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Oxovanadium(IV)-Containing N_2O_2 Chelate Complex; Crystal Structure Determination and DFT

Berat İlhan Ceylan*[1]

[1]University of Istanbul, Engineering Faculty, Department of Chemistry, 34320, Istanbul, Turkey

Abstract: The stable oxovanadium(IV) complex was obtained by template condensation of 2-hydroxynaphthaldehyde S-methylthiosemicarbazone and salicylaldehyde in the presence of $VOSO_4$. The structure of VO(II)-centered metal complex was confirmed by elemental analysis and was characterized by single crystal X-ray diffraction technique and the optimized geometry of the crystal structure was calculated by density functional theory (DFT/B3LYP) with LANL2DZ basis set. Theoretical data were compared with experimental data. The complex crystal is in the form of dark green-colored small sticks. The experimental data of the monoclinic crystalline structure belonging P 21/n space group was compared to those obtained with DFT-B3LYP-LANL2DZ. It was seen that experimental and theoretical values are in a good agreement.

Keywords: Oxovanadium(IV) complexes; thiosemicarbazones; template reaction; crystal structure; DFT.

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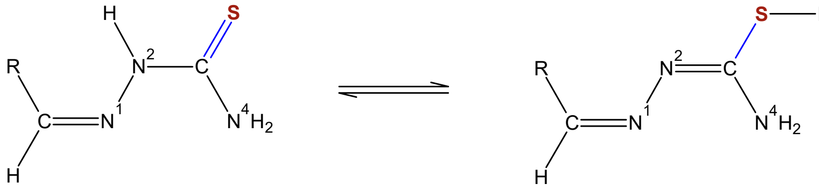
*Corresponding author. E-mail: beril@istanbul.edu.tr.

INTRODUCTION

Thiosemicarbazone compounds have long been known to show biological activities like antibacterial, antifungal, antimalarial, antitumor, antiviral, antitubercular, and anti-HIV activities. In general, biological activities of thiosemicarbazones have been shown to change depending on the metal complex infrastructure in which they are bound to. An important notice in the structure-activity relationship is that complexation not only enhances the strength of the bioactive ligands but also the metal center plays a role in the process (1, 2).

Thiosemicarbazone compounds have the thione-thiol tautomerism (Scheme 1). Studies about metal complexes of the S-alkylated thiosemicarbazones have shown that the molecular geometries of S-alkylthiosemicarbazones and coordinated metal bonding type change and terminal nitrogen (N4) atom takes place in the coordination process instead of the sulfur atom whose donor property has been diminished significantly (3-5).



Scheme 1. Tautomerism of thiosemicarbazones.

The antitumor and insulin-mimetic properties of vanadium-bearing complexes have increased the number of publications in the literature (6, 7). Vanadium thiosemicarbazone complexes have long been known to have potential anticancer activity toward renal tumor cells *in vitro*. In a study, some oxovanadium(IV) complexes were reported to employ DNA interaction through the intercalative mode and can cleave the plasmid pBR322 DNA efficiently (8). The chemical structures include V(IV) and V(V) species; therefore the reaction-based parameters like ligand structure, type of the solvent, and pH value of the medium have an effect on the actual structures: The species might be one or more of the following: $[VO]^{2+}$, $[VO]^{3+}$, $[VO_2]^{+}$, $[V_2O_3]^{n+}$ (n = 2, 3, 4), and $[V_2O_4]^{2+}$ (9).

Nitrogen-fixing bacteria must acquire molybdenum or vanadium in order to form the nitrogenase structure. Since Mo and V are important metal ions, they were investigated in the acquisition mechanism by *Azotobacter vinelandii* and several siderophores (10).

Physicochemical characterization of vanadium complexes can be studied by researching the inorganic pharmacology of them. Oxovanadium(IV) complexes were synthesized containing ONS, N_2O, N_2O_2, and S_2O_2 donor ligands (11). Administration of vanadium (IV) oxide-ligand complexes to the diabetic rats rendered them diabetic, which has had a significant effect over diabetes mellitus by regenerating the B cells of the pancreas (12).

