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Transition metal complexes with thiosemicarbazide-based ligands. Part 57. Synthesis, spectral and structural characterization of dioxovanadium(V) and dioxomolybdenum(VI) complexes with pyridoxal *S*-methylisothiosemicarbazone

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Abstract: This work is concerned with the synthesis of neutral dioxovanadium(V) and dioxomolybdenum(VI) complexes with tridentate ONN pyridoxal *S*-methylisothiosemicarbazone (PLITSC) of the respective formulas [VO₂(PLITSC–H)]·2H₂O and [MoO₂(PLITSC–2H)]. Structural X-ray analysis of the vanadium complex showed that it has an almost ideal square-pyramidal structure, while the molybdenum complex is supposed to have a polymeric octahedral structure. In addition to elemental analysis, both complexes were characterized by conductometric and magnetometric measurements, as well as by IR, UV–Vis, ¹H- and ¹³C-NMR spectra.

Keywords: dioxovanadium(V); dioxomolybdenum(VI); complexes; pyridoxal *S*-methylisothiosemicarbazone; crystal structure; spectra.

INTRODUCTION

Due to their interesting physicochemical, structural, and biological properties, tridentate ONS Schiff-bases derivatives of pyridoxal (one of the forms of vitamin B₆), along with the unsubstituted and substituted thiosemicarbazide (PLTSC), as well as their complexes, have constantly attracted research interest during the last 20 years. As a result, a number of complexes have been prepared and studied with different metals,[1–4] including the most recently synthesized complexes of V(V)[5] and Mo(VI,V)[6] with these ligands. In contrast to the numerous metal complexes with PLTSC, interest in tridentate ONN pyridoxal isothiosemicarbazone is of a more recent date, so that only a limited number of complexes, namely with

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Cu(II), Fe(III) and Co(III),[1] have been prepared and characterized. In view of the biological importance of not only molybdenum,[7,8] but also of vanadium,[9,10] together with the more recently reported biological activity of some isothiosemicarbazones,[11,12] it is not surprising that the synthesis of complexes of these metals with the mentioned ligands aroused also a notable interest. Hence, the objective of this work was to study the syntheses, as well as the spectral and structural characteristics of the neutral complexes of dioxovanadium(V) and dioxomolybdenum(VI) with pyridoxal *S*-methylisothiosemicarbazone (PLITSC) of the formula $[VO_2(PLITSC–H)]\cdot 2H_2O$ and $[MoO_2(PLITSC–2H)]$.

EXPERIMENTAL

Reagents

All the employed chemicals were commercially available products of analytical reagent grade, except for the ligand pyridoxal *S*-methylisothiosemicarbazone and $MoO_2(acac)_2$, which were prepared according to known procedures.[13,14]

Synthesis of the complexes

[VO₂(PLITSC–H)]·2H₂O. Over a mixture of NH_4VO_3 (0.070 g, 0.60 mmol) and $PLITSC\cdot H_2O$ (0.160 g, 0.60 mmol) was poured 3 cm³ ccNH₃ (aq.) and 3 cm³ MeOH and the mixture was refluxed for about 1.5 h. After 50 h standing at room temperature, orange crystals formed which were filtered and washed with MeOH. Yield: 0.14 g (64 %).

[MoO₂(PLITSC–2H)]. Over a mixture of 0.27 g (1.0 mmol) of $PLITSC\cdot H_2O$ and 0.33 g (1.0 mmol) $MoO_2(acac)_2$ was poured 15 cm³ EtOH and the mixture was refluxed for 1 h. The readily soluble reactants formed a red solution from which, while still warm, a microcrystalline orange complex precipitated. After warm filtration, the precipitate was washed with EtOH. Yield: 0.20 g (74 %).

Analytical methods

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

The molar conductivities of freshly prepared DMF solutions ($c = 1.0\times10^{-3}$ mol/dm³) were measured on a Jenway 4010 conductivity meter.

The magnetic susceptibilities were measured on an MSB-MKI magnetic balance (Sherwood Scientific Ltd., Cambridge, England).

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

The electronic UV–Vis spectra in DMF solutions were recorded on a T80+UV/Vis spectrometer, PG Instruments Ltd., in the spectral range of 260–1000 nm.

