

## SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF TITANIUM (III) AND OXOVANADIUM (IV) CONTAINING A 14-MEMBERED MACROCYCLE AND ORGANIC MONOBASIC ACIDS

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(Received July 18, 1995; revised February 28, 1997)

A number of novel mixed ligand complexes of titanium (III) and oxovanadium (IV) containing trans-[14]-diene and organic monobasic acids of compositions, trans-[Ti(L')<sub>2</sub>L<sup>11</sup>]Cl and K[VOL<sup>11</sup>]SO<sub>4</sub> (L<sup>1</sup> = deprotonated acetic acid, propionic acid, butyric acid and benzoic acid and L<sup>11</sup> = trans-[14]-diene) have been isolated and characterized by elemental analyses, conductivity and magnetic measurements, IR and electronic spectral studies. Titanium (III) complexes exhibit 3:1 and oxovanadium (IV) complexes show 2:1 electrolytic behaviour in DMSO as are evident from conductivity measurements. Magnetic measurements, IR and electronic spectral data reveal octahedral stereochemistry for both titanium (III) and oxovanadium (IV) complexes.

**Key Words:** Mixed ligand complexes, Titanium (III), Oxovanadium (IV).

### Introduction

Transition metal complexes containing tetra and pentaazamacrocycles [1-7] constitute a potential part of coordination chemistry. The synthetic and structural works are important because they can act as simple models for realising the naturally occurring structures that are found in metalloproteins. Hay *et al.* reported [1, 3] a number of transition metal complexes of Ni(II), Co(II), Cu(II) and Zn(II) containing 14-membered macrocyclic ligand, 5, 12 dimethyl 1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene. Ferguson *et al.* [4] have studied a number of chromium (III) complexes containing a 14-membered macrocycle, 14-ane N<sub>4</sub>. Limited information is available on complexes with 1, 4, 8, 12 tetraazacyclopentadecane-15-ane N<sub>4</sub> [6, 8, 9]. Xu Jide *et al.* [10] have reported the metal complexes of Ni(II), Cu(II) and Co(II) with 5, 5, 7, 12, 12, 14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-N-acetic acid.

Again metal complexes of phthalic acid exhibit wide therapeutic and industrial applications [11-17]. Carboxylic acids coordinated to metal ions [18] show antiseptic properties on film fibres and fabrics.

Keeping an eye on the above literature survey, we were interested to study the mixed ligand complexes of titanium (III) and oxovanadium (IV) containing trans-14-diene and organic monobasic acids and report herein the synthesis, bonding and structures of these complexes.

### Experimental

Infrared spectra were obtained as KBr discs on a Perkin Elmer 883 IR spectrophotometer and electronic spectra of solid

samples (as nujol mull) on Shimadzu UV-Visible Spectrophotometer. Molar conductivity of the complexes were measured at 30°C in dimethylsulphoxide (DMSO) using 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the complexes with a digital conductometer, Scotte Geratte 857 and a dip type cell with platinized electrodes. Magnetic measurements were carried out on a Sherwood scientific magnetic susceptibility balance at 30°C. Melting points were measured with electrothermal melting point apparatus.

**Reagents.** All chemicals were analytical reagent grade and were used as supplied by Merck and BDH Ltd. except for ethanol which was purified by refluxing with magnesium turnings and iodine and finally distilled and stored over molecular sieves.

**Analyses.** Carbon, hydrogen and nitrogen analyses were carried out at Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow, India. Metals were estimated using standard procedure [19].

**Preparation of the ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (trans-14-diene):** The ligand was prepared in the laboratory using standard procedure [20].

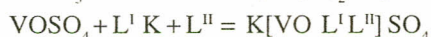
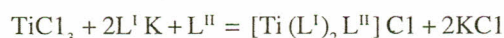
**General method of preparation of the complexes, 1-4, trans-[Ti(L')<sub>2</sub>L<sup>11</sup>]Cl (L<sup>1</sup> = deprotonated acetic acid (1), propionic acid (2), butyric acid (3) and benzoic acid (4) and L<sup>11</sup> = trans-14-diene):** Monobasic acid (0.004 mol) was deprotonated with equimolar KOH. A solution of Ti(III) chloride, hexahydrate (0.002 mol) in ethanol (30 cm<sup>3</sup>) was added to an ethanolic solution (15 cm<sup>3</sup>) of deprotonated monobasic acid, L<sup>1</sup> with continuous stirring. An ethanolic solution (20 cm<sup>3</sup>) of trans-14-diene (0.002 mol) was then added to this mix-

ture and kept under reflux for 6 h. The product that formed was then filtered, washed thoroughly with ethanol and then ether and dried in a vacuum desiccator over fused  $\text{CaCl}_2$ . Yields were 0.48, 0.45, 0.53 and 0.62 g for complexes 1, 2, 3 and 4 respectively.

