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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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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. A dimeric complex of the formula $[\{Cu(\mu\text{-PLITSC})NCS\}_2](NCS)_2\cdot 2MeOH$ was obtained in the presence of excess of ammonium thiocyanate, while in the presence of its nearly equimolar amount, crystals of a polymeric complex $\{[Cu(\mu\text{-PLITSC})NCS]NO_3\cdot MeOH\}_n$ were formed. The complexes were 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 the 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. A 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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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 also their versatile coordination chemistry.[1–3] In addition, 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 the thioureido fragment, –NH–C(NH_2)=S, is used for coordination, differing from isothiosemicarbazones, where coordination through the nitrogen atom of the NH_2-group of the –N=C(–SR)–NH_2 fragment occurs, rather than through the sulfur atom of *S*-alkyl moiety. 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-aldehyde[12] or 2-(diphenylphosphino)benzaldehyde,[13] thus forming complexes with tetradentate N_2O_2, N_3O and N_2OP donors, respectively. It was 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]

The focus of this research was pyridoxal *S*-methylisothiosemicarbazone (PLITSC), one of the isothiosemicarbazone ligands. Complexes of some 3d metals with this ligand have been synthesized and structurally characterized,[9,18,19] and it was found that, without exception, this ligand acts as a tridentate N_2O donor, which is coordinated to the metal ion through the azomethine and isothioamide nitrogen atoms and the 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 occurs) and dianionic (with the additional deprotonation of the pyridine nitrogen atom).[9]

Herein, the molecular and crystal structures of dimeric and polymeric complexes of Cu(II) with PLITSC, of the formulas $[\{Cu(\mu\text{-PLITSC})NCS\}_2](NCS)_2\cdot 2MeOH$ (**1**) and $\{[Cu(\mu\text{-PLITSC})NCS]NO_3\cdot MeOH\}_n$ (**2**) are presented. In the complexes, the tetradentate N_2O_2 manner of coordination of the PLITSC was 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, the preparation of which was described earlier.[20]

Synthesis of the complexes

*[{Cu(*μ*-PLITSC)NCS}$_2$](NCS)$_2$·2MeOH (**1**)*. A mixture of PLITSC (0.060 g, 0.22 mmol) and $Cu(NO_3)_2·3H_2O$ (0.045 g, 0.19 mmol) was poured over by 10 cm^3 MeOH and heated. After 15 min, a solution of NH_4NCS (0.030 g, 0.4 mmol) in 2 cm^3 MeOH was added to the cooled solution, the color of which became intense green. The resulting solution was left at room temperature to evaporate. The obtained dark-green single crystals were filtered and washed with MeOH. Yield: 0.05 g (45 %).

*{[Cu(*μ*-PLITSC)NCS]NO$_3$·MeOH}$_n$ (**2**)*. A mixture of PLITSC (0.060 g, 0.22 mmol) and $Cu(NO_3)_2·3H_2O$ (0.060 g, 0.25 mmol) was dissolved in 8 cm^3 of hot MeOH. After 15 min, a solution of NH_4NCS (0.020 g, 0.26 mmol) in 2 cm^3 MeOH was added to this solution. The resulting solution was left at room temperature to evaporate. The obtained dark-green single crystals were filtered and washed with MeOH. Yield: 0.04 g (38 %).

Analytical methods

Elemental analyses (C, H, N and S) of air-dried compounds were realized by standard micro-methods. Molar conductivity measurements of freshly prepared MeOH solutions (c = = 1.0 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} using the 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_α X-radiation, λ = 0.71073 Å) 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 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 the idealized positions and refined by a riding model. Their displacement parameters were approximated as $U_{iso} = kU_{eq}$ 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 the AFIX 123 command in SHELXL-2018. Hydrogen atoms bonded to heteroatoms 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_{iso} = $1.2U_{eq}$ of the parent atoms. In **2**, this treatment was used for hydrogen atoms bonded to N1 and O2, while for the other heteroatom-bonded hydrogen atoms, a riding model was used. Structure validation and additional geometrical calculations were performed by PLATON.[25] The graphics were plotted with ORTEP3 for Windows.[26] Crystallographic and refinement details are listed in Table S-I of the Supplementary material to this paper and are deposited in The Cambridge Crystallographic Data Centre under CCDC 1890436–1890437.

RESULTS AND DISCUSSION

Syntheses and characterization

Both complexes were obtained in the reaction of MeOH solutions of $Cu(NO_3)_2·3H_2O$, PLITSC and NH_4NCS. In the presence of excess NH_4NCS, the dimeric complex **1** was formed, otherwise, the obtained complex was polymeric complex **2**.