The ¹H- and ¹³C-NMR spectra were collected on a Varian Gemini 200 instrument operating at 200 MHz in DMSO-d_6 solution, with TMS as the internal standard.

Single crystal X-ray experiment of [VO₂(PLITSC–H)]·2H₂O

A single crystal was selected and glued on glass threads. Diffraction data were collected at 150 K on a Bruker Platform three-circle goniometer equipped with SMART 1K CCD detector. The crystal to detector distance was 30 mm. Graphite monochromated MoKα X-radiation ($\lambda = 0.71073$ Å) was employed. A frame width of 0.3° in ω, with 10 s exposure per frame was used to acquire each frame. The data were reduced using the Bruker program Saint

(Siemens, 1995). A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied (program SADABS, Siemens, 1996), and the data were corrected for Lorentz, polarization, and background effects. Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from International Tables for X--ray Crystallography.[15] The structure was solved by SIR92 – a program for automatic solution of crystal structures by direct methods,[16] and the figures were drawn using Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures.[17] Refinements were based on F^2 values and realized by full-matrix least-squares (SHELXL-97)[18] with all non-H atoms anisotropic. The positions of all non-H atoms were located by direct methods. Although all H atoms were possible to find in the ΔF maps, with the exception of the H atoms belonging to the water molecules, all others were positioned geometrically and refined using a riding model. The crystal data and refinement parameters for [VO$_2$(PLITSC–H)]·2H$_2$O are listed in Table I.
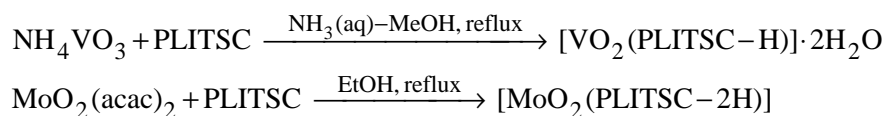
TABLE I. Crystal data and refinement parameters for [VO$_2$(PLITSC–H)]·2H$_2$O

Empirical formula	C$_{10}$H$_{17}$N$_4$O$_6$SV
Formula weight	372.28
Temperature, K	150
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions, Å	$a = 9.1713(2)$, $\alpha = 113.6716(8)°$
	$b = 9.2715(2)$, $\beta = 93.1788(8)°$
	$c = 10.3170(2)$, $\gamma = 107.6116(8)°$
Volume, Å^3	749.91(3)
Mosaicity, °	0.398(2)
Z	2
D_c / g cm^{-3}	1.649
D_0 / g cm^{-3}	1.59
Absorption coefficient, mm^{-1}	0.84
F(000)	384
Crystal size, mm	0.25 x 0.13 x 0.08
Color/shape	orange/prism
Theta range	2.55-27.48°
Index ranges $-h + h$; $-k + k$; $-l +l$	$-11 +11$; $-12 +12$; $-13 +12$
Reflections collected	6514
Unique reflections	3402 ($R_{int} = 0.0167$)
Refinement methods	Full matrix L.S. on F^2
Data/restraints/parameters	3402/0/267
Goodness-of-fit on F^2	1.049
Final R indices ($F_0 > 4$sigF$_0$)	$R1 = 0.0260$
R indices (all data)	$R1 = 0.0298$, $wR2 = 0.0778$
Extinction coefficient	No
Larg. diff. peak and hole, e Å^{-3}	0.41 and -0.30

RESULTS AND DISCUSSION

Synthesis

The dioxo complexes of vanadium(V) and molybdenum(VI) were obtained by the reaction of a warm ammonia–methanolic solution of NH_4VO_3, or an ethanolic solution of $MoO_2(acac)_2$, with pyridoxal *S*-methylisothiosemicarbazone (PLITSC) in a mole ratio 1:1 (Scheme 1).

$$NH_4VO_3 + PLITSC \xrightarrow{\ NH_3(aq)-MeOH,\ reflux\ } [VO_2(PLITSC-H)] \cdot 2H_2O$$

$$MoO_2(acac)_2 + PLITSC \xrightarrow{\ EtOH,\ reflux\ } [MoO_2(PLITSC-2H)]$$

Scheme 1. Formation of the dioxovanadium(V) and dioxomolybdenum(VI) complexes.

