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Transition metal complexes with thiosemicarbazide-based ligands. Part 58. Synthesis, spectral and structural characterization of dioxovanadium(V) complexes with salicylaldehyde thiosemicarbazone

LJILJANA S. VOJINOVIĆ-JEŠIĆ[#], VUKADIN M. LEOVAC^{*#}, MIRJANA M. LALOVIĆ[#],
VALERIJA I. ČEŠLJEVIĆ[#], LJILJANA S. JOVANOVIĆ[#],
MARKO V. RODIĆ[#] and VLADIMIR DIVJAKOVIĆ

Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, Serbia

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Abstract: The first two complexes of dioxovanadium(V) with salicylaldehyde thiosemicarbazone (SALTSC), of the coordination formulas $[\text{VO}_2(\text{SALTSC}-\text{H})\cdot\text{H}_2\text{O}]$ (**1**) and $\text{NH}_4[\text{VO}_2(\text{SALTSC}-2\text{H})]$ (**2**), were synthesized and characterized by elemental analysis, conductometric measurements, IR and UV–Vis spectroscopy and X-ray analysis. The complexes were obtained in the reaction of an aqueous ammoniacal solution of NH_4VO_3 and SALTSC. The results of the characterization showed that SALTSC was coordinated in the usual ONS tridentate mode as monoanion in complex **1** and dianion in complex **2**. In both complexes, the vanadium atom is in a deformed square-pyramidal environment and is slightly shifted towards the apical oxo-ligand ($\approx 0.52 \text{ \AA}$).

Keywords: dioxovanadium(V) complexes; salicylaldehyde thiosemicarbazone; crystal structure; spectra.

INTRODUCTION

Thiosemicarbazones have been the subject of studies not only for coordination chemistry reasons, but for pharmacological as well, due to their good complexing properties and significant biological activity.¹ Among the most examined compounds of this group is certainly salicylaldehyde thiosemicarbazone (SALTSC) and its metal complexes.

Usually, SALTSC is coordinated as a tridentate monoanionic ligand through the oxygen atom of the deprotonated phenolic OH-group, the azomethine nitrogen atom N3 and the thionic sulfur atom. The result of such coordination is the formation of two metallocycles: a six-membered (salicylidene) and five-membered.

* Corresponding author. E-mail: vukadin.leovac@dh.uns.ac.rs

[#] Serbian Chemical Society member.

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bered (thiosemicarbazide) (Fig. 1a). Experiments have shown that SALTSC can also be coordinated as a tridentate dianion (Fig. 1b) after deprotonation of the thiosemicarbazide residue in its thiol form, which is regulated by the pH value. Another two coordination modes of this ligand are bidentate through N3 and S1, by which one 4-membered metallocycle is formed (Fig. 1c)² and monodentate through S1.³ Only one exception to this rule is known and that is the complex of MoO₂(VI), in which SALTSC is coordinated as a tridentate ONN ligand, *via* the amide N1 atom instead of the usual thionic S1 atom (Fig. 1d).⁴ This coordination mode is characteristic for *S*-alkyl-thiosemicarbazide derivatives, *i.e.* isothiosemicarbazides and isothiosemicarbazones.⁵

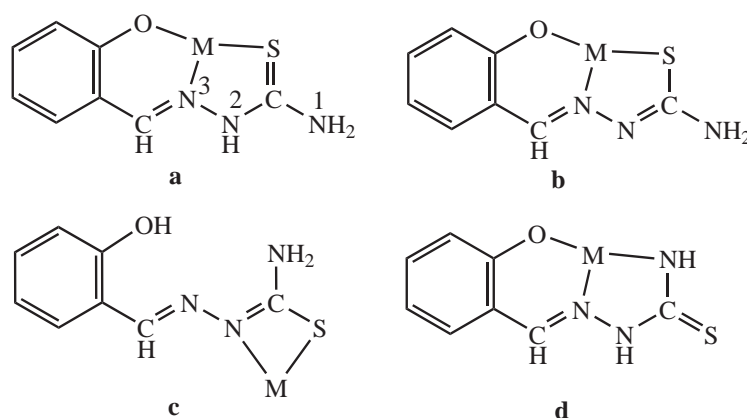


Fig. 1. Selected coordination modes of SALTSC.

The syntheses of the complexes [V(SALTSC-H)(SALTSC-2H)], NH₄[V(SALTSC-2H)₂] and [VO(SALTSC-2H)A] (A = *o*-phen, α,α' -dipy) confirm that this versatile ligand can stabilize +3 and +4 oxidation states of vanadium.^{6,7} The two new complexes of VO₂^{+(V)}, of the formulas [VO₂(SALTSC-H)·H₂O] and NH₄[VO₂(SALTSC-2H)], presented in this paper, certify that the SALTSC can stabilize the maximum oxidation state of vanadium.

