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Please cite this article as M. V. Rodić, M. M. Radanović, Lj. S. Vojinović-Ješić, S. K. Belošević, Ž. K. Jaćimović, V. M. Leovac, *J. Serb. Chem. Soc.* (2019) <https://doi.org/10.2298/JSC190114008R>

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Synthesis and crystal structure of copper(II) complexes with pyridoxal *S*-methylisothiosemicarbazone bearing a new coordination mode

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(Received 14 January; accepted 28 January 2019)

Abstract: The reaction of copper(II) nitrate and pyridoxal *S*-methylisothiosemicarbazone (PLITSC) in the presence of ammonium thiocyanate resulted in the formation of two types of complexes. Dimeric complex of the formula $[\{\text{Cu}(\mu\text{-PLITSC})\text{NCS}\}_2](\text{NCS})_2 \cdot 2\text{MeOH}$ was obtained in the presence of excess of ammonium thiocyanate, while in the presence of its nearly equimolar amount crystals of polymeric complex $\{[\text{Cu}(\mu\text{-PLITSC})\text{NCS}]\text{NO}_3 \cdot \text{MeOH}\}_n$ were formed. Complexes are characterized by elemental analysis, conductometry, IR spectroscopy, and their structures are unequivocally determined by single crystal X-ray crystallography. In both complexes, the copper atom is five-coordinated, situated in a deformed square-pyramidal environment. The basal plane of the square pyramid is defined by oxygen atom of the deprotonated phenol group and terminal nitrogen atoms of the isothiosemicarbazide moiety of the Schiff base, as well as the nitrogen atom of the coordinated thiocyanate ion, while the apical site is occupied by the oxygen atom of the hydroxymethyl group of the neighboring asymmetric unit. This coordination mode of the PLITSC was hitherto unknown. Survey of the Cambridge Structural Database showed that the coordination of the hydroxymethyl group is rare within pyridoxal-based Schiff base metal complexes.

Keywords: dimeric and polymeric Cu(II) complexes; Schiff bases; tetradentate coordination mode; X-ray crystallography

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#Serbian Chemical Society member

<https://doi.org/10.2298/JSC190114008R>

INTRODUCTION

Thiosemicarbazones and their *S*-alkyl derivatives (isothiosemicarbazones) represent a very important group of organic compounds. These compounds are interesting not only due to their chemical properties as organic molecules, but their versatile coordination chemistry.¹⁻³ Besides, these compounds, especially thiosemicarbazones and their metal complexes, have shown a great variety of biological activities, such as antiviral, antibacterial, antimalarial, antitumor, etc.⁴⁻⁸

The mutual property of thiosemicarbazones is that the sulfur atom of thioureido fragment $\text{-NH-C(NH}_2\text{)=S}$ is used for coordination, unlike isothiosemicarbazones where coordination through the nitrogen atom of NH_2 -group takes place, instead of the sulfur atom of *S*-alkyl moiety -N=C(-SR)-NH_2 . This was proven by crystallographic analysis of many complexes obtained with these ligands.^{1-3,9} However, some very rare coordination modes of isothiosemicarbazones are also known, e.g. coordination through the sulfur atom of the *S*-alkyl moiety,¹⁰ or lack of coordination of the isothioureido fragment.¹¹ Coordination of the mentioned NH_2 -group in tridentate isothiosemicarbazones results in its frequent condensation with, for example, salicyl- and pyridine-2-aldehyde¹² or 2-(diphenylphosphino)benzaldehyde,¹³ thus forming complexes with tetradentate N_2O_2 , N_3O , and N_2OP donors, respectively. It is also found that bis(isothiosemicarbazones) of pentan-2,4-dione are able to stabilize some less usual oxidation states: Fe(IV),^{14,15} Ni(III)¹⁶ and Cu(III).¹⁷

