



J. Serb. Chem. Soc. 83 (2) 157–166 (2018)
JSCS–5065

2-Acetylpyridine-aminoguanidine Schiff base – Novel ligand salt and zinc(II) complex containing thiocyanate

MIRJANA M. RADANOVIĆ^{1*#}, SLAĐANA B. NOVAKOVIĆ^{2#}, LJILJANA S. VOJINOVIĆ-JEŠIĆ^{1#}, MARKO V. RODIĆ^{1#} and VUKADIN M. LEOVAC^{1#}

¹Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, Serbia and ²Vinča Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, P. O. Box 522, 11001 Belgrade, Serbia

(Received 22 September, revised 2 November, accepted 7 November 2017)

Abstract: A new salt of Schiff base of aminoguanidine and 2-acetylpyridine, and its zinc(II) complex were obtained and their physicochemical and structural properties studied. The reaction of an aqueous solution of the chloride ligand salt and NH₄NCS resulted in formation of the dithiocyanate ligand salt, L·2HNCS, while the reaction of the obtained salt with zinc(II) acetate gave a neutral complex of the formula [ZnL(NCS)₂]. In this complex, chelate ligand is coordinated in its neutral form, in a common tridentate NNN manner, *via* pyridine, azomethine and imino nitrogen atoms of the aminoguanidine fragment. This coordination mode results in formation of two strained five-membered metallocycles. Zinc(II) is situated in a distorted square-pyramidal environment of the tridentate ligand and one thiocyanate ion in the equatorial and the other thiocyanate ion in the apical position. The crystal structure of the ligand salt is stabilized by N–H···N and N–H···S interactions formed between the cationic and anionic species, while the three-dimensional crystal packing of the complex units is based on weak N–H···S interactions which involve the S acceptors from both NCS ligands.

Keywords: Schiff base; crystal structure; physico-chemical characterization; metal complexes.

INTRODUCTION

Schiff bases are one of the mostly used ligand classes due not only to the ease of their formation and both chemical and structural variety, but also very versatile application possibilities.¹ Pharmacological applications of aminoguanidine and its derivatives are thoroughly investigated.² The guanidine group is found in a large number of biomolecules and it is important for the research in

* Corresponding author. E-mail: mirjana.lalovic@dh.uns.ac.rs

Serbian Chemical Society member.

<https://doi.org/10.2298/JSC170922116R>

the field of natural product synthesis and drug development.³ The pronounced alkalinity of this group,² thus its positive charge, make it important for recognition in chemical and biological systems.⁴ Considering the fact that the bioactivity of metal complexes is usually increased and the side-effects are decreased as compared to the ligands themselves,⁵ it is not surprising that this field of study attracts much attention.^{6–8}

On the other hand, complexes of zinc(II) are particularly interesting because zinc is the second most abundant d-metal in organisms, it is essential for the structure and function of a large number of macromolecules⁹ and has a specific role in numerous bioinorganic processes. Namely, zinc(II) could be four-, five- or six-coordinated, its complexes are kinetically labile and the inter-conversion between the states of different coordination number is fast.⁹

In this paper, the synthesis, physicochemical, and structural properties of 2-acetylpyridine-aminoguanidine Schiff base ((2*E*)-2-[1-(2-pyridinyl)-ethylidene]hydrazinecarboximidamide) dihydrothiocyanate (L·2HNCS) and its zinc(II) complex, of the formula [ZnL(NCS)₂], are discussed.

EXPERIMENTAL

Reagents

All commercially obtained reagent-grade chemicals were used without further purification. 2-Acetylpyridine-aminoguanidine Schiff base dihydrochloride was synthesized according to a previously described procedure.¹⁰

Synthesis of L·2HNCS

2-Acetylpyridine-aminoguanidine Schiff base dihydrochloride (0.50 g, 2.0 mmol) was dissolved in 10 mL H₂O, NH₄NCS (0.30 g, 4.0 mmol) was added and the reaction mixture was slightly heated for a few minutes. The obtained solution was left at the room temperature and after 24 h, the colourless crystals were filtered *in vacuo* and washed with EtOH. Yield: 0.36 g (61 %).

