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Dioxidovanadium(V) complexes with pyridoxal aminoguanidine derivative: synthesis and spectral and structural characterization

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Abstract: Three square–pyramidal complexes of dioxidovanadium(V) with {[3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridyl]methylene}amino}guanidine (PLAG), of the formulas $\text{NH}_4[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**1**), $\text{VO}_2(\text{PLAG}-\text{H})$ (**2**) and $\text{K}[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**3**) were synthesized and characterized by IR and electronic spectra, and in case of **1** and **3** by X-ray crystallography as well. The reaction of aqueous ammoniacal solution of NH_4VO_3 and PLAG resulted in formation of **1**, which in MeOH undergoes spontaneous transformation into **2**, which, in turn, in the reaction with KOH transforms into **3**. In these complexes, PLAG is coordinated in a common tridentate ONN mode, *via* the phenoxide oxygen atom and the nitrogen atoms of the azomethine and imino groups of the aminoguanidine fragment. In all previously characterized complexes, PLAG was coordinated in the neutral form. However, here it was proven that this ligand could be coordinated in both mono- (**2**) and doubly-deprotonated forms (**1** and **3**) as well.

Keywords: pyridoxalaminoguanidine derivative, dioxidovanadium(V), complexes, crystal structure, spectra.

INTRODUCTION

The great interest in vanadium coordination chemistry¹ in the context of medical applications has arisen from the ability of vanadium complexes to promote the insulin-mimetic activity in the treatment of human *Diabetes mellitus*.^{2,3} Other studies involving potential applications of some oxidovanadium(IV) and dioxidovanadium(V) complexes have also been performed in the context of their antitumor, antibacterial and anti-inflammatory activities.^{4–7}

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Concerning the fact that pyridoxal (PL) is a co-enzyme in a large number of enzymatic systems that catalyze biochemical transformations of amino acids, it is not surprising that a large number of vanadium complexes with the Schiff bases of PL have been synthesized and characterized.⁸

Despite the wide range of pharmacological activity^{9–13} of aminoguanidine (AG), vanadium complexes with its Schiff bases are still unknown. Considering the biological importance of vanadium and both ligand precursors, as well as the fact that only a few complexes of pyridoxal aminoguanidine derivative, {[3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridyl)methylene]amino}guanidine (PLAG)^{14–17}, have been synthesized, it seemed worthwhile to examine the synthesis and characteristics of new ones. Herein, a synthesis and spectral study of three dioxidovanadium(V) complexes with PLAG, *viz.* $\text{NH}_4[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**1**), $\text{VO}_2(\text{PLAG}-\text{H})$ (**2**) and $\text{K}[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**3**), is presented together with the structural characterization of two of the complexes.

EXPERIMENTAL

Reagents

All employed chemicals were commercial products of analytical reagent grade, except for the ligand pyridoxal aminoguanidine derivative, which was obtained in the reaction of aqueous solutions of pyridoxal hydrochloride and aminoguanidine hydrogencarbonate in the presence of $\text{Na}_2\text{CO}_3\cdot 10\text{H}_2\text{O}$.¹⁷

Synthesis of the complexes

A mixture of NH_4VO_3 (0.12 g, 1.0 mmol) and PLAG (0.22 g, 1.0 mmol) was heated in $\text{ccNH}_3(\text{aq})$ (5 cm^3) under reflux for 3 h. After 2 days, from the orange solution, orange single crystals of $\text{NH}_4[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**1**) precipitated, which were filtered off and washed with EtOH and Et₂O. When the reaction, with the same quantities of reactants, was performed in MeOH, yellow microcrystals of $\text{VO}_2(\text{PLAG}-\text{H})$ (**2**) were formed. The same product could be obtained by the dissolution of **1** in MeOH. The reaction of **2** with KOH resulted in formation of orange single crystals of $\text{K}[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**3**).

Analytical methods

Elemental analyses (C, H, N) of air-dried complexes were performed by standard micro-methods in the Center for Instrumental Analyses, ICTM in Belgrade.