In the focus of this research is pyridoxal *S*-methylisothiosemicarbazone (PLITSC), one of the isothiosemicarbazone ligands. Complexes of some 3d metals with this ligand are synthesized and structurally characterized,^{9,18,19} and it is found that, without exception, this ligand acts as tridentate N_2O donor, which is coordinated to the metal ion through azomethine and isothioamide nitrogen atoms and phenolic oxygen atom. It should be mentioned that this ligand can be coordinated in three different forms: neutral (zwitterionic), monoanionic (in which deprotonation of isothioureido fragment takes place) and dianionic (with the additional deprotonation of pyridine nitrogen atom).⁹

Here we present molecular and crystal structures of dimeric and polymeric complexes of Cu(II) with PLITSC, of the formulas $[\{\text{Cu}(\mu\text{-PLITSC})\text{NCS}\}_2\text{-(NCS)}_2\cdot 2\text{MeOH}$ (**1**) and $\{\text{Cu}(\mu\text{-PLITSC})\text{NCS}\}\text{NO}_3\cdot \text{MeOH}\}_n$ (**2**) in which tetradentate N_2O_2 way of coordination is found, with additional oxygen atom of the hydroxymethyl group as a fourth donor and bridging ligator.

EXPERIMENTAL

Reagents

All chemicals used were commercially available products of analytical reagent grade, except for the ligand PLITSC whose preparation has been described earlier.²⁰

Synthesis of complexes

[{Cu(μ -PLITSC)NCS}₂](NCS)₂·2MeOH (**1**). The mixture of PLITSC (0.060 g, 0.22 mmol) and Cu(NO₃)₂·3H₂O (0.045 g, 0.19 mmol) is poured with 10 cm³ MeOH and heated. After 15 minutes, to the cooled solution, the solution of NH₄NCS (0.030 g, 0.4 mmol) in 2 cm³ MeOH is added upon which the color becomes intense green. The resulting solution is left at room temperature and evaporated. The obtained dark-green single crystals are filtered and washed with MeOH. Yield: 0.05 g (45%). Anal. Calc. for CuC₁₃H₁₈N₆S₃O₃: C, 33.50; H, 3.89; N, 18.04; S, 20.64. Found: C, 33.38; H, 3.57; N, 17.95; S, 20.36%. Conductivity [$\Lambda_M/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$]: 86 (in MeOH). M.p. 149 °C. Selected IR bands [$\tilde{\nu}/\text{cm}^{-1}$]: 2850(w), 2784(w), 2115(s), 2075(vs), 1558(m), 1305(m).

{[Cu(μ -PLITSC)NCS]NO₃·MeOH}_n (**2**). The mixture of PLITSC (0.060 g, 0.22 mmol) and Cu(NO₃)₂·3H₂O (0.060 g, 0.25 mmol) is dissolved in 8 cm³ of hot MeOH. After 15 minutes to this solution, the solution of NH₄NCS (0.020 g, 0.26 mmol) in 2 cm³ MeOH is added. The resulting solution is left at room temperature and evaporated. The obtained dark-green single crystals are filtered and washed with MeOH. Yield: 0.04 g (38%). Anal. Calc. for CuC₁₂H₁₈N₆S₂O₆: C, 30.66; H, 3.86; N, 17.88; S, 13.64. Found: C, 30.52; H, 3.49; N, 17.71; S, 13.51%. Conductivity [$\Lambda_M/\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$]: 114 (in MeOH). M.p. 195 °C. Selected IR bands [$\tilde{\nu}/\text{cm}^{-1}$]: 2848(w), 2058(vs), 1560(m), 1385(vs), 1329(m).

Analytical methods

Elemental analyses (C, H, N, and S) of air-dried compounds were carried out by standard micro-methods. Molar conductivity measurements of freshly prepared MeOH solutions ($c = 1 \text{ mmol dm}^{-3}$) were performed on a Jenway 4010 conductivity meter. IR spectra were recorded on a Nicolet Nexus 670 (Thermo Scientific) FTIR spectrophotometer, in the range of 400–4000 cm⁻¹, by KBr pellet technique.

