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Synthesis, characterization and biological studies of titanium (III) metal complexes of schiff bases derived from salicylaldehyde and 2- hydroxy-1-naphthaldehyde compound

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Abstract
The complexes of Titanium (III) with Schiff bases derived from the condensation reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with 3-nitro aniline, 4-nitroaniline, phenylthiourea, 3-aminophenol and 2-aminopyridine have been prepared and characterized by elemental analyses, molar conductance, magnetic properties and IR spectral data. All the six ligands function as bidentate coordinating ligands with metal ions through phenolic anionic oxygen and azomethine nitrogen. Octahedral geometry has been proposed for these metal chelates. Complexes have been screened for their antimicrobial activity.

Keywords: synthesis, antimicrobial activity, schiff base, octahedral

Introduction
Metal complexes of Schiff bases have played a central role in the development of coordination chemistry[1]. Most of the bidentate Schiff bases have structures quite suitable for chelation with metal ion Studies on the chelation tendency of various organic compounds have supported the hypothesis that formation of strain free chelate rings and enhances the biological activity [2-4]. The present investigation mainly deals with the preparation and characterization of Ti (III) complexes with Schiff bases. The Schiff bases were prepared by refluxing salicylaldehyde and 2-hydroxy-1- naphthaldehyde complexes with different 10 amines in 1:1 molar ratio. These Schiff bases were characterized and their complexation behavior with Ti (III) has been studied. Recently the characterization and biological studies of bivalent metal complexs of Schiff bases derived from aminothiazole and azosalicyladehyole compound have already been studied [5].

Materials and Methods
All chemicals used were of analytical grade and purified before use. The purity of samples was checked by TLC and characterized by elemental analyses, IR spectral data of Schiff bases and complexes were recorded.

Synthesis of ligands
An equimolar mixture of aldehyde and amine in ethanol was refluxed for about 7 h. on a water bath. The reaction mixture cooled at room temperature and collected by filteration, It was recrystallized from ethanol. The analytical data and physical properties of the synthesized ligands of Schiff bases are shown in Table -1 and IR spectral data are also shown in Table-2.

Table 1: Analytical data and some physical properties of the synthesized ligands (Schiff bases)

Sl. No	Schiff bases	Melting Point (^{0}C)	Elemental analyses found (Calcd. %)			
			C	H	N	S
1.	Salicylaldehyde-3-nitro aniline	135^{0}C	63.92	4.22	10.98	-
	[C13H10N2O3] Mol.wt.=242		(64.46)	(4.13)	(11.57)	
2.	Salicylaldehyde-4-nitro aniline	124^{0}C	63.12	4.02	10.86	-
	[C13H10N2O3] Mol.wt.=242		(64.46)	(4.13)	(11.57)	
3.	Salicylaldehyde-phenyl thiourea	125^{0}C	64.99	4.11	10.66	12.16
	[C14H12N2SO] Mol.wt. = 256		(65.62)	(4.68)	(10.93)	(12.50)
4	2-hydroxy-1-naphthaldehyde-phenyl thiourea	120^{0}C	69.93	3.99	8.88	9.89
	[C18H14N2 OS] Mol.wt. = 306		(70.58)	(4.57)	(9.15)	(10.45)
5	2-hydroxy-1-naphthaldehyde-3-	140^{0}C	76.69	4.54	4.98	-
	amino phenol [C17H13NO2] Mol.wt.		(77.56)	(4.94)	(5.32)	
	= 263					

6.	2-hydroxy-1-naphthaldehyde-2-	115^{0}C	76.92	4.26	10.98	-
	amino pyridine [C16H12N2O]		(77.41)	(4.83)	(11.29)	
	Mol.wt. = 248					

Table 2: Analytical data and some physical properties of the synthesized ligands (Schiff bases)

Sl. No	Composition of Compound	C=N	C-N	NO2	C-O	C=S	OH
1.	[C13H10N2O3]	1629	1357	1495	1278	-	2895
2.	[C13H10N2O3]	1629	1354.1	1505	1280	-	2800
3.	[C14H12N2SO]	1596	1345	-	1290	750	2800
4.	[C18H14N2 OS]	1610	1360	-	1275	775	2800
5.	[C17H13NO2]	1616	1345	-	1281	-	2890
6.	[C16H12N2O]	1620	1350	-	1295	-	2890

Synthesis of metal complexes

Titanium (III) chloride was allowed to react with ligands (Schiff bases) in slight excess in an oxygen free methanol. The preparation of complexes was carried out in an inert atmosphere of nitrogen. The freshly prepared complex was immediately filtered and washed with dry ethanol to remove any excess of ligand. The precipitate was dried in vacuum over anhydrous calcium chloride.

