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Titanium(IV) Complexes with Tridentate Schiff Bases Containing ONO Sequences

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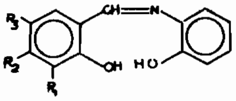
Titanium(IV) chelates have been prepared by a novel method, reacting titanyl perchlorate with tridentate aromatic Schiff bases containing ONO sequences. The complexes are reddish brown microcrystalline substances and have 1:2 stoichiometry, TiL_2, where H_2L is a tridentate Schiff base. Infrared spectra in 4000-250 cm^{-1} region show the coordination through azomethine nitrogen and involment of the OH groups in bond formation. It is argued that the azomethine nitrogen atoms are occupying the axial positions of the octahedron. The electronic and pmr spectra of the complexes are also discussed.

Introduction

This paper deals with titanium(IV) complexes with tridentate aromatic Schiff bases containing ONO sequences. These Schiff bases have been widely used for preparing metal complexes.[1] The complexes formed with such bivalent tridentate Schiff bases are invariably shown to have dimeric structures.[2] Recently a new series of Schiff bases containing ONS sequences have been tried by Theriot and his coworkers.[3] They have shown that the complexes formed with these Schiff bases too are dimeric in nature. Though there is an accumulation of considerable amount of information on titanium(I) Schiff base complexes,[4] very little is known about titanium(IV) complexes of tridentate Schiff bases.

The following Schiff bases were used for preparing titanium(IV) complexes.



	R_1	R_2	R_3
I	H	H	H
II	CH_3	H	H
III	H	CH_3	H
IV	H	H	CH_3
V	OCH_3	H	H

Experimental Section

Materials employed: Salicylaldehyde was of Bush grade and *o*-vanillin was of Fluka grade. *o*-Aminophenol was obtained from Ward Blenkinsop and Co. Ltd., London. Other substituted aldehydes were prepared by Duff[5] method. All the other chemicals used were of reagent grade.

Titanyl perchlorate was prepared by the method known in the literature.[6] Schiff bases were prepared by the method reported elsewhere.[7]

Preparation of the complexes. Titanyl perchlorate in aqueous methanol was treated with a slight excess of Schiff base (slightly more than required for 1:2 stoichiometry) in the same solvent and the reaction mixture was heated for a while, on a water bath. The microcrystalline complex separated was filtered and washed several times with methanol till the complex was free from the excess of ligand, and finally dried in vacuum over phosphorous pentoxide.

Analysis. Titanium in the complexes was determined gravimetrically as TiO_2 and nitrogen by Kjeldahl method. The results of the elemental analysis are given in Table I. Carbon and hydrogen were analysed by microanalytical section of the Osmania University, Hyderabad, India.

Physical measurements. The conductance measurements were done on a ELICO conductivity bridge CM 82 with a cell having cell constant 0.829 cm^{-1}. The ultra-violet spectra of the ligands and the complexes in dioxan were taken with a Hilger UVISPEK H. 700 using 1 cm quartz cells. The substances were dissolved in dioxan and diluted to the required concentration, 10^{-5} *M*. The infrared spectra of the complexes in nujol mulls were recorded on a Beckman IR-20 spectrophotometer in the 4000-250 cm^{-1}. PMR spectra were recorded on a Varian T-60 spectrometer using TMS as internal reference.

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(4) N.S. Biradar and V.H. Kulkarni, *J. Inorg. Nucl. Chem.*, 33, 3847 (1971), and the references therein.

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Table I. Elemental analysis of Titanium(IV) complexes with Schiff bases.