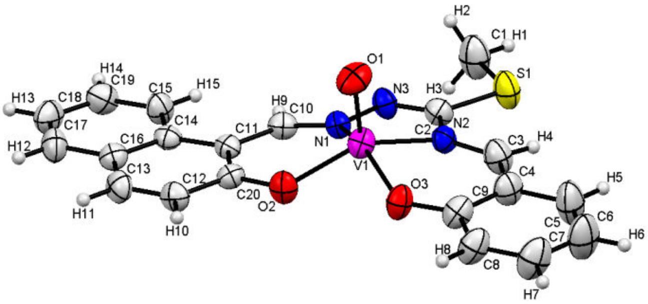


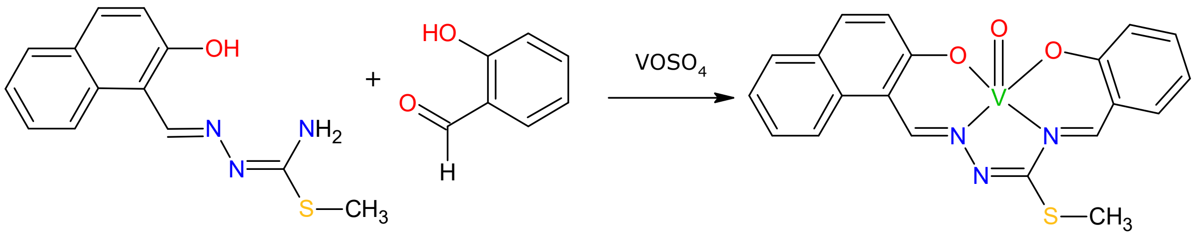
Figure 1. Crystal structure of the oxovanadium(IV) template.

In our previous study, the oxovanadium(IV) complex was synthesized and characterized by electronic, Fourier-transform infrared, ^{1}H-NMR, and electron paramagnetic resonance spectra (11). Here, the molecular and crystal structures of the oxovanadium(IV) complex were investigated by single crystal diffraction technique and the obtained experimental data of the crystal structure was compared to DFT-B3LYP-LANL2DZ results.

EXPERIMENTAL SECTION

Synthesis

The oxovanadium(IV) complex (Scheme 2) was isolated by template condensation of 2-hydroxynaphthaldehyde S-methylthiosemicarbazone and salicylaldehyde in the presence of $VOSO_4$ (11). The structure of VO(II)-centered metal complex was confirmed by elemental analysis.



Scheme 2. Formation of the vanadium template complex.

Crystalline Structure Determination and Refinement

A single crystal of compound with dimensions 0.010 x 0.200 x 0.400 mm was grown by slow evaporation of the ethanolic solution. Crystals were mounted on a cryoloop and attached to a goniometer head on a Bruker D8 VENTURE diffractometer equipped with PHOTON100 detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) and 1.0° Φ-rotation frames. Crystal parameters and refinement results of the complexes are summarized in Table 1. The structure of the complex has been solved by intrinsic method SHELXS-1997 (13) and refined SHELXL-2014/7 (14, 15). ORTEP drawings with the atom numbering schemes are given in Figure 1. Selected bond lengths and bond and torsion angles of compound are given in Tables 2-3.

RESULTS AND DISCUSSION

Template condensation resulted in a thiosemicarbazidato ligand having four functional donor atoms. The VO(II) center has a square pyramidal environment consisted of N1, N2 (azomethine nitrogen) and O2, O3 (deprotonated oxygen) atoms of the thiosemicarbazidato backbone. The square pyramide is distorted because of relatively shorter V-O bond distances compared to V-N bond distances in Table 2.

The optimized geometries of the monomeric and dimeric structures of the template complex were obtained at the DFT/B3LYP method combined with the LANL2DZ basis set by using Gaussian 09 software in order to determine the change in the geometric structure of the synthesized complexes (16). By comparing the theoretical values with the experimental ones, vanadium centered bond distances, vanadium-centered angles, selected torsion angles, and selected bond lengths were presented in Tables 2-3. Although the theoretical values of bond distances and angles are slightly larger, all of the data obtained both methods were seen to be harmonious with each other.

Optimized geometric parameters are found to be nearly the same as those of experimental in solid state by X-ray single diffraction. The reason for the minor discrepancies are due to approximations, basis set incompleteness, and that the molecule is assumed to be isolated in gas phase in the theoretical calculation.

Table 1. Crystal data and structure refinement details for compound.

CCDC number	1506865
Chemical formula	C20H15N3O3SV
Crystal habit	Dark green rod
Crystal size (mm)	0.01 x 0.20 x 0.40 mm
Formula weight (g/mol)	428.35
Temperature (K)	299
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P 21/n
Unit cell parameters	
a, b, c (Å)	8.7158(8) , 12.2954(11), 17.0263(15)
γ, ß, V (Å)	90°, 97.593(2)°, 90°
Cell volume ($Å^3$)	1808.6(3)
Z	4
Density (g/cm^3)	1.573
Absorption coefficient (mm^{-1})	0.692
F000	876
Index ranges	-10<=h<=10, -14<=k<=14, -20<=l<=20
Reflections collected	49049
Independent reflections	3374
Rint	0.1473
Data reflections / parameters	3374 / 254
Goodness of fit indicator	1.074
Final R indices [I>2σ(I)]	R1 = 0.0640, wR2 = 0.1009
Δρmax , Δρmin (e/Å3)	0.314, -0.260

Table 2. Selected bond lengths of compound (Å).