Molar conductivities of freshly prepared complex solutions ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) were measured on a Jenway 4010 conductivity meter.

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

Electronic spectra of DMF solutions were recorded on a T80+ spectrometer (PG Instruments Ltd.) from 270 to 1100 nm.

Single crystal X-ray diffraction

Single crystals of the complexes **1** and **3** were selected, glued on glass fibers and mounted on a Gemini S κ -geometry diffractometer (Agilent Technologies), equipped with Sapphire3 CCD area detector, for diffraction measurements at room temperature. Data were collected in the ω scan mode using graphite-monochromated Mo $K\alpha$ X-radiation ($\lambda = 0.71073 \text{ \AA}$) for **1** and Cu $K\alpha$ X-radiation ($\lambda = 1.54184 \text{ \AA}$) for **3**. Data collection, reduction and cell

refinement were performed with CRYSLISPRO. The structures were solved by direct method using SIR92¹⁸ and refined on F^2 with SHELXL-97 program.¹⁹ Hydrogen atoms bonded to carbon atoms were introduced in idealized positions and refined as riding with U_{iso} fixed as 1.2–1.5 U_{eq} of the parent atoms. Position of hydrogen atoms bonded to heteroatoms were taken from ΔF map and refined isotropically as riding on their parent atoms, since their free refinement did not lead to the most satisfactory geometry. The programs used to prepare material for publication were WINGX²⁰ and ORTEP-3.²¹ Crystal data and refinement parameters are listed in Table I.

TABLE I. Crystallographic data for the $\text{NH}_4[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**1**) and $\text{K}[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**3**)

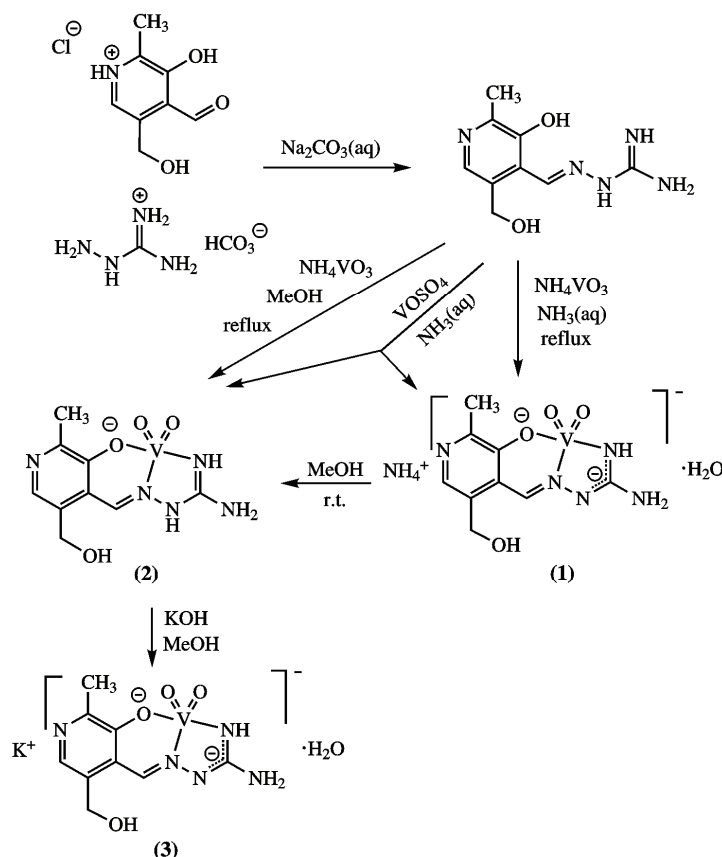
Parameter	1	3
Molecular formula	$\text{C}_9\text{H}_{17}\text{N}_6\text{O}_5\text{V}$	$\text{C}_9\text{H}_{13}\text{KN}_5\text{O}_5\text{V}$
Formula weight	340.23	361.28
Temperature, K	298(2)	294(2)
Wavelength, Å	0.71073	1.54184
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a / \text{Å}$	8.5563(11)	8.5478(9)
$b / \text{Å}$	9.1477(13)	9.1738(8)
$c / \text{Å}$	9.9439(15)	9.7808(9)
$\alpha / ^\circ$	78.943(12)	79.865(8)
$\beta / ^\circ$	86.305(11)	85.467(8)
$\gamma / ^\circ$	63.426(14)	62.052(10)
$V / \text{Å}^3$	682.97(19)	666.94(13)
Z	2	2
$D_c / \text{g cm}^{-3}$	1.654	1.799
μ / mm^{-1}	0.76 (Mo $K\alpha$)	9.33 (Cu $K\alpha$)
$F(000)$	352	368
Crystal size, mm	0.33×0.20×0.05	0.77×0.25×0.23
Color/shape	Orange/prism	Orange/prism
θ range, °	3.3–29.2	4.6–72.3
No. reflections measured	5006	4205
No. unique reflections	3106	2573
R_{int}	0.024	0.024
No. reflections with $I > 2\sigma I$	2429	2390
No. restraints	0	0
No. refined parameters	201	198
Goodness-of-fit on F^2	1.084	1.054
$R / wR [F_o > 4\sigma F_o]$	0.038 / 0.105	0.034 / 0.098
R / wR [all data]	0.052 / 0.110	0.036 / 0.100
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$, e Å ⁻³	0.39 and -0.38	0.34 and -0.44

