

Metal transition complexes of tridentate Schiff base ligands derived from 2-hydrazinopyridine: synthesis, spectroscopic characterization and X-ray structures

Amar Diop¹, Mamou Sarr¹, Mayoro Diop¹, Ibrahima Elhadj Thiam¹, Aliou Hamady Barry², Simon Coles³, James Orton³, Mohamed Gaye¹

Amar DIOP: <https://orcid.org/0000-0003-3170-2622>

Mamou SARR <https://orcid.org/0000-0003-1736-951X>

Mayoro DIOP <https://orcid.org/0000-0003-3594-4901>

Ibrahima Elhadj THIAM <https://orcid.org/0000-0002-4595-8445>

Aliou Hamady BARRY <https://orcid.org/0000-0003-4869-2993>

Simon COLES <https://orcid.org/0000-0001-8414-9272>

James ORTON <https://orcid.org/0000-0002-5362-6969>

Mohamed GAYE: <https://orcid.org/0000-0001-8989-1548>

mlgayeastou@yahoo.fr

Abstract

Mononuclear complexes of 1-(pyridin-2-ylmethylidene)-2-(pyridin-2-yl)hydrazine (HL¹) and 1-(pyridin-2-yl)-2-(1-(pyridin-2-yl)ethylidene)hydrazine (HL²), [Mn(HL¹)(Cl₂)(H₂O)] (**1**), [Zn(HL¹)(CH₃COO)₂](H₂O)₃ (**2**), [Mn(HL²)₂](ClO₄)₂ (**3**) and [Cu(HL²)(NO₃)₂] (**4**), were synthesized and characterized by physico-chemical and spectroscopic methods and X-ray structure determination. The mononuclear compounds **1**, **2** and **4** contain one ligand molecule per metal atom while the manganese (II) atom in the compound **3** is coordinated to two ligand molecules. Both ligands coordinated to the transition metal center in tridentate fashion through two N_{pyridyl} atoms and one N_{imino} atom. The chloride and acetate anions coordinate in monodentate manner respectively in complex **1** and in complex **2**. In complex

¹ Department of Chemistry, University Cheikh Anta Diop, Dakar, Sénégal

² Department of Chemistry, University de Nouakchott, Nouakchott, Mauritanie

³ UK National Crystallography Service, School of Chemistry, Faculty of Engineering and Physical Sciences, University of Southampton, UK. SO17 1BJ

3 the perchlorate groups remain uncoordinated. In complex **4** the nitrate anions act in unidentate fashion. The molar conductance value indicates that the complexes obtained from HL¹ are non-electrolytes while those obtained from HL² are 2:1 electrolytes in DMF solutions. The X-ray structures reveal octahedral geometry for complexes **1**, **3**, **4** and trigonal bipyramidal environment for **2**.

Keywords

Schiff base, Complex, NMR, IR, UV, Crystal structure.

Introduction

Although largely explored, the coordination chemistry of metal transition remains very interesting owing to the variability of the structures [1–3] and the possibility of applications in industries [4–6] of the complexes synthesized in this kind of chemistry. According to the metal center used, several degrees of oxidation, [7,8] different coordination numbers and original geometries that are not always easily predicted can be observed. The involvement of transition metal ions in various important biological processes [9–11], increases the interest of chemists in coordination chemistry. The examples provided by the nature encourage scientists to increase their interest in biomimetic process. The involvement of transition metal centers in biological processes depends on several parameters such as the degree of oxidation [12] and the number of coordination in the complex [13]. Schiff bases in the presence of carboxylate, perchlorate or nitrate anions can react with transition metal ions to generate a wide range of coordination types with widely varying architectures [14,15]. Polydentate ligands containing both hard donor sites and soft donor sites are designed to provide special topological structures [16,17]. For this, both the synthesis of the ligand and that of the complex must be controlled [18,19]. In this context, the Schiff bases 1-(pyridin-2-ylmethylidene)-2-(pyridin-2-yl)hydrazine (HL¹) [20,21], which provide three soft donating N atoms from two pyridine rings and one imino nitrogen atom were used together with metal transition salts to yield metal transition complexes in which acetate and nitrate anions can act with hard oxygen-binding sites. The synthetic procedures adopted are essential for yielding complexes with peculiar structure. The two organic molecules HL¹ and HL² (1-(pyridin-2-yl)-2-(1-(pyridin-2-yl)ethylidene)hydrazine) can adopt two configurations type of *E* and *Z* [22]. In the *E* configuration, the ligand offer a terpyridine-like coordination environment [23,24] in which the relative position of the nitrogen atoms allows to form stable five-membered metallo-cycles after the coordination of the three soft nitrogen binding sites to the same metal atom. The ligand HL¹ was used in our previous attempts to prepare new mono- and binuclear complexes. We used a one-pot synthesis method for the synthesis of dinuclear lanthanide complexes [25–27] and a heptacoordinated Mn(II) complex [28]. Ongoing our study of the behavior, in the presence of metal ions, of this ligand and its homologue in which the acidic proton is substituted by a methyl group (HL²), the corresponding

mononuclear complexes of manganese, copper and zinc are prepared and characterized by spectroscopic and X-ray diffraction analysis.

