Scientific paper

Synthesis and Structure of (4-methylpyridine-N-oxide) oxo-(salicylaldehyde 4-phenylthiosemicarbazonato) vanadium(IV)

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Dedicated to the memory of Professor Ljubo Golič

Abstract

New title complex has been synthesized by the reaction of salicylaldehyde 4-phenylthiosemicarbazone with 4-methylpyridine-*N*-oxide and [VO(acac)$_2$].The tetragonal pyramidal coordination about vanadium atom is realized through O,N,S-donors of a doubly deprotonated thiosemicarbazonato ligand, oxygen atom from 4-methylpyridine-*N*-oxide molecule and in the apical position completed by an oxo group. The complex molecules are held together by hydrogen bonds and by π–π interactions between the aromatic rings of the ligand. The title complex has been characterized by chemical analysis, IR spectroscopy, TG and X-ray crystallography.

Keywords: Vanadium, oxo-vanadium complexes, thiosemicarbazonato complexes, crystal structure

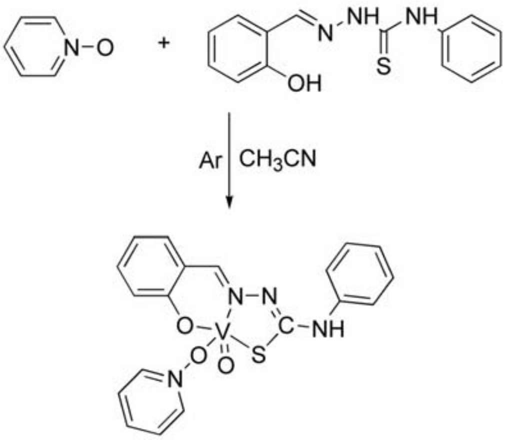
1. Introduction

The coordination chemistry of both oxovanadium(IV) and oxovanadium(V) is becoming significantly relevant to the bioinorganic chemistry.[1] Some of these complexes with ligands such as thiosemicarbazones may be used as models for a better understanding of vanadium role in biomolecules. In addition, metal complexes with thiosemicarbazone ligands are of increasing interest due to their antibacterial, antifungal, antitumor as well as antiviral activities.[2,3] Such activities are most probably connected with their structure similarly as it has been found for the copper(II) thiosemicarbazone complexes.[4–6]

The salicylaldehyde 4-phenylthiosemicarbazone ligand may react in tridentate manner either in its thione form coordinating through deprotonated phenolic-oxygen, imino-nitrogen and thiocarbonyl-sulphur atoms or in its thiol form by loosing another proton from the mercapto group.[7]

In the continuation of our investigations on molybdenum(V) and molybdenum(VI) thiosemicarbazonato complexes we have extended our studies to the analogous vanadium complexes. [8–11]

2. Results and Discussion



Scheme 1.

The title complex was prepared by the reaction of salicylaldehyde 4-phenylthiosemicarbazone with 4-methylpyridine-*N*-oxide and [VO(acac)$_2$] in acetonitrile as shown in Scheme 1. The complex is air-stable, soluble in

DMF, DMSO, acetone and scarcely in $CHCl_3$ and CH_2Cl_2. The results of elemental analysis are in good agreement with the assigned formula.

Thermogravimetric analysis of the complex reveals several decomposition steps: 115–150 °C, 150–293 °C, 293–427 °C, 427–526 °C. Although it was not possible to correlate the weight losses in each step to the decomposed organic fragments, the remaining residue was found to be in good agreement with the formation of V_2O_5.

In its IR spectrum the title complex exhibits single strong band at 3320 cm^{-1} which is attributed to N–H stretching frequency. The disappearance of two out of three spectral bands found at 3338, 3150 and 2992 cm^{-1} in the spectrum of free ligand suggests deprotonation of phenolic OH and N–H group. The strong single absorption band in the IR spectrum of the complex found at 969 cm^{-1} is indicative for the V=O stretching. The bands about 1600 cm^{-1} are assigned to the stretching of C=N bonds of the thiosemicarbazones. The absorption bands located at about 1317 and 763 cm^{-1} are attributed to the coordinated C–S(thiol) stretching. These data and the remaining frequencies in the IR spectrum are in accordance with the literature data for the same type of complexes.[12,13]

2. 1. Description of the Crystal Structure

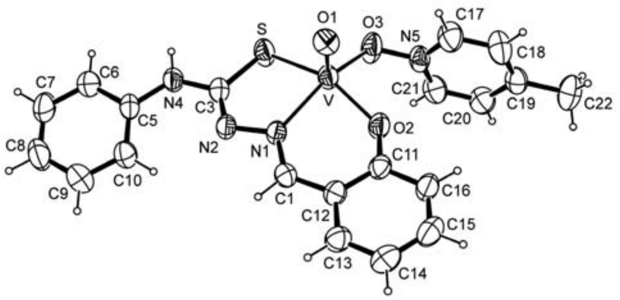


Figure 1. View of the molecule with the numbering scheme and displacement ellipsoids for non-hydrogen atoms drawn at the 50% probability level. The hydrogen atoms are shown as spheres of the arbitrary radius.