Synthesis of [ZnL(NCS)₂]

The ligand, L·2HNCS (0.15 g, 0.50 mmol) was dissolved in 15 mL of H₂O and Zn(OAc)₂·2H₂O (0.11 g, 0.50 mmol) was added. After one week, the formed rod-like single crystals were filtered off and washed with EtOH. Yield: 0.12 g (67 %).

Analytical methods

Elemental analyses (C, H, N and S) of the air-dried compounds were carried out by standard micro-methods in the Center for Instrumental Analyses, IHTM, in Belgrade. Molar conductivity measurements of freshly prepared 1 mM solutions were performed on a Jenway 4010 conductivity meter. IR spectra were recorded on a Nicolet Nexus 670 FTIR (Thermo Scientific) spectrophotometer, in the range of 400–4000 cm⁻¹ using the KBr pellet technique.

Single crystal X-ray diffraction

Single-crystal X-ray diffraction data for compounds L·2HNCS and [ZnL(NCS)₂] were collected on an Oxford Gemini S diffractometer equipped with a CCD detector, using monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction and empirical absorption correction were performed with CrysAlisPRO.¹¹ The structures were solved by direct methods

using SHELXS and refined on F^2 by full-matrix least-squares using SHELXL.¹² All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed at the geometrically calculated positions with the C–H distances fixed to 0.93 and 0.96 Å from the aromatic and methyl C atoms, respectively. H atoms attached to N atoms were located in difference Fourier maps and refined using distance restraints. The U_{iso} values of the H atoms were approximated by U_{eq} values of their carrier atoms. The compound L·2HNCS was refined as a racemic twin resulting in twin fractions of 0.30(9) and 0.70(9). Crystallographic details for structure analysis of L·2HNCS and $[\text{ZnL}(\text{NCS})_2]$ are summarized in Table S-I of the Supplementary material to this paper. The figures were produced using ORTEP¹³ and MERCURY.¹⁴ WINGX,¹⁵ PLATON¹⁶ and PARST¹⁷ software were used for the preparation of the materials for publication.

RESULTS AND DISCUSSION

Syntheses and characterization

The reaction of warm aqueous solution of L·2HCl¹⁰ and an excess of NH_4NCS yielded colourless plate-like single crystals of the thiocyanate ligand salt, *i.e.*, L·2HNCS. In the reaction with $\text{Zn}(\text{OAc})_2$ and the obtained ligand, colourless single crystals of the complex $[\text{ZnL}(\text{NCS})_2]$ were formed.

The ligand and the complex are solid compounds, stable in air and high temperatures. The ligand is well soluble in water and less soluble in EtOH and MeOH, while the complex is poorly soluble in all the mentioned solvents. However, both compounds are well soluble in DMF.

The characterization data for the ligand and the complex are given in the Supplementary material.

The molar conductivity of a DMF solution of the ligand corresponds to a 2:1 electrolyte type, which is in concordance with the given formula. On the contrary, in the DMF solution of the complex, partial substitution of the NCS-ligand with solvent molecules occurs and thus, the value of the molar conductivity is lower than those for 1:1 type of electrolytes, but significantly higher than the one expected for non-electrolytes.

On comparison of the IR spectrum of the ligand with that of the complex, it could be proven that the chelating ligand is coordinated in a tridentate NNN manner, *via* the pyridine, azomethine and imino nitrogen atoms of the aminoguanidine moiety. In the spectrum of the ligand, the strong band ascribed to $\nu(\text{C}=\text{N})$ vibrations is found at 1680 cm^{-1} , but upon coordination, it is shifted towards the lower energy region (1659 cm^{-1}). Similarly, the band that is a result of guanidine group vibrations, located at 1628 cm^{-1} in the spectrum of the ligand, underwent a negative shift of *ca.* 30 cm^{-1} on complexation. The broad low intensity bands in the region $3100\text{--}2800\text{ cm}^{-1}$ in the spectrum of the ligand implicate protonation of the pyridine nitrogen atom. The absence of these bands in the spectrum of the complex indicates deprotonation, and the band at 633 cm^{-1} suggests coordination of this atom. Additionally, the sharp, very strong band at

