SYNTHESIS AND STUDY OF SOME DIOXOVANADIUM(V) COORDINATION COMPOUNDS BASED ON ISONICOTINOYLHYDRAZONE OF SALICYLALDEHYDE AND ITS DERIVATIVES

***[1], [2]Gusina Liudmila, [1]Dragancea Diana, [2]Verejan Ana, [1]Bulhac Ion**

[1]Institute of Chemistry, Academy of Sciences of Moldova – Chişinău, Moldova
[2]Technical University of Moldova – Chişinău, Moldova

***Gusina Liudmila, lgusina@gmail.com**

Abstract: Three mononuclear dioxovanadium(V) complexes, $[VO_2(HL^1)]$ (**1**), $[VO_2(HL^2)]\cdot 1.2H_2O$ (**2**) and $[VO_2(HL^3)]\cdot DMF\cdot H_2O$ (**3**) with tridentate ONO ligands derived from isonicotinoylhydrazide and salicylaldehyde (H_2L^1), *o*-vanillin (H_2L^2) and 3-carboxy-salicylaldehyde (H_2L^3), respectively, have been synthesized and characterized by elemental analysis, IR-spectroscopy and single crystal X-Ray diffraction studies. The V(V) in all complexes has a distorted square pyramidal geometry with ONOO2 donor atoms set.

Keywords: oxovanadium(V) complexes, ONO donors, Schiff base, X-Ray crystal structure

1. Introduction

The catalytic properties of vanadium compounds and their effects in biological systems or as therapeutic agents have led to an increasing interest in the coordination chemistry of this element. Among the vanadium complexes that have been synthesized as models for biologically active compounds or as therapeutic agents with insulin-mimetic properties the oxovanadium (V) chelates demonstrate an essential activity [1-3]

In most cases oxygen–nitrogen donor ligands, which have a tendency to stabilize the vanadium in its highest oxidation state, are used[4,5]. Hydrazone ligands derived from the condensation of an acid hydrazide with aromatic carbonyl compounds are important tridentate ONO-functional ligands containing a combination of donor sites such as protonated/deprotonated amide oxygen, an imine nitrogen of hydrazone moiety and additional donor site (usually N or O) provided from the aldehyde or ketone forming the Schiff base. The number of coordination compounds with isonicotinohydrazone of salicylaldehyde and its derivatives is comparatively limited. [4, 6-8] These ligands possess a fourth nitrogen donor atom in the isonicotinoyl part that could link metal moieties into higher dimensional structures[7].

In this paper we report the preparation and characterization of three new dioxovanadium (V) complexes $[VO_2(HL^1)]$ (**1**), $[VO_2(HL^2)]\cdot 1.2H_2O$ (**2**) and $[VO_2(HL^3)]\cdot DMF\cdot H_2O$ (**3**) of salicylaldehyde isonicotinoylhydrazone (H_2L^1), *o*-vanillin isonicotinoylhydrazone (H_2L^2) and 3-carboxy-salicylaldehyde isonicotinoylhydrazone (H_2L^3) (Scheme 1).

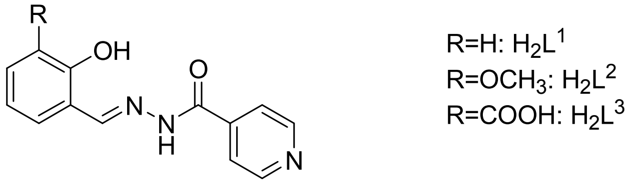


Fig. 1. Salicylaldehyde based sonicotinoylhydrazone Schiff base ligands.

2. Experimental

2.1 Materials

Solvents and reagents (isonicotinic acid hydrazide, salicylaldehyde, *o*-vanillin) were obtained from commercial sources and used without further purification. [$VO(acac)_2$] and was prepared as described in the literature [9, 10].

2.2. Physical measurements

Elemental analyses of carbon, nitrogen and hydrogen were carried out on a Vario EL III CHNOS Elemental Analyzer. IR spectra were recorded with a Perkin-Elmer FTIR spectrometer. NMR spectra for ligands were performed on a Bruker 400 spectrometer in DMSO-*d6* solution using TMS as internal reference.