Characterization of metal complexes

The melting points of complexes were determined using Toshniwal's melting point apparatus. The complexes were also subjected to IR spectral studies and elemental analyses for C, H, N and Cl. The metal was estimated by standard method. Their molar conductance at 10^{-3} M concentration was measured in DMSO/DMF. These analytical data have suggested 1:2 (M: L) stoichiometry for all the synthesized complexes. The analytical data and some physical properties of the synthesized Titanium (III) complexes are given in Table -3 and IR- spectral absorption of Titanium (III) complexes with azomethines (cm^{-3}) are shown in Table -4. The comparison of infra-red spectra of ligand and complex helped in ascertaining that ligands, coordinating in bidentate manner and indicating the coordination sites [6]. The IR- spectral data of all the ligands shows important bands in the range of 2800-2895 cm^{-1} assignable to intra molecular hydrogen bonding [7-8] in between phenolic (-OH) and azomethine nitrogen and 1275-1295 cm^{-1}. for vC-O (phenolic) [9]. In spectra of all the complexes the band disappeared indicating that during complexation deprotonation has taken place. This data has been further supported by upward shift in v(C-O) phenolic to the positive shift of 8-20 cm^{-1}. The IR-spectral data of all the ligands shows important bands in the range of 1596-1629 cm^{-1} assignable to v(C=N) vibrations. These bands appear in spectra of complexes at 1586.3-1597.1 cm^{-1} with low energy shift suggesting the involvement of azomethine nitrogen in coordination [10]. The IR-spectra of all chelates show peaks around 3380 cm^{-1} and 929-720 cm^{-1} due to the presence of coordinated water molecules.[11] The presence of non-ligand bands in IR spectra of the complexes in the region of 600 – 300 cm^{-1} may be assigned vM-O, vM-N and vM-Cl [12, 13]. The molar conductance of complexes 1 and 4 in DMF at 10^{-3} M concentration at 25^{0}C were found to be 2.5 and 3.8 ohm^{-1} cm^2 mol^{-1}. The values suggested non-electrolyte [14] nature in DMF and complexes 2, 3, 5 and 6 in DMF at 25^{0}C were found the values 60, 76, 62 and 67 suggested 1:1 electrolyte nature in DMF. The electronic spectra of Titanium (III) complexes were recorded in DMF solution. The spectra show a band in the range 18400 - 18500 cm^{-1} due to $^2T_{2g} \rightarrow {}^2E_g$ transition for an octahedral geometry [15].

Table 3: Analytical data and some physical properties of the synthesized Titanium (III) complexes

Sl. No	Molecular formula of compound	Elemental analyses found (Calcd. %)						M.P. 0C	Magn etic mome nt B.M.	molar condu ctance ohm^{-1} cm^2 mol^{-1}
		C %	H %	N %	M %	Cl %	S %			
1.	[Ti (C13H9N2O3)2 (H2O) Cl] Mol. wt. = 583.5	52.96 (53.47)	3.21 (3.42)	9.08 (9.59)	7.98 (8.22)	5.98 (6.08)	-	180	1.69	2.5
2.	[Ti (C13H9N2O3)2 (H2O)2] Cl Mol. wt. = 601.5	50.88 (51.87)	3.28 (3.65)	9.05 (9.37)	7.20 (7.98)	4.98 (5.90)	-	165	1.72	60
3.	[Ti (C14H11N2OS)2 (H2O)2] Cl Mol. wt. = 629.5	52.85 (53.37)	3.92 (4.13)	8.16 (8.89)	7.30 (7.62)	4.48 (5.63)	9.98 (10.16)	> 250	1.70	76
4.	[Ti (C18H13N2OS)2 (H2O) Cl] Mol. wt. = 711.5	59.86 (60.71)	2.98 (3.93)	6.98 (7.87)	5.94 (6.74)	3.96 (4.98)	7.98 (8.99)	190	1.69	3.8
5.	[Ti (C17H12NO2)2 (H2O)2] Cl Mol. wt. = 643.5	61.56 (63.40)	4.08 (4.35)	3.85 (4.35)	7.00 (7.45)	4.42 (5.51)	-	175	1.71	62
6.	[Ti (C16H11N2O)2 (H2O)2] Cl Mol. wt. = 613.5	60.56 (62.59)	3.86 (4.23)	58.92 (9.12)	7.56 (7.82)	4.98 (5.78)	-	> 250	1.70	67

Table 4: Important IR- spectral absorption of Titanium (III) complexes with azomethines (cm^{-1})

Sl. No	Molecular formula of complexes	ν(C=N)	ν (NO2)	ν(-OH)	□(-OH) bending	ν (C-O) phenolic	ν(C=S)	ν (MX)
1.	C26 H20N4O7.TiCl	1598	1495	3402	821.2 719.4	1290	-	360
2.	C26 H22N4O8.TiCl	1594.1	1505	3406	929 720.2	1288	-	-
3.	C28 H26N4O4S2.TiCl	1586.3	-	3380	813.1 763.4	1306	750	-
4.	C36 H28N4O3S2.TiCl	1595.2	-	3502	827.6 773.1	1295	775	380
5.	C34 H28N2O6.TiCl	1590	-	3408	844 765.1	1298	-	-
6.	C32 H26N4O6 TiCl	1597.1	-	3400.6	922.1 748	1307	-	-