Crystal structure determination

Diffraction experiments were conducted on a Gemini S (Oxford Diffraction) four-circle diffractometer equipped with a Mo-anode sealed tube (Mo $K\alpha$ X-radiation, $\lambda = 0.71073 \text{ \AA}$) and a Sapphire3 CCD detector. Diffraction data were processed with the *CrysAlis^{Pro}*.²¹ Analytical absorption corrections were performed based on face indexed crystal models. Structure solution and space group determination were performed by *SHELXT-2018*.²² Full-matrix least-squares refinements were performed by *SHELXL-2018*²³, using the *ShelXle*²⁴ as a graphical interface. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms were introduced in idealized positions and refined by riding model. Their displacement parameters were approximated as $U_{\text{iso}} = kU_{\text{eq}}$ of the parent atoms ($k = 1.2$ and 1.5 for sp^2 and sp^3 hybridized carbon atoms, respectively). Disorder of methyl group of the pyridoxal moiety was treated by AFIX 123 command in *SHELXL-2018*. Hydrogen atoms bonded to hetero-atoms were discovered in the residual density map and were refined by application of distance restraints (N–H = 0.86 Å; O–H = 0.82 Å), with their $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atoms. In **2**, this treatment was used for hydrogen atoms bonded to N1 and O2, while for other heteroatom-bonded hydrogen atoms a riding model was used. Structure validation and additional geometrical calculations were performed by *PLATON*.²⁵ Graphics were plotted with the *ORTEP3 for Windows*.²⁶ Crystallographic and refinement details are listed in Table I.

CCDC 1890436–1890437 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

TABLE I. Crystallographic and refinement details

Crystal data	1	2
Chemical formula	C ₂₆ H ₃₆ Cu ₂ N ₁₂ O ₆ S ₆	C ₁₂ H ₁₈ CuN ₆ O ₆ S ₂
M _r	466.05	469.98
Crystal system	Triclinic	Orthorhombic
Space group	P1	Pbcn
Temperature, K	295	295
<i>a</i> / Å	8.7640(5)	13.4682(4)
<i>b</i> / Å	9.4490(6)	12.6874(3)
<i>c</i> / Å	12.2731(5)	22.3679(4)
α / °	82.134(4)	90
β / °	83.863(4)	90
γ / °	75.190(5)	90
<i>V</i> / Å ³	970.59(10)	3822.15(16)
<i>Z</i>	2	8
Radiation type	Mo K α	Mo K α
μ / mm ⁻¹	1.47	1.40
Crystal size, mm	0.55 × 0.29 × 0.16	0.57 × 0.50 × 0.23
Data collection		
Diffractometer	Gemini S (Oxford Diffraction)	
Absorption correction	Analytical	Analytical
<i>T</i> _{min} , <i>T</i> _{max}	0.578, 0.805	0.546, 0.739
Measured reflections	10369	36990
Independent reflections	3950	3909
Observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3536	3442
<i>R</i> _{int}	0.016	0.030
(<i>sin</i> θ / λ) _{max} / Å ⁻¹	0.625	0.626
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.029	0.034
<i>wR</i> (<i>F</i> ²)	0.073	0.081
<i>S</i>	1.05	1.15
No. of reflections	3950	3909
No. of parameters	252	253
No. of restraints	5	2
H-atom treatment	Mixed	Mixed
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	0.35, -0.22	0.31, -0.28

RESULTS AND DISCUSSION

Syntheses and characterization

Both complexes are obtained in the reaction of MeOH solutions of Cu(NO₃)₂·3H₂O, PLITSC and NH₄NCS. In the presence of the excess of NH₄NCS, dimeric complex **1** is formed, otherwise, the obtained complex is polymeric complex **2**. Complexes are crystal substances, soluble in MeOH and DMF, while poorly soluble in H₂O and Me₂CO. Molar conductivities of MeOH solutions of complex **1** and **2** are in concordance with the values characteristic for 1:1 type of electrolytes.²⁷

