

Oxotitanium (IV) Complexes with Diazo Compounds

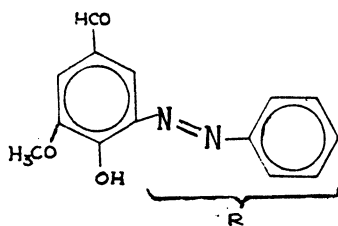
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Oxotitanium (IV) complexes have been prepared by treating oxotitanium (IV) perchlorate with diazocompounds. The complexes are characterized by elemental analyses, molecular weight, infrared and electronic spectral studies. The results suggest that the complexes are five coordinated and have bipyramidal geometry.

INTRODUCTION

Diazocompounds are widely used in industry as dyes for textiles. They may cause environmental pollution through discharge of the contents of plating baths from textile industries into rivers¹. These complexes of diazo ligands also show bacteriostatic and other biochemical activities^{2,3}. Although some organometallic complexes of Ti(IV) and Mo(IV) with diazo compounds are known^{4,5}, the complexes of oxotitanium (IV) with diazocompounds have not been studied. The object of the present investigation is to synthesise complex of oxotitanium (IV) with a series of diazocompounds and study their structural features. The diazocompounds complexes were obtained by reacting diazotised aniline derivatives with vanilline (A).



R = aniline (L_1H); o^- -anisidine (L_2H); o^- -chloroaniline (L_3H); m -chloroaniline (L_4H); o -phenetidine (L_5H).

EXPERIMENTAL

All reagents were of Analytical grade. Diazo ligands were synthesized by diazotization of primary amines and coupling with vanilline at low temperatures.

The product obtained was washed with water and crystallized from ethanol. The crystals were dried in vacuum.

Preparation of complexes: Oxotitanium (IV) perchlorate (0.01 mole) dissolved in minimum quantity of aqueous alcohol was treated with the diazo compound (0.02 mole) with vigorous stirring. The precipitate was allowed to settle. The complex formed was filtered, washed with aqueous alcohol and dried at 110°C.

Titanium was determined gravimetrically as TiO_2 and C, H and N by microanalytically. The results of the analysis are given in Table. 1.

TABLE 1
ELEMENTAL ANALYSIS AND CONDUCTIVITY DATA FOR
OXOTITANIUM (IV) DIAZO COMPLEXES

Ligand number	Complex	Found (Calc)				Conductance $Ohm^{-1}cm^2mol^{-1}$
		Ti	N	C	H	
I	$TiO(L_1)_2$	8.00 (8.35)	4.79 (4.88)	57.94 (58.55)	3.79 (3.83)	8.0
II	$TiO(L_2)_2$	8.05 (7.94)	4.56 (4.64)	59.92 (59.71)	4.22 (4.31)	5.0
III	$TiO(L_3)_2$	7.85 (7.74)	4.61 (4.52)	58.39 (58.16)	4.15 (4.20)	7.2
IV	$TiO(L_4)_2$	7.40 (7.45)	4.31 (4.35)	52.06 (52.26)	3.21 (3.11)	6.0
V	$TiO(L_5)_2$	7.35 (7.45)	4.29 (4.35)	52.45 (52.26)	3.20 (3.11)	6.5

Conductance measurements were made in DMF at room temperature using Elico conductivity bridge type 82. The proton NMR spectra were recorded on a Varian spectrometer operating at 60 MHz using TMS as internal reference. The infrared spectra were recorded as CsI pellets in the $4000-200\text{ cm}^{-1}$ region on Perkin Elmer 621 grating spectrophotometer. Electronic spectra of the complexes were recorded using Carl zeiss UR-10 spectrophotometer.

RESULTS AND DISCUSSION

Oxotitanium (IV) forms complexes with 1 : 2 stoichiometry (Table 1). The complexes are brown coloured and are soluble in pyridine, DMF and DMSO. The molecular weight in nitrobenzene of one complex agree with the empirical formula showing that the complex is monomeric in nitrobenzene. The molar conductance values in DMF (Table 1) show that the complexes behave as electrolytes in DMF.

