ligands due to n - π^* transitions of the azomethine group $>C=N-$, undergoes a hypsochromic shift in the metal complexes due to polarization within the $>C=N-$ chromophore caused by the metal-ligand interaction. In the corresponding 1:1 titanium complexes an additional charge transfer band at around 405-415 nm is observed. All complexes are diamagnetic.

IR spectra: Two sharp bands are observed at 1632 - 1615 cm^{-1} and 1612 - 1587 cm^{-1} in the spectra of all these complexes, compared to one at 1620 - 1606 cm^{-1} in the ligands may be attributed to $\nu(C=N)$ group [15]. The band at lower frequency in the titanium (IV) complexes indicates the coordination of the azomethine nitrogen to the titanium atom whereas the other one is due to uncoordinated azomethine group. The spectra of the uncomplexed ligand showed bands in the region 3286 - 3130 cm^{-1} assignable to $\nu(NH)$, which disappeared in all the complexes indicating coordination. The bands at 1690 - 1660 cm^{-1} and 1025 - 1010 cm^{-1} due to $\nu(C=O)$ and $\nu(C=S)$, respectively are shifted towards lower side in the complexes, indicating coordination of oxygen or sulphur to the central metal atom and formation of Ti-O and Ti-S types of bonds. Bands in the region 620 - 610 , 533 - 510 and 350 - 345 cm^{-1} are attributed to $\nu(Ti-O)$, $\nu(Ti\leftarrow N)$ and $\nu(Ti-S)$ respectively. The IR stretching frequencies of $>C=O$ and $>C=N-$ can be easily distinguished on the basis of their intensity, as the $\nu(C=O)$ will be more intense than $\nu(>C=N-)$ [16]. The results are recorded in table 3.

Table 3: IR spectral data of the ligands and their corresponding titanium (IV) compounds

Compound	$\nu(>C=N-)$	$\nu(>C=O)$	$\nu(>C=S)$	$\nu(N-H)$	$\nu(Ti-O)$	$\nu(Ti\leftarrow N)$	$\nu(Ti-S)$
$C_7H_{14}N_6O_2$ (L^1H_2)	1615 s	1690	-	3286 m	-	-	-
$TiC_{17}H_{22}N_6O_2$	1607 s 1620 s	-	-	-	615	533	-
$C_7H_{14}N_6S_2$ (L^2H_2)	1618 s	-	1025	3280 m	-	-	-
$TiC_{17}H_{22}N_6S_2$	1611 s 1627 s	-	-	-	-	530	350
$C_{12}H_{16}N_6O_2$ (L^3H_2)	1606 s	1680	-	3280 m	-	-	-
$TiC_{22}H_{24}N_6O_2$	1587 s 1615 s	-	-	-	610	512	-
$C_{12}H_{16}N_6S_2$ (L^4H_2)	1620 s	-	1022	3130 m	-	-	-
$TiC_{22}H_{24}N_6S_2$	1595 s 1625 s	-	-	-	-	510	355
$C_4H_8N_6O_2$ (L^5H_2)	1618 s	1660	-	3250 m	-	-	-
$TiC_{14}H_{16}N_6O_2$	1612 s 1632 s	-	-	-	620	520	-
$C_4H_8N_6S_2$ (L^6H_2)	1610 s	-	1010	3240 m	-	-	-
$TiC_{14}H_{16}N_6S_2$	1597 s 1620 s	-	-	-	-	524	345

m = medium; s = strong

1H NMR spectra: 1H NMR data showed a singlet at 3.38-3.57 ppm in the uncomplexed ligands as well as in titanium (IV) complexes due to the non-participation of NH_2 group in complexation. The NH proton signals in the spectra of ligands completely disappeared in all complexes suggesting ONX ($X = O$ or S) donor nature of the ligand. A broad signal observed at δ 6.5-7.6 ppm which may be assigned to phenyl resonance region in the spectra of ligands as well as complexes. In the complexes additional slightly broad singlet appeared at δ 6.7 for π - C_5H_5 . In the spectra of the ligands azomethine proton signal ($H-C=N$) appeared at δ 8.45 ppm and a singlet occurs in the region δ 1.63-1.90 ppm due to $-C(CH_3)=N-$. The

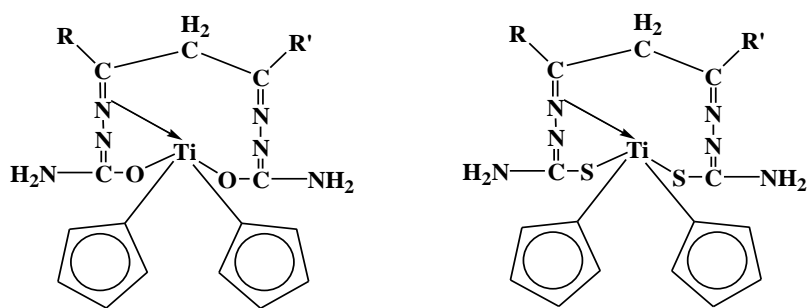
position of above two signals in complexes is downfield, suggesting the formation of the coordination bond between the titanium (IV) ion and azomethine nitrogen atom. The results are summarized in table 4.