In the IR spectra of both complexes bands in the region 2780–2850 cm^{-1} could be ascribed to $\nu(\text{NH}^+)$ vibrations of the protonated pyridine nitrogen atom of the zwitterionic ligand form, which is formed by migration of the hydrogen atom located on a phenolic oxygen atom to pyridinic nitrogen atom.^{9,19} The azomethine band is located at *ca.* 1560 cm^{-1} in the spectra of both complexes. In comparison to the same band in the spectrum of free ligand (1655 cm^{-1}), it is shifted to lower energy, due to coordination of azomethine nitrogen atom. Coordination of oxygen atom of the deprotonated phenolic OH-group leads to a positive shift of $\nu(\text{C}-\text{O})$ band. Namely, this band is located at 1255 cm^{-1} in the spectra of the free ligand, while its positions in the spectra of complexes **1** and **2** are at 1305 and 1329 cm^{-1} , respectively.¹⁹

Finally, in the spectrum of complex **1**, the doublet band at 2115 and 2075 cm^{-1} , corresponds to $\nu(\text{CN})$ vibrations of coordinated and non-coordinated NCS-groups, respectively. Unlike this, in the spectrum of complex **2** in the same region only one band is found (2058 cm^{-1}).²⁸ Besides, in the spectrum of the latter complex very strong band at 1385 cm^{-1} undoubtedly originates from $\nu(\text{NO})$ vibrations of NO_3^- -group.²⁸

Crystal structure description

Complex **1** consists of dinuclear centrosymmetric complex cations $[\{\text{Cu}(\mu\text{-PLITSC})\text{NCS}\}_2]^{2+}$ and NCS^- ions, while complex **2** is comprised of polymeric complex cations $[\{\text{Cu}(\mu\text{-PLITSC})(\text{NCS})\}]^+_n$ and NO_3^- ions. Both structures contain methanol molecules as a solvent of crystallization. Molecular structures of the dinuclear centrosymmetric complex cation of **1** and polymeric complex cation of **2** are given in Fig. 1, and selected structural parameters are noted in Table II.

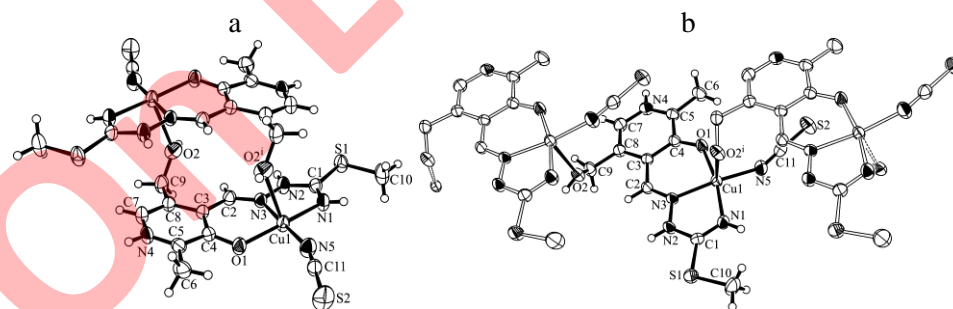


Fig. 1. Molecular structures of cations $[\{\text{Cu}(\mu\text{-PLITSC})\text{NCS}\}_2]^{2+}$ of **1** (a) and $[\{\text{Cu}(\mu\text{-PLITSC})(\text{NCS})\}]^+_n$ of **2** (b). In (b) repeating unit is depicted with filled bonds, and neighboring units were drawn without hydrogen atoms for the sake of clarity. Symmetry codes are given in Table II caption.

In both complexes, the ligand is coordinated as N_2O_2 tetradentate donor, in a way that isothioamide and azomethine nitrogen atoms and phenoxide oxygen atom are making bonds to one copper atom, while oxygen atom of the

hydroxymethyl group binds second copper atom. In **1** this results in dimeric complex, while in **2** it results in polymeric catenation.

Table II. Selected structural parameters (Å, °) of cations in **1** and **2**.