RESULTS AND DISCUSSION

Synthesis

Orange single crystals of the monoanionic complex $\text{NH}_4[\text{VO}_2(\text{PLAG}-2\text{H})]\cdot\text{H}_2\text{O}$ (**1**) were obtained in the reaction of warm ammoniacal solutions of

NH_4VO_3 and PLAG in the mole ratio 1:1. The MeOH solution of **1** is unstable, thus the dissolution of **1** in MeOH resulted in the formation of a yellow neutral microcrystalline complex of the formula $\text{VO}_2(\text{PLAG-H})$ (**2**). Compound **2** could also be obtained in the reaction of MeOH solutions of NH_4VO_3 and PLAG in the mole ratio 1:1. The mixture of complexes **1** and **2** could be obtained in the reaction of ammoniacal solutions of VOSO_4 and PLAG, which indicates that, under these conditions, the oxidation of V(IV) to V(V) occurred. The identities of the complexes obtained in this reaction were proved by X-ray analysis data (for complex **1**) and by elemental analysis data and IR spectrum identical to those obtained in other two ways of synthesis (for complex **2**). In the reaction with KOH in MeOH, complex **2** transforms into $\text{K}[\text{VO}_2(\text{PLAG-2H})]\cdot\text{H}_2\text{O}$ (**3**). Details of the synthetic procedure to the complexes are summarized in Scheme 1.



Scheme 1. Reaction scheme of the syntheses of the ligand and the complexes.

In all previously described complexes,^{14–17} PLAG was coordinated in the neutral but dipolar zwitter-ionic form, which was the result of prototropic tauto-

merism, *i.e.*, the migration of an H-atom from the phenolic OH-group to pyridine nitrogen of the pyridoxal moiety. However, complexes **1** and **3** are the first two examples of metal complexes in which PLAG is coordinated as a dianionic ligand, because of deprotonation of both the pyridinium and hydrazine nitrogen atoms. As was already mentioned, in these complexes PLAG is coordinated as tridentate ONN ligand, *via* the oxygen atom of the deprotonated OH-group and the nitrogen atoms of the azomethine and imino groups of the aminoguanidine fragment, forming one six-membered (pyridoxylidene) and one five-membered (aminoguanidine) metallocycle.