EXPERIMENTAL

Reagents

All chemicals used were commercial products of analytical reagent grade, except for the ligand salicylaldehyde thiosemicarbazone, which was prepared by the reaction of EtOH solutions of salicylaldehyde and thiosemicarbazide.⁸

Synthesis of the complexes

[VO₂(SALTSC-H)·H₂O] (1) and NH₄[VO₂(SALTSC-2H)] (2). A mixture of NH₄VO₃ (0.060 g, 0.5 mmol) and SALTSC (0.098 g, 0.5 mmol) was overpoured with 5 cm³ ccNH₃ (aq) and heated for 5 min to complete the dissolution. After 12 days of standing at the room

temperature, the yellow (**1**) and orange (**2**) single crystals obtained from the orange solution were filtered and washed with EtOH. Yield (of the mixture): 0.025 g.

Analytical methods

Elemental analyses (C, H, N and S) of air-dried complexes were realized by standard micromethods in the Center for Instrumental Analyses, ICTM in Belgrade.

Molar conductivities of freshly prepared H₂O and DMF complex solutions ($c = 1.0 \times 10^{-3}$ mol dm⁻³) were measured on a Jenway 4010 conductivity meter.

IR spectra were recorded using KBr pellets on a Thermo Nicolet (NEXUS 670 FTIR) spectrophotometer in the range of 4000–400 cm⁻¹.

UV–Vis spectra in DMF solutions were recorded on a T80+ UV/Vis spectrometer PG Instruments Ltd., in the spectral range of 270–1100 nm.

Single crystal X-ray experiment of [VO₂(SALTSC–H)]·H₂O (**1**) and NH₄[VO₂(SALTSC–2H)] (**2**)

Single crystals of **1** and **2** were selected and glued on a glass fiber. Diffraction measurements were performed on an Oxford Diffraction Gemini S diffractometer equipped with a Sapphire CCD detector. The crystal to detector distance was 45 mm, and graphite monochromated MoK α (0.71073 Å) radiation was used. The data were reduced using the Oxford Diffraction program CrysAlisPRO. A semi-empirical absorption-correction was applied, and the data were corrected for Lorentz, polarization, and background effects. The structures were solved by the direct method using SIR92⁹ and refinement was performed by full-matrix least-square methods on F^2 using the SHELXL-97 program.¹⁰ All non-H atoms were refined with anisotropic displacement parameters. The positions of all H atoms were found by inspection of ΔF maps. In the final stage of refinement, the H atoms belonging to SALTSC were positioned geometrically (N–H, 0.86; C–H, 0.93 and 0.97 Å for CH and CH₃, respectively) and refined using the riding model with U_{iso} equal to 1.2 (for NH and CH) and 1.5 (for CH₃) U_{eq} of the parent atoms. Positions of the H atoms corresponding to H₂O in complex **1** and NH₄⁺ in **2** were refined with restrained N–H and O–H distances (O–H = 0.82; N–H = 0.86 Å) with U_{iso} equal to 1.5 U_{eq} of the parent atoms. The material for publication was prepared by the WINGX¹¹ and PLATON¹² programs. The crystal data and refinement parameters are listed in Table I.

TABLE I. Crystal data and refinement parameters for [VO₂(SALTSC–H)]·H₂O (**1**) and NH₄[VO₂(SALTSC–2H)] (**2**)

Empirical formula	C ₈ H ₁₀ N ₃ O ₄ SV (1)	C ₈ H ₁₁ N ₄ O ₃ SV (2)
Formula weight	295.19	294.21
Temperature, K	295(2)	295(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>Cc</i>	<i>P2₁/c</i>
Unit cell dimensions, Å	<i>a</i> = 7.7751(3) <i>b</i> = 11.2828(5) <i>c</i> = 12.8995(4) β = 92.254(4)°	<i>a</i> = 14.104(5) <i>b</i> = 6.363(5) <i>c</i> = 13.829(5) β = 113.169(5)°
Volume, Å ³	1130.73(8)	1141.0(11)
<i>Z</i>	4	4
D_c , g cm ⁻³	1.734	1.713
Absorption coefficient, μ /mm ⁻¹	1.068	1.054

