



Synthesis, Spectroscopy and X-ray Crystallography Structure of Pyridine 4-Carbaldehyde Semicarbazone Schiff Base Ligand



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ARTICLE INFO

Received: 09 November 2019

Revised: 16 December 2019

Accepted: 05 January 2020

Available online: 22 January 2020

KEYWORDS

Semicarbazone

Schiff base ligand

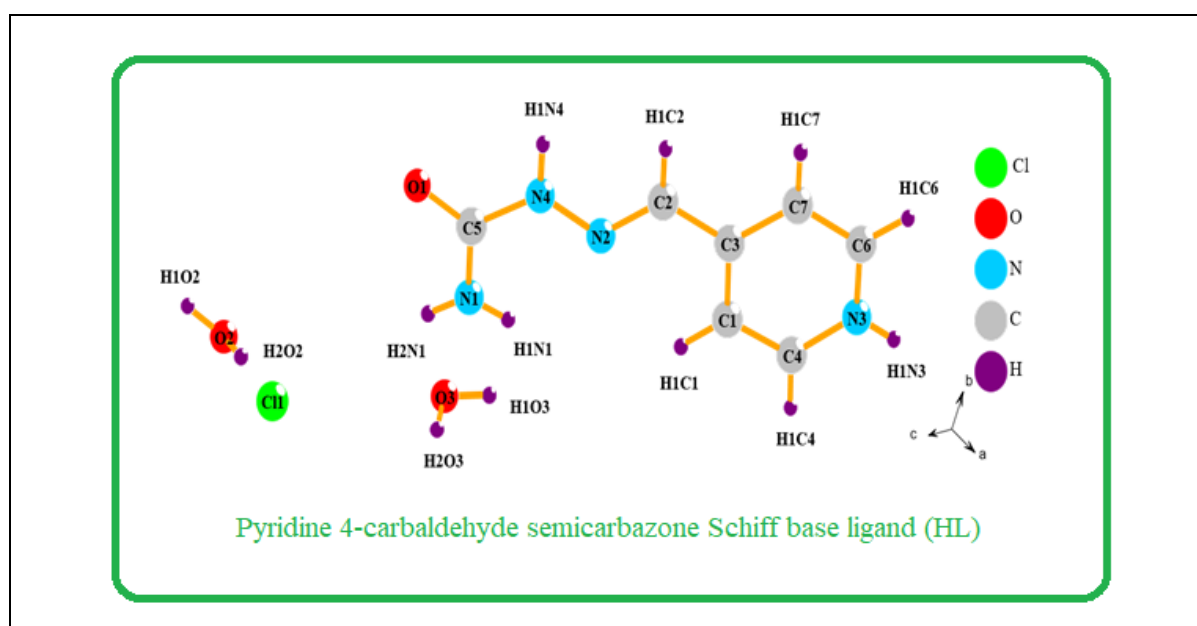
Crystal structure

Spectroscopy

ABSTRACT

In this work, pyridine 4-carbaldehyde semicarbazone Schiff base ligand (HL) was synthesized with condensation of pyridine 4-carbaldehyde and semicarbazide hydrochloride in reflux method. The HL was characterized using the CHN elemental analysis, FT-IR, UV-Vis, and ¹H NMR spectroscopy. The single crystals of HL prepared and used for the X-ray crystallography. Single-crystal X-ray diffraction revealed that, HL crystallized in a triclinic system with the space group P-1. The FT-IR spectra and X-ray crystallography results suggested that the HL ligand is in keto form.