Experimental	Calculated
1.583(3)	1.600
1.923(3)	1.934
1.917(3)	1.928
2.030(3)	2.037
2.047(3)	2.082
1.750(4)	1.831
1.797(5)	1.885
1.322(4)	1.329
1.300(5)	1.327
1.300(5)	1.330
1.408(4)	1.419
1.306(5)	1.334
1.403(5)	1.411
1.279(5)	1.310

Table 3. Selected angular values and torsion angles of compound (°).

	Experimental	Calculated
O1-V1-O3	108.64(14)	109.20
O1-V1-O2	109.01(14)	109.90
O3-V1-O2	91.12(12)	91.50
O1-V1-N1	105.51(14)	105.10
O3-V1-N1	144.88(13)	143.60
O2-V1-N1	85.35(12)	86.30
O1-V1-N2	107.04(15)	106.10
O3-V1-N2	87.75(13)	86.30
O2-V1-N2	142.25(13)	143.70
N1-V1-N2	74.57(13)	76.50
C20-O2-V1	129.6(2)	131.80
C9-O3-V1	131.0(3)	133.30
C10-N1-V1	127.8(3)	129.1
N3-N1-V1	118.3(2)	116.30
C3-N2-V1	125.2(3)	125.90
C2-N2-V1	113.4(3)	111.1
V1-O2-C20-C11	27.85	18.27
V1-O3-C9-C4	−15.38	-20.50
V1-N2-C3-C4	9.39	11.06
V1-N1-C10-C11	-6.86	-10.12
O2-C20-C11-C10	-0.59	-1.96
N1-N3-C2-N2	-0.20	0.79
O3-C9-C4-C3	-5.40	3.89

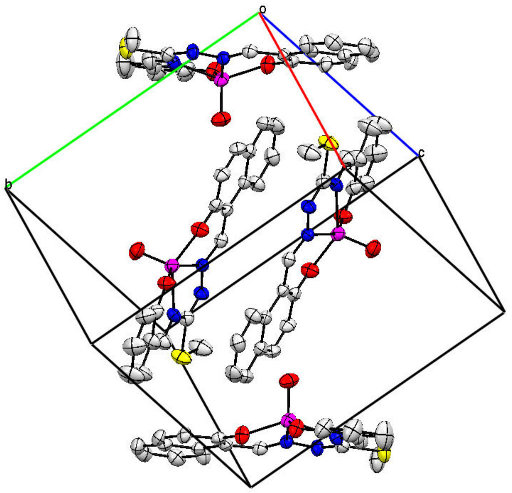


Figure 2. Molecular packing of the complex.

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REFERENCES

1. Pahontu E, Julea F, Rosu T, Purcarea V, Chumakov Y, Petrenco P, et al. Antibacterial, antifungal and in vitro antileukaemia activity of metal complexes with thiosemicarbazones. Journal of Cellular and Molecular Medicine. 2015; 19(4): 865–78. DOI: 10.1111/jcmm.12508.

2. Da S. Maia PI, Pavan FR, Leite CQF, Lemos SS, de Sousa GF, Batista AA, et al. Vanadium complexes with thiosemicarbazones: Synthesis, characterization, crystal structures and anti-Mycobacterium tuberculosis activity. Polyhedron. 2009; 28(2): 398–406. DOI: 10.1016/j.poly.2008.11.017.

3. Ülküseven B. Studies of the S-Ethylthiosemicarbazones with Cu(I), Zn(II), Cd(II), Hg(II) Chloride Salts. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry. 1995; 25(9): 1549–60. DOI: 10.1016/j.poly.2008.11.017.

4. Bourosh P, Gerbeleu N, Revenko M, Simonov Y, Belskii V, Byrotosu N. Preparation and crystal structure of salicylaldehyde S-methyl-4-phenylthiosemicarbazone (H2L) and its copper complex [Cu(HL)H2O] NO3. Russ J Inorg Chem. 1987; 32:1446–50.

5. Lewis NA, Liu F, Seymour L, Magnusen A, Erves TR, Arca JF, et al. Synthesis, Characterisation, and Preliminary In Vitro Studies of Vanadium(IV) Complexes with a Schiff Base and Thiosemicarbazones as Mixed Ligands. European Journal of Inorganic Chemistry. 2012; 4: 664–77. DOI: 10.1002/ejic.201100898.