*General method of preparation of the complexes, 5-8,  $\text{K}[\text{VOL}^{\text{I}} \text{L}^{\text{II}}] \text{SO}_4$ ;  $\text{L}^{\text{I}}$  = deprotonated acetic acid (5), propionic acid (6), butyric acid (7), benzoic acid (8) and  $\text{L}^{\text{II}}$  trans-14-diene:* Monobasic acid (0.004 mol) was deprotonated with equimolar KOH. A solution of vanadyl sulphate (0.002 mol) in ethanol (30  $\text{cm}^3$ ) was mixed with ethanolic solution (15  $\text{cm}^3$ ) of the deprotonated acid,  $\text{L}^{\text{I}}$  with continuous stirring. While stirring an ethanolic solution (25  $\text{cm}^3$ ) of trans-14-diene (0.002 mol) was added to this mixture and refluxed for 5 h. The solid product that appeared was separated, washed thoroughly with ethanol and then with ether and finally dried *in vacuo* over fused  $\text{CaCl}_2$ . Yields were 0.76, 0.79, 0.72 and 0.75 g for complexes 5, 6, 7 and 8 respectively.

### Results and Discussion

The complexes are prepared by the following general reactions.



where  $\text{L}^{\text{I}} \text{K}$  = potassium salt of monobasic acids e. g. acetic acid, propionic acid, butyric acid and benzoic acid.

and  $\text{L}^{\text{II}}$  = trans-14-diene (5, 7, 7, 12, 14, 14-hexamethyl, 1, 4, 8, 11-tetraazacyclo-tetradeca-4, 11-diene).

The colour and analytical data of the complexes are summarized in Table 1. The complexes have been formulated on the basis of this analytical data and their structures proposed by conductivity and magnetic measurements, IR and electronic spectral studies. Conductivity measurements (Table 2) indicate that the titanium (III) complexes are 3:1 electrolytes and oxovanadium (IV) complexes are 2:1 electrolytes in DMSO and DMF respectively [21].

*IR studies.* The IR spectral data of the complexes 1-8 are presented in Table 3. Free acetic acid and its analogues exhibit  $\nu_a(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  modes at  $\sim 1560$  and  $\sim 1416 \text{ cm}^{-1}$ , respectively and when these acids are coordinated to metals  $\nu(\text{C}=\text{O})$  mode appears at higher frequency than  $\nu_a(\text{CO}_2)$  and  $\nu(\text{C}-\text{O})$  mode occurs at lower frequency than  $\nu_s(\text{CO}_2)$  absorption [22, 23]. The present complexes 1-8 display  $\nu(\text{C}=\text{O})$  modes at  $1570\text{-}1600 \text{ cm}^{-1}$  significantly higher than  $\nu_a(\text{CO}_2)$  modes of the free acid ligands and  $\nu(\text{C}-\text{O})$  modes  $1390\text{-}1405 \text{ cm}^{-1}$  sufficiently lower than the  $\nu_s(\text{CO}_2)$  modes of the free acid ligands, thereby suggesting that these acid ligands are coordinated to the metals through carboxylate anion [22, 23]. The metal-oxy-