The molecule of the title complex is shown in Figure 1. The vanadium(IV) ion is coordinated by an oxo-oxygen atom, a doubly deprotonated tridentate thiosemicarbazonato ligand, and by a 4-methylpyridine-*N*-oxide molecule. Whereas the thiosemicarbazone ligand is meridionally bonded through the sulphur atom (S), imine-nitrogen (N1) and the deprotonated phenolic-oxygen (O2) thus forming 5- and 6-membered rings with the vanadium ion, the 4-methylpyridine-*N*-oxide molecule is bonded to vanadium ion through the oxygen atom O3. Consequently, the coordination sphere around vanadium is tetragonal–pyramidal with the doubly bonded oxo-oxygen O1 in the apical position and with the other coordinating atoms occupying the basal plane of the pyramid. The maximum deviation from the best plane defined by S, N1, O2, O3 is that of O2 being 0.0311(17) Å. The vanadium atom is 0.6175(4) Å out of the basal plane realizing thus an almost ideal tetragonal-pyramidal geometry as indicated by a τ value of 0.025, where τ = I<(S–V–O2) – <(O3–V–N1) I/60º (τ = 0 for ideal tetragonal pyramid, τ = for an ideal trigonal bipyramid).[14] The V = O1, V–S, V–N1 and V–O2 bond lengths (Table 1) fall in the range of the corresponding bond lengths observed for thiosemicarbazonato-ONS complexes with a VO^{2+} core.[15–20] The V–O3 bond distance of 1.9803(17) Å is somewhat longer than the corresponding distances observed in oxo-bis(pyridine-2-thiolato-*N*-oxide-*O,S*)vanadium(IV), $VO(pto)_2$ [1.952(3) and 1.961(3) Å in one report on $VO(pto)_2$,[21] 1.958(5) and 1.969(5) Å in another structural report on the same complex],[22] which can be attributed to the chelate binding mode of the ligand molecule in $VO(pto)_2$. Until now, as far as we know, the aforementioned chelate complex was the only example of an X-ray structurally characterized vanadium complex with a derivative of pyridine-*N*-oxide molecule as a ligand.

Table 1. Selected bond distances (Å) and angles (°).

V–S	2.3562(7)	C11–C12	1.410(3)
V–O1	1.5994(18)	O2–C11	1.318(3)
V–O2	1.9088(17)	S–V–O1	107.38(7)
V–O3	1.9803(17)	S–V–O2	144.15(6)
V–N1	2.0666(18)	S–V–O3	85.47(5)
S–C3	1.743(2)	S–V–N1	79.89(5)
N2–C3	1.297(3)	O1–V–O2	108.19(8)
N4–C3	1.365(3)	O1–V–O3	110.01(9)
N4–C5	1.410(3)	O1–V–N1	103.97(8)
N1–N2	1.397(2)	O2–V–O3	86.60(7)
N1–C1	1.280(3)	O2–V–N1	87.41(7)
C1–C12	1.444(3)	O3–V–N1	145.67(8)

The thiosemicarbazonato ligand consists of three parts: salycil (O2, C11–C16 and C1), thiosemicarbazonyl (N1, N2, C3 and N4) and *N*–phenyl (C5–C10) moieties. The salicyl and the thiosemicarbazonyl fragments are nearly coplanar – a dihedral angle between the least-square best planes defined by their atoms amounts to 3.14(8)º – while the *N*–phenyl ring is inclined to the thiosemicarbazonyl moiety by an angle of 16.88(11)º. Nevertheless, both dihedral angles allow a high degree of π-electron delocalization throughout the thiosemicarbazonato ligand as suggested by bond lengths given in Table 1. The observed bond lengths N2–C3 and S–C3 are typical for the vanadium thiosemicarbazonato complexes in which the thiosemicarbazone molecule is bonded through its deprotonated =N–NH– group.[15–20,23] As a consequence of the relatively small angle between the thiosemicarbazonyl and the *N*–phenyl fragments, an intramolecular

