

## Cationic Mixed Ligand Complexes of Oxovanadium(IV) Containing a $\beta$ -Carbonylenolate & a Neutral Heterocyclic Bidentate Nitrogen Base

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Received 5 September 1985; revised and accepted 10 February 1986

Mixed ligand complexes of the type  $[\text{VOAL}]\text{ClO}_4$  where A = 2,2'-dipyridyl (dipy) or 1,10-phenanthroline (*o*-phen) and HL = (i)  $\beta$ -diketone: acetylacetone (Hacac), benzoylacetone (HBzac), dibenzoylmethane (Hdbm); (ii)  $\beta$ -ketoesters: ethyl acetoacetate (Hetacac), ethyl benzoylacetate (Hetbzac); and (iii)  $\beta$ -ketoanilides: acetoacetanilide (Hac-*o*-anld), acetoacet-*o*-toluidide (Hac-*o*-tld), acetoacet-*o*-aniside (Hac-*o*-ansd) have been synthesised. They have been characterised by elemental analyses, electronic and infrared spectra, molar conductance and magnetic susceptibility measurements.

For understanding the significant biological role of vanadium and the reaction mechanism of complex formation reactions of vanadium, studies on some model oxovanadium(IV) complexes have been carried out in solution as well as in the solid state<sup>1-4</sup>.

A lot of work has been done on oxovanadium(IV) complexes containing acetylacetone<sup>5,6</sup>. Mixed ligand complexes of oxovanadium(IV) with acetylacetone and some hydrazine ligands and 1,10-phenanthroline have been also studied<sup>5,3,7</sup>. In the present investigation the mixed complexes of the type  $[\text{VOAL}]\text{ClO}_4$  have been prepared and characterised.

All the chemicals and solvents used were of A.R. grade.

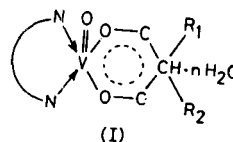
### Preparation of $[\text{VOAL}]\text{ClO}_4$

To 0.01 mmol of 2,2'-dipyridyl or 1,10-phenanthroline in 20 ml of ethanol was added 0.01 mmol of HL in 20 ml of ethanol. The resulting mixture of the two ligands was added slowly with constant stirring to 0.01 mmol of  $\text{VOSO}_4 \cdot \text{H}_2\text{O}$  in 30 ml of water. The pH of the solution was raised to four by dropwise addition of dilute aqueous ammonia in cases of complexes involving HL =  $\beta$ -diketone and  $\beta$ -ketoesters. In the cases of complexes where HL =  $\beta$ -ketoanilides, it was not necessary to raise the pH. After digesting the mixture on a water-bath for 15 min, it was filtered, and a saturated solution of sodium perchlorate was added to the filtrate. The complex so precipitated was digested on a water-bath for 30 min, and then filtered, washed thoroughly with cold water, and 50% ethanol before drying *in vacuo*.

All the complexes are stable at room temperature and soluble in methanol. Elemental analytical results are shown in Table I. Magnetic susceptibility measurements were made on a Gouy type balance in all the cases. Conductivities of the complexes were measured using a Toshniwal Conductivity Bridge. Electronic spectra were recorded using a Carl Zeiss UV/Visible spectrophotometer. All these data are included in Table I. IR spectra were recorded in KBr or nujol mull using Perkin Elmer model 427 spectrophotometer. Relevant bands have been discussed in the text.

All the complexes were kept overnight *in vacuo* so as to remove associated water or solvent molecules.

The elemental analyses (Table I) of the complexes indicate that complexes of the type  $[\text{VOAL}]\text{ClO}_4(\text{I})$  are formed where A = a heterocyclic bidentate nitrogen base and HL = a  $\beta$ -diketone,  $\beta$ -ketoester or  $\beta$ -ketoanilide.



where,

$\overline{\text{N}}\text{N}$  = 2,2'-dipyridyl or 1,10-phenanthroline

For ligands of type (i):  $\text{R}_1 = \text{R}_2 = \text{CH}_3$

$\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{C}_6\text{H}_5$

$\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$

For ligands of type (ii):  $\text{R}_1 = \text{OC}_2\text{H}_5$ ,  $\text{R}_2 = \text{CH}_3$