Table 4: ^1H NMR spectral data (in δ , ppm) of ligands and their corresponding titanium (IV) complexes

Compound	-NH	H-CN	CH ₃ -CN	-NH ₂	Aromatic
C ₇ H ₁₄ N ₆ O ₂	7.10	-	1.63	3.48	-
C ₇ H ₁₄ N ₆ S ₂	7.13	-	1.67	3.45	-
C ₁₂ H ₁₆ N ₆ O ₂	7.20	-	1.71	3.41	6.9-7.4m
C ₁₂ H ₁₆ N ₆ S ₂	7.34	-	1.90	3.51	7.1-7.6m
C ₄ H ₈ N ₆ O ₂	7.16	8.45	-	3.42	-
C ₄ H ₈ N ₆ S ₂	7.22	8.45	-	3.38	-
TiC ₁₇ H ₂₂ N ₆ O ₂	-	-	1.72	3.52	-
TiC ₁₇ H ₂₂ N ₆ S ₂	-	-	1.79	3.47	-
TiC ₂₂ H ₂₄ N ₆ O ₂	-	-	1.97	3.44	6.5-7.2m
TiC ₂₂ H ₂₄ N ₆ S ₂	-	-	2.01	3.57	7.2-7.4m
TiC ₁₄ H ₁₆ N ₆ O ₂	-	8.57	-	3.45	-
TiC ₁₄ H ₁₆ N ₆ S ₂	-	8.57	-	3.39	-

m=multiple

^{13}C NMR spectra: ^{13}C NMR spectra of ligands a signal observed at δ 155.60 ppm has been assigned to carbon of azomethine group which shows downfield shift on complexation. The signals of $>\text{C}=\text{O}$ or $>\text{C}=\text{S}$ group carbons also shift on complexation, indicating the participation of these groups in bonding. In the complexes additional signal for $\pi\text{-C}_5\text{H}_5$ also observed. On the basis of above spectral studies, the following possible structure may be assigned to titanium (IV) complexes. The results are recorded in table 5. The structure of the complexes shown in fig 2.

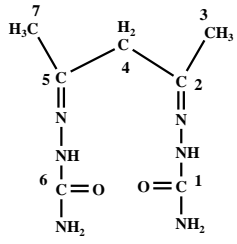
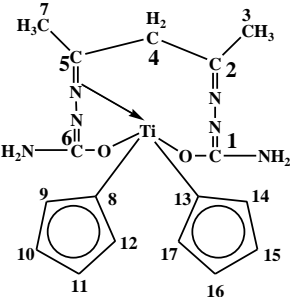


Where $\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$

$\text{R}' = \text{H}, \text{CH}_3$

Fig 2: Structure of complexes

Table 5: ^{13}C NMR spectral data of the ligands and their corresponding titanium (IV) complexes

Compounds	Chemical shift value in δ ppm								
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	
	161	155.6	9.3	34.3	155.6	161	9.3		
	163	155.6	10.2	24.1	164.6	163	16.2	121.2	124.0
	125.0	125.0	124.0	121.2	124.0	125.0	125.0	124.0	

APPLICATIONS

Antibacterial activity: The activity of the ligands and their corresponding titanium (IV) complexes against *Escherichia coli*, *Proteus Mirabilis*, *Staphylococcus Aureus* and *Bacillus Thuringiensis* bacterial strains were evaluated by Paper Disc Plate Method [17-18]. The nutrient agar medium was used as a culture medium for bacterial growth and streptomycin was used as reference drug for this technique. The compounds were dissolved in DMSO in 500 and 1000 ppm concentrations. Paper disc of Whatman No. 1 with a diameter of 5 mm were soaked in these solutions and placed in appropriate medium previously seeded with tested organism in Petri dishes. The Petri plates were stored in incubator at $28 \pm 2^\circ\text{C}$ after 24 h. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm.