The assignment of characteristic frequencies for a typical oxotitanium (IV) complex are given in Table 2. A strong band is observed near 1600 cm^{-1} in the spectra of the ligands which may be assigned to a coupled $N = N + C = C$ stretching

mode⁴. In the complexes, this band shifts towards the low frequency indicating the coordination of the N=N group to oxotitanium through diazo nitrogen.

An intense band at 1285 cm⁻¹ in diazo ligand can be assigned to the phenolic C-O stretching vibration. In the complexes it shifts towards higher frequency indicate bonding of the ligand to the metal ion through oxygen. A discrete Ti=O moiety in the complexes gives a sharp band in the multiple bonded metal-oxygen stretching region, 1100-900 cm⁻¹. An intense band observed in square pyramidal TiO(acac)₂ at 1087 cm⁻¹ has been assigned to Ti=O stretching mode^{6,7}. In all the complexes studied, an intense band in the region 1040-1000 cm⁻¹, which is attributed to the Ti=O stretching vibration was observed. A decrease in observed Ti=O stretching frequency for titanyl diazo complexes (Table-2) leads us to believe that oxotitanium (IV) complexes of diazo compounds may have different symmetry from that of TiO(acac)₂.

TABLE 2
INFRARED FREQUENCIES (cm⁻¹) OF OXOTITANIUM (IV)
COMPLEX OF L₁H

Ligand L ₁ H	TiO(L ₁) ₂	Assignments
1600 s	1585 s	ν N=N + ν C=C
1590 s	1580 s	
1545 s	1550 s	
1285 s	1300 s	ν CO (Phenolic)
	1040 sb	ν Ti=O
—	525 m	ν Ti-N
—	425 s	ν Ti-O
—	365 m	

The metal nitrogen bands are reported to occur in the range 600-400 cm⁻¹ for schiff base complexes^{8,9}. The band found around 520 cm⁻¹ in the case of titanium (IV) schiff base complexes has been assigned to ν(Ti-N) vibration¹⁰. Accordingly a band in the region 555-520 cm⁻¹ has been assigned as to ν (Ti-N) vibration. The presence of only one band in these complexes suggests that the complexes exist in the form shown later.

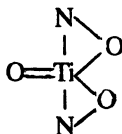
The data available on (M-O) stretching vibrations of the metal complexes fix the region between 500-400 cm⁻¹ for (M-O) stretching mode¹¹. Another band due to (Ti-O) stretching is found in the region 380-340 cm⁻¹. The observed bands in the (M-O) stretching region¹² suggests that the oxygen atoms occupy the *cis* position in the trigonal bipyramidal structure.

The electronic spectra of the complexes were measured in ethanol. The bands appearing near 255, 320 and 350 nm are due to π - π* (benzoid), π - π* (diazo) and n - π* (diazo) transitions, respectively¹³. These bands shift to shorter wave

length after complexation and it could be attributed due to coordination of diazo nitrogen and phenolic oxygen of the ligands.

The ^1H NMR spectrum of diazo ligand shows two proton signal at 7.20 and 12.3 ppm attributable to phenyl and OH proton resonances respectively. In the complexes, the phenyl resonance is shifted. The resonance due to hydroxy group at 12.3 ppm disappears after complexation indicating that deprotonation of the ligand occurs with complexation.

All these observations suggest that these oxotitanium (IV) complexes have a coordination number of five. Several complexes of coordination number five have been reported in the literature¹⁴ and a majority of the complexes have trigonal bipyramidal (D_{3h}) stereochemistry¹⁵. A limited number complexes also have square-pyramidal structure. It may be suggested that diazo complexes of oxotitanium (IV) may also possess a trigonal bipyramid geometry as shown below.



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