

## CHARACTERISATION OF MIXED LIGAND COMPLEXES OF V(IV) AND Ti (III) HOMOPHTHALATE WITH HETEROCYCLIC AMINES

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The octahedral mixed ligand complexes of the type  $[\text{VO}(\text{A})\text{L}_3]$ ,  $[\text{VO}(\text{A})\text{L}'(\text{H}_2\text{O})]$ ,  $\text{K}[\text{VO}(\text{A})\text{L}''(\text{H}_2\text{O})]$ ,  $\text{K}[\text{Ti}(\text{A})_2\text{L}_2]$  and  $\text{K}[\text{Ti}(\text{A})_2\text{L}']$  where A = deprotonated homophthalic acid; L=quinoline, isoquinoline,  $\alpha$ -picoline or  $\gamma$ -picoline; L' = 2-aminopyridine and L'' = 8-hydroxyquinoline were prepared and characterised on the basis of elemental analysis, infrared and electronic spectra, conductance and magnetic measurements.

**Key words:** Mixed ligand homophthalate complexes with amines.

### Introduction

A survey of the available literature revealed that the complexes of oxovanadium (IV) with dithiocarbamates [1-3] amine bases [4-7] and organic acids [8-12] have been extensively studied. The complexes of titanium (III) have also been characterised both in the solid state and in solution [13-16]. The magnetic susceptibilities of some Ti(III) complexes from 80-300°K have also been measured [17]. The present communication deals with the preparation and characterisation of mixed ligand complex of oxovanadium (IV) and titanium (III) with homophthalic acid ( $\text{AH}_2$ ) as primary and heterocyclic amines i.e. quinoline (A), isoquinoline (IQ),  $\alpha$ -picoline ( $\alpha$ -pic),  $\delta$ -picoline ( $\delta$ -pic), 2-aminopyridine (Apy) and 8-hydroxyquinoline (HOX) as secondary ligands.

### Experimental

**Physical measurements.** Infrared spectra of the present complexes were recorded on a Pyc Unicam SP3-300 infrared spectrophotometer as KBr pellets. The electronic spectra of the complexes were run on a Ultroslope K4053 spectrophotometer as nujol mull spreaded on a piece of filter paper. Magnetic measurements were carried out on a Princeton Applied Research model VSM-155 digital vibrating sample magnetometer with an attachment of EG and G, PARC model -152 cryogenic temperature controller, under a magnetic field of 5000 gauss produced by polytronic electromagnet type H.E.M. 200. Conductivity measurements were carried out at room temperature using a WPA CM35 conductivity meter and dipcell with a platinized electrodes in N,N, dimethylformamide. Melting points were obtained with an Electrothermal Melting Point Apparatus.

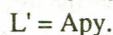
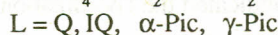
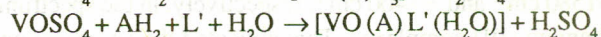
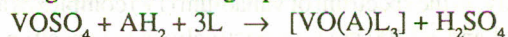
**Reagent and chemicals.** Homophthalic acid was supplied by Fluka AG Buchs SG (Switzerland). All other chemicals were of A.R. grade. The solvents were also obtained from B.D.H. and were used as supplied except for ethanol which was purified by refluxing the 99% crude with magnesium turnings and iodine and finally distilled and stored over molecular sieves.

**Preparation of complexes.** For the preparation of vanadium (IV) complexes,  $\text{VOSO}_4 \cdot \text{H}_2\text{O}$  (0.1M) was dissolved in water to which solution of homophthalic (0.1M) acid in ethanol was added. The mixture was then heated at 60° for about 15 min. and then calculated amount of an alcoholic solution of heterocyclic amines (Q, IQ,  $\alpha$ -pic and  $\delta$ -pic = 0.3M and HOX and Apy = 0.1M) was then added (the solution of heterocyclic amines such as 8-hydroxyquinoline was prepared in one equivalent of alcoholic potassium hydroxide). The mixture was again heated for half an hour and allowed to stand for over night. The crystals formed were filtered, washed several times with distilled water, and finally with ethanol and then dried in *Vacuo* over  $\text{P}_4\text{O}_{10}$ .