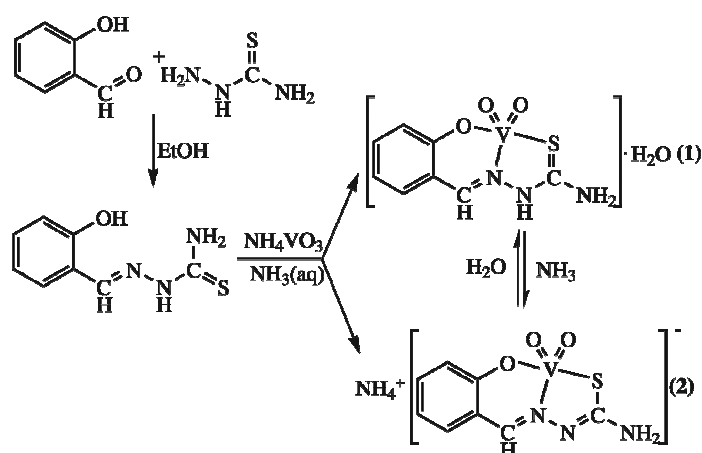
TABLE I. Continued

$F(000)$	600	600
Crystal size, mm	$0.5 \times 0.2 \times 0.1$	$0.6 \times 0.3 \times 0.1$
Color/shape	Yellow/prism	Orange/prism
Theta range, °	3.16–25.00	2.96–25.00
Index ranges $-h + h$; $-k + k$; $-l + l$	$-9 + 7$; $-9 + 13$; $-15 + 14$	$-10 + 16$; $-7 + 7$; $-16 + 16$
Reflections collected	2307	5554
Unique reflections	1433 ($R_{\text{int}} = 0.0204$)	2011 ($R_{\text{int}} = 0.0285$)
Reflections with $I > 2\sigma I_o$	1346	1680
Refinement methods	Full matrix L. S. on F^2	Full matrix L. S. on F^2
Data/restraints/parameters	1433/2/162	2011/4/170
Goodness-of-fit on F^2	1.045	1.101
Final R indices [$F_o > 4\sigma F_o$]	$R1 = 0.0308$	$R1 = 0.0398$
R indices (all data)	$R1 = 0.0338$, $wR2 = 0.0654$	$R1 = 0.0519$, $wR2 = 0.0921$
Extinction coefficient	no	no
Larg. diff. peak and hole, $e\text{Å}^{-3}$	0.26 and -0.21	0.36 and -0.23

RESULTS AND DISCUSSION

Synthesis

The ligand, SALTSC, was obtained by the reaction of warm EtOH solutions of salicylaldehyde with thiosemicarbazide in the mole ratio 1:1. The reaction of warm ammonia solutions of NH_4VO_3 and SALTSC in a mole ratio 1:1 resulted in the formation of two types of complexes: the neutral yellow $[\text{VO}_2(\text{SALTSC}-\text{H})]\cdot\text{H}_2\text{O}$ (**1**) and the monoanionic orange $\text{NH}_4[\text{VO}_2(\text{SALTSC}-2\text{H})]$ (**2**) (Scheme 1). In both complexes, SALTSC is coordinated in its usual ONS tridentate mode as a monoanion (complex **1**), formed by the deprotonation of the phenolic hydroxyl, and as a dianion (complex **2**), formed by further deprotonation of the thioureido $-\text{NH}-\text{C}(=\text{S})-\text{NH}_2$ group.



Scheme 1. Reaction scheme for the synthesis of SALTSC ligand.

Magnetic measurements showed that the obtained complexes are diamagnetic, which is further evidence of the isolation of V(V) complexes.

Complexes are stable in air, soluble in DMF, and sparingly soluble in MeOH and EtOH. Unlike complex **1**, complex **2** is soluble in water.

Molar conductivity of **1** in DMF indicates its non-electrolytic nature while the molar conductivity of **2** in both H₂O and DMF points to 1:1 electrolyte type, which is in accordance with the coordination formulas.^{13,14}

Since **2** is a strong base, the protonation of the nitrogen atom N2 of the coordinated thiosemicarbazide moiety in aqueous solution leads to the formation of **1**. The reconversion to the complex **2** can be achieved by deprotonation of the neutral complex **1** in NH₃. A similar reversible reaction was described for the complex NH₄[VO₂(salhyph)], where salhyph stands for the dianion of the tridentate ONO Schiff base derived from salicylaldehyde and benzoic acid hydrazide.¹⁵

The presented reactions involved no essential chemical transformations of SALTSC. This is emphasized here because it is known that the reaction in a similar environment, *i.e.*, aqueous–ammonia solution of VO₂SO₄ and SALTSC, leads to the partial decomposition of SALTSC to thiosemicarbazide and salicylaldehyde moieties.⁷ Here, salicylaldehyde is condensed with an amide NH₂-group of the undecomposed SALTSC and a square-pyramidal complex of VO²⁺ with *in situ* obtained tetradentate O₂N₂ ligand bis(salicylidene)-thiosemicarbazide is formed. This leads to the conclusion that, unlike VO²⁺, VO₂⁺ is not a suitable template center for the mentioned SALTSC transformation.

