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Dioxovanadium(V) complexes with N,N,O-donor monoanionic ligands: Synthesis, structure and properties

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Abstract

Dioxovanadium(V) complexes having the general formula [VO_2(phsalR)] have been synthesized in 52–63% yields by reacting one mole equivalent each of $VOSO_4 \cdot 5H_2O$, 4-R-2-(pyridin-2-yl-hydrazonomethyl)-phenols (HphsalR, where R = H, OCH_3, Cl, Br and NO_2) and $N(C_2H_5)_3$ in water–acetonitrile (1:1.3) mixture. The complexes have been characterized by elemental analysis, magnetic susceptibility and spectroscopic (IR, UV–Vis, NMR and EPR) measurements. The physical properties of the complexes are consistent with the +5 oxidation state of the metal ion in them. The X-ray structure of a representative complex, [VO_2(phsal)] (R = H) has been determined. The metal centre in [VO_2(phsal)] is in square-pyramidal N_2O_3 coordination sphere. The monoanionic pyridine-N, imine-N and phenolate-O donor phsal$^-$ and one of the two oxo groups form the N,N,O,O basal plane and the other oxo group satisfies the fifth apical coordination site. This square-pyramidal molecules form weakly associated dimeric units due to the participation of the oxo group at the basal plane in the V–O–V bridge formation. The structure of [VO_2(phsal)]$_2$ can be described as two edge-shared VN_2O_4 octahedra. In the crystal lattice, these dimeric units form infinite one-dimensional chain structure via intermolecular N–H···O=V hydrogen bonding interaction.

Keywords: Dioxovanadium(V) complexes; Schiff base; Square-pyramidal; Dimerisation; Crystal structure

1. Introduction

Coordination complexes of oxovanadium(V) (VO^{3+}) and dioxovanadium(V) (VO_2^+) have invoked considerable current interest for their bioinorganic relevance in the context of haloperoxidation, phosphorylation and insulin mimicking [1–6]. Such species have been also found to be very useful as catalysts in oxidation reactions of various substrates in presence of peroxides [7–9]. We have been working on vanadium(V) complexes [10–14] with tridentate Schiff bases derived from aroylhydrazines using [VO(acac)$_2$](Hacac = acetylacetone) as the precursor commonly used for the synthesis of such complexes [9]. In methanolic media, the O,N,O-donor dianionic deprotonated benzoic acid (5-R-2-hydroxy-benzylidene)-hydrazides provide complexes containing the $\{VO(OMe)\}^{2+}$ motif [10]. On the other hand, complexes containing the $\{OV(\mu\text{-}O)VO\}^{4+}$ core with the same ligand system have been isolated from non-protic acetonitrile media [11]. The N,N,O-donor monoanionic deprotonated 4-R-benzoic acid pyridin-2-ylmethylene-hydrazides are found to be very efficient in stabilizing the VO_2^+ unit. In this case, either a dimeric species (two edge-shared octahedra) formed by a square-pyramidal complex of VO_2^+ [12] or mononuclear trigonal-bipyramidal complexes of VO_2^+ [13,14] have been isolated. In our attempts to prepare complexes of VO_2^+ with a similar N,N,O-donor Schiff base system 4-R-2-(pyridin-2-yl-hydrazonomethyl)-phenol (HphsalR) using the same precursor [VO(acac)$_2$], we have isolated some ternary oxovanadium(IV) complexes [VO(phsalR)(acac)] [15]. To explore further the coordination chemistry of oxovanadium species with HphsalR, we have used $VOSO_4 \cdot 5H_2O$ as the precursor and isolated dioxovanadium(V) complexes

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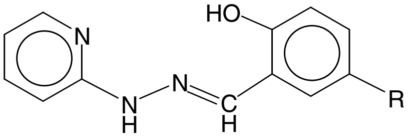
with the general formula [VO_2(phsalR)]. In the following account, we have described the synthesis, characterization and physical properties of these complexes. The molecular structure of a representative complex has been determined by X-ray crystallography.