GRAPHICAL ABSTRACT



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Introduction

Schiff bases are known as imines or azomethines and are used as ligands for synthesis of complexes using different metal ions. They are obtained from condensation reaction of primary amines and aldehydes or ketones. Often, aldehydes react faster and better than ketones because of the steric and electronic effects [1-3]. For many years, they have been introduced as chelating ligands in transition metal coordination chemistry, because of easy synthesis routes, extensive availability and versatility of structure related to their potential applications in catalysis, analytical, pharmacological, and magnetism [4-5]. Schiff bases are also used as significant intermediates for synthesis of various bioactive materials [6-9]. Countless Schiff bases and their coordination complexes with outstanding antimicrobial activity, antifungal, and anticancer abilities have been reported [8-13]. The Schiff bases with pyridine ring have received more attention in literature [14-15]. The semicarbazones and thiosemicarbazones usually behave as chelating ligands, which are versatile in both neutral and anionic forms [16-18]. Metal complexes of semicarbazones and thiosemicarbazones have gained special attention due to their importance in medicine and biological system [19-20]. Furthermore, the metal complexes of semicarbazones have demonstrated antimicrobial [21,22], anticancer [23], and antiviral activities [24,25]. The first report for synthesis of pyridine 2-carbaldehyde semicarbazone ligand dates in 1955 [26,27], discovering its antifungal activity. Keeping on that, we reported several transition metal compounds based on this ligand [25, 28-30]. Herein we synthesized a new semicarbazone ligand by the reaction of semicarbazide hydrochloride and pyridine 4-carbaldehyde under reflux conditions and characterized it with several analyses. Furthermore the structure of the HL was determined using the X-ray crystallography and discussed completely.

Experimental

General

The chemicals and solvents contains pyridine 4-carbaldehyde, semicarbazide hydrochloride and ethanol were purchased from Merck. Fourier-transform infrared spectra were recorded on Shimadzu FT-IR 8400 S (Japan) using KBr pellet. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. The uncorrected melting point was measured on an Electrothermal 9100 apparatus. ^1H NMR spectra were recorded on a Bruker AVANCE 300-MHz instruments at room temperature with the signal of the free deuterated methanol, CD_3OD solvent using TMS as internal reference. UV-Vis spectrum was recorded on a Carry 100 Conc Varian spectrophotometer.

Synthesis of pyridine 4-carbaldehyde semicarbazone (HL)

At first, semicarbazide hydrochloride (10 mmol, 1.1 g) was added to 40 mL ethanol in a round bottom flask and heated at 75 °C. It refluxed for 2 h at this temperature till dissolved completely in ethanol. Then pyridine 4-carbaldehyde (10 mmol, 1 mL) was dissolved in 10 mL ethanol and was added dropwise to the above solution under reflux condition. The mixture was refluxed on water bath for 6 h at 75 °C and the precipitate of HL was formed. After cooling the solution to room temperature, the precipitate was collected, washed with ethanol, dried in air and used without further purification. Yield: 1.8 g (83%), [m.p. 153 °C]. For synthesis of single crystals of HL with slow evaporation method, after collecting the precipitate, the solution of reaction was kept at room temperature. After 5 days, the white crystals of HL were formed at vessel of reaction. The crystals were collected and dried at room temperature. Anal. Calcd for $\text{C}_7\text{H}_{13}\text{ClN}_4\text{O}_3$: C, 35.5; H, 5.65; N, 23.67. Found: C, 35.7; H, 5.52; N, 23.80. Characteristic FT-IR data (KBr, cm^{-1}):

3386 m, ν ($-\text{NH}_2$); 3220 m, ν (N-H); 1704 s, ν (C=O); 1604 s, ν (C=N); 1087 s, ν (N-N).

Scheme 1. Synthesis of pyridine 4-carbaldehyde semicarbazone Schiff base ligand (HL)

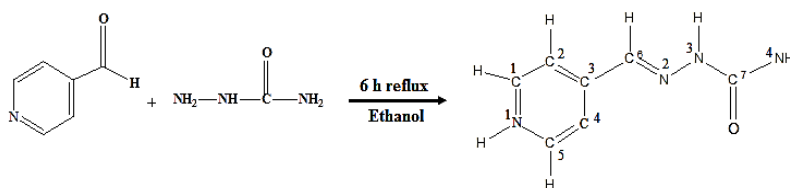


Table 1. Crystal and structure refinement data for HL

Chemical Formula	C7H13CIN4O3
Formula weight	236.66
Crystal description	Plate, transparent
Crystal size (mm)	0.13 × 0.13 × 0.04
Temperature (K)	95
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	4.6415 (1)
<i>b</i> (Å)	8.8704 (3)
<i>c</i> (Å)	14.1176 (5)
α (°)	104.918 (3)
β (°)	95.654 (3)
γ (°)	100.799 (3)
Volume (Å ³)	545.08 (3)
<i>Z</i>	2
ρ calculated (g/cm ³)	1.442
μ (mm ⁻¹)	3.112
Largest diff. peak and hole (eÅ ⁻³)	0.28-0.31
Final R indices [<i>I</i> > 3 σ (<i>I</i>)]	0.0352 (2033)
Final R indices (all data)	0.0953 (2194)

Crystallographic analysis

The single crystal X-ray diffraction experiments were performed using a Super Nova four circles diffractometer equipped with an Atlas S2 detector and an micro focus source (Cu-K α_{average} = 1.54184 Å). The data were collected at 95 K on a single crystal of suitable size (0.13 × 0.13 × 0.04 mm³), using ω scans and detector-sample distance 53 mm. The diffracted intensities were collected up to 75.420° ($-5 \leq h \leq 5$; $-11 \leq k \leq 10$ and $-17 \leq l \leq 16$). The experimental details are summarized in Table 1.