Analytical and spectral characteristics

[VO₂(SALTSC–H)]·H₂O (**1**). Anal. Calcd. for C₈H₁₀N₃O₄SV (*FW* = 295.19): C, 32.55; H, 3.41; N, 14.23; S, 10.86 %. Found: C, 32.48; H, 3.30; N, 14.08; S, 10.49 %. FTIR (KBr, cm⁻¹): 3154, 1638, 1549, 915, 902, 761. UV–Vis (λ_{\max} / nm (log (ϵ / mol⁻¹ dm³ cm⁻¹)): 276 (4.20), 307*sh* (4.11), 336 (3.53), 350*sh* (3.08), 382 (3.28) (*sh*-shoulder). λ_M (DMF, 1.0×10⁻³ mol dm⁻³): 9.5 S cm² mol⁻¹.

NH₄[VO₂(SALTSC–2H)] (**2**). Anal. Calcd. for C₈H₁₁N₄O₃SV (*FW* = 294.20): C, 32.66; H, 3.77; N, 19.04; S, 10.90 %. Found: C, 32.48; H, 3.66; N, 18.83; S, 10.69 %. FTIR (KBr, cm⁻¹): 3144, 1620, 1550, 915, 890, 767. UV–Vis (λ_{\max} / nm (log (ϵ / mol⁻¹ dm³ cm⁻¹)): 275*bp* (4.15), 320*sh* (3.28), 384 (3.73) (*bp*-broad peak). λ_M (H₂O, 1.0×10⁻³ mol dm⁻³): 99 S cm² mol⁻¹. λ_M (DMF, 1.0×10⁻³ mol dm⁻³): 47 S cm² mol⁻¹.

IR spectra

X-Ray analysis of the obtained complexes (*vide infra*) showed that the SALTSC was coordinated in the usual way,⁸ *i.e.*, *via* the phenolic group oxygen, azomethine nitrogen and sulfur atom of the thionic (complex **1**) or thiolic (complex **2**) group. This mode of coordination was confirmed by the IR spectra.

In the IR spectrum of SALTSC, the characteristic $\nu(\text{OH})$ band is observed at 3444 cm^{-1} . The absence of this band in the IR spectra of the complexes indicates the coordination through the phenolic oxygen O1. Additional evidence of O1 coordination is the positive shift of the $\nu(\text{C-O})$ band ($\approx 10\text{ cm}^{-1}$) in the IR spectra of the complexes, compared to the IR spectrum of the ligand.¹⁶

The IR band $\nu(\text{CH=N})$ appearing at 1616 cm^{-1} in the free ligand spectrum is shifted towards higher wavenumbers in the spectra of the complexes (1638 and 1620 cm^{-1} , respectively) due to the involvement of the azomethine nitrogen in coordination.^{16–22}

Unlike aforementioned bands, the $\nu(\text{C=S})$ band is shifted to the lower energy region in the IR spectra of both complexes (761 and 767 cm^{-1}) in comparison to the IR spectrum of the free SALTSC (777 cm^{-1}).¹⁷

The strong band at 3170 cm^{-1} can be attributed to $\nu(\text{N}^2\text{-H})$ vibrations. In free SALTSC, the N2 is involved in a H-bond with the sulfur atom of an adjacent molecule,²² but in the complexes this bond disappears as a consequence of sulfur atom coordination. However, in the structure of complex **1**, instead of the $\text{N}^2\text{-H}\cdots\text{S}1$, an H-bond with O4 is formed. Since the H-bond with oxygen is stronger than with the sulfur atom, $\nu(\text{N}^2\text{H})$ is found to undergo a downfield shift after complexation.

Very strong bands observed in the region characteristic for the *cis*- VO_2 group, *i.e.*, 915 and 902 cm^{-1} in **1** and 915 and 890 cm^{-1} in **2**, arise from $\nu_{\text{sym/asym}}(\text{VO}_2^+)$ vibrations.^{23,24}

Electronic spectra

In the available spectral range in DMF ($270\text{--}1100\text{ nm}$), the two complexes absorbed only at wavelengths up to 450 nm . The spectral characteristics resemble those reported previously for iron(III) complexes with the same deprotonated ligand forms in this solvent.^{25,26} Generally, the absorptions at $\lambda < 350\text{ nm}$ appear as unresolved bands resulting from the intraligand transitions ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$). Similarly to the mentioned Fe(III) and other previously reported VO_2^+ complexes with pyridoxal thiosemicarbazone derivatives,²³ the band registered at higher λ ($\approx 380\text{ nm}$) is attributable to ligand-to-metal charge-transfer (LMCT) complex. As expected, no d–d interactions could be observed in the visible spectral range.