The complexes are stable in air. Complexes **1** and **3** are soluble in H₂O, MeOH and DMF, and partially in EtOH, whilst **2** is soluble in DMF. The molar conductivity of **1** and **3** in H₂O suggest a 1:1 type of electrolyte,²² which is in accordance with the coordination formulas, whilst the conductivity of **1** in MeOH and DMF had slightly lower values. This can be explained by the lower mobility of the voluminous complex anion as well as the gradual transformation into **2**. The value for the molar conductivity of **2** in DMF indicates its non-electrolyte nature.

It should be mentioned that, concerning the similar reactions in analogous complexes with similar ligands,²³ the transformation of **1** into **2** is expected to be reversible. It was experimentally shown that neutral complex **2** cannot be deprotonated by NH₃(aq) as those with similar ligands,²³ but by strong bases only. Thus, dissolution of complex **2** in warm MeOH in the presence of equimolar amount of KOH gives an orange solution, from which the orange single crystals of **3** were formed.

Analytic and spectral characteristics

$NH_4[VO_2(PLAG-2H)] \cdot H_2O$ (**1**). Yield: 67 %; Anal. Calcd. for C₉H₁₇N₆O₅V: C, 31.77; H, 5.04; N, 24.70 %. Found: C, 31.75; H, 4.98; N, 24.41 %; FTIR (KBr, cm⁻¹): 3384, 3187, 3010, 1655, 1597, 1542, 1499, 1398, 920, 890; UV-Vis (DMF) (λ_{max} / nm (log (ϵ / dm³ mol⁻¹ cm⁻¹))) : < 270 (\approx 4.15), 353 (3.76), 404 (3.82); Molar conductivity, A_M (S cm² mol⁻¹): 120 (H₂O), 55 (MeOH), 35 (DMF).

$VO_2(PLAG-H)$ (**2**). Yield: 96 %; Anal. Calcd. for C₉H₁₂N₅O₄V: C, 35.42; H, 3.96; N, 22.95 %. Found: C, 35.58; H, 4.02; N, 22.77 %; FTIR (KBr, cm⁻¹): 3271, 3132, 1659, 1592, 1563, 1372, 1319, 953, 925, 897; UV-Vis (DMF) (λ_{max} / nm (log (ϵ / dm³ mol⁻¹ cm⁻¹))) : <270 (\approx 4.15), 373 (3.67); Molar conductivity, A_M (S cm² mol⁻¹): 18 (DMF).

$K[VO_2(PLAG-2H)] \cdot H_2O$ (**3**). Yield: 42 %; Anal. Calcd. for C₉H₁₃KN₅O₅V: C, 29.89; H, 3.60; N, 19.37 %. Found: C, 30.25; H, 3.73; N, 19.65 %; FTIR (KBr, cm⁻¹): 3366, 3319, 3133, 1658, 1598, 1540, 1501, 1396, 922, 885; Molar conductivity, A_M (S cm² mol⁻¹): 110 (H₂O).

IR spectra

Using a comparative analysis of the IR spectra of the ligand and the complexes, a tridentate ONN coordination mode of PLAG could be established. The positive shift of the $\nu(\text{C}-\text{O})$ band from 1290 cm^{-1} in the spectrum of the ligand to 1370 cm^{-1} in the spectra of the complexes indicates the coordination of the oxygen atom of the deprotonated phenolic OH-group.^{14–17,24} In contrast to this band, bands originating from the vibrations of guanidino and azomethine group, which were observed at 1631 and 1697 cm^{-1} , respectively, in the spectrum of the ligand were shifted toward the lower energy region by 35 and 40 cm^{-1} , respectively, due to the coordination of nitrogen atoms of the imino and azomethine groups of the aminoguanidine fragment.^{14–17} The broad bands in the region $2700\text{--}3000\text{ cm}^{-1}$, which can be ascribed to $\nu(\text{NH}^+)$ vibrations, were observed in all previously characterized complexes with PLAG.^{14–17} However, the absences of these bands in the IR spectra of the complexes **1–3** confirmed the deprotonation of the nitrogen atom of PL-residue, *i.e.*, the anionic form of the ligand.^{25,26} Apart from these, in the spectra of complexes **1–3**, very strong bands characteristic for $\nu_{\text{sym/asym}}(\text{VO}_2^+)$ vibrations were observed at 920 and 890 cm^{-1} , 925 and 897 cm^{-1} , and 922 and 885 cm^{-1} , respectively.²³