The complexes are crystal substances, soluble in MeOH and DMF, while poorly soluble in H_2O and Me_2CO. 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 $\nu(NH^+)$ 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 a 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 the free ligand (1655 cm^{-1}), it is shifted to a lower energy, due to coordination of the azomethine nitrogen atom. Coordination of oxygen atom of the deprotonated phenolic OH-group leads to a positive shift of the ν(C–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 ν(C–N) vibrations of coordinated and non-coordinated NCS-groups, respectively. Unlike this, in the spectrum of complex **2**, only one band is found in the same region (2058 cm^{-1}).[28] In addition, in the spectrum of the latter complex, very strong band at 1385 cm^{-1} undoubtedly originates from ν(NO) vibrations of the NO_3-group.[28]

Analytical and IR spectral data for the complexes are given in the Supplementary material to this paper.

Crystal structure description

Complex **1** consists of dinuclear centrosymmetric complex ion $[\{Cu(\mu\text{-PLITSC})NCS\}_2]^{2+}$ and NCS^-, while complex **2** is comprised of polymeric complex ions $\{[Cu(\mu\text{-PLITSC})(NCS)]^+\}_n$ and NO_3^-. 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 S-II of the Supplementary material.

In both complexes, the ligand is coordinated as a N_2O_2 tetradentate donor, in a way that the isothioamide and azomethine nitrogen atoms and phenoxide oxygen atom make bonds to one copper atom, while the oxygen atom of the hydroxymethyl group binds a second copper atom. In **1**, this results in a dimeric complex, while it results in polymeric catenation in **2**.

A survey of the Cambridge Structural Database (CSD)[29] version 5.40 (Nov, 2018) revealed over 200 structures with a pyridoxal-based Schiff base metal complex. It should not escape notice that in a significant number of these (80), the 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 a coordinated hydroxymethyl function, illustrating how this coordination mode is rare. In a sub-set of these containing copper(II) as a central atom, the hydroxymethyl group plays the role in dimerization of Cu(II) atoms in six complexes (CSD refcodes: ARALAG,[30] IVEPAC,[31] KAHGIM,[32] KAHGOS,[32] PEBWEA[33] and QEKRII[34]), while in three complexes, the hydroxymethyl group plays the role in polymerization of Cu(II) atoms (CSD refcodes: QEKREE,[34] EBAQOQ[35] and FIVKAW[36]).

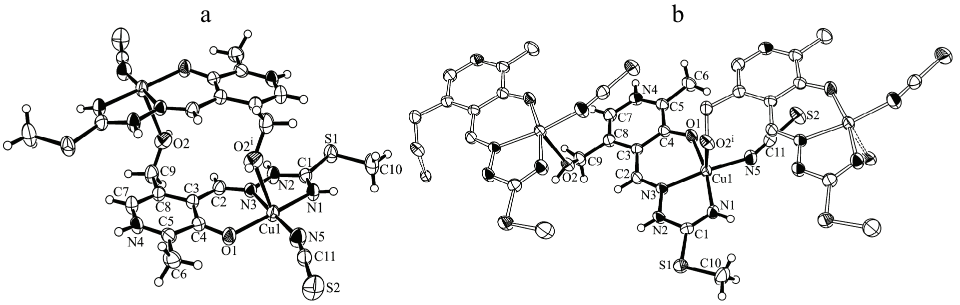

Fig. 1. Molecular structures of cations $[\{Cu(\mu\text{-PLITSC})NCS\}_2]^{2+}$ of **1** (a) and $\{[Cu(\mu\text{-PLITSC})(NCS)]^+\}_n$ of **2** (b). In (b), the repeating unit is depicted with filled bonds, and neighboring units are drawn without hydrogen atoms for the sake of clarity. Symmetry codes are: (i) $-x+1$, $-y$, $-z+1$ (for **1**); $-x+½$, $y+½$, z (for **2**).

The intra-ligand bond lengths have typical values in accordance with those found in structurally related complexes.[9] The bond lengths of the C1–N1 and C2–N3 bonds are typical for localized double bonds, and the C4–O1 bond length clearly indicates electron delocalization of the phenoxide function. Similarly, the valence angles of the isothiosemicarbazide moieties of the two complexes match within 1–2°. Finally, it is worth noting that the C5–N4–C7 angles have values greater than 120° (*ca.* 124°) which is representative for a 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 the Holmes method[38] (using 174° as the value of the idealized *trans*-basal angles) indicates that transition along the Berry pseudorotation coordinate ($D_{3h} \rightarrow C_{2v} \rightarrow C_{4v}$) for the coordination polyhedrons of the complexes is 89 % for **1**, and 84 % for **2**, meaning that the coordination polyhedron of **2** is slightly more deformed.