TABLE 1. COLOUR AND ANALYTICAL DATA OF THE COMPLEXES

S. No.	Complexes	Colour	Analytical data			
			Metal %	C %	H %	N %
1.	$[\text{Ti}(\text{AC})_2 \text{L}] \text{Cl}$ ( $\text{TiC}_{20}\text{H}_{38}\text{O}_4\text{H}_4\text{Cl}$ )	Off white	9.90 (9.95)	49.89 (49.85)	7.85 (7.89)	11.60 (11.63)
2.	$[\text{Ti}(\text{Pro})_2 \text{L}] \text{Cl}$ ( $\text{TiC}_{22}\text{H}_{42}\text{O}_4\text{N}_4\text{Cl}$ )	Cream	9.45 (9.40)	51.88 (51.83)	8.28 (8.25)	10.95 (10.99)
3.	$[\text{Ti}(\text{But})_2 \text{L}] \text{Cl}$ ( $\text{TiC}_{24}\text{H}_{46}\text{O}_4\text{N}_4\text{Cl}$ )	Off white	8.88 (8.91)	53.55 (53.60)	8.52 (8.56)	10.40 (10.42)
4.	$[\text{Ti}(\text{Ben})_2 \text{L}] \text{Cl}$ ( $\text{TiC}_{30}\text{H}_{42}\text{O}_4\text{N}_4\text{Cl}$ )	Cream	7.85 (7.91)	59.40 (59.47)	6.90 (6.94)	9.20 (9.25)
5.	$\text{K}[\text{VO}(\text{Ac})\text{L}]\text{SO}_4$ ( $\text{KVC}_{18}\text{H}_{35}\text{O}_7\text{N}_4\text{S}$ )	Green	8.86 (8.84)	37.48 (37.86)	6.00 (6.07)	9.77 (9.71)
6.	$\text{L}[\text{VO}(\text{Pro})\text{L}]\text{SO}_4$ ( $\text{KVC}_{19}\text{H}_{37}\text{O}_7\text{N}_4\text{S}$ )	Olive	8.60 (8.63)	38.59 (38.61)	6.25 (6.27)	9.45 (9.48)
7.	$\text{K}[\text{VO}(\text{But})\text{L}]\text{SO}_4$ ( $\text{KVC}_{20}\text{H}_{39}\text{O}_7\text{N}_4\text{S}$ )	Bluish Green	8.48 (8.43)	39.68 (39.70)	6.42 (6.45)	9.24 (9.26)
8.	$\text{K}[\text{VO}(\text{Ben})\text{L}]\text{SO}_4$ ( $\text{KVC}_{23}\text{H}_{37}\text{O}_7\text{N}_4\text{S}$ )	Green	7.95 (9.98)	43.26 (43.22)	5.78 (5.80)	8.75 (8.77)

(Calculated Values are in the Parentheses). L = trans-14-diene, Ac = Anion of acetic acid, Pro = Anion of propionic acid, But = Anion of butyric acid, Ben = Anion of benzoic acid.

TABLE 2. SOME PHYSICAL PROPERTIES OF THE COMPLEXES.

Compound	Melting point ( $^{\circ}\text{C}$ )	Magnetic moment, $\mu_{\text{eff}}$ (B.M.)	Molar conductivity, $\Lambda_{\text{M}}$ ( $\text{ohms}^{-1} \text{cm}^2 \text{mol}^{-1}$ )
1.	280	1.57	105
2.	300	1.65	107
3.	280	1.72	110
4.	300	1.62	102
5.	300(d)	1.56	130
6.	300(d)	1.70	125
7.	280(d)	1.58	115
8.	300(d)	1.69	112

d = decomposition.

gen bonding is further supported by the appearance of  $\nu$  (MO) modes at  $300\text{-}325 \text{ cm}^{-1}$  in the far IR region of the spectra of the complexes [22]. The disappearance of  $\nu(\text{OH})$  stretching mode observed at  $\sim 3500 \text{ cm}^{-1}$  for free acids clearly provides an additional support for coordination through carboxylate anion.

Complexes 1-8 exhibit  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{N})$  bands at  $2940\text{-}2990 \text{ cm}^{-1}$  and at  $1630\text{-}1640 \text{ cm}^{-1}$  respectively. These values are sufficiently lower than the corresponding trans-14-diene ligand values  $3040 \text{ cm}^{-1}$ , respectively, thereby suggesting the coordination of N donors of  $\text{L}^{\text{II}}$  to the metals in these complexes. The appearance of  $\nu(\text{MN})$  modes at  $420\text{-}430 \text{ cm}^{-1}$  in the far IR region of the spectra of the complexes provides further support to the metal to nitrogen coordination [6]. Further com-

TABLE 3. INFRARED SPECTRAL BANDS OF THE COMPLEXES (BAND MAXIMA,  $\text{cm}^{-1}$ ).