Electronic spectra

Electronic spectra of the complexes **1** and **2** in DMF (available wavelength range $270\text{--}1100\text{ nm}$) were, similarly to previous reports on alike complexes,^{17,23,27} rather simple. The observed strong band with $\lambda_{\text{max}} < 270\text{ nm}$ is due to intraligand $\pi \rightarrow \pi^*$ transitions. The other bands of medium intensity at $353\text{--}404\text{ nm}$ were ascribed to $\text{L} \rightarrow \text{M}$ charge transfer. No $d\text{--}d$ transitions were recorded, as expected for VO_2^+ complexes.

Crystal structure of **1** and **3**

Molecular structures of the complexes **1** and **3** are shown in Fig. 1 whilst selected bond distances and angles for the complexes are given in Table II. The asymmetric unit of the complexes contained a mono cation (NH_4^+ for **1** and K^+ for **3**), a complex anion consisting of PLAG chelating VO_2^+ , and one water molecule. The vanadium atom is pentacoordinated in a slightly distorted square-pyramidal arrangement ($\tau = 0.109$ for **1** and $\tau = 0.044$ for **3**). The complexes **1** and **3** are isomorphous and isostructural, which was expected considering the tolerant difference in the radius of NH_4^+ and K^+ ($r(\text{NH}_4^+)/r(\text{K}^+) = 1.48\text{ \AA}/1.33\text{ \AA}$). The basal plane of the pyramid is defined by two nitrogen atoms (N1 and N3) and one oxygen atom (O1) of the tridentate Schiff base and one oxygen atom (O3) of dioxido-group. The apex of the pyramid is occupied by the other oxygen atom (O4) of dioxido moiety. The vanadium atom is displaced from the basal plane toward the apical oxygen by $0.529(1)$ and $0.524(1)\text{ \AA}$ in **1** and **3**, respecti-

vely. The VO₂-group is in the *cis*-configuration with the usual value of O–V–O angle (108.79(9)° for **1** and 109.53(10)° for **3**).

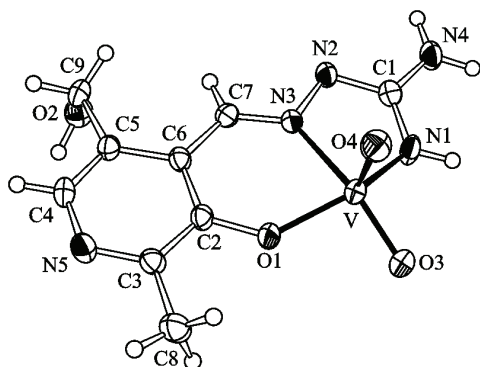


Fig. 1. The structure of the complex anion [VO₂(PLAG-2H)]⁻.

TABLE II. Selected bond lengths and valence angles for **1** and **3**

Bond(s)	Complex	
	1	3
	Distance, Å	
V–O1	1.8851(17)	1.8960(17)
V–N1	1.972(2)	1.965(2)
V–N3	2.1816(19)	2.1935(19)
V–O3	1.6536(17)	1.6490(17)
V–O4	1.6292(19)	1.6379(18)
C1–N1	1.331(3)	1.325(3)
C1–N2	1.350(3)	1.345(3)
C1–N4	1.339(3)	1.348(3)
C7–N3	1.296(3)	1.288(3)
N2–N3	1.395(3)	1.394(3)
C2–O1	1.338(3)	1.332(3)
	Angle, °	
N1–V–N3	71.90(8)	71.99(8)
O1–V–N3	81.58(7)	81.65(7)
O4–V–N1	103.31(10)	102.13(10)
O3–V–O4	108.79(9)	109.53(10)
O1–V–N1	141.44(9)	143.47(8)
O3–V–N3	148.02(9)	146.08(9)
C3–N5–C4	118.4(2)	118.7(2)