Bonds	1	2
Cu1–O1	1.9163(14)	1.9106(15)
Cu1–O2 ⁱ	2.4706(16)	2.3707(17)
Cu1–N1	1.9595(17)	1.9728(19)
Cu1–N3	1.9760(16)	1.9926(17)
Cu1–N5	1.9331(18)	1.958(2)
C1–N1	1.281(3)	1.288(3)
C1–N2	1.357(2)	1.357(3)
N2–N3	1.378(2)	1.374(2)
C2–N3	1.285(2)	1.288(3)
C4–O1	1.293(2)	1.292(3)
O1–Cu1–N5	91.95(7)	90.77(8)
O1–Cu1–N3	89.38(6)	88.77(7)
N1–Cu1–N3	80.56(7)	79.67(8)
N1–Cu1–N5	98.08(7)	100.05(8)
O1–Cu1–O2 ⁱ	87.68(6)	96.31(7)
N1–Cu1–O2 ⁱ	98.46(7)	88.99(8)
N3–Cu1–O2 ⁱ	86.10(6)	102.15(6)
N5–Cu1–O2 ⁱ	94.25(7)	88.51(8)
O1–Cu1–N1	167.78(7)	168.09(8)
N3–Cu1–N5	178.64(7)	169.32(8)
N1–C1–N2	117.80(17)	117.1(2)
C1–N2–N3	115.13(16)	115.58(17)
N2–N3–C2	118.65(16)	117.42(17)
N3–C2–C3	121.92(17)	123.0(2)
C5–N4–C7	124.19(17)	124.80(19)

Symmetry codes: (i) $-x+1, -y, -z+1$ (for **1**); $-x+\frac{1}{2}, y+\frac{1}{2}, z$ (for **2**)

Survey of the Cambridge Structural Database (CSD)²⁹ version 5.40 (Nov 2018) reveals over 200 structures with pyridoxal-based Schiff base metal complexes. It has not escaped our notice that in a significant number of these (80), ligands are pyridoxal semi-, thiosemi-, or isothiosemicarbazones (and their derivatives), as well as pyridoxal-aminoguanidine. Furthermore, only 16 of structurally characterized pyridoxal-based Schiff base metal complexes contain coordinated hydroxymethyl function, illustrating how that coordination mode is rare. In sub-set of these containing copper(II) as a central atom, hydroxymethyl group has a role of dimerization of Cu(II) atoms in six complexes (CSD refcodes: ARALAG³⁰, IVEPAC³¹, KAHGIM³², KAHGOS³², PEBWEA³³, QEKRII³⁴), while in three complexes hydroxymethyl group has a role of polymerization of Cu(II) atoms (CSD refcodes: QEKREE³⁴, EBAQOQ³⁵, FIVKAW³⁶).

Intra-ligand bond lengths have typical values in accordance with those found in structurally related complexes.⁹ Bond lengths of C1–N1 and C2–N3 bonds are typical for localized double bonds, and C4–O1 bond lengths clearly indicate electron delocalization of the phenoxide function. Similarly, valence angles of the isothiosemicarbazide moieties of the two complexes are matching within 1–2°. Finally, it is worth noting that C5–N4–C7 angles have values greater than 120° (*ca.* 124°) which is representative for protonated pyridine moiety.^{9,37}

In **1** and **2**, the copper atom is five-coordinated, situated in a deformed square-pyramidal environment. The basal plane of the square pyramid is defined by Schiff base donor atoms and the nitrogen atom of the coordinated thiocyanate ion, while the apical site is occupied by the oxygen atom of the hydroxymethyl group of the neighboring asymmetric unit. Both coordination polyhedrons deviate from the ideal square-pyramid towards trigonal-bipyramid. The application of Holmes' method³⁸ (using 174° as the value of the idealized *trans*-basal angles) indicates that transition along Berry pseudorotation coordinate ($D_{3h} \rightarrow C_{2v} \rightarrow C_{4v}$) for coordination polyhedrons of complexes is 89% for **1**, and 84% for **2**, meaning that the coordination polyhedron of **2** is slightly more deformed.

It has been shown³⁹ that in certain classes of copper(II) complexes, the formally five-coordinate (square-pyramidal) copper complexes could alternatively be described as six-coordinate (octahedral) if the sum of corresponding covalent radii is increased by *ca.* 0.1 Å. As copper atom of dimeric complex **1** has an additional short contact (2.9879(16) Å) with phenoxide oxygen atom O1ⁱⁱ (symmetry code (ii) $-x, -y, -z+1$) of the neighboring asymmetric unit, the coordination polyhedron of copper atom in **1** could be described as quasi-octahedral (5+1 coordination) in lieu of square-pyramid. That would also render complex cation of **1** 1-D polymeric in nature, with repeating unit being “dimer”, and with crystallographic axis *a* as a propagation direction. It is of interest to note that the bridging role of phenoxide oxygen in pyridoxal Schiff base complexes is remarkably rare, as it is found only in one complex (CSD refcode ELUVIR⁴⁰).