Crystal structure of $[\text{VO}_2(\text{SALTSC-H})]\cdot\text{H}_2\text{O}$ (**1**) and $\text{NH}_4[\text{VO}_2(\text{SALTSC-2H})]$ (**2**)

Molecular structures of the obtained complexes are shown in Figs. 2 and 3, respectively, and selected bond distances and angles for the complexes and free ligand are given in Table II. The asymmetric unit of **1** contains the neutral complex molecule and one water molecule involved in H-bonding with the complex molecule. The complex molecule consists of a tridentate monodeprotonated li-

gand, chelating the VO_2^+ . In the asymmetric unit of **2**, there are the complex anion and the NH_4^+ , which are linked by a dominant electrostatic interaction and a moderate H-bond.

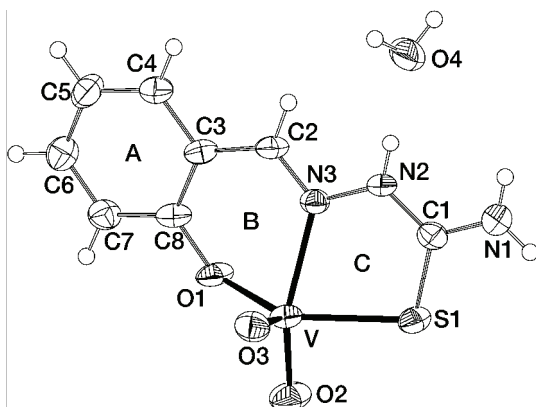


Fig. 2. Molecular structure of $[\text{VO}_2(\text{SALTSC-H})]\cdot\text{H}_2\text{O}$ (**1**).

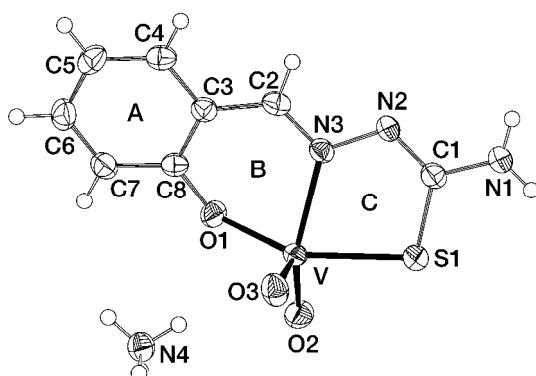


Fig. 3. Molecular structure of $\text{NH}_4[\text{VO}_2(\text{SALTSC-2H})]$ (**2**).

In both complexes, tridentate coordination of the SALTSC results in a square-pyramidal configuration usual for VO_2^+ -complexes with one oxo-ligand in the basal plane and the other in the apical position. It is interesting to notice that the vanadium atom is in an almost ideal square-pyramidal environment ($\tau = 0.052$) in **2**, unlike the vanadium atom in **1**, in which the square-pyramidal environment is significantly distorted. The vanadium atom is shifted from the basal O1-N3-S1-O2 plane towards the apical oxo-ligand in both complexes ($\approx 0.52 \text{ \AA}$). The VO_2 -group is in the *cis*-configuration with the usual value of the O-V-O angle²³ ($108.2(2)$ in **1** and $108.7(1)^\circ$ in **2**). As mentioned above, the SALTSC is coordinated in a common tridentate ONS mode, which results in the formation of two metallocycles: one six-membered (B, salicylidene) and one five-membered (C, thiosemicarbazide). In **1**, the SALTSC is coordinated as a monoanion formed by

deprotonation of the phenolic OH-group. However, in **2**, a further deprotonation of the thiolic group occurs, resulting in a dianion of the ligand.