$\text{R}_1 = \text{OC}_2\text{H}_5$ ,  $\text{R}_2 = \text{C}_6\text{H}_5$

For ligands of type (iii):  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{NHC}_6\text{H}_5$

$\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{NHC}_6\text{H}_4\text{CH}_3$

$\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{NHC}_6\text{H}_4\text{OCH}_3$

The carbon analyses of the complexes  $[\text{VO}(\text{dipy})]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  and  $[\text{VO}(\text{o-phen})]\text{ClO}_4$  show some deviation from the expected values in spite of repeated crystallizations. This may be due to the high solubility of the complexes in the solvent which makes it impossible to remove the last traces of the soluble impurities of the ligands.

In the case of complex  $[\text{VO}(\text{dipy})]\text{ClO}_4$ , there was a mass loss corresponding to two water molecules on heating at 120°C. There was no further mass loss on heating at 130°C and 150°C. The complexes  $[\text{VO}(\text{dipy})]\text{ClO}_4$ ,  $[\text{VO}(\text{o-phen})]\text{ClO}_4$ ,  $[\text{VO}(\text{dipy})]\text{ClO}_4$  and  $[\text{VO}(\text{dipy})]\text{ClO}_4$  showed a mass loss corresponding to one water molecule at 120°C. There was no further loss in mass at 130°C and 150°C. This shows that  $[\text{VO}(\text{dipy})]\text{ClO}_4$

Table 1—Analytical, Electronic Spectral, Magnetic Susceptibility and Molar Conductance Data of Ternary Complexes of Oxovanadium(IV)

Complex	Found (Calc.) %				Electronic spectra (cm <sup>-1</sup> )	$\mu_{eff}$ (B.M.)	$\Lambda_M$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
	V	N	C	H			
[VO(dipy) (acac)]ClO <sub>4</sub> ·2H <sub>2</sub> O	11.88 (11.14)	6.16 (6.12)	36.62 (39.34)	3.70 (3.27)	710	2.13	98
[VO( <i>o</i> -phen) (acac)] ClO <sub>4</sub>	11.73 (11.47)	9.26 (9.44)	48.20 (45.89)	3.52 (3.59)	720	1.70	102
[VO(dipy) (bzac)] ClO <sub>4</sub> ·H <sub>2</sub> O	10.98 (10.18)	5.79 (5.59)	47.76 (47.95)	3.94 (3.39)	700	1.95	101
[VO( <i>o</i> -phen) (bzac)] ClO <sub>4</sub> ·H <sub>2</sub> O	10.86 (9.73)	5.45 (5.33)	56.23 (54.90)	3.91 (3.24)	670	1.70	100
[VO(dipy) (dbm)] ClO <sub>4</sub>	10.13 (9.34)	4.93 (5.13)	54.55 (54.99)	3.34 (3.48)	700	1.80	99
[VO( <i>o</i> -phen) (dbm)] ClO <sub>4</sub>	8.15 (8.95)	4.81 (4.91)	56.69 (56.89)	3.54 (3.33)	675	2.10	99
[VO(dipy) (etacac)] ClO <sub>4</sub>	9.68 (9.59)	5.02 (5.26)	46.92 (47.41)	3.75 (3.57)	695	1.71	97
[VO( <i>o</i> -phen) (etacac)] ClO <sub>4</sub>	10.06 (9.48)	5.66 (4.20)	51.68 (51.34)	3.58 (3.53)	690	1.96	92
[VO(dipy) (Etbzac)] ClO <sub>4</sub> ·H <sub>2</sub> O	9.68 (9.59)	5.02 (5.26)	46.92 (47.41)	3.75 (3.57)	700	1.87	95
[VO( <i>o</i> -phen) (Etbzac)] ClO <sub>4</sub>	10.06 (9.48)	5.66 (5.20)	51.68 (51.34)	3.58 (3.53)	650	2.09	100
[VO(dipy) (ac- <i>o</i> -anld)] ClO <sub>4</sub> ·H <sub>2</sub> O	10.10 (9.87)	7.93 (8.87)	45.82 (46.46)	3.53 (3.48)	705	1.72	100
[VO( <i>o</i> -phen) (ac- <i>o</i> -anld)] ClO <sub>4</sub>	9.69 (9.76)	7.55 (8.03)	50.05 (50.52)	3.61 (3.44)	710	2.00	100
[VO(dipy) (ac- <i>o</i> -tld)] ClO <sub>4</sub>	9.47 (9.95)	9.40 (8.19)	48.75 (49.17)	3.57 (3.90)	700	2.05	100
[VO( <i>o</i> -phen) (ac- <i>o</i> -tld)] ClO <sub>4</sub>	9.37 (9.50)	8.13 (7.82)	51.54 (51.44)	3.55 (3.72)	725	2.08	100
[VO(dipy) (ac- <i>o</i> -ansd)] ClO <sub>4</sub>	9.46 (9.64)	8.30 (7.94)	48.16 (47.68)	3.96 (3.78)	710	1.92	98
[VO( <i>o</i> -phen) (ac- <i>o</i> -ansd)] ClO <sub>4</sub>	10.76 (9.18)	8.00 (7.57)	50.27 (49.77)	3.86 (3.96)	700	1.90	98