Metal–ligand bond lengths are in accordance with those observed in similar Cu(II) complexes with pyridoxal-based thiosemi-, isothiosemi-, and semicarbazones.⁹ As expected, phenoxide oxygen O1 participate in the shortest metal–ligand bond, which is in accordance with formal negative charge located on that atom. In general, bond lengths within coordination polyhedron are comparable in **1** and **2**, with the exception of apical Cu1–O2 bonds. Namely, this bond is by 0.1 Å longer in complex **1**.

Cis-valence angles within the basal plane of the coordination polyhedron are very similar (within 2° tolerance), while *cis*-valence angles involving apical O2 are significantly different for two complexes. Among these, O2–Cu1–N3 and O2–Cu1–O1 are smallest in **1**, while O2–Cu1–N5 and O2–Cu1–N1 are smallest in

2, which reveals that Cu1–O2 apical bond is inclined in opposite directions with respect to the basal plane in those complexes. The magnitude of inclination is rather similar, as acute angles between Cu1–O2 apical bond vector and least squares plane through basal atoms (O1, N1, N3, N5) are 83.05(6)° for **1**, and 82.06(7)° for **2**.

The rationale for the difference in coordination polyhedra geometry can be expressed as follows. As in **1** Cu1–O2 bond is longer, and inclined away from coordinated thiocyanate ion, the steric repulsion between these two groups is lower in **1**. This allows for a wider trans basal angle N3–Cu1–N5 in **1** (178.64(7)°), whereas in **2**, this angle is narrower (169.32(8)°) due to the repulsion of the coordinated water molecule and thiocyanate ion. As a consequence of bigger N3–Cu1–N5 angle in **1**, Cu(II) ion is less displaced from the mean basal plane in **1** (0.0602(3) Å) than in **2** (0.1254(3) Å). An additional reason for wider trans basal angle N3–Cu1–N5 in **1** may be found in the existence of O1ⁱⁱ atom occupying the sixth quasi-octahedral site.

A further difference between cations in **1** and **2** is a degree of planarity of the coordinated ligands (abstracting hydroxymethyl group). Namely, the ligand is quite planar in **2**, which is also true for five- and six-membered metallocycles. On the other hand, coordinated ligand significantly deviates from planarity in **1**, which renders six-membered metallocycle puckered. The conformation of Cu1–O1–C4–C3–C2–N3 ring is ¹S₂ screw-boat, slightly deformed towards ⁴T₂ twist-boat (nomenclature after Boeyens⁴¹), according to Cremer & Pople⁴² puckering parameters $Q=0.2494(14)$ Å, $\theta=63.4(4)^\circ$, $\varphi=34.9(5)^\circ$.

Polymeric cations of **2** are propagating in crystallographic *b* direction, with repeating units being symmetry related by a glide plane. Closest Cuⁱⁱ–Cuⁱⁱ distances are found between neighboring dimers/chains in both complexes (Cuⁱⁱ–Cuⁱⁱ = 3.7035(6) Å, symmetry code (ii) $-x, -y, -z+1$ for **1**, and Cuⁱⁱ–Cuⁱⁱ = 3.9228(6) Å, symmetry code (ii) $-x+1, y, -z+3/2$ for **2**), while intradimer Cuⁱ–Cuⁱ separation is 7.1439(6) Å in **1**, and intra-chain Cuⁱ–Cuⁱ separation is 7.1064(3) Å in **2** (symmetry codes as in Table II).

Both structures have developed and complex hydrogen bonding networks that connect structural units in 3-D network (**1**) or double layers parallel to *bc* plane (**2**). Common to both hydrogen bonding patterns is that all hydrogen donors are involved in hydrogen-bonding interactions (with exception of N4H4 group in **2**) and that N2H2 groups and MeOH molecules are donating hydrogen bonds to the uncoordinated anion. Hydrogen bonding geometry is presented in Table III.