2058 cm^{-1} in the spectrum of the ligand, originates from free NCS^- . Due to coordination of two NCS^- -ligands, in the spectrum of the complex, in this region doublet band at 2109 and 2084 cm^{-1} is present.¹⁸

Crystal structure analysis

Molecular structures of compounds including the atom labelling schemes are presented in Fig. 1, while selected geometrical parameters are listed in Table I. The asymmetric unit of $\text{L} \cdot 2\text{HNCS}$ contains the ligand molecule, protonated at the N atoms of the pyridine ring and imino group of the aminoguanidinium (AG) fragment, and two thiocyanate counter-ions (Fig. 1). Among the four C–N bonds of the ligand, the imino bond C2–N3 displays the shortest length (1.283(3) Å), typical for a pure double bond (Table I). The torsion angle N2–N3–C2–C3, involving this bond, has a value of 180.0(2)° and reveals the *E* configuration of the present Schiff base. The C–N bonds belonging to the AG fragment display intermediate lengths (between single and double bonds) with similar distances for the C1–N1 and C1–N4 bonds involving the two amino groups (Table I). The partial double-bond character is also present in the N–N bond (1.366(3) Å), which shows notable shortening with respect to the length of a typical single bond (1.41 Å).

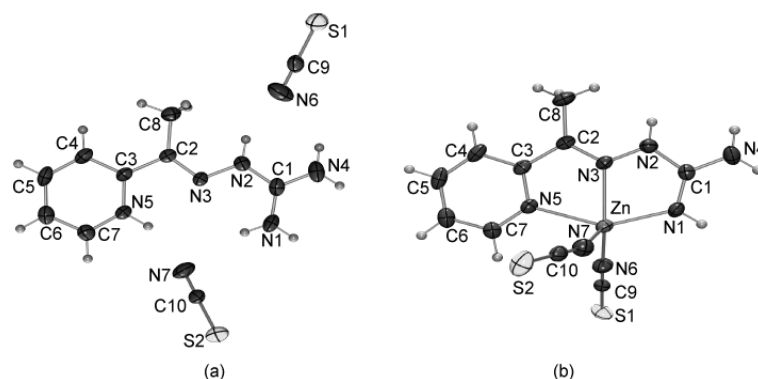


Fig. 1. Molecular structure of: a) $\text{L} \cdot 2\text{HNCS}$ and b) $[\text{ZnL}(\text{NCS})_2]$ with the atom labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level.

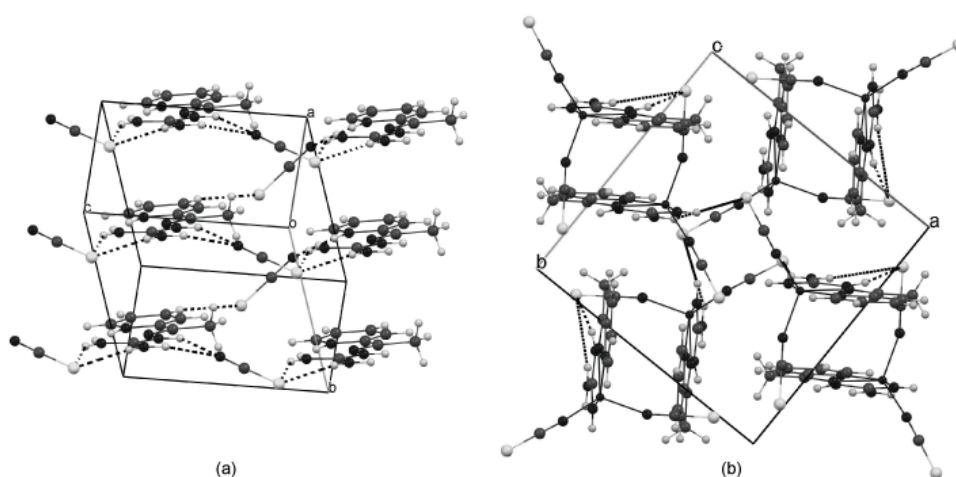
The intermediate bond lengths accompanied by sets of sp^2 angles at each non-H atom in the aliphatic chain (the sum of the angles at the atom centres is 360°, with exception of methyl C8) indicate overall charge delocalization within the ligand molecule. All non-H atoms of the ligand are therefore coplanar with mean deviations from their respective plane of 0.024 and the maximal deviation of pyridine N5 of $-0.03(1)$ Å. The plane of the pyridine ring is only slightly twisted from the plane of the AG fragment, forming the dihedral angle of 1.2(1)°. The described geometrical features of the cation in $\text{L} \cdot 2\text{HNCS}$ are closely com-