Com-pound	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{MN})$	$\nu(\text{MO})$	$\nu(\text{V}=\text{O})$
1.	2965m	1635 s	1570 m	1405 sh	425 sh	325 m	
2.	2970sh	1640s	1575 w	1400 sh	430 sh	330 m	
3.	2960sh	1630 s	1570 w	1405 sh	425 sh	325 m	
4.	2980sh	1640 m	1570 w	1406 sh	420 w	310 m	
5.	2940w	1630 w	1580 s	1400 sh	420 sh	320 m	970 m
6.	2990m	1640 sh	1595 s	1390 sh	420 sh	300 s	960 s
7.	2995m	1630 sh	1600 s	1395 sh	425 sh	300 s	960 s
8.	2970m	1630 s	1570 s	1400 sh	420 w	315 m	950 m

The symbols s,m,w and sh are employed to mean strong, medium weak and shoulder, respectively.

TABLE 4. ELECTRONIC SPECTRAL BANDS OF THE TITANIUM (III) COMPLEXES (BAND MAXIMA,  $\text{cm}^{-1}$ ) WITH TRANSITIONS.

Compound	${}^2T_{2g} \longrightarrow {}^2E_g$
1	19608
2	19417
3	18707
4	18553

TABLE 5. ELECTRONIC SPECTRAL BANDS OF THE OXAVANADIUM COMPLEXES (BAND MAXIMA,  $\text{cm}^{-1}$ ) WITH TRANSITION.

Compound	${}^2B_2 \longrightarrow {}^2E$	${}^2B_2 \longrightarrow {}^2B_1$	${}^2B_2 \longrightarrow {}^2A_1$
5	12453	18182	21645
6	12546	18587	22421
7	12480	18282	22124
8	12525	18349	22222

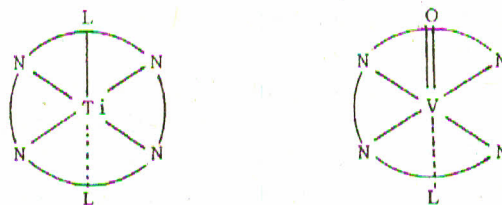
plexes 5-8 show characteristic  $\nu(\text{V}=\text{O})$  bands at 950 - 970  $\text{cm}^{-1}$ .

*Magnetic and electronic spectral studies.* All the complexes 1-8 show effective magnetic moment,  $\mu_{\text{eff}} = 1.56 - 1.72$  B. M. (Table 2) corresponding to one unpaired electron. This indicates the octahedral stereochemistry for these complexes. The magnetic data argue that Ti(III) complexes are not oxidized to the corresponding Ti (IV) ones.

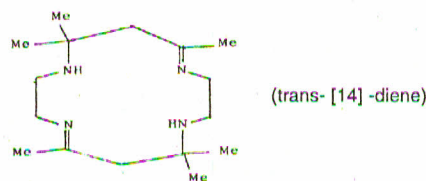
Electronic spectral bands are presented in Tables 4 and 5. Complexes 1-4 display one characteristic d-d band at 18553-19608  $\text{cm}^{-1}$  corresponding to the transition,  ${}^2T_{2g} \longrightarrow {}^2E_g$ . This reveals the octahedral geometry with  $O_h$  symmetry of the Ti (III) complexes [24, 25]. Complexes 5-8 exhibit electronic bands at 12453 - 12246  $\text{cm}^{-1}$ , 18587 - 18182  $\text{cm}^{-1}$  and 22421 - 21645  $\text{cm}^{-1}$ . These bands are assignable to the transitions,  ${}^2B_2 \longrightarrow {}^2E$ ,  ${}^2B_2 \longrightarrow {}^2B_1$  and  ${}^2B_2 \longrightarrow {}^2A_1$  and are characteristic of octahedral geometry of the oxovanadium (IV) complexes [26].

From the above discussion, the proposed structures of the Ti (III) and VO (IV) complexes can be shown by the following general octahedral skeletal structures, where Ti(III)

complexes assume trans-configuration with two L situated at the trans-positions of an octahedron.



L = Acetic acid, propionic acid, butyric acid or benzoic acid



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