As can be seen in Table II, the chelate ligand donors–vanadium distances in **1** and **3** vary systematically in the expected fashion. Due to the deprotonation of the phenolic OH-group, the negative charge associated with the formed phenoxide group makes it the best electron donor among the PLAG ligands, which is why the V–O1 bond is the shortest. This fact is in concordance with all the earlier characterized complexes with this ligand.^{14–17} The significantly longer (0.21 Å

for **1** and 0.23 Å for **3**) V–N3 bond compared to the V–N1 distance can be correlated with the presence of multiple-bonded O3 and single-bonded O1 atoms in the basal plane, *i.e.*, the stronger *trans* influence of the O3 oxygen atom compared to O1.^{27,28}

It should be noted that C2–O1 bond is slightly longer (1.338(3) and 1.332(3) Å for **1** and **3**, respectively) compared with the C–O[−] bond in the zwitter-ion of a similar ligand, *i.e.*, pyridoxal thiosemicarbazone (1.29 Å),²⁹ which could be explained by means of the excess electron density transfer from the phenoxide oxygen to the metal ion *via* coordinative bonding. The intraligand bond distances fall within the expected values based on mentioned structural reports.^{14–17} Accordingly, C7–N3 bond length corresponds to pure Csp²–Nsp² azomethine double bond, whilst C1–N1, C1–N2 and C1–N4 bond lengths have values between those characteristic for pure single and double C–N bonds due to extensive delocalization of the electron density within the aminoguanidine moiety. Although the deprotonation of pyridinic (N5) and hydrazine nitrogen (N2) atoms is evident from difference electron density maps calculated during structural analysis, additional confirmation is given by the following facts. The deprotonation of N2 and N5 is unambiguously proved by the fact that these nitrogen atoms are acceptors in strong H–bonds, and the value of C3–N5–C4 angle, which is lower than 120° (118.4(2)° for **1** and 118.7(2)° for **3**) is another proof for the deprotonation of the PL residue.²⁶

SUPPLEMENTARY MATERIAL

Fig. S-1, showing the crystal packing, as well as Tables S-I and S-II with hydrogen bonding descriptions are available electronically at <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

Crystallographic data reported for the complex NH₄[VO₂(PLAG–2H)]·H₂O (**1**) and K[VO₂(PLAG–2H)]·H₂O (**3**) have been deposited with the CCDC, No. CCDC-870175 and 926853. Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk.

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ИЗВОД

КОМПЛЕКСИ ДИОКСИДОВАНАДИЈУМА(V) СА АМИНОГВАНИДИНСКИМ ДЕРИВАТОМ ПИРИДОКСАЛА— СИНТЕЗА, СПЕКТРАЛНА И СТРУКТУРНА КАРАКТЕРИЗАЦИЈА

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Три комплекса диоксидованадијума(V) са {(3-хидрокси-5-(хидроксиметил)-2-метил-4-пиридил)метилен}аминогванидином (PLAG), формула NH₄[VO₂(PLAG–2H)]·H₂O (**1**), VO₂(PLAG–H) (**2**) и K[VO₂(PLAG–2H)]·H₂O (**3**), су синтетисана и спектрално

окарактерисана, а за комплексе **1** и **3** урађена је и рендгенска структурна анализа. Реакцијом амонијачног раствора NH_4VO_3 и PLAG добијен је комплекс **1**, који у MeOH подлеже спонтаној трансформацији у комплекс **2**. Комплекс **2** у реакцији са KOH даје комплекс **3**. У овим комплексима PLAG је координован на уобичајен тридентатни ONN начин, преко атома кисеоника депротоноване OH-групе и атома азота азометинске и имино групе аминогванидинског фрагмента. У свим до сада окарактерисаним комплексима нађена је координација PLAG у неутралној форми, док је у комплексима описаним у овом раду лиганд по први пут координован у моно- (**2**) и двоструко депротонованој (**1** и **3**) форми.

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