ClO<sub>4</sub> complex molecule contains two water molecules, whereas [VO(dipy) (bzac)] ClO<sub>4</sub>, [VO(*o*-phen) (bzac)] ClO<sub>4</sub>, [VO(dipy) (etbzac)] ClO<sub>4</sub>, [VO(dipy) (ac-*o*-anld)] ClO<sub>4</sub> complexes, have one water molecule each. In cases of the rest of the complexes there was no loss in mass on heating up to 120°C; hence, these complex molecules contain no water.

The observed molar conductance values (Table 1) of the complexes are in the expected range for 1:1 electrolytes in methanol<sup>8</sup>. Magnetic moments are as expected, for one unpaired electron.

In the electronic spectra of the ternary complexes, [VOAL]ClO<sub>4</sub>, three bands are observed at ~14,900, ~19,000 and ~35,900 cm<sup>-1</sup> which may be assigned to the transitions <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>, <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>B<sub>1g</sub> and <sup>2</sup>B<sub>2g</sub> → <sup>2</sup>A<sub>1g</sub>, respectively.

These assignments correspond to the square-pyramidal geometry of the complexes, where chelating ligands occupy square-planar positions and the oxygen is at the axial position<sup>5,9,10</sup>.

The IR spectra of the compounds [VO(dipy) (acac)] ClO<sub>4</sub>, [VO(dipy) (bzac)] ClO<sub>4</sub>, [VO(*o*-phen) (bzac)] ClO<sub>4</sub>, [VO(dipy) (etbzac)] ClO<sub>4</sub>, and [VO(dipy) (ac-*o*-anld)] ClO<sub>4</sub> exhibit a broad band in the region 3600 cm<sup>-1</sup> corresponding to -OH stretching, confirming the presence of water molecules.

However, a similar band is absent in rest of the compounds, thereby confirming the absence of water molecule in these complexes.

A band observed at 985 ± 5 cm<sup>-1</sup> in the spectra of complexes is characteristic of νV=O<sup>11,12</sup>. IR spectral bands of ClO<sub>4</sub><sup>-</sup> confirm that it is not coordinated. Two IR bands, a weak band at 920 cm<sup>-1</sup> due to the symmetric stretching, and a strong band at 1100 cm<sup>-1</sup> due to asymmetric stretching, are observed. This shows that ClO<sub>4</sub><sup>-</sup> has T<sub>d</sub> symmetry, and is ionic in nature<sup>13</sup>.

It has been well established that β-diketonate chelates exhibit ν(C=O) and ν<sub>as</sub> (C=C=C) bands in the region 1,500-1,600 cm<sup>-1</sup>. The present oxovanadium complexes display the carbonyl band at 1,600 cm<sup>-1</sup>. The decrease in frequency of >C=O band is

attributed to the pseudo-aromatic character of the  $\beta$ -diketone ring. Similar change in  $>C=O$  stretch is observed in  $\beta$ -ketoesters and  $\beta$ -ketoanilide complexes also.

Complexes containing  $\beta$ -ketoanilide, show  $\nu N-H$  band<sup>13</sup> at  $\sim 3,300\text{ cm}^{-1}$ .

The  $\beta$ -ketoesters complexes show  $\nu C-O$  at  $\sim 1,220\text{ cm}^{-1}$ , thus indicating the presence of  $-COOR'$  group.

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