TABLE II. Selected bond distances and bond angles for $[\text{VO}_2(\text{SALTSC-H})]\cdot\text{H}_2\text{O}$ (**1**), $\text{NH}_4[\text{VO}_2(\text{SALTSC-2H})]$ (**2**) and SALTSC

Bond	Distance, Å		SALTSC
	1	2	
V–O1	1.895(2)	1.906(2)	–
V–N3	2.217(4)	2.186(3)	–
V–S1	2.383(1)	2.358(2)	–
V–O2	1.626(3)	1.639(3)	–
V–O3	1.629(3)	1.631(2)	–
O1–C8	1.336(5)	1.340(4)	1.356(3)
C2–N3	1.287(5)	1.296(4)	1.276(3)
N3–N2	1.382(5)	1.394(4)	1.380(4)
C1–N2	1.319(5)	1.300(4)	1.346(4)
C1–N1	1.324(5)	1.350(5)	1.317(4)
C1–S1	1.717(4)	1.734(3)	1.689(4)
	Angle, °		
	1	2	
O3–V–O2	108.3(2)	108.7(1)	–
O1–V–S1	139.32(9)	149.44(8)	–
N3–V–O2	155.6(1)	146.3(1)	–
O1–V–O2	98.5(1)	95.6(1)	–
O2–V–S1	88.2(1)	87.63(9)	–
S1–V–N3	76.99(9)	77.30(7)	–
N3–V–O1	81.2(1)	83.6(1)	–

Based on a previously known crystal structure of the free ligand²⁷ and two new structures of its complexes with VO_2^+ presented in this paper, it is possible to make comparative analysis of the corresponding geometric parameters. In neutral, uncoordinated SALTSC, the thiocarbonylic sulfur atom is in a *trans*-position with respect to the other two ligators N3 and O1. In the complexation reaction, rotation around the C1–N2 bond brings all the ligators into *cis*-positions that are maintained in the complexes.

The chelate ligand donors–vanadium bond distances V–O1, V–N3 and V–S1 in **1** are 1.895(2), 2.217(4) and 2.383(1) Å and in **2** 1.906(2), 2.186(3) and 2.358(2), respectively. In **1**, the V–N3 bond is slightly longer compared to the same bond in **2**, probably because of the stronger *trans*-influence of the O2 oxygen, which in this complex is placed at a shorter distance from the vanadium atom. It is noticeable that the V–S1 bond is shorter in **2** than in **1**, which is in accordance with better electron-donor properties of the thiol compared to the thione sulfur atom. The two oxo-ligands are at the almost same distance from the vanadium atom in **1**, unlike the complex **2** in which apical oxo-ligand O2 forms a

shorter bond with vanadium atom than the basal oxygen O3. Since the thiosemi-carbazide residue is in its thiolate form, both oxo-ligands in **2** are further from the vanadium atom than in **1**.

The average V=O distances 1.627 Å in **1** and 1.635 Å in **2**, being slightly longer than the normal V=O double bond length of 1.595 Å, indicate that the oxygens are involved in moderate hydrogen-bonding interactions.²⁴

The C2–N3 and N3–N2 bond distances have the values of localized double and single bond, respectively, in both complexes and in the free ligand as well. However, the slight elongation of these bonds in the complexes is a consequence of the involvement of the nitrogen N3 in the coordination. The other two C–N bonds, *i.e.*, C1–N1 and C1–N2, in the complexes are, due to the delocalization, shorter than a formal single, but longer than a formal double bond.²

It is also worth mentioning that the C1–N1 bond in free SALTSC is shorter (1.317(4) Å) than in the complexes, especially in **2**. This is evidence of the effect of the sulfur atom on the movement of electron density towards the metal atom. The shortening of the C1–N2 bond in **2** compared to the bond length in **1** can be explained by the deprotonation of the nitrogen atom N2, as well as by the involvement of an additional electron in the delocalization.

As expected, it was found that the thioketo C1–S1 bond in **1** is longer than the same bond in the free ligand, due to the coordination effect. In **2**, the increased single-bond character expected in the deprotonated form of the thioureido group makes this bond even longer. A similar elongation trend of the C1–S1 bond was found in some other structures containing the thioketoureido fragment.²⁸ In both complexes, the C8–O1 bond is shorter than the single C(*sp*²)–O bond found in the free ligand (1.356(3) Å). Namely, the oxygen atom O1 is deficient in electron density as a consequence of the coordination, and the π -electron cloud is shifted from the benzene ring towards the oxygen O1. This process results in contraction of the C8–O1 bond.

As expected, the whole ligand molecule, which possesses an extended system of conjugated double bonds, in **1** is planar (the maximum distance of the mean plane 0.110 Å for the N3). Hence, the five-membered chelate ring (C) has an envelope conformation (E₁) and the six-membered (B) is in the conformation close to a half-chair. In **2**, the ligand is distorted and twisted along the C2–C3 bond with a torsion angle C8/C2/C3/N2 of –10.4°, and, as a result, the C ring becomes planar, but the B ring remains in the conformation close to a half-chair. These conformations of the B and C rings result in a decreased difference between the trans-basal angles and, therefore, in a decreased value of the τ -parameter with respect to **1**.