Ligand no.	Complex no.	Empirical formula	% Ti found	% Ti calcd.	% C found	% C calcd.	% H found	% H calcd.	% N found	% N calcd.
I	VI	$Ti(C_{13}H_9NO_2)_2$	9.95	10.20	—	66.39	—	3.88	5.82	5.96
II	VII	$Ti(C_{14}H_{11}NO_2)_2$	10.06	9.62	67.70	67.47	4.80	4.42	4.85	5.60
III	VIII	$Ti(C_{14}H_{11}NO_2)_2$	10.02	9.62	65.75	67.47	4.61	4.42	5.49	5.60
IV	IX	$Ti(C_{14}H_{11}NO_2)_2$	10.06	9.62	—	67.47	—	4.42	5.62	5.60
V	X	$Ti(C_{14}H_{11}NO_3)_2$	8.99	9.03	62.52	63.39	4.32	4.15	4.62	5.30

Table II. Electronic spectral data for tridentate Schiff bases and their Titanium(IV) complexes in dioxan.

Ligand No.	λ_{max}(nm)	ε_{max}(log)	Complex	λ_{max}(nm)	ε_{max}(log)
I	235	4.19	VI	249	4.70
	269	4.13		326	4.56
	357	4.17		413	4.14
II	233	4.07	VII	254	4.71
	273	4.09		325	4.62
	358	4.06		411	4.17
III	237	4.15	VIII	249	4.66
	274	4.10		332	4.53
	360	4.14		414	4.10
IV	237	4.22	IX	—	—
	270	4.12			
	362	4.16			
V	235	4.25	X	244	4.66
	277	4.15		330	4.53
	346	4.13		422	4.09

Results and Discussion

The complexes are reddish brown coloured microcrystalline substances and soluble to a limited extent in common organic solvents such as chloroform, dioxan, pyridine, acetonitrile, DMF and DMSO. This limited solubility of the complexes in various organic solvents did not permit the determination of the molecular weight of the complexes. The complexes do not respond to the test for perchlorate,[8] showing that they do not contain any perchlorate impurity. The elemental analysis in Table I agrees with the composition containing two ligand molecules and one titanium atom. It seems from these observations that titanyl perchlorate has lost its both perchlorate ions during the reaction with Schiff bases. The complexes of titanium(IV) prepared in alcohol medium with these ligands using titanium(IV) chloride instead of titanyl perchlorate also agree with the same stoichiometry.

Conductance measurements. The molar conductance values of the complexes in DMF at the concentration 10^{-3} *M* fall in the range of 0-1 ohm^{-1} cm^2/mole. This value is too small to account for any dissociation of the complexes in that solvent. Hence the complexes can be regarded as non-electrolytes.

Electronic Spectra. The absorption bands of the free ligands in dioxan are listed in Table II. All these ligands possess three bands around 235, 260, and 350 nm. The bands around 230 nm and 270 nm are respectively assigned to Φ - Φ^* and π - π^* benzenoid transitions, in view of the previous assignments.[9] The comparison of the spectra of the complexes with those of ligands shows that there is no much change in the nature of the absorption spectra except that the bands in the spectra of the complexes are broader and more intense than those of the ligands. The band around 250 nm in the complex is midway between 235 nm and 270 nm bands. Hence, in the complex, Φ - Φ^* band might have merged with π - π^* benzenoid band to give rise to a broad, intense band. The band around 250 nm, may, therefore, be considered to be the π - π^* benzenoid band. Then the observed shift towards lower wavelength may be due to the unsymmetrical nature of the metal-ligand bonding or increasing metal-ligand π-interactions and increase in the conjugation.

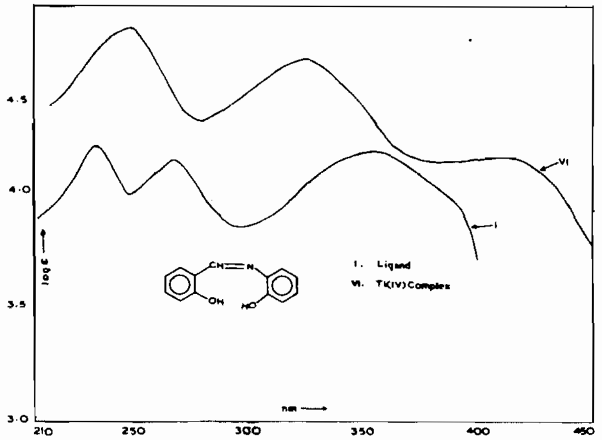

Figure 1.