2.3. Synthesis of the ligands

The tridentate Schiff base ligands, salicylaldehyde isonicotinoylhydrazone (H_2L^1), *o*-vanillin isonicotinoylhydrazone (H_2L^2) and 3-carboxy-salicylaldehyde isonicotinoylhydrazone (H_2L^3) were prepared by condensing isonicotinic acid hydrazide with salicylaldehyde, o-vanillin or 3-carboxy-salicylaldehyde as previously reported procedure [11, 12] and were characterized by IR and NMR spectroscopy.

*2.4. Synthesis of dioxovanadium complexes **1-3***

*Synthesis of $VO_2(HL^1)$ (**1**)*

A mixture of 0.22g (1 mmol) of $VOSO_4{\cdot}3H_2O$ and 0.21g (1 mmol) of 2-hydroxybenzaldehyde isonicotinoylhydrazone (H_2L^1) in 20 mL of a MeOH/DMSO mixture (1:1) was stirred at room temperature to give a clear brown solution, which was filtered and allowed to stand 2-3 days. The brown prisms crystals which appeared were filtered off and air-dried.

Yield: 67%. *Anal.* Calcd. for $C_{13}H_{10}N_3O_4V$: C, 48.31; H, 3.12; N, 13.0. Found: C, 48.17; H 3.24; N 12.43.

The complexes **2** and **3** were prepared in the same way as for **1**, except using $VO(acac)_2$, *o*-vanillin isonicotinoylhydrazone (H_2L^2) and 3-carboxy-salicylaldehyde isonicotinoylhydrazone (H_2L^3) ligands, and MeOH and MeOH/DMF (1:1) mixture for **2** and **3**, respectively.

The complexes are soluble in polar and/or coordinating solvents such as pyridine, DMF and DMSO, and sparingly soluble in MeOH.

For **2**: Yield: 62%. *Anal.* Calcd. for $C_{14}H_{14.4}N_3O_{6.2}V$: C, 44.86; H 3.87; N 11.21. Found: C, 45.13; H 4.21; N 11.22.

For **3**: Yield: 58%. *Anal.* Calcd. for $C_{17}H_{19}N_4O_8V$: C, 50.12; H 4.70; N 13.75. Found: C, 49.65; H 4.21; N 13.22.

3. Results and discussion

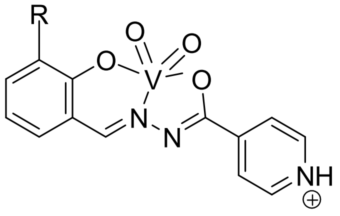
Three novel V^V isonicotinohydrazone complexes with the formula $[VO_2(HL^1)]$ (**1**), $[VO_2(H_2L^2)]\cdot 1.2H_2O$ (**2**) and $VO_2(HL^3)\cdot DMF\cdot H_2O$ (**3**), where L = salicylaldehyde isonicotinohydrazide (H_2L^1), o-vanilin isonicotinohydrazide (H_2L^2) and 3-carboxy-salicylaldehyde isonicotinohydrazide (H_2L^3), have been synthesized in good yields and high purity. The products are characterized by spectroscopic data, elemental analyses and single crystal X-Ray diffraction studies.

3.2 Spectral characteristics

In the IR spectra of complexes **1-3**, a strong band at about 1630–1650 cm^{-1} may be attributable to the carbonyl resonance and it is red-shifted from 1680–1700 cm^{-1} in the free ligands. Deprotonation of the hydrazone and salicylaldehyde OH groups enhances the electron delocalization across the ligand system, reduces the double bond character and increases the donor strength of the carbonyl group as a consequence[13]. For the oxovanadium(V) complexes, two new bands appear at about 900–930 and 950–970cm^{-1} These two bonds for the previously reported VO^{2+} complexes are assigned to the ν_{asim} and ν_{sim} stretching of the *cis*-dioxovanadium(V) moiety, respectively[14].