The crystal lattice of both complexes is stabilized by an inter- and intramolecular hydrogen-bond network. The H-bond parameters are given in Tables III and IV.

In the asymmetric unit of **1**, the complex molecule is linked by the moderate H-bond²⁹ N2–H2N...O4 to water, and in **2**, by the moderate H-bond N4–H4B...O3 formed between the complex anion and NH₄⁺.

TABLE III. Hydrogen-bonding geometry in [VO₂(SALTSC–H)]·H₂O (**1**); equivalent positions: *i*) $x+1/2, -y+3/2, z-1/2$; *ii*) $x+1/2, y-1/2, z$; *iii*) $x+1/2, -y+3/2, z-1/2$; *iv*) $x, -y+2, z-1/2$

<i>D</i> –H... <i>A</i>	Distance, Å		<i>D</i> –H... <i>A</i> angle, °
	<i>D</i> – <i>A</i>	H... <i>A</i>	
N2–H2N...O4	2.653(5)	1.79	179.1
N1–H1A...O2 ^{<i>i</i>}	3.043(5)	2.24	155.8
N1–H1B...O3 ^{<i>ii</i>}	2.917(5)	2.12	153.7
O4–HW1...O1 ^{<i>iii</i>}	2.820(5)	2.01(7)	166(6)
O4–HW2...O3 ^{<i>iv</i>}	2.698(5)	1.86(9)	163(8)

TABLE IV. Hydrogen-bonding geometry in NH₄[VO₂(SALTSC–2H)] (**2**); equivalent positions: *i*) $-x+2, -y+1, -z+2$; *ii*) $-x+1, -y, -z+2$; *iii*) $-x+1, y-1/2, -z+3/2$; *iv*) $x, -1+y, z$

<i>D</i> –H... <i>A</i>	Distance, Å		<i>D</i> –H... <i>A</i> angle, °
	<i>D</i> – <i>A</i>	H... <i>A</i>	
N4–H4B...O3	2.850(4)	2.00(3)	169(4)
N1–H1A...N2 ^{<i>i</i>}	3.050(4)	2.30	146.4
N4–H4A...O1 ^{<i>ii</i>}	3.028(4)	2.17(3)	173(4)
N4–H4C...O2 ^{<i>iii</i>}	2.866(4)	2.04(3)	158(3)
N4–H4D...O3 ^{<i>iv</i>}	2.904(4)	2.01(3)	175(4)

The packing of the structural units in **1** is shown in Fig. 4, from which it can be seen that the complex molecules form C-layers that are parallel to the *ab* plane

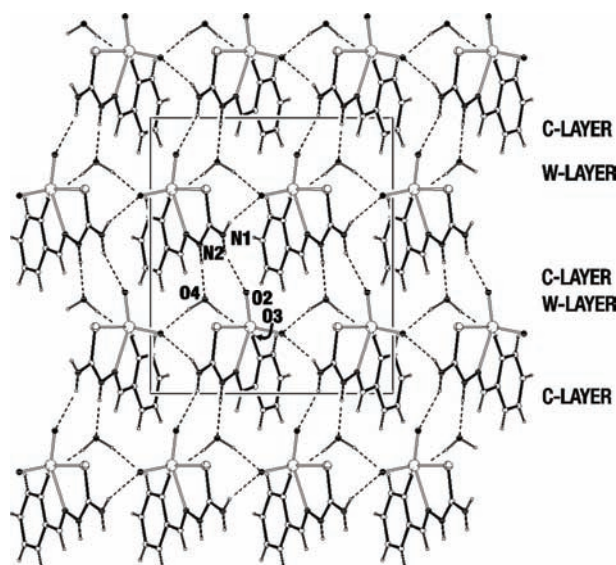


Fig. 4. Crystal packing diagram of complex **1** viewed perpendicular to the *bc* plane.

at the levels $c = 0$, $c = 1/2$ and $c = 1$. At the levels $c = 1/4$ and $c = 3/4$, water molecules form a W-layer, with one apical oxo-ligand between two water molecules. Within one C-layer, there is the N1–H1B...O3 H-bond, linking the molecules and another H-bond, N1–H1B...O3, which ties in the adjacent C-layers. Three moderate H-bonds, *i.e.*, N2–H2N...O4, O4–HW1...O1 and O4–HW2...O3, associate the W-layer with the neighboring C-layers.