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Table III. Infrared frequencies (in cm^{-1}) of Ti^{IV} complexes and their assignments.[a]

VI	VII	VIII	IX	X	Assignments
1610s	1610s	1610s	1610s	1608s	νC=N
1595s	1595s	1590s	1595s	1590s	
1580s	1581s	1560s	1585s	1565s	νC=C
1550s	1540s	—	1550s	1550s	
1310s	1310s	1310s	1310s	1305s	νC=O
555s	555s	555s	553s	548s	νTi—N
413sh	405sh	415s	415sh	421s	νTi—O
398sh	392s	398s	402s	398s	

[a] Numbers VI to X represent the serial numbers of the complexes. C=N stretching of the ligand occurs around 1623 cm^{-1} and the phenolic C-O vibration is found around 1280 cm^{-1}.

Barnum[10] and Waters *et al*[11] have fully commented on such interactions.

It is known that the free imine type ligands exhibit a band near 400 nm in neutral solutions[12] and it has been attributed to an ene-amine form and quinonoid tautomer, π-π* transition. In the ligand this band occurs near 350 nm. In the complexes, the nature of the band remains undisturbed but shows a bathochromic shift of 60 nm, and an increase in the intensity.

The observed broad band of high intensity around 330 nm may be regarded as a σ-d charge transfer transition in view of the previous assignments.[11]

Infrared Spectra. The infrared frequencies along with their tentative assignments are listed in Table III. Baker and Shulgin[13] have studied salicylidene-*o*-hydroxyaniline in chloroform and reported two types of stretching vibrations, one around 3545 cm^{-1} due to π-hydrogen bonded -OH group of aniline residue and the other at 2730 cm^{-1} due to azomethine nitrogen hydrogen bonded -OH of the aldehyde residue. In the spectra of these ligands in nujol mull, we do not observe any band around 3500 cm^{-1} but a broad band of medium intensity around 2700 cm^{-1}. This has been attributed to the intramolecular hydrogen bonded -OH. In the complexes of titanium(IV), this band disappears and the band due to the phenolic C-O vibration around 1280 cm^{-1} shifts to higher frequency (Table III). The high intensity band around 1623 cm^{-1} in the ligands attributable to the C=N stretch is found around 1610 cm^{-1} in the complexes showing that the coordination has taken place through the azomethine nitrogen and as a result of this the bond order of carbon to nitrogen link is decreased. The three high intensity bands in the region 1600-1500 cm^{-1} observed for the ligands as well as the complexes are assigned to the aromatic C=C stretching vibrations.

It is reported that[14] titanyl acetylacetonate exhibits a strong band at 1087 cm^{-1} attributable to the Ti=O stretching vibration. The complexes[15] of tetradentate Schiff bases with titanyl perchlorate also exhibit a band around 1090 cm^{-1}. The complexes under present investigation do not show any band around 1090 cm^{-1}. This proves that these complexes contain no Ti=O species in them. The spectra of the complexes prepared from titanium(IV) chloride are identical with the spectra of the complexes under present investigation. These observations show that titanyl perchlorate has lost not only its perchlorate ions but also the π-bonded oxygen during the reaction with the tridentate Schiff bases.

The complexes exhibit a strong band around 550 cm^{-1} and it is assigned to ν(Ti-N) vibration in view of the previous assignments.[15]

It is known that *cis* complexes give rise to two metal ligand M-N vibrations where as *trans* complexes give rise to only one infrared active band.[17] The presence of only one ν(Ti-N) band suggests that the complexes exist in the *trans* form. The bands observed around 415 cm^{-1} and 398 cm^{-1} are attributed to ν-(Ti-O) vibration. These bands are known to be sensitive to the coordination number and oxidation state of the central metal ion.[18] The observed constancy in the vibration attributable to ν(Ti-O) is the proof that titanium has the same oxidation state in these complexes and they have the same coordination number.