The structure has a triclinic unit cell with $a = 4.6415$ Å, $b = 8.8704$ Å, $c = 14.1176$ Å, $\alpha = 104.918^\circ$, $\beta = 95.654^\circ$ and $\gamma = 100.799^\circ$. The data reduction and absorption correction were done by the software Crys Alis Pro [31], merging of symmetry equivalent reflections yielded $R_{\text{int}} = 0.056$. The structure was solved by charge

flipping (Super flip [32]) for space group *P*-1. The refinement was performed with the software Jana 2006. The anisotropic displacement parameters (ADP) were used for N, C, O and Cl. The hydrogens atoms were inserted are insert by symmetry and positions were refined for nitrogen and oxygen atoms. The hydrogen ADP are restrained for 1.2 times U_{eq} . The final merit factor are $R_{\text{obs}} = 3.52\%$ and $wR_{\text{all}} = 9.53\%$.

Results and discussions

Most of the semicarbazone ligands display keto-enol tautomerism in coordination to metal ion centers as neutral or deprotonated ligands [16-20]. Preparation of the pyridine 4-carbaldehyde semicarbazone ligand (HL) was revealed by infrared spectroscopy (Figure 1). The FT-IR spectrum of HL revealed a strong

band at 1704 cm^{-1} and two medium bands at 3386 and 3220 cm^{-1} for C=O, -NH₂ and N-H stretching, and a sharp band at 1087 related to N-N bond. Observation of sharp band corresponding to C=O bond, suggests the keto form for HL and interestingly presence of a strong band at 1604 cm^{-1} reveals the imine functionality in HL. The bands at 2754 and 2986 cm^{-1} correspond to C-H bond of aldehyde. The strong bands at 1419 cm^{-1} and $1450\text{--}1580\text{ cm}^{-1}$ are related to aliphatic C-N bonds and aromatic C=C bonds, respectively. The low energy in-plane and out of plane vibrations of pyridine

ring are observed at 655 and 451 cm^{-1} respectively. Interestingly observation of bands at 3429 and 1640 cm^{-1} corresponding to stretching and bending vibrations of water, confirms presence of lattice water molecules in structure of HL.

The ¹H NMR spectrum of HL is demonstrated in Figure 2. The singlet resonances are observed at $\delta=10.413$, 10.391 and 9.963 ppm, which are assigned to semicarbazide NH (³NH), hydrogenated pyridine nitrogen (¹NH) and aldehyde CH groups (⁶CH), respectively.