As was to be expected, the obtained complexes were diamagnetic, which means that no change occurred in the metal oxidation state during the reaction.

Both complexes were stable in air. The mass loss after isothermal heating at 110 °C of the vanadium complex was 9.58 %, which corresponds to the departure of two water molecules (9.67 %).

The complexes were sparingly soluble in H_2O, MeOH and EtOH, and better in DMF.

The low values of the molar conductivities of DMF solutions of the complexes are in accordance with their coordination formulas. As is evident from the formulas, the vanadium complex contained a monoanionic, and molybdenum complex a dianionic form of the tridentate ONN ligand PLITSC. The monoanionic form of the ligand, as well as in its complexes with some other metals,[1] is formed by deprotonation of the isothiosemicarbazide, while the dianionic form by additional deprotonation of the pyridoxal moiety, which results in the formation of neutral complexes in both cases.

The deprotonation of the pyridinium moiety of PLITSC in the molybdenum complex is facilitated by the good proton-acceptor properties of both substituted acetylacetonato anions.

Analytic and spectral characteristics

PLITSC·H$_2$O ligand. FTIR (KBr, cm^{-1}): 3368, 3094, 2850, 1662, 1491, 1254, 1152, 1020. ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 12.12, 11.72 (1H, *s*, phenolic OH), 8.69, 8.58 (1H, *s*, azomethine), 7.89 (1H, *s*, pyridine C-6); 7.23, 7.21 (2H, *s*, NH$_2$), 5.31, 5.28, (1H, *t*, *J* = 5.22 Hz, OH, hydroxymethyl), 4.60, 4.58 (2H, *d*, *J* = 5.22 Hz, CH$_2$), 2.47, 2.41 (3H, *s*, CH$_3$–S); 2.39, 2.38 (3H, *s*, CH$_3$–Py). ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 167.36, 162.83 (N=C(N)–S), 152.26, 151.04 (CH=N), 148.37 (C-3, Py), 146.95 (C-2, Py), 138.88, 138.71 (C-6, Py), 132.45, 132.14 (C-5, Py), 121.06 (C-4, Py), 58.95 (CH$_2$), 19.07 (CH$_3$–Py),

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12.81 (CH$_3$–S). UV–Vis (DMF; λ_{max}/ nm (log (ε / mol^{-1} dm^3 cm^{-1})): 325 (4.45), 352 (4.43), 365 (4.38).

[VO$_2$(PLITSC–H)]·2H$_2$O. Yield: 0.14 g (64 %), Anal. Calcd. for C$_{10}$H$_{17}$N$_4$O$_6$SV (FW = 372.28): C, 32.26; H, 4.50; N, 15.05; S, 8.61 %. Found: C, 32.48; H, 4.31; N, 14.83; S, 8.40 %. FTIR (KBr, cm^{-1}): 3401, 3265, 2852, 2730, 2070, 1650, 1613, 1455, 1375, 920, 907. ^{1}H-NMR (200 MHz, DMSO-d_6, δ / / ppm): 8.83 (1H, *s*, azomethine), 7.96 (1H, *bs*, NH), 7.88 (1H, *s*, pyridine C-6), 5.72 (2H, very *bs*, hydroxymethyl OH and pyridinium H), 4.76 (2H, *s*, CH$_2$), 2.51 (3H, *s*, CH$_3$–S), 2.48 (3H, *s*, CH$_3$–Py). ^{13}C-NMR (50 MHz, DMSO-d_6, δ / / ppm): 172.90 (N=C(N)–S), 157.65 (CH=N), 146.46 (C-3, Py), 142.13 (C-2, Py), 135.73 (C-6, Py), 128.00 (C-5, Py), 127.26 (C-4, Py), 58.76 (CH$_2$), 16.82 (CH$_3$–Py), 13.73 (CH$_3$–S). UV–Vis (DMF; λ_{max} / nm (log (ε / mol^{-1} dm^3 cm^{-1})): 273 (4.22), 356 (3.92), 418 (4.02). Λ_M (DMF) = 3.2 S cm^2 mol^{-1}.

