Ultra Chemistry Vol. 9(2), 274-278 (2013).

Peroxidovanadium(V) Complexes Ligated by Heterocyclic Thioamides

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(Acceptance Date 10th July, 2013)

Abstract

A new Peroxidovanadium(V) complexes ligated with 1-substituted tetrazoline-5-thione of the coordination formulas $Na[VO(0\text{-}0)_2(ligand)(H_2O)].2H_2O$ were synthized and characterized by elemental analysis, conductometric measurements, IR, UV-vis and 'H NMR Spectroscopy. The results of the characterization showed that all mono nuclear complexes were hepta-coordinated Vanadium atom and donor atoms occupy the position of a distorted pentagonal bipyramid configuration. The bonding of thioamide ligand occurs through thione sulphur atom.

Key words : Peroxidovanadium(V), Thioamides, hepta-coordination.

Introduction

Peroxidovanadium (V) complexes are intensively studied due to their importance in bio-coordination Chemistry which represent synthetic, structural and functional models for the peroxo form of the Vanadium haloperoxidase enzyme (VHPO)[1], insulin mimetic properties[2-5] and antitumor activity[6-7]. The present paper aims at a thorough investigation to elucidate the structure of diperoxido Vanadium(V) Complexes ligated with heterocyclic thioamides. The general features in their molecular structure and intermolecular interactions are discussed herein.

Experimental

All the chemicals used were of AR or CP-grade 1-substituted tetrazoline-5-thione was prepared by the method of Lieber *et al*.[8].

Table 1. Selected IR (cm^{-1}) bands of ligands and Complexes

Compounds	Complexes			Thioamide Bands			
	υ(0-0)	υ(0-V-0)	υ(V-0)	Band I	Band II	Band III	Band IV
($C_7H_6N_4S$) 1PT5TH(L)	-	-	-	1500 (s)	1300 (s)	1000 (ms)	800 m
$Na[VO(0\text{-}0)_2(L)(H_2O)].2H_2O$	935 (s)	655 m 590 m	535m	1505 (s)	1295 (s)	980 m	760 m
P-CH_3-L (ligand)	_	_	_	1500 ms	1280 s	1044 m	810 m
$Na[VO(0\text{-}0)_2$(P-CH_3-L) $(H_2O)].2H_2O$	920 (vs)	6455 590 m	530 m	1510 m	1285 m	1035 m	780 m
P-CH_3O-L (ligand)	-	-	-	1505 (s)	1290 (s)	1050 (m)	800 (m)
$Na[VO(0\text{-}0)_2$(P-CH_3O-L) $(H_2O)].2H_2O$	940 (vs)	640 (s) 585(s)	535 (m)	1515 (ms)	1280 (m)	1020 (m)	780 (m)
P-Cl-L (Ligand)	-	-	-	1498 (s)	1280 (s)	1055 (m)	780 (m)
$Na[VO(0\text{-}0)_2$(P-Cl-L) $(H_2O)].2H_2O$	935 (vs)	647 M 590 M	545 (s)	1510 (ms)	1282 (s)	1020 m	745 m
P-EtO-L (ligand)	-	-	-	1515 (s)	1285 (m)	1060 (m)	805 (m)
$Na[VO(0\text{-}0)_2$(P-EtO-L) $(H_2O)].3H_2O$	925 (vs)	640 m 592 m	530 (m)	1510 (s)	1280 (m)	1020 (m)	790 (m)

Preparation of Complexes :

0.5 g of $NaVO_3$ was dissolved in 30% ice-cooled H_2O_2 (30 ml) and 0.01 mols of 1-substituted tetrazoline-5-thione in 100 ml methanol was mixed to get yellow-red solution. The mixture was kept at 0ºC overnight and 10 ml of 2N NaOH solution was added and shaked vigorously for 30 minutes. A grayish-violet solid was precipitated which was further filtered off and washed with methanol and cold ether (1:1) and dried over P_2O_5 (yield = 82%).

Sl. No. 1 :

$Na[VO(0\text{-}0)_2(1PT5TH)(H_2O)].2H_2O$: Calculated (%) for **$NaVC_7H_{12}N_4O_8S$** : C = 21.76; H = 3.10; N = 14.50; V = 13.21; Found (%) : C = 21.77; H = 3.12; N = 14.52; V = 13.20;

Sl. No. 2 :

$Na[VO(0\text{-}0)_2(1PtT5TH)(H_2O)].2H_2O$: Calculated (%) for **$NaVC_8H_{14}N_4O_8S$** : C = 24.00; H = 3.50; N = 14.00; V = 12.75; Found (%) : C = 24.30; H = 3.52; N = 14.08; V = 12.32;

Sl. No. 3 :