Antifungal activity: The antifungal activity was evaluated against *Aspergillus flavus*, *Fusarium oxysporum* and *Aspergillus niger* by the Radial Growth Method [19]. In this method, the Czapek's agar medium used was potato dextrose agar medium (composition : potato slices – 200 gm, dextrose-20g, agar-agar- 15g and distilled water 1000 ml). The solutions of the compounds in different concentration (50, 100 and 200ppm) in dimethylformamide were then mixed with the medium. Seven days old cultures of these organisms grown on potato dextrose agar medium were used. All the glassware used were sterilised in an autoclave before use. Three replicates were used and the linear growth of the fungus was obtained by measuring the fungal colony diameter after 96 hours at $28 \pm 2^\circ\text{C}$. The average of linear growth in all replicates was recorded and the amount of growth inhibition was calculated by the equation. Micostatin was used as reference compound for antifungal activities.

Antimicrobial results: The results of the antimicrobial screening of semicarbazones/thiosemicarbazones and their titanium (IV) complexes against Gram negative (*Proteus mirabilis*, *Escherichia coli*) & Gram positive (*Staphylococcus aureus*, *Bacillus thuringiensis*) bacteria and some selected fungi (*Aspergillus*

niger, *Aspergillus flavus* and *Fusarium oxysporum*) have been found. The experimental data indicate that antimicrobial activity of the complexes enhances as compared to its ligands [20-21] which indicates that complexation increases the activity. It is also found that the activity increased with increasing the concentration. The compounds inhibit the growth of bacteria and fungi to a great extent as the concentration is increased. The results are summarized in tables 6, 7.

Table 6: Antibacterial screening data of semicarbazones/thiosemicarbazones and their titanium (IV) complexes

Compounds	Diameter of Inhibition Zone (mm)							
	Proteus milamilis (-)		Staphylococcus aureus (+)		Bacillus thuringiensis (+)		Escherichia coli (-)	
	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm	500 ppm	1000 ppm
C ₇ H ₁₄ N ₆ O ₂ (L ¹ H ₂)	5	8	7	9	6	7	6	7
C ₇ H ₁₄ N ₆ S ₂ (L ² H ₂)	7	9	8	10	7	9	7	8
C ₁₂ H ₁₆ N ₆ O ₂ (L ³ H ₂)	6	8	6	9	7	9	7	6
C ₁₂ H ₁₆ N ₆ S ₂ (L ⁴ H ₂)	7	9	7	9	8	10	8	7
[(CH ₃) ₂ SnC ₇ H ₁₂ N ₆ O ₂]	7	9	8	10	9	10	8	11
[(CH ₃) ₂ SnC ₇ H ₁₂ N ₆ S ₂]	8	13	11	12	11	12	10	12
[(CH ₃) ₂ SnC ₁₂ H ₁₄ N ₆ O ₂]	8	10	10	12	11	12	9	11
[(CH ₃) ₂ SnC ₁₂ H ₁₄ N ₆ S ₂]	9	11	11	13	12	13	11	13
Streptomycin	12	15	15	17	14	16	17	18

Table 7: Antifungal screening data of semicarbazones/thiosemicarbazones and their titanium (IV) complexes

Compounds	Percent Inhibition after 96h (conc in ppm)								
	Organism Aspergillus niger			Organism Aspergillus flavus			Organism Fusarium oxysporum		
	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm	50 ppm	100 ppm	200 ppm
C ₇ H ₁₄ N ₆ O ₂ (L ¹ H ₂)	53	65	73	47	52	78	62	71	82
C ₇ H ₁₄ N ₆ S ₂ (L ² H ₂)	56	67	82	54	65	81	54	73	84
C ₁₂ H ₁₆ N ₆ O ₂ (L ³ H ₂)	58	62	67	51	62	67	44	65	75
C ₁₂ H ₁₆ N ₆ S ₂ (L ⁴ H ₂)	62	68	70	56	66	69	51	68	72
[(CH ₃) ₂ SnC ₇ H ₁₂ N ₆ O ₂]	56	68	76	53	62	81	65	74	83

$[(CH_3)_2SnC_7H_{12}N_6S_2]$	59	70	84	59	69	86	56	78	86
$[(CH_3)_2SnC_{12}H_{14}N_6O_2]$	61	71	72	54	65	72	48	67	79
$[(CH_3)_2SnC_{12}H_{14}N_6S_2]$	65	76	79	61	68	80	52	73	80
Mycostatin	70	91	100	69	86	98	72	82	96

CONCLUSIONS

In our present studies semicarbazones/thiosemicarbazones and their titanium (IV) complexes were synthesized and screened for antimicrobial activity. On the basis of above evidences, pentacoordinated structure may be concluded for resulting complexes. The antimicrobial results shows that complexes are more potent compare to corresponding ligands, which indicates that the coordination increase their bioactivity. The more investigations are going on with this hope that some of these compounds may be used as antimicrobial agent.

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