[MoO$_2$(PLITSC–2H)]. Yield: 0.20 g (74 %); Anal. Calcd. for C$_{10}$H$_{12}$MoN$_4$O$_4$S (FW = 380.43): C, 31.57; H, 3.18, N; 14.73; S, 8.43 %. Found: C, 31.69; H, 3.27; N, 14.70; S, 8.44 %. FTIR (KBr, cm^{-1}): 3294, 1638, 1450, 1344, 1160, 945, 926, 908. ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 9.41 (1H, *s*, NH), 8.68 (1H, *s*, azomethine), 7.91 (1H, *s*, pyridine C-6), 5.54, (1H, *t*, J = 5.22 Hz, OH, hydroxyme-thyl), 4.62 (2H, *d*, J = 5.22 Hz, CH$_2$), 2.48 (3H, *s*, CH$_3$–S), 2.33 (3H, *s*, CH$_3$–Py). ^{13}C-NMR (50 MHz, DMSO-d_6, δ / ppm): 172.58 (N=C(N)–S), 153.56 (CH=N), 148.68 (C-3, Py), 146.49 (C-2, Py), 139.71 (C-6, Py), 134.12 (C-5, Py), 123.50 (C-4, Py), 59.31 (CH$_2$), 19.92 (CH$_3$–Py), 14.51 (CH$_3$–S). UV–Vis (DMF; λ_{max} / / nm (log (ε / mol^{-1} dm^3 cm^{-1})): 308 (4.22), 364 *sh* (3.81), 441 (3.50). Λ_M(DMF) = = 7.5 S cm^2 mol^{-1}.

IR Spectra

The X-ray analysis of the square-pyramidal vanadium complex (*vide infra*) showed that the PLITSC was coordinated in the usual way,[1] *i.e.*, *via* the oxygen of the phenolic group, the azomethine nitrogen and the nitrogen atom of the de-protonated amino group of the isothioamide fragment (Figs. 1 and 2). In addition, the analysis showed that the pyridoxal moiety occurred in a zwitterionic form, with the protonated pyridine nitrogen and deprotonated aromatic phenolic group. The occurrence of a protonated pyridine nitrogen atom, apart from the X-ray analysis, is also suggested by the appearance of a broader ν(NH$^+$) band in the IR spectrum in the range 2730–2850 cm^{-1},[1,4] which was missing from the spectrum of the molybdenum complex, in which this ligand is coordinated as a dianion.

In the IR spectra of both complexes, the characteristic bands of the *cis*-MO$_2^{n+}$ group, recognizable by their strong intensity, can easily be identified Thus, the $\nu_{sym/asym}$(VO$_2^+$) bands were observed at 920 and 907 cm^{-1}, respectively, *i.e.*, in the range characteristic for the *cis*-VO$_2$ moiety.[19,20] As X-ray structural analysis of the MoO$_2^{2+}$ complex was not possible in that study[19,20], which was the case in