The same procedures was applied for the preparation of Ti (III) complexes as described earlier, with acid solutions of titanium chloride as the starting material ( For monodentate ligands the molar ratio was maintained as 1: 2: 2, while for bidentate ligands this ratio was 1 : 2 : 1).

### Results and Discussion

The oxovanadium (IV) complexes were obtained according to the following equations:



Similarly Ti (III) complexes are also prepared from  $\text{TiCl}_3$  with homophthalic acid ( 2 mole) and L (2 mole) or L' (1 mole).

The complexes of oxo vanadium (IV) and of titanium (III) were soluble in N,N, dimethylformamide. Analytical data of the complexes are given in Table 1, and some physical properties, viz. melting points, molar conductance and magnetic moments are given in Table 2. The molar conductance values of the complexes, 1, 2, 4, 5, and 6 indicated their non-electrolytic nature while the complexes 3, 7, 8, 9, and 10 behaved as 1 : 1 electrolyte

**I.R. studies.** The strong bands obtained at 1700  $\text{cm}^{-1}$  and 1440  $\text{cm}^{-1}$  due to  $\nu$  as COO and  $\nu$ s COO in the spectrum of



TABLE 1. ANALYTICAL DATA, PERCENTAGE CALCULATED (FOUND).

Complex No.	Complexes	Colour	Metal	Carbon	Hydrogen
1.	[VO (A)(Q) <sub>3</sub> ]	Pastel green	8.05 (7.98)	68.29 (68.02)	4.27 (4.23)
2.	[VO (A) (IQ) <sub>3</sub> ]	Light grey	8.05 (8.14)	68.29 (68.87)	4.27 (4.22)
3.	K[VO(A)(HOX)(H <sub>2</sub> O)]	Deep blue	11.42 (11.34)	48.39 (48.14)	3.14 (3.09)
4.	[VO(A)(γ-pic) <sub>3</sub> ]	Dark grey	9.72 (9.79)	61.82 (61.14)	3.24 (3.20)
5.	[VO(A)(α-pic) <sub>3</sub> ]	Grey	9.72 (9.63)	61.82 (61.28)	3.24 (3.28)
6.	[VO(A)(Apy) (H <sub>2</sub> O)]	Light green	14.26 (14.05)	47.03 (47.52)	3.92 (3.88)
7.	K[Ti(A) <sub>2</sub> (IQ) <sub>2</sub> ]	Yellowish brown	6.83 (6.78)	61.57 (61.02)	3.71 (3.75)
8.	K[Ti(A) <sub>2</sub> (Q) <sub>2</sub> ]	Green	6.83 (6.79)	61.57 (61.12)	3.71 (3.68)
9.	K[Ti(A) <sub>2</sub> (Apy)]	Cream	8.91 (8.84)	51.36 (50.89)	3.43 (3.46)
10.	K[Ti (A) <sub>2</sub> (γ-pic) <sub>2</sub> ]	-do-	7.62 (7.54)	57.21 (57.84)	4.13 (4.17)
11.	K[Ti (A) <sub>2</sub> (α-pic) <sub>2</sub> ]	White	7.62 (7.72)	57.21 (56.91)	4.13 (4.08)

A=C<sub>5</sub>H<sub>6</sub>O<sub>4</sub> (deprotonated), Q and IQ=C<sub>5</sub>H<sub>7</sub>N, α-pic and γ-pic=C<sub>6</sub>H<sub>7</sub>N, Apy=C<sub>5</sub>H<sub>6</sub>N<sub>2</sub> and HOX=C<sub>5</sub>H<sub>6</sub>NO.

TABLE 2. PHYSICAL PROPERTIES OF COMPLEXES.

Complex No. *	Molar conductance Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Magnetic moment (B.M.)	Melting point (± 0.5°C)
1.	10.05	1.65	285-290(d)
2.	11.78	1.72	270-275(d)
3.	90.25	1.74	250
4.	15.20	1.71	245-250(d)
5.	12.45	1.69	240-245(d)
6.	20.40	1.70	300
7.	95.56	1.66	87
8.	105.50	1.69	80
9.	110.05	1.83	290-295(d)
10.	100.06	1.81	200-205(d)
11.	90.61	1.79	250-255(d)

d = decompose., \* Complex no. are as indicated in Table 1.