parable to those of similar protonated ligands in two recently reported salts $L \cdot 2HCl$ and $L \cdot H_2SO_4$.¹⁰ For $L \cdot 2HNCS$, $L \cdot 2HCl$ and $L \cdot H_2SO_4$, slight variations can be observed in the values of torsion angles $N5-C3-C2-N3$ ($0.3(3)$, -2.01 and -3.24° , respectively) and $C2-N3-N2-C1$ ($-177.5(3)$, 180.0 and 175.8° , respectively).

TABLE I. Selected bond lengths (Å) and bond angles ($^\circ$)

Bond	[ZnL(NCS) ₂]		Angle	[ZnL(NCS) ₂]	
	L·2HNCS	[ZnL(NCS) ₂]		L·2HNCS	[ZnL(NCS) ₂]
Zn1–N1	–	2.037(4)	N1–Zn1–N3	–	75.0(2)
Zn1–N3	–	2.150(4)	N3–Zn1–N5	–	71.5(1)
Zn1–N5	–	2.220(4)	N1–Zn1–N5	–	146.5(2)
C1–N1	1.302(5)	1.289(6)	N6–Zn1–N7	–	113.1(2)
C1–N2	1.343(4)	1.367(6)	N2–N3–C2	116.5(2)	123.2(4)
C1–N4	1.317(4)	1.356(6)	N3–N2–C1	118.0(3)	114.9(4)
C2–N3	1.283(3)	1.286(6)	N1–C1–N2	120.8(3)	118.5(4)
N2–N3	1.364(3)	1.346(5)	N3–C2–C3	113.4(2)	113.2(4)

The crystal structure of $L \cdot 2HNCS$ is mainly stabilized by $N-H \cdots N$ and $N-H \cdots S$ interactions formed between the cationic and anionic species. It can be noticed that the six $N-H$ hydrogen donors of the ligand act in pairs, each pair engaging the single anion acceptor (N or S) and thus forming three-centre bifurcated hydrogen bonds (Fig. 2a, Table II). Similar bifurcated interactions with equivalent spatial distribution of the anions containing the acceptors were observed for the crystal structures of $L \cdot 2HCl$ and $L \cdot H_2SO_4$.¹⁰ In the case of $L \cdot 2HNCS$, the bifurcated interactions involving the two guanidinium donor pairs and corresponding N or S acceptors from the $N6-C9-S1$ anion link the cations into a chain extending along the c crystallographic axis (Fig. 2a, Table II). The

Fig. 2. Crystal packing of: a) $L \cdot 2HNCS$ and b) $[ZnL(NCS)_2]$.

second anion, N7–C10–S2, forms a short bifurcated interaction (N5–H5···N7 and N1–H1a···N7) by engaging the remaining py and AG donor pair (Table II), while the S acceptor serves to connect two adjacent chains by weak C–H···S interactions (Fig. 2a, Table II). In this arrangement, the flat molecules form parallel stacks in the *a* direction with the partial overlap between the guanidinium fragment –C1(NH₂)₂ and the pyridine ring. The interplane distance between the adjacent ligand molecules is 3.47 Å. A similar partial overlap with the interplane distances of 3.35 and 3.54 Å could be observed in the crystal structures of L·2HCl and L·H₂SO₄.¹⁰

TABLE II. Geometrical parameters for intermolecular interactions in crystal structures of L·2HNCS and [ZnL(NCS)₂]