the present work, the number and position of the $\nu(MoO_2^{2+})$ bands may indicate the role of the MoO_2 group (terminal, bridging) and, thus, also the structure (monomer, dimer, polymer) of the complex. Namely, it is known from the literature[6,8] that the great majority of these complexes have an octahedral structure. In the case of the very frequent neutral monomeric complexes of MoO_2^{2+} with tridentate dianionic ligands, the tendency of MoO_2 to enter the hexacoordination was so pronounced that the sixth coordination site, apart from the typical neutral monodentate donors (Py, DMSO, DMF, PPh_3, H_2O), could also be occupied by some more weakly coordinated ligands, such as EtOH, MeOH, acetaldehyde.[14] The spectra of such complexes have, as a rule, two very strong bands in the region of 950–880 cm^{-1}, of which the one at the higher energy corresponds to the symmetric and the other to asymmetric stretching vibrations of the *cis*-MoO_2 group.[21] In some cases, these bands are split due to the crystal packing effect.[22] In the absence of a monodentate donor, the hexacoordination of molybdenum is most often realized *via* the intermolecular molybdenum···oxygen interaction, with the formation of a double oxygen bridge Mo_2O_2 (μ-O)$_2$[6,23,24] or the Mo=O···Mo interaction in polymeric complexes,[6,14,25,26] which results in the appearance of very strong bands in the 850–800 cm^{-1} region of the IR spectra.[27–29] In view of the composition of the present tridentate complex and absence of a band in the region of 850–800 cm^{-1}, together with the presence of three bands that correspond to the terminal (bridging) *cis*-MoO_2 group (945, 926 and 908 cm^{-1}), the isolated complex can be thought of as having either a pentacoordinated structure,[6,30] very rare for MoO_2^{2+}, or the usual dimer/polymer octahedral structure, but without the participation of the Mo=O···Mo bridge. This means that the dimer/polymer octahedral structure of the present complex in the coordination of PLITSC may be realized, apart from the oxygen atom of the phenoxy group, *via*
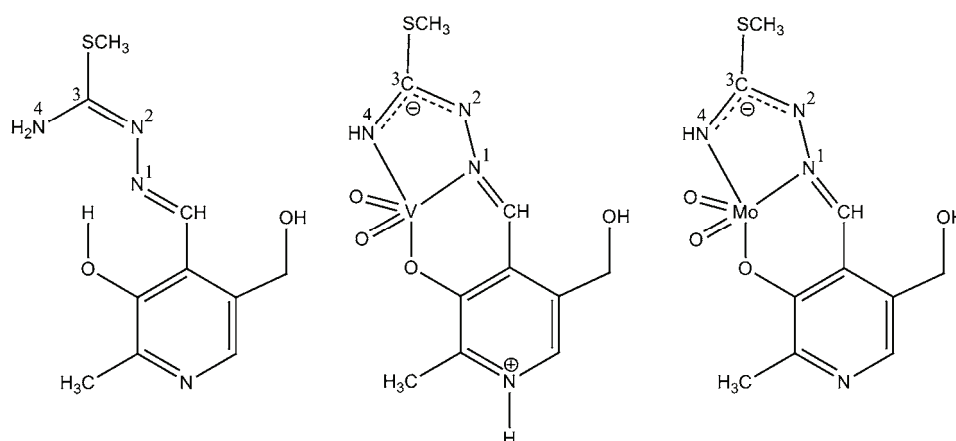

Fig. 1. Chemical structures of the ligand, and the [VO$_2$(PLITSC–H)]·2H$_2$O and [MoO$_2$(PLITSC–2H)] complexes.

two nitrogen atoms of the isothiosemicarbazide fragment and the bridging coordination of the oxygen atom of the hydroxymethyl group. The latter coordination mode of the pyridoxal moiety was also assumed in a similar MoO$_2^{2+}$ complex with pyridoxal 4-phenylthiosemicarbazone,[6] and unambiguously found in the structures of some complexes of Cu(II)[2] and Ni(II)[31] with pyridoxal thiosemi- and semicarbazone.
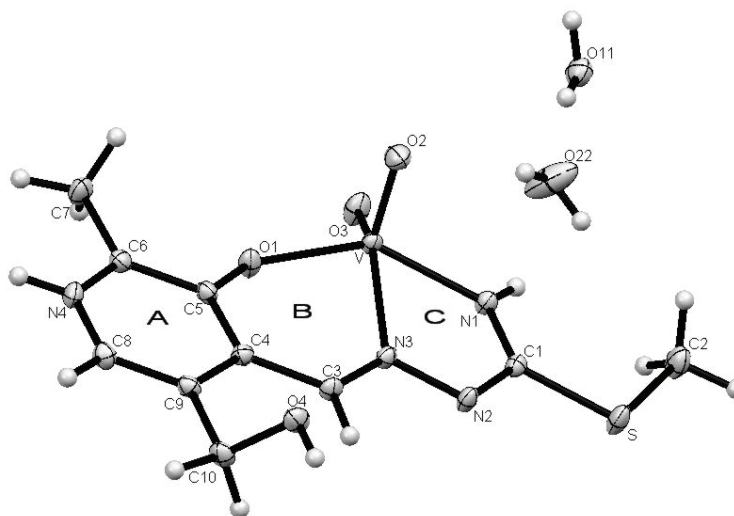

Fig. 2. MERCURY view of [VO$_2$(PLITSC–H)]·2H$_2$O shown with 50 % probability level of the thermal ellipsoids.

