

OXOTITANIUM(IV) COMPLEXES WITH 2-OH-ACETOPHENONE OXIMES

N. S. BIRADAR,* M. D. PATIL AND V. B. MAHALE

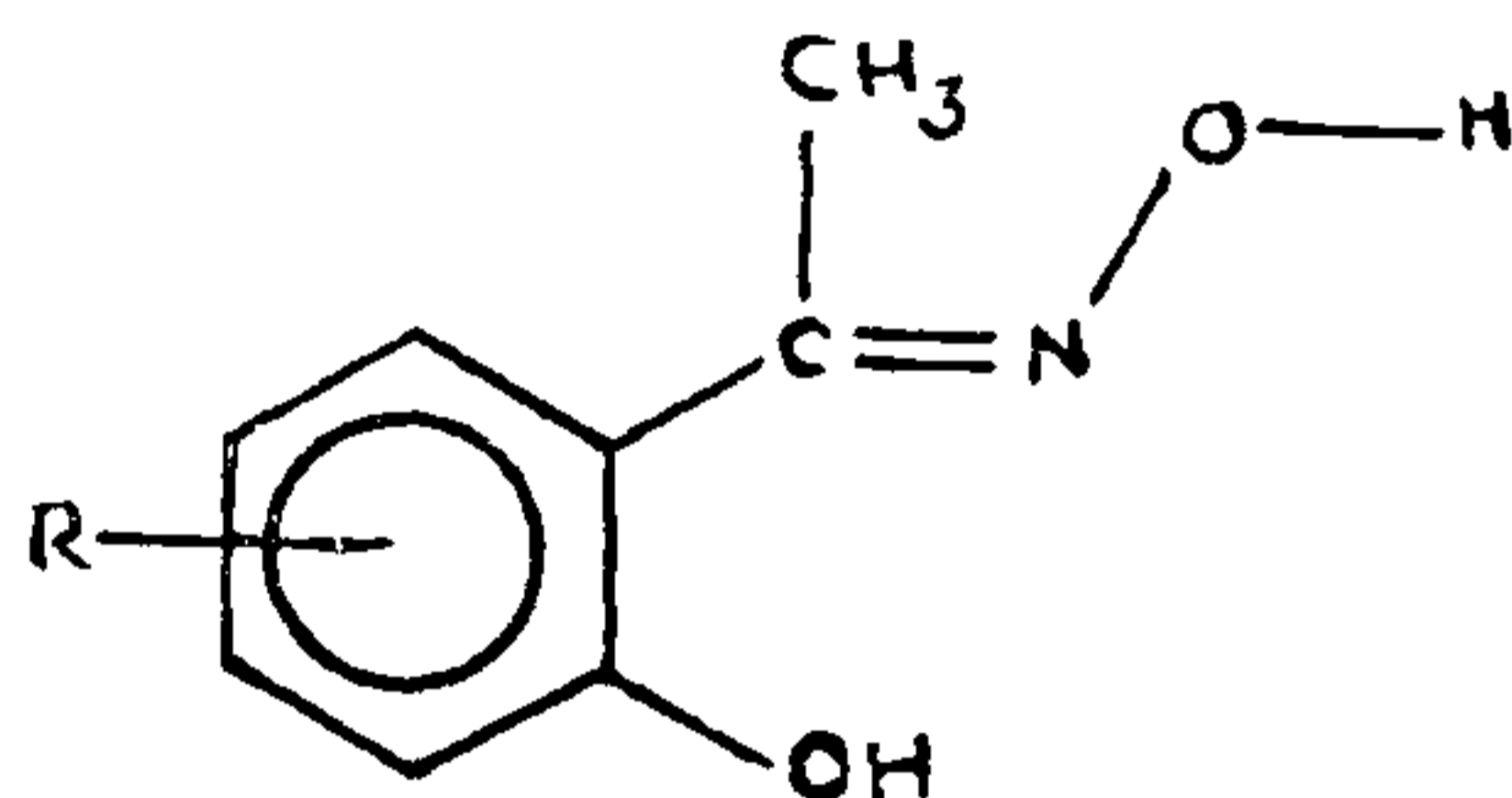
Department of Chemistry, Karnatak University, Dharwar 580 003