Antimicrobial studies

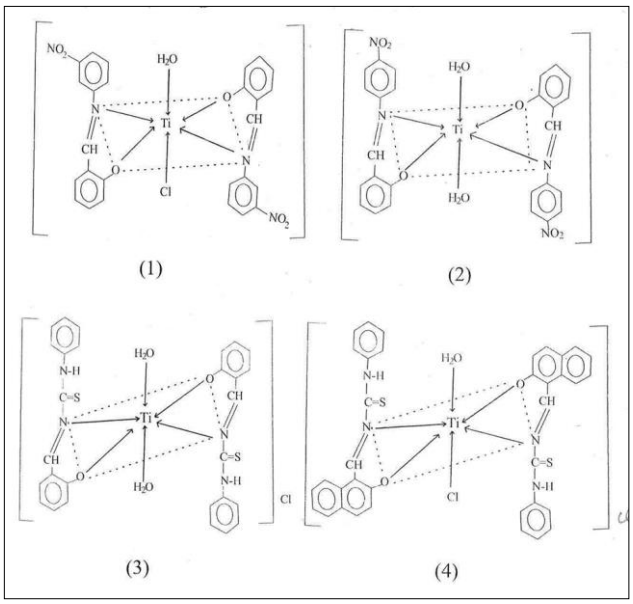
The antimicrobial screening of ligands (Schiff bases) and their metal chelates were carried out against the bacteria, *Escherichia coli and Salmonella typhi* by the disc diffusion method[16], using agar nutrient as medium and DMF as solvent. The results are comparable with that of standard compound drug streptomycin. The stock solutions were prepared by dissolving the compounds in dimethyl formamide at 100 μg/ml. All the blank discs (whatmann filter paper No.1) of diameter 6mm were dipped in stock solution (100 Disc/ml). Each absorbing about 0.01 ml of solution, after the impregnation of compounds these discs were placed on the surface of the nutrient agar plates previously spread with 0.1 ml. of overnight cultures of microorganism. After 36 hr. of incubation of 37^0C, the diameter of inhibition zones were measured and results are represented in Table-5.

Results and Discussion

The azomethine and their metal complexes were screened for antimicrobial activity against *Escheriachia coli* and *Salmonella typhi* by disc diffusion method. The reference was taken as streptomycin (100 ug/ml) in each case and inhibition zone (mm) were measured The Titanium (III) complexes display moderate to weak activity against the above organisms. On the above mentioned analysis and spectral studies of these Titanium (III) complexes have been tentatively assigned and octahedral geometry of Titanium (III) ligand are shown in the in the following structures 1, 2, 3, 4, 5 and 6.

Table 5: Antibacterial activity of azomethines (ligands) and it's Titanium (III) chelates (zone of inhibition in mm)

S.No.	Ligand (L) /Complex (C)	*Escherichia coli* L	(C)	*Salmonella typhi* L	(C)
1.	Salicylaldehyde-m-nitro aniline titanium (III) chloride	11	(13)	08	(14)
2.	Salicylaldehyde-p-nitro aniline titanium (III) chloride	09	(12)	08	(15)
3.	Salicylaldehyde-phenylthiourea titanium (III) chloride	08	(16)	10	(17)
4.	2-hydroxy-1-naphthaldehyde-phenylthioureatitanium (III) chloride	11	(15)	12	(17)
5.	2-hydroxy-1-naphthaldehyde-3 amino phenol titanium (III) chloride	09	(16)	09	(18)
6.	2-hydroxy-1-naphthaldehyde-2-amino pyridine titanium (III) chloride	10	(18)	08	(15)
7.	Streptomycin	20		21	



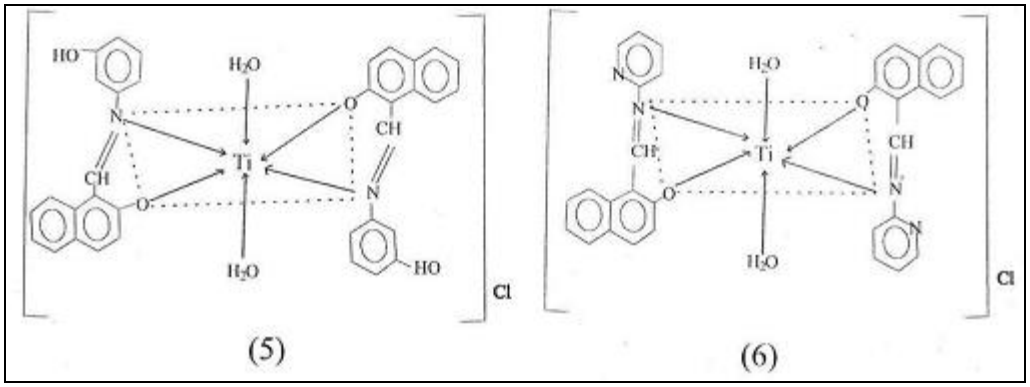


Fig 1

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