NMR Spectra

The ^{1}H-NMR spectrum of the ligand in DMSO-d_6 solution was recorded with a systematic pattern of isomer peaks of all protons, with the exception of the pyridine one at the C-6 position, which was poorly resolved and appeared as a singlet. The *syn/anti* isomerism results from the double bond in the azomethine group (CH=N1) (Fig. 1).[32] In the ^{1}H-NMR spectrum of the ligand, the *syn* and *anti* isomers were defined by the dual peak system with a 23:77 integral ratio, respectively. The *cis/trans* isomerism occurred with respect to the N2=C3 double bond of the amide group. The chemical shifts of the two isomeric phenolic protons were at 12.12 and 11.72 ppm, with a *cis/trans* integral ratio 82:18. The absence of a resonance of both these signals for OH in the spectrum of the vanadium complex is in accordance with the coordination of the phenolate oxygen to vanadium. The spectrum of the complex contains no isomer peaks for CH=N1, indicating the fixed geometry after coordination and existence of the complex in only one isomeric form (Fig. 1). The significant downfield shift of the azomethine proton in the complex ($\Delta^* = 0.14$ ppm), with respect to the corresponding free ligand, confirms the coordination of the azomethine nitrogen. A similar down-

field shift was observed for the carbon atom of the azomethine group in its ^{13}C--NMR spectrum.

A comparison of the ^{1}H-NMR spectra of the ligand and its dioxomolybdenum complex revealed that the ligand behaved as a tridentate binegative ONN donor. The disappearance of the signals at 12.12 and 11.72 ppm was ascribed to the fact that the ligand also underwent deprotonation of the phenolic group during complexation. Similarly, the appearance of a new signal at 9.41 ppm with integral intensity of 1.0 suggests that the complexation was followed by deprotonation of the terminal amino group. Finally, the absence of two isomeric peaks of the azomethine group of the free ligand indicates coordination to molybdenum with a fixed geometry, without the possibility for any isomerism.

Electronic spectra

In the available spectral range in DMF, the complexes displayed spectra with three bands of high and medium intensities. The two bands at shorter λ values (below 400 nm) can be ascribed to intraligand $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions.[5,13,33] The third one (above 400 nm) belongs to an LMCT, *i.e.*, charge transfer from the highest occupied ligand orbital to an empty d-orbital of the metal atom.[34] As expected for MoO_2^{2+} and VO_2^+, (d^0), no d–d transitions were observed in the visible spectral range.

Crystal structure of [VO$_2$(PLITSC–H)]·2H$_2$O

The asymmetric unit consists of a tridentate ONN monodeprotonated ligand chelating the VO_2^+ and two water molecules. The well-separated complex units of [VO$_2$(PLITSC–H)] and H_2O are connected by hydrogen bonds. The vanadium atom is pentacoordinated in an almost ideal square-pyramidal environment ($\tau =$ = 0.042) (Fig. 2), with the apical O2 atom at a distance V–O2 = 1.641(1) Å and the equatorial O3 at a distance V–O3 = 1.630(1) Å (Table II). The VO$_2$ group is in the *cis*-configuration with an O–V–O angle of 108.03(6)° (Table II). A very similar square-pyramidal arrangement around the vanadium(V) ion was also found in the crystal structure of ammonium(2,4-dihydroxybenzaldehyde *S*-methylthiosemicarbazonato)dioxovanadate(V).[35] The chelate ligand donors–vanadium bond distances V–O1, V–N1 and V–N3 are 1.917(1), 2.006(1) and 2.200(1) Å, respectively. Thus, as with some other tridentate ONN isothiosemicarbazones,[36] the V–N3 bond is longer than the V–N1 bond. However, while these differences for non-oxo metal complexes are significantly smaller (≈0.05 Å),[36] the difference in the case of this complex is much more pronounced, amounting to even 0.195 Å. The significant elongation of the V–N3 bond is a consequence of the stronger *trans* effect of the basal oxo O3 ligand bound to vanadium by a double bond, compared to the *trans* effect of the (also basal) oxygen atom O1 bonded to vanadium by a single bond.