3.3 Crystallographic study

X-ray crystallography revealed that compound **1-3** have a molecular structure built from mononuclear $[VO_2(HL^{1-3})]$ entities (Figure 1) [15]. and solvate water[16] and DMF/water molecules for compound **2** and **3**, respectively. In each complex vanadium(V) atom adopts a square-pyramidal geometry coordinated by the tridentate Schiff base ligand stabilized in E form and two oxygen atoms in *cis* positions.



R=H: (**1**)
R=OCH$_3$: (**2**)
R=COOH: (**3**)

Fig. 2. The structure of **1-3**, solvent molecules are omitted

The N–N, N–C and C–O bond distances observed in the =N–N=C(O–)-fragment of the ligands put in evidence the enolate form of the amide functionality. The average V=O and V–O bond lengths are comparable to those observed in other vanadium(V) Schiff base complexes [17, 18]. X-ray diffraction study has demonstrated the protonation of the pyridine ring, which was also observed earlier in V^V complexes with a related ligand [13,18]. The crystal structure of **1** is stabilized by a strong intermolecular N–H···O H-bonds, involving the protonated pyridinic nitrogen and the equatorial oxo ligand. The crystal structure of **2** represents a supramolecular 3D network, sustained by the N-H…O, O-H…O hydrogen bonds and $\pi\cdots\pi$ stacking interactions.

References

1. R.R. Eady, *Coord. Chem. Rev.*, 237, **2003**, 23-30.
2. S. Gambarotta, *Coord. Chem. Rev.*, **2003**, 229-243.
3. K.H. Thompson, J.H. McNeill, C. Orvig. *Chem. Rev.*, 99, **1999**, 2561–2571.
4. M.R. Maurya, S. Khurana, C. Schulzke, D. Rehder. *Eur. J. Inorg. Chem.*, **2001**, 779-788.
5. R. Dinda, P. Sengupta, S. Ghosh, T.C.W. Mak. *Inorg. Chem.*, 41, **2002,** 1684-1688.
6. Chun-Hua Ge, Ai-Li Cui, Zhong-Hai Ni, Yun-Bo Jiang, Li-Fang Zhang, Joan Ribas, Hui-Zhong Kou. *Inorg. Chem.*, **2006**, 45, 4883-4885.
7. V. Vrdoljak, B. Prugovecki, D. Matkovic-Calogovic, J. Pisk, R. Dreos, and P. Siega. *Cryst. Growth Des.*, **2011**, 11, 1244–1252.
8. J.-X Wang, X.-Z. Li, L.-N Zhu, J.-Y. Wan g, H. Qu., *J Chem Crystallogr*, V. 40, **2010**, 726–730.
9. R.A. Rowe, M.M. Jones, *Inorg. Synth*. 5, **1957**, 113.
10. J. C. Duff and E. J. Bills, *J. Chem. Soc.*, **1932**, 1987.
11. B. Liu, R.X. Xu, Z.F. Chen, X.B. Chen, Chin. *J. Struct. Chem.*, 21, **2002**, 414.
12. D.-S. Yang, *J. Chem. Crystallogr.*, 37, **2007**, 343-348.
13. Richardson D.R., Bernhardt P.V., *J. Biol. Inorg. Chem.*, **1999**, 266-273.
14. Zhang, X. M.; You, X. Z.; Wang, X. *Polyhedron* **1996**, 15, 1793–1796.
15. L. Gusina, I. Bulhac, D. Dragancea, Yu. Simonov, S. Shova. *26th European Crystallographic Meeting*, Darmstadt, Germany, 29 August - 2 September, **2010**, p. s266.
16. L. Gusina, I. Bulhac, D. Dragancea, S. Shova. *5th Conference on Materials Science and Condensed Matter Physics MSCMP* **2010**, September 13 - 17, 2010, Chisinau, Moldova, p. 149.
17. P. Nobli, E.J. Baran, L. Otero, et al. *Eur. J. Inorg. Chem*. **2004**, 322-328.
18. Yu, Q., Li, Ch.-Y., Bian, H.-D., et al. *Chinese. J. Struct. Chem.*, **2007**, 37-40.