ABSTRACT

Oxotitanium (IV) complexes have been prepared by treating oxotitanium (IV) perchlorate with 2-OH-acetophenone oxime in aqueous alcohol medium. The complexes are orange-yellow to orange-red in colour. These complexes are characterised by elemental analysis, molecular weight, conductometric and spectral data. Five coordinate trigonal bipyramidal structure has been suggested for these complexes.

INTRODUCTION

COMPLEXES with oximes have been the subject-matter of a large number of investigators^{1,2}. This paper deals with a study of complexes of oxotitanium (IV) with the following ketoximes (I-V).



= LH

	R
I	- H
II	- 3-CH ₃
III	- 4-CH ₃
IV	- 5-CH ₃
V	- 5-Cl

EXPERIMENTAL

2-OH-acetophenone and substituted 2-OH-acetophenones were prepared by known method³. Hydroxylamine hydrochloride was of reagent grade. The ketoximes were prepared by heating a solution of 1 g of 2-OH-acetophenone, 1 g of hydroxylamine hydrochloride and 2 g of sodium acetate in 10 ml of ethanol on a steam bath for an hour. The ketoximes thus prepared were recrystallised from aqueous ethanol. Titanyl perchlorate was prepared according to the method reported in the literature⁴.

Complexes were prepared by reacting oxotitanium (IV) perchlorate (10 m mole) dissolved in aqueous ethanol with ketoxime (22 m mole) in aqueous ethanol with vigorous shaking. Sufficient time was allowed for the precipitate to settle. The complex formed was filtered, washed with aqueous ethanol and dried at 110° C.

The complexes were analysed for titanium and nitrogen contents by standard methods. The molecular weights of the complexes in nitrobenzene were determined by the Beckman freezing point method. The infrared spectra of the complexes and the ligands in nujol mull were recorded on Perkin-Elmer-337 in the region 4000-400 cm⁻¹.

RESULTS AND DISCUSSION

The elemental analysis of the complexes (Table I) show that oxotitanium (IV) perchlorate reacts with ketoxime in 1 : 2 ratio, losing two of its perchlorate ions. The complexes are orange-yellow to orange-red in colour and highly soluble in common organic solvents. Molecular weights of the complexes determined in nitrobenzene agree well with the empirical formulae and the monomeric nature in nitrobenzene. These complexes show negative test for perchlorate ion. The molar conductance values in nitrobenzene at 10⁻³ M fall in the range 0-3.0 ohm⁻¹ cm²/mole, indicating that these are nonelectrolytes in nitrobenzene.

Infrared Spectra.—The important infrared frequencies are given in Table II along with their assignments. The IR spectra of the ligands under investigation show two bands, one around 3340 cm⁻¹ and other around 2600 cm⁻¹; the former is broad with high intensity and the latter is weak. The band around 3340 cm⁻¹ is due to intermolecular hydrogen bonded -OH, and that around 2600 cm⁻¹ to intramolecular hydrogen bonded -OH. In case of salicylaldoximes the band due to intramolecular hydrogen bonded -OH is observed around 3200 cm⁻¹. This shows that the intramolecular hydrogen bonding in ketoximes is stronger than that present in salicylaldoximes. In the complexes the band at 2600 cm⁻¹ vanishes and the band around 3340 cm⁻¹ is retained, which indicates the presence of intermolecular hydrogen bonding -OH.

In view of the previous assignments^{5,6} the high intensity band in the region 1640-1630 cm⁻¹ in ligands is attributed to C=N stretch. In complexes this band is observed in the region 1550-1530 cm⁻¹. This shift towards the lower frequency indicates the coordination of the C=N group to oxotitanium,

* For correspondence.