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TABLE II. Selected bond distances and bond angles for [VO$_2$(PLITSC–H)]·2H$_2$O

Bond	Bond distances, Å	Bond	Bond angles, °
V–O1	1.917(1)	O1–V–O2	103.65(5)
V–O2	1.641(1)	O1–V–O3	96.83(5)
V–O3	1.630(1)	O1–V–N1	143.96(5)
V–N1	2.006(1)	O1–V–N3	80.89(5)
V–N3	2.200(1)	O2–V–O3	108.03(6)
O1–C5	1.315(2)	O2–V–N1	106.22(5)
N1–C1	1.317(2)	O2–V–N3	105.07(5)
N2–N3	1.381(2)	O3–V–N1	92.71(5)
N2–C1	1.337(2)	O3–V–N3	146.37(6)
		N1–V–N3	72.27(5)
		C6–N4–C8	123.8(1)

The whole ligand molecule, which possesses an extended system of conjugated double bonds and, hence, should be planar, is on the contrary significantly distorted. The dihedral angle between the mean planes of the pyridoxal moiety (A) and the six-membered chelate ring (B) is 7.8°, the dihedral angles between the average plane of five-membered chelate ring (C) and the A and B rings are 8.7 and 12.0°, respectively. The basal plane (O1, N1, O3, N3) of the coordination polyhedron is slightly tetrahedrally deformed, with the distances from the least squares plane being between 0.0137(1) and 0.0159(1) Å. The vanadium atom is displaced towards the apical O2 atom by 0.5146(1) Å. The pyridoxal ring adopts the role of a zwitterion.[1] The bond distances and angles in the pyridoxal ring are in agreement with those found in some other compounds containing the same moiety when a zwitterion was adopted. The C6–N4–C8 angle of the pyridine ring (123.8(1)°) is significantly increased with respect to the C–N–C angle of about 120°, which could be expected for a non-protonated pyridyl-N.[1,3] This is also in agreement with the N4···O11 distance (2.677(2) Å), corresponding fairly well to a strong hydrogen bond (Table III) and with the O1–C5 distance (1.317(2) Å), which is intermediate between a single (1.43 Å) and a double C=N bond (1.23 Å). All the other bond distances and bond angles in the PLITSC chelate ligand are in agreement with the corresponding bonds found in the related pyridoxal isothiosemicarbazone ligand.[1] The packing of the structural units is determined by an extended 3D network of hydrogen bonds, listed in Table III.

Two of them: O4–H···N2 (2.762(2) Å) and N1–H···O3 (2.969(2)) bind the complex molecules along the *x* and *y* directions, respectively (Fig. 3), forming layers parallel to the ab plane at the levels *c* = 0 and *c* = 1 (C-layers). As can be seen from Fig. 4, between these layers, at the *c*/2 level, there is a layer composed of the crystalline water molecules H$_2$O11 and H$_2$O22, mutually connected by the hydrogen bond O11–H11···O22 (2.723(3)), along the (110) direction. The water layers (W-layers) and layers of the complex (C-layers) alternate along the *z*-direction and are interconnected by the relatively strong pairs: O11–H12···O4

(2.735(2) Å) and N4–H···O11 (2.674(2) Å), as well as by O22–H21···O2 (2.799(2) Å) and O22–H22···O2' (2.991(2) Å).

TABLE III. Hydrogen-bonding geometry (Å, °)

D–H	D···A	H···A	D–H···A	Equivalent position[a]
O11–H11	O11···O22	H16···O22	O11–H16···O22	(0)
0.78(4)	2.723(3)	1.96(4)	167(4)	
O4–H4	O4···N2	H8···N2	O4–H8···N2	(1)
0.84(4)	2.762(2)	1.93(4)	172(3)	
N1–H1	N1···O3	H9···O3	N1–H9···O3	(2)
0.88(3)	2.969(2)	2.11(3)	167(3)	
N4–H4A	N4···O11	H10···O11	N4–H10···O11	(3)
0.88(2)	2.674(2)	1.80(2)	172(3)	
O11–H12	O11···O4	H15···O4	O11–H15···O4	(4)
0.81(3)	2.735(2)	1.93(4)	171(3)	
O22–H21	O22···O2	H14···O2	O22–H14···O2	(4)
0.86(3)	2.799(2)	1.94(3)	177(3)	
O22–H22	O22···O2	H17···O2	O22–H17···O2	(5)
0.77(4)	2.991(2)	2.24(3)	167(4)	

