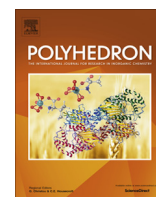


Contents lists available at [ScienceDirect](http://ScienceDirect.com)

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Fist oxidovanadium complexes containing chiral derivatives of dihydrophenanthroline and diazafluorene

Yakov S. Fomenko^a, Artem L. Gushchin^{a,b,*}, Aleksey V. Tkachev^{b,c}, Evgene S. Vasilyev^c, Pavel A. Abramov^a, Vladimir A. Nadolinny^a, Mikhail M. Syrokvashin^a, Maxim N. Sokolov^{a,b,d}^a Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia^b Novosibirsk State University, 2, Pirogova Str., 630090 Novosibirsk, Russia^c Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia^d Kazan Federal University, Kremlyovskaya St., 18, Kazan 420008, Russia

ARTICLE INFO

Article history:

Received 21 April 2017

Accepted 4 July 2017

Available online 8 July 2017

Keywords:

Chiral ligands
Oxido complexes
Vanadium
Crystal structure
EPR

ABSTRACT

Reactions of VCl_3 with chiral derivatives of dihydrophenanthroline (2*R*,4*R*,9*R*,11*R*)-3,3,10,10-tetramethyl-1,2,3,4,6,7,9,10,11,12-decahydro-2,4:9,11-dimethanodibenzo[*b,j*][1,10]phenanthroline (**L1**) and diazafluorene (1*R*,3*R*,8*R*,10*R*)-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1*H*-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b'*]diquinoline (**L2**) in acetonitrile in air yield mixtures of $[V^{III}(\mathbf{L1}/\mathbf{L2})(CH_3CN)Cl_3]$ and $[V^{IV}O(\mathbf{L1}/\mathbf{L2})(CH_3CN)Cl_2]$ (**I**, **II**) which were characterized by elemental analysis, IR spectroscopy and magnetic susceptibility data. The behavior of these mixtures in different solvents was investigated by ^{51}V NMR and EPR spectroscopies as well as optical rotation. Recrystallization of a $[V^{III}(\mathbf{L1})(CH_3CN)Cl_3]/[V^{IV}O(\mathbf{L1})(CH_3CN)Cl_2]$ mixture from CH_2Cl_2/Et_2O affords a V(IV) complex, $[V^{IV}O(\mathbf{L1})(H_2O)Cl_2] \cdot nCH_2Cl_2$ (**III**). Recrystallization from MeOH/Et₂O leads to complete oxidation to V(V) complex $[V^{VO}(\mathbf{L1})(OMe)Cl_2]$ (**IV**), which was characterized by X-ray crystallography, IR, ^{51}V and 1H NMR spectroscopies.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Oxido complexes containing the $V^{IV}=O$ and $V^V=O$ moieties are ubiquitous in the coordination chemistry of vanadium [1]. They demonstrate efficient catalytic oxidase reactivity in various transformations such as olefin epoxidation [2], aromatization of α,β -unsaturated cyclohexanone derivatives [3], alcohol oxidation [4], C–C bond cleavage of glycols to give the corresponding ketones [5], naphthol coupling [6], and α -oxidation of hydroxyl esters and amides [7]. In addition, they are part of vanadium-dependent haloperoxidases [8,9].

N-donor ligands play an important role in the chemistry of vanadium oxido complexes. In particular, much attention received the complexes with Schiff bases (N- or N, O-donor bi- or tetradentate ligands) that exhibit biological activity and catalytic properties in various oxidation reactions [2,10].

A separate group is vanadium oxido complexes with N-donor heterocyclic diimines (2,2'-bipyridine (bpy), 1,10-phenanthroline

(phen) and their derivatives). In particular, binuclear complexes $[(VO)_2(L)_2(bta)(H_2O)_2]$ (L = bpy, phen; $H_4bta = 1,2,4,5$ -benzenetetracarboxylic acid) catalyze the conversion of phenol red to bromophenol blue in the presence of H_2O_2 and Br^- , which mimics vanadium-dependent haloperoxidases [11]. Among mononuclear complexes, bis-substituted complexes with general formula $cis-[V^{IV}O(X)(L)_2]^+$ (X = OH^- , Cl^- , SO_4^{2-} , F^- ; L = bpy, phen and their derivatives) are the most common [12,13]. The $cis-[V^{IV}O(F)(dbbpy)_2]ClO_4$ complex (dbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine) with mainly ionic V–F bond can be used as a fluorinating agent and can convert quantitatively^o, for example, $(CH_3)_3Si-Cl$ to $(CH_3)_3SiF$ [13]. Oxido complexes with only one diimine ligand are less common. There are some mixed-ligand complexes, for example, $[V^{IV}O(sal-mdtc)(bpy)]$, $[V^{IV}O(sal-mdtc)(phen)]$ ($sal-mdtcH_2 =$ salicylaldehyde S-methyldithiocarbazone) [14], $[V^{IV}O(bpy)(H_2cit)] \cdot 2H_2O$, $[V^{IV}O(Hmal)(bpy)] \cdot H_2O$ and $[V^{IV}O(H_2cit)(phen)] \cdot 1.5H_2O$ ($H_4cit =$ citric acid; $H_3mal = R,S$ -malic acid) [15]. The oxido complexes of vanadium(V) include oxido-peroxido derivatives such as $[V^{VO}(O_2)(pca)(bpy)]$ and $[V^{VO}(O_2)(pca)(phen)]$ ($pca = 2$ -pyrazinecarboxylic acid) [16], dioxido derivatives such as $[V^{VO}_2(dbbpy)_2](BF_4)$ [17] and a dinuclear complex $[(V^{VO})_2(\mu_2-O)_2(\mu_2-SO_4)(dbbpy)_2]$ [18]. Vanadium oxido complexes with chiral diimine ligands are still unknown.

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia.

E-mail address: gushchin@niic.nsc.ru (A.L. Gushchin).