Figure 1. FT-IR spectrum of HL

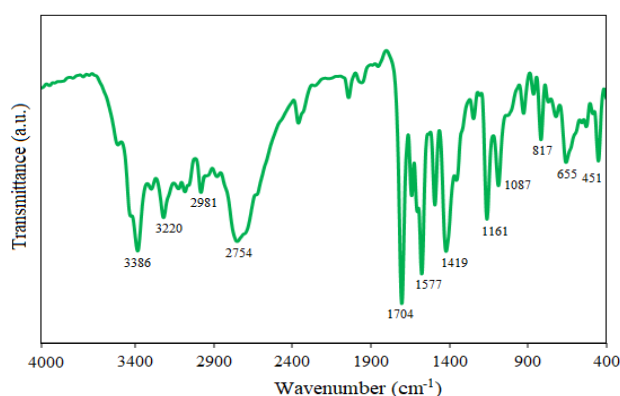
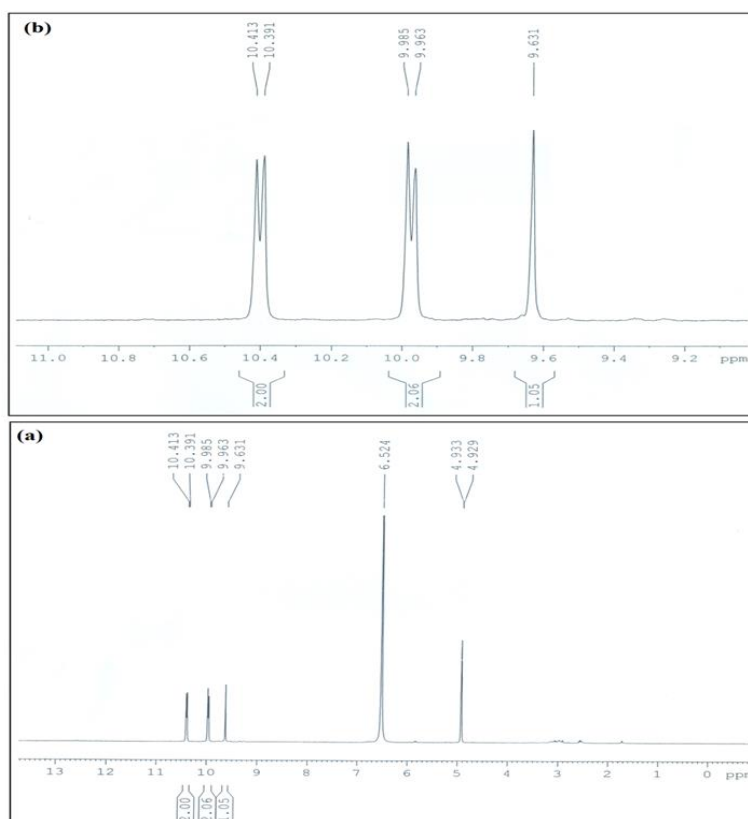


Figure 2. ¹H NMR spectrum of HL in CD₃OD



The broad small peaks at the range of 9.2-9.4 ppm are related to NH_2 group of semicarbazone ($^4\text{NH}_2$). The observed peaks at $\delta=9.985$ and 9.631 ppm belong to the pyridine protons. The peaks at 6.524 ppm can assigned to water molecules in structure of HL and the peaks at 4.929 and 4.933 ppm are related to use CD_3OD solvent for analysis.

Electronical spectra of the HL measured in methanol solvent (Figure 3). Observation of absorption bands at 224 and 328 nm corresponding to intra-ligand $\pi \rightarrow \pi^*$ transitions of the pyridin ring and imine group confirms successful synthesis of HL [28-30].

Structure of the HL is depicted in Figure 4. It crystallizes in a triclinic system, with the space group of $P-1$. X-ray crystal analysis revealed that, the structure of the HL contained a Schiff base molecule, two water molecules, and one anionic chlorine atom. The structural formula of the HL can be summarized as $[\text{H}_2\text{L}]^+\text{Cl} \cdot (\text{H}_2\text{O})_2$. According to the FI-IR data, the HL is not deprotonated and it is in inert form of ligand. In fact, the HL by keeping its hydrogen atom located on N3 atom exists in keto form. Moreover, the nitrogen of the pyridine ring is protonated, giving the ligand a positive charge,

and a chlorine atom is located in the structure as a counter-ion. The observed chlorine atom in the structure of HL is from the semicarbazide hydrochloride, which used for synthesis of HL.

The shortest bond distances of the pyridine ring are 1.347 and 1.339 Å for $\text{N3}-\text{C4}$ and $\text{N3}-\text{C6}$ respectively. The C-C or C=C distances of pyridine ring are between 1.375 Å and 1.400 Å. The selected bond distances and angles of HL are summarized at Table 2. The C=N bond length of HL is 1.285 Å which is in good consistent with the C=N bond distances in similar ligands [20-29]. Although the HL contains an aromatic cycle, there is no π - π stacking interaction in its structure. Presence of two water molecules and chlorine ion in structure of HL plays an important role in hydrogen bond interactions, expanding the structure in three dimensions. Table 3 provides more details on the hydrogen bonding interactions in HL. Figure 5a illustrates the available individual hydrogen bonds in the structure of HL. The $\text{N}_4-\text{H}_1\text{N}_4 \cdots \text{O1}$ and $\text{O}_3-\text{H}_1\text{O}_3 \cdots \text{O1}$ hydrogen bonds connect molecules into layers (Figure 5b), and the layers are interconnected by hydrogen bonds of the water molecules and chloride ions.