[a](0): x, y, z; (1): $-x+1, -y+2, -z$; (2): $-x+2, -y+1, -z$; (3): $x+1, +y+1, +z$; (4): $-x+1, -y+2, -z+1$; (5): $x-1, +y, +z$
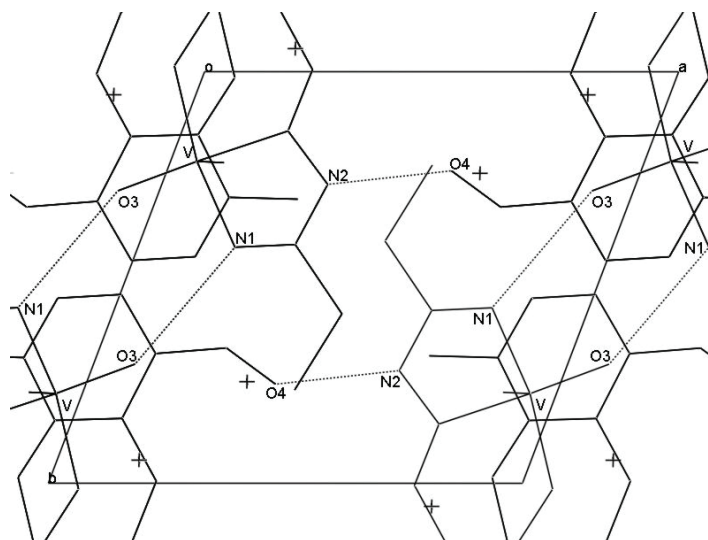

Fig. 3. Projection of the structure parallel to the (001) direction. Water oxygens are marked with +.

Crystallographic data reported for the complex [VO$_2$(PLITSC–H)]·2H$_2$O have been deposited with CCDC, No. CCDC-641145. 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).
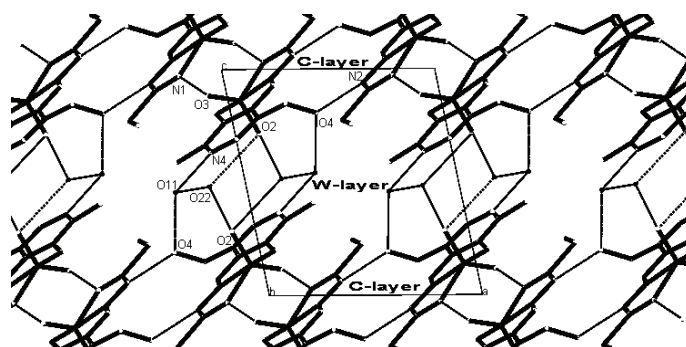
Fig. 4. Projection of the structure parallel to the (010) direction.
H-atoms are omitted for the sake of clarity.

И З В О Д

КОМПЛЕКСИ ПРЕЛАЗНИХ МЕТАЛА СА ЛИГАНДИМА НА БАЗИ ТИОСЕМИКАРБАЗИДА. ДЕО 57. СИНТЕЗА, СПЕКТРАЛНА И СТРУКТУРНА КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА ДИОКСОВАНАДИЈУМА(V) И ДИОКСОМОЛИБДЕНА(VI) СА *S*-МЕТИЛИЗОТИОСЕМИКАРБАЗОНОМ ПИРИДОКСАЛА

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Описана је синтеза неутралних комплекса диоксованадијума(V) и диоксомолибдена(VI) са тридентатним ONN *S*-метилизотиосемикарбазоном пиридоксала (PLITSC), формула [VO$_2$(PLITSC–H)]·2H$_2$O и [MoO$_2$(PLITSC–2H)]. Структурна анализа комплекса ванадијума је показала да исти има скоро идеалну квадратно-пирамидалну структуру, а за комплекс мо-либдена је претпостављена полимерна октаедарска структура. Оба комплекса су, осим еле-менталном анализом, окарактерисана кондуктометријским и магнетометријским мерењима, те IR-, UV–Vis и ^{1}H- и ^{13}C-NMR спектрима.

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