6. Noblıa P, Vieites M, Torre M.H, Costa-Filho A.J, Cerecetto H, Gonzalez M, Laura Lavaggi M, Adachi Y, Sakurai H, Gambino D. Journal of Inorganic Biochemistry. 2006; 100: 281–87. DOI :10.1016/j.jinorgbio.2005.11.012.

7. Sanna D, Ugone V, Pisano L, Serra M, Micera M, Garribba E, Journal of Inorganic Biochemistry. 2015; 153: 167–77. DOI:10.1016/j.jinorgbio.2015.07.018.

8. Ying P, Zeng P, Lu J, Chen H, Liao X, Yang N. New Oxidovanadium Complexes Incorporating Thiosemicarbazones and 1, 10-Phenanthroline Derivatives as DNA Cleavage, Potential Anticancer Agents, and Hydroxyl Radical Scavenger. Chemical Biology & Drug Design. 2015; 86(4): 926–37. DOI: 10.1111/cbdd.12535.

9. Rubčić M, Milić D, Horvat G, Đilović I, Galić N, Tomišić V, et al. Vanadium-induced formation of thiadiazole and thiazoline compounds. Mononuclear and dinuclear oxovanadium(v) complexes with open-chain and cyclized thiosemicarbazone ligands. Dalton Transactions. 2009; 44: 9914. DOI: 10.1039/b913653c.

10. Springer SD, Butler A. Microbial ligand coordination: Consideration of biological significance. Coordination Chemistry Reviews. 2016; 306: 628–35. DOI: 10.1016/j.ccr.2015.03.013.

11. Ilhan-Ceylan B, Tuzun E, Kurt Y, Acikgoz M, Kahraman S, Atun G, et al. Oxovanadium(IV) complexes based on S -alkyl-thiosemicarbazidato ligands. Synthesis, characterization, electrochemical, and antioxidant studies. Journal of Sulfur Chemistry. 2015; 36(4): 434–49. DOI: 10.1080/17415993.2015.1050396.

12. Yanardag R, Demirci TB, Ülküseven B, Bolkent S, Tunali S, Bolkent S. Synthesis, characterization and antidiabetic properties of N1-2,4-dihydroxybenzylidene-N4-2-hydroxybenzylidene-S-methyl-thiosemicarbazidato-oxovanadium(IV).European Journal of Medicinal Chemistry. 2009; 44(2): 818–26. DOI: 10.1016/j.ejmech.2008.04.023.

13. Sheldrick G. SHELXS-97, Program for Crystal Structure Solution, Univ. Göttingen, Germany. 1997

14. Sheldrick G. SHELXL2014/1 Programs for the Solution and Refinement of Crystal Structures. University of Göttingen; 2014.

15. Sheldrick GM. A short history of SHELX. Acta Crystallographica Section A Foundations of Crystallography. 2008; 64(1): 112–22.

16. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson. Gaussian 09, Revision A. 02, Gaussian, Inc., Wallingford, CT, 2009; 200.

Türkçe Öz ve Anahtar Kelimeler

Oksovanadyum(IV) İçeren N_2O_2 Kelat Kompleksleri; Kristal Yapı Tayini ve DFT

Berat İlhan Ceylan

Öz: Kararlı oksovanadyum(IV) kompleksi, 2-hidroksinaftaldehit S-metiltiyosemikarbazon ve salisilaldehidin $VOSO_4$ varlığındaki template kondensasyonu ile elde edilmiştir. VO^{2+}-merkezli metal kompleksinin yapısı elementel analiz ile doğrulanmış ve X-ışını saçılması tekniği ile karakterize edilmiştir, kristal yapının optimize geometrisi yoğunluk fonksiyonel teorisi (DFT/B3LYP) LANL2DZ baz seti kullanılarak hesaplanmıştır. Teorik veriler deneysel verilerle karşılaştırılmıştır. Kompleks kristali, koyu yeşil renkli küçük çubuklar halinde elde edilmiştir. P 21/n uzay grubuna bağlı olan monoklinik kristal yapısına ait deneysel veriler DFT-B3LYP-LANL2DZ ile elde edilenlerle karşılaştırılmıştır. Deneysel ve teorik değerlerin iyi bir uyum içinde olduğu bulunmuştur.

Anahtar kelimeler: Oksovanadyum(IV) kompleksleri; tiyosemikarbazonlar; template tepkimesi; kristal yapısı; DFT.

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