Hphsal (R = H)
HphsalOMe (R = OCH_3)
HphsalCl (R = Cl)
HphsalBr (R = Br)
HphsalNO_2 (R = NO_2)

2. Experimental

2.1. Materials

The Schiff bases (HphsalR) were prepared in 70–80% yield by condensation reactions of 2-hydrazinopyridine with the corresponding 5-substituted salicylaldehyde in methanolic media [15–17]. All other chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

2.2. Physical measurements

Microanalytical (C, H, N) data were obtained with a Thermo Finnigon Flash EA1112 series elemental analyzer. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. A Sherwood Scientific balance was used for magnetic susceptibility measurements. A Shimadzu 3101-PC UV/Vis/NIR spectrophotometer was used to record the electronic spectra. The ^1H ($Si(CH_3)_4$ as internal standard) and ^{51}V ($VOCl_3$ as external standard) NMR spectra were recorded with the help of a Bruker 400 MHz NMR spectrometer. A Jeol JES-FA200 spectrometer was used for EPR experiments. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter.

2.3. Synthesis of [VO_2(phsal)] (**1**)

An aqueous solution (15 ml) of $VOSO_4 \cdot 5H_2O$ (100 mg, 0.4 mmol) was added to an acetonitrile solution (20 ml) of Hphsal (85 mg, 0.4 mmol) and $N(C_2H_5)_3$ (0.07 ml, 51 mg, 0.5 mmol). The mixture was refluxed for 1 h. The resulting brown solution was kept in air at room temperature for slow evaporation. Dark brown crystalline material separated in about 2 days was collected by filtration, washed with acetonitrile and finally dried in air. Yield: 60 mg (51%).

The other four complexes [VO_2(phsalOMe)] (**2**), [VO_2(phsalCl)] (**3**), [VO_2(phsalBr)] (**4**) and [VO_2(phsalNO_2)] (**5**) reported in this work were synthesized by using one mole equivalent each of $VOSO_4 \cdot 5H_2O$, $N(C_2H_5)_3$ and the corresponding Schiff base in 50–60% yields by following the same procedure as described above.

2.4. X-ray crystallography

Single crystal of [VO_2(phsal)] (**1**) was collected directly from the product precipitated in the synthetic reaction mixture. The unit cell parameters and the intensity data were obtained on a Bruker-Nonius SMART APEX CCD single crystal diffractometer, equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 2.0 kW. The detector was placed at a distance of 6.0 cm from the crystal. Data were collected at 298 K with a scan width of 0.3° in ω and an exposure time of 5 s/frame. The SMART software was used for data acquisition and the SAINT-Plus software was used for data extraction [18]. The SADABS program [19] was used for the absorption correction. The complex crystallizes in the space group $P\bar{1}$. The structure was solved by direct method and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atom of the NH group in the hydrazine fragment of the ligand was located on a difference map and refined with $U_{iso}(H) = 1.2U_{eq}(N)$. The other hydrogen atoms were added at idealized positions by using a riding model. The SHELX-97 programs [20] were used for structure solution and refinement. The ORTEX6a [21] and PLATON [22] packages were used for molecular graphics. Selected crystallographic data for **1** are listed in Table 1.

Table 1
Crystallographic data for [VO_2(phsal)] (**1**)

Chemical formula	$VC_{12}H_{10}N_3O_3$
Formula weight	295.17
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	6.9432(13)
b (Å)	7.8457(15)
c (Å)	11.359(2)
α (°)	91.024(3)
β (°)	99.877(3)
γ (°)	101.149(3)
V (Å^3)	597.3(2)
Z	2
ρ (g cm^{-3})	1.641
μ (mm^{-1})	0.837
Reflections collected	6960
Reflections unique	2768
Reflections [$I \geqslant 2\sigma(I)$]	2260
Parameters	175
R_1, wR_2 [$I \geqslant 2\sigma(I)$]	0.0459, 0.1054
R_1, wR_2 (all data)	0.0598, 0.1113
Goodness-of-fit on F^2	1.080
Largest difference in peak and hole (e Å^{-3})	0.506 and −0.256