D–H···A	D–H (Å)	H···A (Å)	D–H···A (°)	Symmetry codes
L·2HNCS				
N1–H1a···N7	0.89(2)	2.32(3)	157(3)	<i>x, y, z</i> +1
N1–H1b···S1	0.87(2)	2.96(4)	136(3)	<i>x, y, z</i> +1
N2–H2···N6	0.83(2)	2.04(3)	158(2)	<i>x, y, z</i>
N4–H4a···S1	0.84(2)	2.52(4)	166(3)	<i>x, y, z</i> +1
N4–H4b···N6	0.86(2)	2.35(4)	144(2)	<i>x, y, z</i>
N5–H5···N7	0.89(4)	1.943(4)	154(4)	<i>x, y, z</i> +1
C5–H5a···S2	0.93	2.88	159	<i>x</i> +1, <i>y, z</i>
[ZnL(NCS) ₂]				
N1–H1···S1	0.85(3)	2.69(3)	159(5)	– <i>x</i> +1, – <i>y</i> +1, <i>z</i> +0.5
N2–H2···S2	0.86(3)	2.63(3)	157(5)	– <i>x, –y</i> +2, <i>z</i> +0.5
N4–H4a···S1	0.90(3)	2.98(4)	132(5)	– <i>x</i> +1, – <i>y</i> +1, <i>z</i> +0.5
N4–H4a···S1	0.90(3)	2.77(5)	132(5)	– <i>y</i> +1, <i>x, z</i> +1.5
N4–H4b···S2	0.91(3)	2.89(4)	141(5)	– <i>x, –y</i> +2, <i>z</i> +0.5

The crystal packing of [ZnL(NCS)₂] consists of discrete complex units, where the Zn atom is five-coordinated by the three N atoms belonging to the neutral Schiff base, and two N atoms from the thiocyanate ligands. The Addison τ parameter¹⁹ calculated from the equation $\tau = (\beta - \alpha)/60$ has a value of 0.29 (α and β are the largest angles in the coordination sphere; $\tau = 0$ for a perfect square pyramid, and $\tau = 1$ for a perfect trigonal bipyramid). Hence, the five-coordinate geometry of the Zn centre could be described as a distorted square pyramid, with the three N donors of chelate ligand, and one thiocyanate N donor defining the basal plane, and the second thiocyanate N donor occupying the apical position. According to the geometrical parameters summarized in Table II, the significant distortion of the coordination geometry is mainly related to the small bite angles of the tridentate ligand. The Zn–N coordination bonds are comparable to those in previously reported Zn complexes comprising a similar tridentate (NNN) Schiff base and NCS anion as ligands.^{20–26} In [ZnL(NCS)₂], the Zn–N bond involving the pyridine N atom is the longest and that involving the imino N is the shortest

bond with the chelate ligand (Table I). A similar trend was observed in two previously reported Cu(II) complexes comprising the same tridentate ligand.¹⁰ The geometries of the two linear NCS ligands in $[\text{ZnL}(\text{NCS})_2]$ are mutually similar, but they form noticeably different distances and angles with the central metal atom (Zn1–N6 1.974(4) and Zn1–N7 1.998(4) Å, Zn1–N6–C9 (175.4(4) and Zn1–N7–C10 161.4(4)°).

By coordination to the Zn atom, the tridentate ligand forms two strained five-membered chelate rings. As evidenced by the torsion angles C3–C2–N3–Zn and C1–N2–N3–Zn of -4.8 and 4.5° , respectively, both chelate rings display slight twists at the bonds involving the central N3 donor. Among the three fused rings of the chelate ligand, the largest dihedral angle of $1.4(2)^\circ$ is found between the mean planes of the pyridine ring and guanidinium metallocycle. In general, the coordinated Schiff base retains a high degree of planarity (root mean square deviation of the non-H atoms does not exceed 0.02 Å) and the same *E*-configuration at C2–N3 bond as observed for the protonated ligand. The deprotonation of the ligand at pyridine N does not particularly affect the lengths of the vicinal bonds, while deprotonation at N1 results in a shortening of C1–N1 and an elongation of C1–N2 and C1–N4 bonds (Table II). The overlay of the crystal structures belonging to the free and coordinated ligand (Fig. 3) reveals only slight conformational changes, which mainly occur at the N3 donor atom (angle C2–N3–N2 is $116.5(2)$ and $123.2(4)^\circ$ in L·2HNCS and $[\text{ZnL}(\text{NCS})_2]$, respectively). Upon coordination of the rigid ligand to the metal centre, the distance between the terminal donor atoms N5 and N1 shortens from 4.48 to 4.08 Å. The three-dimensional crystal packing of the $[\text{ZnL}(\text{NCS})_2]$ complex units is based on weak N–H...S interactions which involve the S acceptors from both NCS ligands (Table II). It is noteworthy that the existence of a fourfold axis between the complex units causes the linear N–C–S ligands to accumulate into square-like formations (Fig. 2b).