TABLE I
 Elemental analysis of oxotitanium (IV) complexes with 2-OH-acetophenone oximes

No.	Complex	Empirical formulae	Ti%		N%		Molecular weight by cryoscopic method	
			Found	Calcd.	Found	Calcd.	Found	Calcd.
1.	Bis (2-OH-acetophenone oximate) oxotitanium (IV)	TiO (C ₈ H ₈ O ₂ N) ₂	12.90	13.18	7.63	6.69	375	364
2.	Bis (3-Me-2-OH-acetophenone oximate) oxotitanium (IV)	TiO (C ₉ H ₁₀ O ₂ N) ₂	12.03	12.25	7.20	7.14	412	392
3.	Bis (4-Me-2-OH-acetophenone oximate) oxotitanium (IV)	TiO (C ₉ H ₁₀ O ₂ N) ₂	12.40	12.25	7.05	7.14	410	392
4.	Bis (5-Me-2-OH-acetophenone oximate) oxotitanium (IV)	TiO (C ₉ H ₁₀ O ₂ N) ₂	11.95	12.25	7.26	7.14	415	392
5.	Bis (5-Cl-2-OH-acetophenone oximate) oxotitanium (IV)	TiO (C ₈ H ₇ O ₂ NCl) ₂	12.10	11.09	6.56	6.46	446	433

TABLE II
 Infrared spectra (cm⁻¹) of complexes and ligands

Sl. No.	Intermolecular hydrogen bonded -OH		Intramolecular hydrogen bonded -OH		γ C = N		Phenolic C-O		γ Ti=O	γ M-N	γ M-O
	Ligand	Chelate	Ligand	Chelate	Ligand	Chelate	Ligand	Chelate	Chelate	Chelate	Chelate
I	3340 b.s	3300 b.w	2600 b.w	..	1635 s	1535 s	1290 s	1310 s	1020 b.m	520 s	425 s
II	3330 b.s	3300 b.w	2650 b.w	..	1630 s	1535 s	1285 s	1300 s	1025 b.m	523 s	455 s
III	3340 b.s	3300 b.w	2650 b.w	..	1635 s	1550 s	1290 s	1310 s	1020 b.m	520 s	430 s
IV	3345 b.s	3300 b.w	2650 b.w	..	1638 s	1538 s	1285 s	1300 s	1040 b.m	530 s	420 s
V	3330 b.s	3300 b.w	2650 b.w	..	1635 s	1538 s	1295 s	1310 s	1030 b.m	580 s	480 s

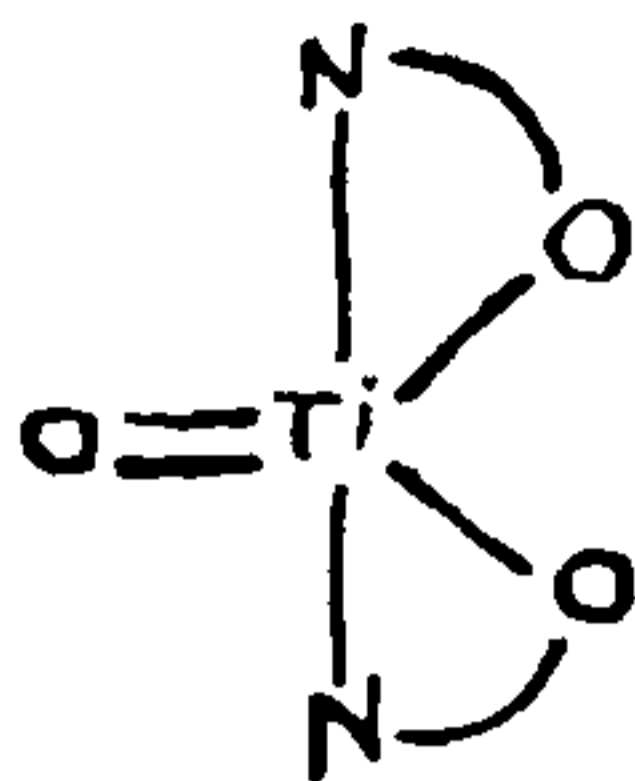
through nitrogen and lowering of the bond order of the carbon to nitrogen link. The strong band in the region 1280-1300 cm⁻¹ of the ligands, due to the phenolic C-O is found in the region 1300-1310 cm⁻¹ in the complexes. This is indicative of titanium-oxygen bond formation with oxygen of the *o*-OH group of the ketoximes.