It has been shown[39] that in certain classes of copper(II) complexes, 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 the copper atom of the dimeric complex **1** has an additional short contact (2.9879(16) Å) with the phenoxide oxygen atom $O1^{ii}$ (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–pyramidal. That would also render the complex cation of **1** 1-D polymeric, with the repeating unit being a "dimer" and with the crystallographic axis *a* as the 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 ELUVIR[40]).

The 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, the phenoxide oxygen O1 participates in the shortest metal–ligand bond, which is in accordance with the formal negative charge located on this atom. In general, the bond lengths within the coordination polyhedron are comparable in **1** and **2**, with the exception of the 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 a 2° tolerance), while the *cis*-valence angles involving the apical O2 are significantly different for the two complexes. Among these, O2–Cu1–N3 and O2–Cu–O1 are the smallest in **1**, while the O2–Cu1–N5 and O2–Cu1–N1 are smallest in **2**, which reveal that Cu1–O2 apical bond is inclined in opposite directions with respect to the basal plane in these complexes. The magnitude of inclination is rather similar, as the acute angles between the Cu1–O2 apical bond vector and the least squares plane through the 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 could be expressed as follows. As the Cu1–O2 bond is longer in **1**, and inclined away from the 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 the thiocyanate ion. Due to the larger N3–Cu1–N5 angle in **1**, the 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 the wider trans basal angle N3–Cu1–N5 in **1** may be found in the existence of the $O1^{ii}$ atom occupying the sixth quasi-octahedral site.

A further difference between the cations in **1** and **2** is the 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, the coordinated ligand significantly deviates from planarity in **1**, which renders the six-membered metallocycle puckered. The conformation of the Cu1–O1–C4–C3–C2–N3 ring is $^{1}S_{2}$ screw-boat, slightly deformed towards $^{4}T_{2}$ twist-boat (nomenclature after Boeyens[41]), according to the Cremer & Pople[42] puckering parameters $Q = 0.2494(14)$ Å, $\theta = 63.4(4)°$, $\varphi = 34.9(5)°$.

Polymeric cations of **2** propagate in the crystallographic *b* direction, with the repeating units being symmetry related by a glide plane. Closest Cu···Cu distances were found between neighboring dimers/chains in both complexes (Cu···Cu^{ii} = 3.7035(6) Å, symmetry code (ii) –*x*, –*y*, –*z*+1 for **1**, and Cu···Cu^{ii} = 3.9228(6) Å, symmetry code (ii) –*x*+1, *y*, –*z*+³⁄₂ for **2**), while the intra-dimer Cu···Cu^{i} separation is 7.1439(6) Å in **1**, and intra-chain Cu···Cu^{i} separation is 7.1064(3) Å in **2** (symmetry codes as in Table S-II).

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

TABLE I. Selected hydrogen-bond parameters

D–H···*A*	*D*–H / Å	H···*A* / Å	*D*···*A* / Å	*D*–H···*A* / °	Symmetry operation on *A*
			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*-½
O6–H6···O5	0.82	1.99	2.799 (3)	169.9	

CONCLUSIONS

The obtained results show that the ligand, pyridoxal *S*-methylisothiosemicarbazone, besides the usual tridentate N_2O mode of coordination (terminal nitrogen atoms of the isothiosemicarbazide moiety, and the oxygen atom of deprotonated phenolic OH-group), can also be coordinated as a tetradentate ligand. In this case, the oxygen atom of the hydroxymethyl group acts as an additional donor atom of the chelate ligand. In **1**, this resulted in a dimeric complex, while in **2**, it resulted in polymeric catenation. A perusal of the Cambridge Structural Database showed that coordination of the hydroxymethyl group is rare within pyridoxal-based Schiff base metal complexes.

SUPPLEMENTARY MATERIAL

Additional analytical and crystallographic data are available electronically from http:// //www.shd.org.rs/JSCS/, or from the corresponding author on request, or are deposited in the Cambridge Crystallographic Data Centre under CCDC 1890436–1890437, obtainable free of charge from www.ccdc.cam.ac.uk/structures.

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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 $[\{Cu(\mu\text{-PLITSC})NCS\}_2](NCS)_2\cdot 2MeOH$ је добијен у присуству вишка амонијум-тиоцијаната, док је полимерни комплекс формуле $\{[Cu(\mu\text{-PLITSC})NCS]NO_3\cdot MeOH\}_n$ 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-координован и налази се у квадратно-пирамидалном окружењу. Базалну раван квадратне пирамиде чине атом кисеоника депротоноване фенолне групе, и терминални атоми азота изотиосемикарбазидног остатка Шифове базе, као и атом азота координованог 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 Cambridge Structural Database је показала да је координација хидроксиметил групе ретка код комплекса метала са Шифовим базама пиридоксала.

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