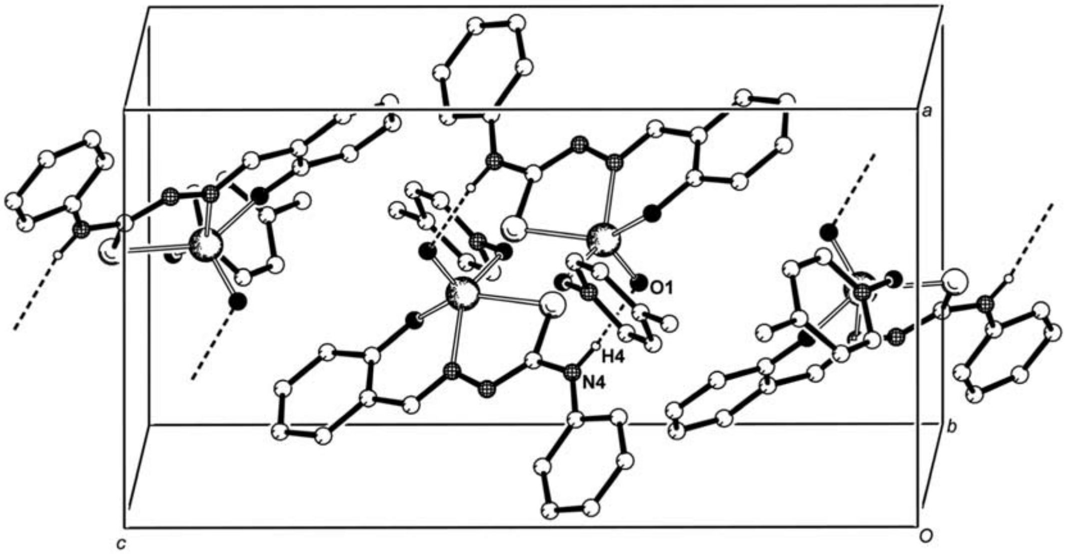


Figure 2. View of the unit cell. The molecules are connected by hydrogen bonds in the centrosymmetrical dimers. The carbon-bonded hydrogen atoms are omitted for better clarity. The intermolecular hydrogen bonds are represented by dashed lines.

hydrogen bond C10–H10···N2 [*d*(H10···N2) = 2.34 Å, *d*(C10···N2) = 2.917(3) Å, <(C10–H10···N2) = 120º] is observed. The planar molecule of 4-methylpyridine-*N*-oxide is inclined to the salicyl moiety at almost right angle [84.88(10)º] while the V–O3–N5 angle amounts to 119.61(13)º.

In the crystal of the title complex two molecules are held together in centrosymmetrical dimers forming the N4–H4···O1 (1 – *x*, 2 – *y*, –*z*) hydrogen bonds [*d*(H4···O1) = 2.27(2) Å, *d*(N4···O1) = 3.052(3) Å. <(N4–H4···O1) = 151.2(19)º] described by graph–set notation $R_2^2(12)$ (Figure 2). The dimers are further packed *via* plethora of π···π interactions between the aromatic rings of the ligands.

3. Experimental

3. 1. Materials

Salicylaldehyde, 4-phenylthiosemicarbazide, 4-methylpyridine-*N*-oxide, acetylacetone, triethylamine and V_2O_5 were commercially available and used as purchased. The ligand salicylaldehyde 4-phenylthiosemicarbazone was prepared by literature procedure.[24] [VO(acac)$_2$] was prepared by slightly modified well established method using triethylamine instead Na_2CO_3.[25] Acetonitrile was dried over phosphorus pentoxide followed by distillation.

3. 2. Methods

Elemental analyses (C, H, N and S) were provided by Analytical Services Laboratory of Rudjer Bošković Institute, Zagreb. Infrared spectra were recorded as KBr pellets using Perkin-Elmer Fourier-Transform Spectrum RX1 spectrophotometer in the 4500–450 cm^{-1} region. Thermogravimetric analysis was performed on a Mettler-Toledo TGA/SDTA851^{e} thermobalance using aluminium crucibles under oxygen atmosphere with the heating rate 5 °C min^{-1}. Temperature ranged from 25 to 600 °C. The results were developed by applying the Mettler STAR^{e} 9.01 software.