PMR Spectra. The pmr spectrum of salicylidene-*o*-aminophenol is characterised by four signals at -13.80, -9.76, -9.07, -7.11 ppm and they have been attributed to the various proton resonances due to *o*-OH of salicylidene group, *o*-OH— of amine group, HC=N and phenyl groups respectively. The spectrum of 4-methyl-salicylidene-*o*-aminophenol possess an extra signal at -2.4 ppm assignable to the resonance due to the methyl protons.

In the spectra of the complexes, the resonances due to the *o*-OH groups both on aldehyde and amine residues disappear and the resonance due to the azomethine proton shifts to upfield due to shielding effect and merges with phenyl proton signal at -7.35 ppm. These observations are suggestive that both the hydroxy groups have taken part in the reaction and azomethine nitrogen has formed the coordination bond with tita-

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(12) L.A. Kazitsyna, N.B. Kupletskaya, L.L. Polstyanko, B.S. Kikot, Yu.A. Kolesnik, and A.P. Terentev, *J. General Chem., USSR*, *31*, 286 (1961).

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(17) S.C. Jain and R. Rivest *J. Inorg. Nucl. Chem.*, *32*, 1117 (1970).

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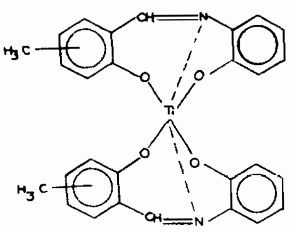
nium(IV). These observations support the infrared conclusions.

The single signal of methyl group in 4-methylsalicylidene-*o*-aminophenol splits into two signals (-2.32, -2.36 ppm) in the complex indicating that both the methyl groups in the complex are not in the identical environment. This leads to the unsymmetrical arrangement in the complex molecule. Similar observations have been made by Holm *et al.*[1] in the case of *tris* (salicylidene-methylamine) cobalt(III), and they have assigned *trans* structure to the complex, depending on the observed separate signals for methyl-protons. Hence, it may be said that these titanium(IV) complexes under investigation contain *trans* structure. The analogous inference has been achieved with the aid of infrared spectra. This leads to the following structures I and II.



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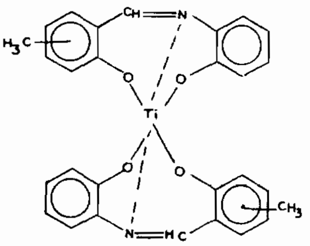
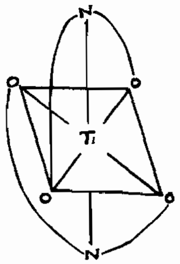


II

The observed splitting of the methyl group proton signal can be explained on the basis of structure I in which nitrogen atoms are in the *trans* position and aldehyde oxygen atoms are in the *cis* position. The structure II is more symmetrical and may give rise to single methyl signal.

Conclusions

The Schiff bases considered here are the planar tridentates with two active centres and one donor site.[1] They can coordinate to an octahedral metal atom and occupy six coordination positions. The elemental analysis show that these complexes have 1:2 stoichiometry. The spectral evidences prove that these complexes contain no Ti=O bonding and are identical with complexes formed with titanium(IV) chloride. On the basis of spectral observations it is suggested that the azomethine nitrogen atoms are in the *trans* positions to each other. Hence they should occupy the axial positions of the octahedron. Thus these complexes contain two Schiff base molecules arranged in two equatorial planes at right angles, to give rise to an octahedral structure of the following type:



This seems possible in view of the known six coordinate complexes of titanium(IV).[19]

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