$Na[VO(0\text{-}0)_2(P\text{-}Mt5TH)(H_2O)].2H_2O$: Calculated (%) for **$NaVC_8H_{14}N_4O_9S$** : C = 23.07; H = 3.36; N = 13.46; V = 12.25; Found (%) : C = 23.01; H = 3.46; N = 13.56; V = 12.24;

Sl. No. 4 :

$Na[VO(0\text{-}0)_2(1PClPT5TH)(H_2O)].2H_2O$: Calculated (%) for **$NaVC_7H_{11}N_4O_8SCl$** : C = 19.97; H = 2.61; N = 13.31; V = 12.12; Found (%) : C = 20.01; H = 2.65; N = 13.32; V = 12.20;

Sl. No. 5 :

$Na[VO(0\text{-}0)_2(1PET5TH)(H_2O)].2H_2O$: Calculated (%) for **$NaVC_9H_{16}N_4O_9S$** : C = 25.11; H = 3.72; N = 13.02; V = 11.86; Found (%) : C = 25.01; H = 3.78; N = 13.11; V = 11.88;

Elemental analysis, magnetic measurement, IR, UV-vis and 'H NMR Spectra were obtained as reported in our previous paper[9].

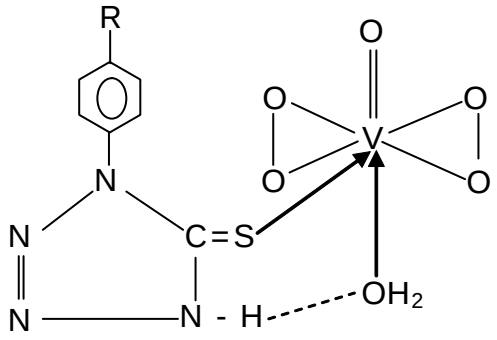
Results and Discussion

Elemental analysis of the complexes correspond to $Na[VO(0\text{-}0)_2$ (ligand)$H_2O].2H_2O$ stoichiometry. The molar conductance in DMF(10^{-3}M) were found in the range of 75-87$\wedge^{-1}$ cm^2 mol^{-1} indicating them as 1:1 electrolyte[10]. All solid products were diamagnetic as expected for d^o (V^{+5}) complexes. The electronic spectra of 1-substituted tetrazoline-5-thione exhibits two absorption maxima at 335 nm and 305 nm assignable to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively. These transitions are observed around 300 nm and 265 nm on complexation indicating the presence of coordinated thioamide ligand. An another weak transition band at 543 nm was also observed in complexes due to charge transfer[11]. The quantum chemical calculations (time- dependent DFT) of many peroxidovanadium(V) complexes indicates that LMCT transition is combination of ligand-to-ligand transition[12-13].

IR Spectra :

All peroxidovanadium(V) complexes display stretching vibrations of the $VO(O_2)^+$ moiety to quite narrow ranges for $\upsilon v = 0$ (985

cm^{-1}), υ 0-0(935–940cm^{-1}) υ O-V-O(650 & 590cm^{-1}) and υ V-0(590-535cm^{-1}) are agreement with earlier report[14-16]. The mononuclear molecular structure of complexes may be proposed with hepta-coordinated vanadium atom and donor atoms occupy the position of a distorted pentagonal bipyramid configuration (Str. I). The positions in the coordination polyhedron are occupied cis arranged η^2 peroxido ligands and oxido oxygen atom bond in one apical position. The υ ($\eta^2 - O_2$) group is more or lesss asymmetric.



(Str. I)
(R = H, CH_3 -, CH_3O-, CH_3CH_2O- Cl-)

Thioamide band III and band IV of 1-substituted tetrazoline-5-thione has major contribution from υC⋯S and observed around 1000 cm^{-1} and 800 cm^{-1} undergoes red shift to lower wave number on complexation (table 1) indicating bonding of thioamide ligand through thione sulphur following our previous observations[17-19]. New band of weak intensity at 310 cm^{-1} in complexes also suggest the formation of V-S bond and are assigned due to stretching mode.

'H NMR Spectra :

The metal ligand bonding is further substantiated by 'H NMR Spectra of 1-substituted tetrazoline-5-thione and complexes. All derivatives of 1-substituted tetrazoline-5-thione display broad multiplet in the range of δ7.2 – 7.70 PPM due to phenyl protons[20]. The broad nature of peak may be due to large quadrupole resonance broadening effect of four tetrazole nitrogen atoms. These protons signal are slightly low shifted on complexation and the integral intensities of these signals agree well with the formulation of the complexes. The methyl protons (δ2.4 PPM), (δ3.74 PPM) and imino proton (δ1.31-1.42 PPM) of ligand are also low field shifted and their integral intensities of the signals support the assigned structure (Str. I). The imino proton remain intact on complexation and bonding of thioamide ligands occurs through thione sulphur. These observations are consistent with conclusions drawn from IR Spectral data.

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