3. 3. Synthesis of (4-methylpyridine-N-oxide)oxo(salicylaldehyde 4-phenyl thiosemicarbazonato)vanadium(IV)

Salicylaldehyde 4-phenylthiosemicarbazone (100 mg, 0.37 mmol) and 4-methylpyridine-*N*-oxide (40 mg, 0.37 mmol) were dissolved in dry acetonitrile (10 mL) and the solution was refluxed under argon atmosphere for 15 minutes before addition of stoichiometric amount of [VO(acac)$_2$]. After addition of [VO(acac)$_2$], the reaction mixture was refluxed for an additional hour in argon atmosphere. On cooling, green-brown crystals separated from the solution. Crystals were filtered off and washed with small amount of cold acetonitrile.

Yield: 130 mg (79%). *Anal.* Calcd. for $C_{20}H_{18}N_4O_3SV$ (M_r = 445.39): C 53.93; H 4.07; N 12.58; S 7.20; V 11.44%. Found: C 53.84; H 4.01; N 12.49; S 7.15; V 10.90%. IR (cm^{-1}): 3320 (N–H); 1601, 1548 (C=N); 1317, 763 (C–S), 969 (V=O).

3. 4. X-ray structure analysis

The X-ray data of the title complex were collected on the Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ =

Table 2. Crystal data, data collection and structure refinement.

Chemical formula	$C_{20}H_{18}N_4O_3SV$	T_{min}/T_{max}	0.793/0.933
M_r	445.38	θ_{max} / °	28.0
Crystal color, habit	green-brown prism	Limiting indices	$-13 \le h \le 13$
Crystal size / mm^3	0.11 × 0.20 × 0.60		$-13 \le k \le 13$
Crystal system	monoclinic		$-24 \le l \le 24$
Space group	$P2_1/c$ (no. 14)	Data total/unique	14 001/4813
a / Å	10.2007(3)	Observed data [$I > 2\acute{o}(I)$]	3209
b / Å	10.4696(3)	R_{int}	0.028
c / Å	18.8090(6)	Parameters/restraints	267/1
β /	90.840(2)	$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	*0.0440, 0.1077*
V / Å^3	2008.53(10)	R_1, wR_2 (all data)	0.0746, 0.1190
Z	4	S^c	1.025
D_{calc} / (g cm^{-3})	1.473	$\Delta\rho^{max\ /\ e\ Å-3}$	0.787
$\mu(MoK_\alpha)$ / mm^{-1}	0.627	$\Delta\rho_{min}$ / e Å^{-3}	–0.297

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o\text{đ} - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
[c] $S = [(\Sigma w(|F_o| - |F_c\text{đ})^2 + \Sigma w_r(P_{calc} - P_{targ})^2)/(N_{ref} + N_{restr} - N_{par})]^{1/2}$ (the restraint applied in the refinement is explicitly included).

0.71073 Å) at room temperature. The crystallographic data are summarized in Table 2. The data reduction (including the empirical absorption correction using spherical harmonics) was performed using the CrysAlis sofware package.[26] Solution, refinement and analysis of the structure were done using the programs integrated in WinGX system.[27] The structure was solved by direct methods (SHELXS)[28] and refined by full-matrix least-squares method based on F^2 against all reflections (SHELXL-97).[28] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps. The H-atom attached to the N-atom was refined isotropically with the restrained N–H distance (0.87 Å); for the methyl H-atoms only the torsion angles were refined keeping fixed the methyl-group geometry with $U_{iso}(H) = 1.5U_{eq}(C)$ while the remaining non-methyl H-atoms attached to carbon atoms were refined using the riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. Geometrical calculations were performed using PLATON.[29] The figures were made using ORTEP[30] and PLATON.[29] CCDC 676029 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre *via* www.ccdc.cam. ac.uk/data_request/cif.

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Povzetek

Nov kompleks smo sintetizirali z reakcijo med salicilaldehid 4-feniltiosemikarbazonom in 4-metilpiridin-*N*-oksidom ter [VO(acac)$_2$]. Tetragonalno piramidalno koordinacijo okrog vanadijevega atoma sestavljajo O,N,S-donorji dvojno deprotoniziranega tiosemikarbazonato liganda, kisikovi atomi iz 4-metilpiridin-N-oksida in okso skupine v vertikalni poziciji. Kompleksne molekule so povezane z vodikovimi vezmi in s π–π interakcijami med aromatskimi obroči liganda. Kompleks smo okarakterizirali s kemijsko analizo, IR spektroskopijo, TG in rentgensko kristalografijo.