It is evident from the previous reports^{7,8}, that a discrete Ti=O group in the complexes gives a sharp band in the multiple bonded metal-oxygen stretching region, 1100-900 cm⁻¹. In all the complexes studied, a high intensity broad band is observed in the region 1040-1020 cm⁻¹. This is attributed to the Ti=O stretching vibration.

The metal-nitrogen bands are reported to occur in the range 600-500 cm⁻¹ for the Schiff base⁹ and oxime¹ complexes. In view of these assignments, we have assigned the band in the region 560-520 cm⁻¹ to (Ti-N) vibration. The presence of the only one band in these complexes suggests that the complexes exist in the *trans* form. The region 500-400 cm⁻¹ is attributed to M-O stretching vibrations^{10,11} in the complexes. In the light of these observations a medium intensity band found around 400 cm⁻¹ is assigned to (M-O) vibration.

All these observations suggest that these oxotitanium (IV) complexes have coordination number five. On the basis of the previous literature¹² a

trigonal bi-pyramidal structure with intermolecular hydrogen bonding is proposed for the present series.



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PREVALENCE OF SOLUBLE COMPLEMENT FIXING (SCF) ANTIBODY TO JAPANESE ENCEPHALITIS (JE) VIRUS IN CASES OF JE VIRUS INFECTION

JAGDISH RAI, N. P. GUPTA** AND S. N. GHOSH‡

ABSTRACT

Serial samples of human sera belonging to confirmed cases of Japanese encephalitis (JE) virus infection were studied for the presence of antibody to soluble complement fixing (SCF) antigen of JE virus.

All the convalescent phase sera (39) out of a total of 44 sera tested, were positive for JE SCF antibodies whereas all the acute phase sera (5) were negative for these antibodies. There was complete correlation between results of complement fixation (CF) and Agarose gel diffusion (AGD) tests with JE SCF antigens. Use of JE SCF antigen as a useful reagent for specific serodiagnosis of JE virus infection by CF and AGD tests is suggested.

FALKLER *et al.* (1973) detected SCF antibodies exclusively in sera of secondary dengue cases in convalescent phase of the infection. They were unable to detect SCF antibodies in acute and primary convalescent phase sera of patients with dengue infection.

Presence of SCF antibodies in human sera in Japanese encephalitis (JE) virus infection has been demonstrated recently (Rai *et al.*, 1975) by complement fixation (CF) and Agarose gel double diffusion (AGD) tests. However, only a limited

number, mostly secondary type convalescent phase sera were found to be positive for JE SCF antibodies.

In view of the absence of correlation between HI, CF and/or neutralizing antibodies and SCF antibodies, more sera from confirmed cases of JE virus infection were tested.

MATERIAL AND METHODS

Viruses.—JE Virus (VRC Strain P 20778) plaque purified in Vero cells was used for preparation of JE SCF antigen. SCF antigens of West Nile (Strain G 22886), DEN-1 (Hawaii), DEN-2 (Strain P 23085 and TR 1751), DEN-3 (Strain 633798), DEN-4 (Strain 642069 and 611319) and Chikungunya (CHIK strain 634029) viruses were also prepared.

* Lt. Col. Jagdish Rai, AMC, Virus Section, Armed Forces Medical College, Poona-1.

** Dr. N. P. Gupta, Director, Virus Research Centre, Poona-1.

‡ Dr. S. N. Ghosh, Assistant Director and Head, Division of Immunology, Virus Research Centre, Poona-1.