Figure 3. UV-Vis spectra of HL

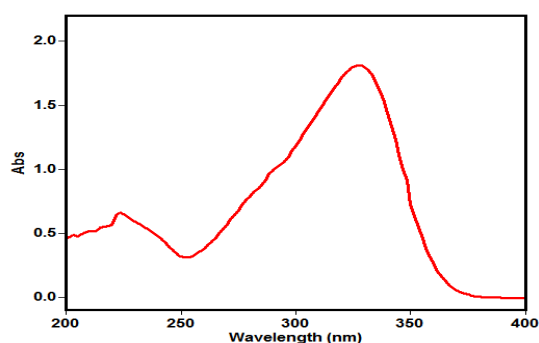


Figure 4. Crystal structure of HL

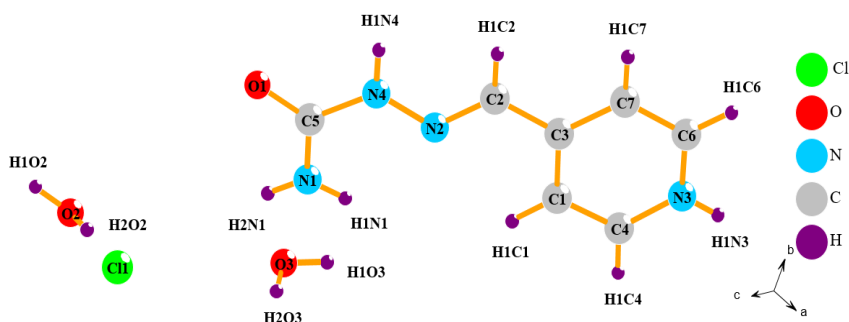


Figure 5. (a) View of hydrogen bonding interactions in HL, (b) Expansion of HL with intermolecular interactions in three dimensions (green)