homophthalic acid were shifted to  $\approx 1550$  cm<sup>-1</sup> and  $\approx 1400$  cm<sup>-1</sup>, respectively, in the spectrum of vanadium (IV) complexes and  $\approx 1580$  cm<sup>-1</sup> and  $\approx 1400$  cm<sup>-1</sup>, respectively, in the spectrum of titanium (III) complexes. This indicated the coordination of homophthalic acid through carboxyl groups. From the spectra of the complexes no. 3 and 6 the band obtained at about 3400 cm<sup>-1</sup> may be due to  $\nu$  (OH), indicated the coordination of water. The vibrational bands at about  $\approx 600$  cm<sup>-1</sup> and  $\approx 800$  cm<sup>-1</sup> in these complexes (3 and 6) are due to rocking and wagging modes of coordinated water, which suggest the presence of water molecule inside the coordination sphere [18]. The bands due to  $\nu$  V = O in oxovanadium complexes were observed at  $\approx 960$  cm<sup>-1</sup> [19].

The characteristic ring vibrations of the heterocyclic amine bases in the ring 1600- 1450 cm<sup>-1</sup> generally showed significant changes on complexation [20] which could not be distinguished because of mixing or overlapping with  $\nu$  COO

stretching bands. The inplane and out of plane ring deformation modes at  $\approx 500$  cm<sup>-1</sup> and  $\approx 700$  cm<sup>-1</sup> respectively, undergo a positive shifts in the mixed ligand complexes confirming their coordination through the nitrogen.

*Magnetic moments and electronic spectral studies.* The magnetic moments of the oxovanadium (IV) complexes were to be 1.65-1.74 B.M. at room temperature while the titanium (III) complexes gave 1.66-1.83 B.M. as given in Table 2. The observed values are in good agreement with the published values [21].

The electronic spectra of oxovanadium (IV) complexes gave four bands in the region 17000-18000, 22500-23500, 32000-32500 and 38300-38700 cm<sup>-1</sup>. These spectra are typical for oxovanadium (IV) complexes. The former two bands were assigned the transitions:  ${}^2B_2 \longrightarrow {}^2B_1$  ( $b_2 \longrightarrow b_1^*$ ) and  ${}^2B_2 \longrightarrow {}^2A_1$  ( $b_2 \longrightarrow a^*$ ), while the latter two regions correspond to the charge transfer bands. The electronic spectra of the oxovanadium (IV) complexes are summarized in Table 3. A band at 14500-20400 cm<sup>-1</sup> with a shoulder at 18420-19000 cm<sup>-1</sup> was observed for titanium (III) complexes and it was assigned to the transition  ${}^2T_{2g} \longrightarrow {}^2E_g$  for an symmetry. The electronic spectral data of titanium (III) complexes are given in Table 4.

From the above results, the structure given in Fig 1. is assigned to the vanadyl complex of homophthalic acid and 2-

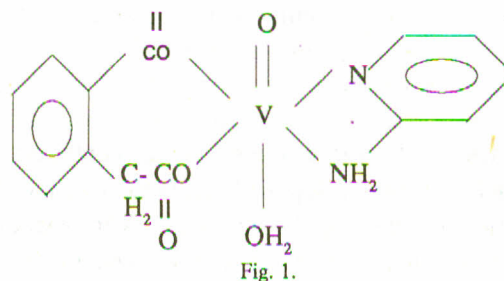


TABLE 3. ELECTRONIC SPECTRAL DATA OF OXOVANADIUM (IV) COMPLEXES.

Complex No.*	Spectral bands (cm <sup>-1</sup> ) with assignment			
	${}^2B_2 \rightarrow {}^2B_1$	${}^2B_2 \rightarrow {}^2A_1$	Charge transfer bands	
1.	17300	22500	32450	38600
2.	17000	22600	32130	38760
3.	18000	23100	32520	38700
4.	17860	23050	32570	38550
5.	17500	23500	32320	38400
6.	17400	22460	32420	38300

Complex no\*. are as indicated in Table1.

TABLE 4. ELECTRONIC SPECTRAL DATA OF TITANIUM (III) COMPLEXES.

Complex No*.	Spectral band (cm <sup>-1</sup> ) with assignment	
	${}^2T_{2g}$	$\rightarrow {}^2E_g$
7.		19000
8.		19500
9.		20100
10.		19780
11.		20450

Complex no\*. are as indicated in Table1.

aminopyridine. Similarly the structure of other complexes may also be given.

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