The packing of the structural units in **2** is shown in Fig. 5. C-double layers are formed by the complex anions placed in the bc plane at the levels $a = 0$ and $a = 1$ linked by the N1–H1A...N2 H-bond. The NH_4^+ ions form A-layers parallel to the bc plane at $a = 1/2$. Between the C-double-layers and the A-layers, there are moderate H-bonds, *i.e.*, N4–H4B...O3, N4–H4A...O1, N4–H4C...O2 and N4–H4D...O3. A similar layered structure was reported for the abovementioned complex $\text{NH}_4[\text{VO}_2(\text{saltyph})]$.¹⁵

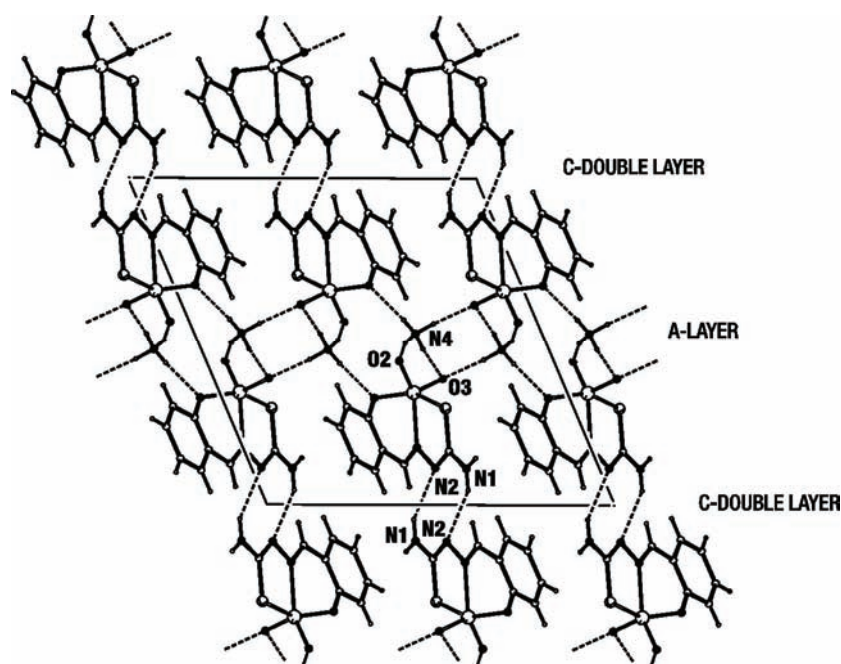


Fig. 5. Crystal packing diagram of complex **2** viewed perpendicular to the ac plane.

Crystallographic data reported for the complex $[\text{VO}_2(\text{SALTSC-H})]\cdot\text{H}_2\text{O}$ and $\text{NH}_4[\text{VO}_2(\text{SALTSC-2H})]$ have been deposited under the CCDC Nos. CCDC-801721 and 801722. Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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ИЗВОД

КОМПЛЕКСИ ПРЕЛАЗНИХ МЕТАЛА СА ЛИГАНДИМА НА БАЗИ
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КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА ДИОКСОВАНАДИЈУМА(V) СА
ТИОСЕМИКАРБАЗОНОМ САЛИЦИЛАЛДЕХИДА

ЉИЉАНА С. ВОЈИНОВИЋ-ЈЕШИЋ, ВУКАДИН М. ЛЕОВАЦ, МИРЈАНА М. ЛАЛОВИЋ, ВАЛЕРИЈА И.
ЧЕШЉЕВИЋ, ЉИЉАНА С. ЈОВАНОВИЋ, МАРКО В. РОДИЋ И ВЛАДИМИР ДИВЈАКОВИЋ

Prirodno–matemati–ki fakultet, Univerzitet u Novom Sadu, Trg D. Obradovića 3, 21000 Novi Sad

Описане су синтезе и структуре прва два комплекса диоксованадијума(V) са триден-
татним ONS тиосемикарбазоном салицилалдехида (SALTSC), формула $[\text{VO}_2(\text{SALTSC}-\text{H})\cdot\text{H}_2\text{O}]$ (**1**) и $\text{NH}_4[\text{VO}_2(\text{SALTSC}-2\text{H})]$ (**2**). Комплекси су добијени као смеша кристала у
реакцији водено-амонијачног раствора NH_4VO_3 и SALTSC. Комплекси су окарактерисани
елементалном и рендгено-структурном анализом, кондуктометријским мерењима, IR- и UV-
–Vis спектрима. Рендгено-структурна анализа је показала да комплекс **1** има деформисану, а
комплекс **2** скоро идеалну квадратно-пирамидалну геометрију са атомом ванадијума поме-
реним ка апикалном оксо-лиганду за око 0,52 Å.

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