TABLE III. Selected hydrogen-bond parameters

<i>D</i> –H [⋯] <i>A</i>	<i>D</i> –H / Å	H [⋯] <i>A</i> / Å	<i>D</i> –H [⋯] <i>A</i> / Å	<i>D</i> –H [⋯] <i>A</i> / °	Symmetry operation on <i>A</i>
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1					
O2–H2B···S3	0.782 (16)	2.431 (17)	3.2046 (17)	170 (3)	
N1–H1···S2	0.827 (16)	2.786 (17)	3.5706 (18)	159 (2)	$-x, -y-1, -z+1$
N2–H2···N6	0.827 (16)	2.045 (16)	2.871 (3)	176 (2)	
N4–H4···O3	0.825 (16)	1.868 (16)	2.693 (2)	178 (2)	$x, y, z+1.$
O3–H3···N6	0.777 (17)	2.16 (2)	2.906 (3)	161 (3)	
2					
O2–H2O···O6	0.822 (17)	1.820 (17)	2.640 (2)	176 (3)	
N2–H2···O3	0.86	1.96	2.772 (3)	157.7	
N4–H4···O5	0.86	1.95	2.802 (2)	171.1	$x, -y+1, z-1/2$
O6–H6···O5	0.82	1.99	2.799 (3)	169.9	

CONCLUSION

These results have shown that the ligand, pyridoxal *S*-methylisothiosemicarbazone, besides the usual tridentate N₂O mode of coordination (terminal nitrogen atoms of the isothiosemicarbazide moiety, and the oxygen atom of deprotonated phenolic OH-group), can be coordinated as a tetradentate ligand, as well. In this case, the oxygen atom of the hydroxymethyl group acts as the additional donor atom of the chelate ligand. In **1** this resulted in dimeric complex, while in **2** it resulted in polymeric catenation. A perusal of the Cambridge Structural Database showed that the coordination of the hydroxymethyl group is rare within pyridoxal-based Schiff base metal complexes.

Acknowledgements. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants Nos. 172014 and III41010).

ИЗВОД

СИНТЕЗА И КРИСТАЛНА СТРУКТУРА КОМПЛЕКСА БАКРА(II) СА НОВИМ НАЧИНОМ КООРДИНАЦИЈЕ S-МЕТИЛИЗОТИОСЕМИКАРБАЗОНА ПИРИДОКСАЛА

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Реакцијом бакар(II)-нитрата и *S*-метилизотиосемикарбазона пиридоксала (PLITSC) у присуству амонијум-тиоцијаната добијена су два типа комплекса. Димерни комплекс формуле $\{[\text{Cu}(\mu\text{-PLITSC})\text{NCS}]_2(\text{NCS})_2 \cdot 2\text{MeOH}\}$ је добијен у присуству вишка амонијум-тиоцијаната, док је полимерни комплекс формуле $\{[\text{Cu}(\mu\text{-PLITSC})\text{NCS}]\text{NO}_3 \cdot \text{MeOH}\}_n$ добијен у присуству приближно еквимоларне количине амонијум-тиоцијаната. Комплекси су окарактерисани елементалном анализом, кондуктометријом и IR спектроскопијом, а њихове структуре су недвосмислено утврђене рендгенском структурном анализом. У оба комплекса је атом бакра пента-координан и налази се у квадратно-пирамидалном окружењу. Базалну раван квадратне пирамиде чине атом кисеоника депротонване фенолне групе, и терминални атоми азота изотиосемикарбазидног остатка Шифове базе, као и атом азота координаног тиоцијанатног јона, док је апикално место заузето атомом кисеоника хидроксиметил групе из суседне асиметричне јединице. Наведени начин

координације PLITSC је први пут нађен у овим комплексима. Претрага Кембричке банке структурних података је показала да је координација хидроксиметил групе ретка код комплекса метала са Шифовим базама пиридоксала.

(Примљено 14. јануара; прихваћено 28. јануара 2019)

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