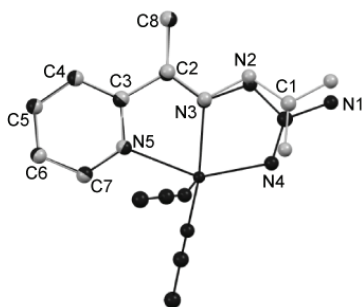


Fig. 3. Overlay of Schiff base in uncoordinated (light grey) and coordinated (dark grey) form. The least-square fit is based on atoms of the pyridine ring. H-atoms are excluded for clarity.

CONCLUSIONS

Syntheses, physicochemical properties and structural characterization of thiocyanate salt of the Schiff base 2-acetylpyridine-aminoguanidine and its complex with zinc(II) are presented. Single crystals of the Schiff base are obtained in the reaction of its chloride salt and an excess of NH_4SCN , while the reaction of aqueous solution of $\text{Zn}(\text{OAc})_2$ and the obtained ligand resulted in the formation of single crystals of the complex.

The ligand and complex were characterized by elemental analysis, IR spectroscopy, conductometric measurements and X-ray analysis. The last method showed that the isolated ligand is in its doubly protonated form, with protonated nitrogen atoms of pyridine ring and imino group of the aminoguanidinium fragment. In the obtained complex, the chelate ligand is coordinated in its neutral form through pyridine, azomethine and imino groups of the aminoguanidine residue. Zinc(II) is situated in a distorted square-pyramidal environment of the tridentate Schiff base and one NCS^- ligand in the equatorial plane and the other NCS^- ligand in the apical position. Considering the great pharmacological importance of zinc(II) complexes and the described Schiff base, as well as the possibilities for applications in many other areas, further characterization of these compounds should be the aim of future research.

SUPPLEMENTARY MATERIAL

CCDC 1575327 and 1575328 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (<https://summary.ccdc.cam.ac.uk/structure-summary-form>). The characterization data and pertinent crystallographic and refinement details are given in the Supplementary material to this paper, available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

Acknowledgement. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 172014).

ИЗВОД

ШИФОВА БАЗА 2-АЦЕТИЛПИРИДИН-АМИНОГВАНИДИН – НОВА ЛИГАНДНА СО И ТИОЦИЈАНАТО КОМПЛЕКС ЦИНКА(II)

МИРЈАНА М. РАДАНОВИЋ¹, СЛАЂАНА Б. НОВАКОВИЋ², ЉИЉАНА С. ВОЈИНОВИЋ-ЈЕШИЋ¹, МАРКО В. РОДИЋ¹ и ВУКАДИН М. ЛЕОВАЦ¹

Природно-математички факултет, Универзитет у Новом Саду, Три Д. Обрадовића 3, 21000 Нови Сад и ¹Институт за нуклеарне науке "Винча", Лабораторија за теоријску физику и физику кондензоване материје, 11001 Београд

Синтетисана је нова, тиоцијанатна со Шифове базе аминогванидина и 2-ацетилпиридина, као и њен комплекс са цинком(II) и испитане физичко-хемијске и структурне карактеристике добијених једињења. Реакцијом воденог раствора хлоридне соли лиганда са NH_4NCS изоловани су монокристали тиоцијанатне соли лиганда, док је реакција добијене соли са цинк(II)-ацетатом резултовала настанком монокристала неутралног комплекса формуле $[\text{ZnL}(\text{NCS})_2]$. У овом комплексу хелатни лиганд је координан

у својој неутралној форми, на уобичајен тридентатни NNN начин, преко пиридинског, азометинског и атома азота имино групе аминогванидинског фрагмента. Цинк(II) је смештен у деформисаном квадратно-пирамидалном окружењу тридентатног лиганда и једног тиоцијанатног јона у базалној равни и другог тиоцијанатног јона у апикалном положају. Кристална структура соли лиганда стабилизована је N–H…N и N–H…S водоничним интеракцијама, док је тродимензионално паковање структурних јединица добијеног комплекса остварено slabим N–H…S интеракцијама.