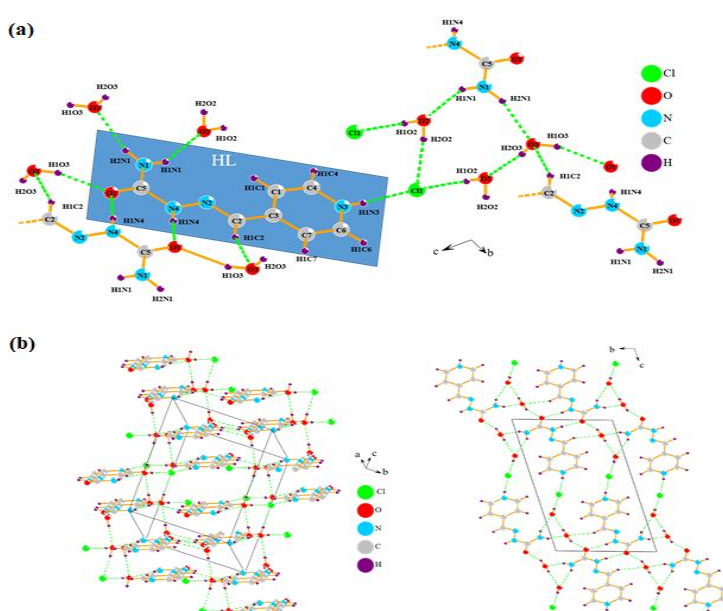


Table 2. Selected Bond Distances (Å) and Angles (°) of HL

Atom 1	Atom 2	distance (Å)	Atom 1	Atom 2	distance (Å)		
C5	O1	1.2450 (18)	N4	C5	1.3833 (19)		
	N1	1.3259 (18)	H1N4	C3	0.87 (2)		
O2	H1O2	0.85 (2)	C1	C4	1.4002 (19)		
	H2O2	0.87 (2)		H1C1	0.96		
O3	H1O3	0.83 (3)	C2	C3	1.463 (2)		
	H2O3	0.75 (2)		H1C2	0.96		
N1	H1N1	0.84 (2)	C3	C7	1.397 (2)		
	H2N1	0.84 (2)	C4	H1C4	0.96		
N2	N4	1.3527 (18)	C6	C7	1.380 (2)		
	C2	1.2846 (19)		H1C6	0.96		
N3	C4	1.347 (2)	C7	H1C7	0.96		
	C6	1.3391 (19)	Cl1	N3	3.0579 (14)		
	H1N3	0.82 (2)					
Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
H1O2	O2	H2O2	100 (2)	N2	C2	C3	118.40 (12)
H1O3	O3	H2O3	110 (2)	N2	C2	H1C2	120.8
C5	N1	H1N1	119.4 (14)	C3	C2	H1C2	120.8
C5	N1	H2N1	119.3 (15)	C1	C3	C2	121.85 (13)
H1N1	N1	H2N1	120.3 (19)	C1	C3	C7	118.95 (13)
N4	N2	C2	116.77 (11)	C2	C3	C7	119.20 (12)
Cl1	N3	C4	113.31 (9)	N3	C4	C1	120.04 (13)
Cl1	N3	C6	124.17 (10)	N3	C4	H1C4	119.98
C4	N3	C6	122.50 (14)	O1	C5	N1	124.89 (14)
C4	N3	H1N3	117.7 (14)	O1	C5	N4	117.78 (12)
C6	N3	H1N3	119.7 (14)	N1	C5	N4	117.33 (13)
N2	N4	C5	119.41 (11)	N3	C6	C7	119.76 (14)
N2	N4	H1N4	121.5 (14)	N3	C6	H1C6	120.12
C5	N4	H1N4	117.7 (14)	C7	C6	H1C6	120.12
C3	C1	C4	119.23 (14)	C3	C7	C6	119.52 (13)
C3	C1	H1C1	120.38	C3	C7	H1C7	120.24

Symmetry codes: (i) $x-1, y, z+1$; (ii) $x+1, y, z-1$

Table 3. Selected hydrogen bonding parameters in HL (D = donor, H = hydrogen and A = acceptor)

D-H.A	D (D-H) (Å)	D (H.A) (Å)	D (D.A) (Å)	(D-H.A) (°)
C2-H1C2...O3 ⁱⁱⁱ	0.96	2.49	3.4013 (18)	158.72
N1-H1N1...O2 ^{iv}	0.84 (2)	2.26 (2)	3.0087 (18)	149.6 (17)
N1-H2N1...O3 ^{iv}	0.84 (2)	2.04 (2)	2.8602 (16)	163.7 (19)
N4-H1N4...O1 ^v	0.87 (2)	1.97 (2)	2.8370 (16)	174.2 (18)
O3-H1O3...O1 ^{vi}	0.83 (3)	1.98 (2)	2.7833 (17)	160.7 (18)
O3-H2O3...O2 ^{vi}	0.75 (2)	2.11 (3)	2.8555 (18)	173 (2)
O2-H1O2...Cl1 ^{vii}	0.85 (2)	2.28 (2)	3.1281 (12)	177 (2)
O2-H2O2...Cl1	0.87 (2)	2.28 (2)	3.1418 (11)	173 (2)

Symmetry codes: (ii) $x+1, y, z-1$; (iii) $-x+2, -y+1, -z$; (iv) $-x+1, -y, -z$; (v) $-x+1, -y+1, -z$; (vi) $x+1, y, z$; (vii) $x-1, y, z$.

Conclusion

In this research study, a Schiff base ligand named pyridine 4-carbaldehyde semicarbazone (HL) was synthesized and fully characterized. The results of the CHN elemental analysis, FT-IR, UV-Vis and ¹H NMR spectroscopies confirmed the successful synthesis of the HL. The X-ray crystallography of single crystals of HL revealed its structural formula as $[H_2L]^+Cl \cdot (H_2O)_2$. Presence of several hydrogen bonding interaction in structure of HL expanded its structure in three dimensions. Also it was found that, the HL can be utilized as an interesting tridentate NNO donor ligand for synthesis of novel complexes with different metal ions.

Appendix A. supplementary data

CCDC 1494841 contains the supplementary crystallographic data for the structure reported in this paper. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgment

The authors would like to acknowledge Lorestan University for supporting this work. The crystallographic part was supported by the project 18-10504S of the Czech Science

Foundation using instruments of the ASTRA lab established within the Operation program Prague Competitiveness-project CZ.2.16/3.1.00/24510.

Disclosure statement

No potential conflict of interest was reported by the authors.

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How to cite this manuscript: Farzaneh Mahmoudi, Saeed Farhadi, Michal Dusek, Morgane Poupon, Synthesis, Spectroscopy and X-ray Crystallography Structure of Pyridine 4-Carbaldehyde Semicarbazone Schiff Base Ligand, *Adv. J. Chem. A*, **2020**, *3*(4), 534–541.