(Примљено 22. септембра, ревидирано 2. новембра, прихваћено 7. новембра 2017)

REFERENCES

1. R. Hernández-Molina, A. Mederos, in *Comprehensive Coordination Chemistry II*, J. A. McCleverty, T. J. Meyer, Eds., Elsevier, Oxford, 2003, p. 411
2. L. S. Vojinović-Ješić, M. M. Radanović, *Coordination chemistry of aminoguanidine and its Schiff bases*, Faculty of Sciences, Novi Sad, 2017 (in Serbian)
3. E. A. Buvaylo, V. N. Kokozay, O. Y. Vassilyeva, B. W. Skelton, O. V. Nesterova, A. J. L. Pombeiro, *Inorg. Chem. Commun.* **78** (2017) 85
4. T. G. Kapp, M. Fottner, O. V. Maltsev, H. Kessler, *Angew. Chem. Int. Ed.* **55** (2016) 1540
5. P. Khatkar, S. Asija, N. Singh, *J. Serb. Chem. Soc.* **82** (2017) 13
6. M. Jafari, M. Salehi, M. Kubicki, A. Arab, A. Khaleghian, *Inorg. Chim. Acta* **462** (2017) 329
7. J. Adhikary, P. Chakraborty, S. Samanta, E. Zangrando, S. Ghosh, D. Das, *Spectrochim. Acta, A* **178** (2017) 114
8. V. M. Jiménez-Pérez, M. C. García-López, B. M. Muñoz-Flores, R. Chan-Navarro, J. C. Berrones-Reyes, H. V. R. Dias, I. Moggio, E. Arias, J. A. Serrano-Mireles, A. Chavez-Reyes, *J. Mater. Chem., B* **3** (2015) 5731
9. L. Taghizadeh, M. Montazerzohori, A. Masoudiasl, S. Joohari, J. M. White, *Mater. Sci. Eng., C* **77** (2017) 229
10. L. S. Vojinović-Ješić, M. M. Radanović, M. V. Rodić, V. Živković-Radovanović, L. S. Jovanović, V. M. Leovac, *Polyhedron* **117** (2016) 526
11. Rigaku Oxford Diffraction, *CrysAlisPro Software system*, Rigaku Corporation, Oxford, 2015
12. G. M. Sheldrick, *Acta Crystallogr., A* **64** (2007) 112
13. L. J. Farrugia, *J. Appl. Crystallogr.* **30** (1997) 565
14. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* **39** (2006) 453
15. L. J. Farrugia, *J. Appl. Crystallogr.* **32** (1999) 837
16. A. L. Spek, *J. Appl. Crystallogr.* **36** (2003) 7
17. M. Nardelli, *J. Appl. Crystallogr.* **28** (1995) 659
18. K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds. Part B, Applications in coordination, organometallic, and bioinorganic chemistry*, Wiley, New York, 2009
19. A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349
20. L.-W. Xue, G.-Q. Zhao, Y.-J. Han, Y.-X. Feng, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **41** (2011) 141
21. D.-H. Shi, Z.-L. Cao, W.-W. Liu, R.-B. Xu, L.-L. Gao, Q. Zhang, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **42** (2012) 864.

22. S. Satapathi, S. Das, K. Bhar, R. K. Kuar, T. K. Maji, B. K. Ghosh, *Polyhedron* **30** (2011) 387
23. N. S. Gwaram, H. M. Ali, H. Khaledi, M. A. Abdulla, A. H. A. Hadi, T. K. Lin, C. L. Ching, C. L. Ooi, *Molecules* **17** (2012) 5952
24. P. Chakraborty, S. Purkait, S. Mondal, A. Bauzá, A. Frontera, C. Massera, D. Das, G. Polidori, R. Spagna, H. A. Sparkes, M. Towrie, *CrystEngComm* **17** (2015) 4680
25. X.-W. Li, *Acta Crystallogr., E* **67** (2011) m829
26. G. Chen, Z.-P. Bai, S.-J. Qu, *Acta Crystallogr., E* **61** (2005) m2483.