Experimental section

Starting materials and Instrumentations

Commercially available 2-pyridinecarbaldehyde, 2-acetylpyridine, 2-hydrazinopyridine and metals transition salts were purchased from Aldrich and used without further purification. The analyses for carbon, hydrogen and nitrogen were carried out using a LECO CHNS-932 instrument. The IR spectra were recorded on a Perkin Elmer Spectrum Two spectrophotometer (4000-400 cm^{-1}). UV-VIS spectra were recorded in methanol solution concentration of 10^{-3} M at 25 °C and wavelength was reported in nm using a Perkin Elmer Lambda 365 UV/VIS spectrophotometer. The molar conductance of 10^{-3} M solution of the metal complex in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibility of the powdered sample was measured using a Johnson Matthey scientific magnetic susceptibility balance (calibrant $\text{Hg}[\text{Co}(\text{SCN})_4]$).

Synthesis of Ligands

HL¹ The Schiff base ligand 1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine (HL¹) was synthesized as follow : 2-hydrazinopyridine (1.0913 g, 10 mmol) in 20 mL of ethanol was added to a solution of 2-pyridinecarbaldehyde (1.0711 g, 10 mmol) dissolved in 25 mL of methanol. The resulting mixture was stirred under reflux during 30 min. After cooling, the solution was completed to 100 mL with ethanol and stored in the refrigerator. 10 mL of this solution was evaporated to dryness and the NMR spectrum of the resulting liquid was recorded. δ_{H} (250 MHz, DMSO- d_6): 11.185 (1H, s, H-N-N); 8.542 (1H, d, J 4.75 Hz, H-Py); 8.144 (1H, s, H-C=N); 6.82-8.54 (8H, mult, H-Py). δ_{C} (250 MHz, DMSO- d_6): 106.500 (C_{Ar}), 115.528 (C_{Ar}), 118.810 (C_{Ar}), 122.88 (C_{Ar}), 136.42 (C_{Ar}), 137.99 (C_{Ar}), 139.16 (C=N), 147.80 (C_{Ar}), 149.18 (C_{Ar}), 154.26 (C_{Ar}), 156.66 (C_{Ar}). UV-Vis (λ , nm) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 290 (1.06), 310 (1.02), 330 (2.95), 360 (1.09). IR (cm^{-1} in DMSO): 3204, 1635, 1600, 1571, 1293, 765.

HL² The same procedure used for the synthesis of HL¹ was repeated for the synthesis of HL²; 2-acetylpyridine was used instead 2-pyridinecarbaldehyde. On cooling a yellow powder was afforded (80%). Melting point: 54 °C. δ_{H} (250 MHz, DMSO- d_6): 11.185 (1H, s, H-N-N); 6.60-8.83 (8H, mult, H-Py); 1.144 (3H, s, $\text{CH}_3\text{-C=N}$). δ_{C} (250 MHz, DMSO- d_6): 13.800 (CH_3); 109.50 (C_{Ar}), 113.51 (C_{Ar}), 123.98 (C_{Ar}), 126.35 (C_{Ar}), 136.12 (C_{Ar}), 138.510 (C_{Ar}), 145.16 (C=N), 148.38 (C_{Ar}), 149.10 (C_{Ar}), 153.87 (C_{Ar}), 155.95 (C_{Ar}). UV-Vis (λ , nm) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) 294 (1.03), 312 (1.09), 332 (2.90), 358 (1.03). IR (cm^{-1}): 3230, 3230, 1651, 1600, 1569, 1287, 768.

Synthesis of complexes (1-4)

To a solution of 1 mmol of the desired ligand (HL¹ or HL²) in 10 mL of ethanol was added a solution of 1 mmol of the MX₂·nH₂O (M²⁺ = Mn²⁺ and X = Cl⁻, ClO₄⁻, n = 4; M²⁺ = Cu²⁺ and X = NO₃⁻, n = 3; M²⁺ = Zn²⁺ and X = CH₃COO⁻, n = 2). The mixture was stirred under reflux for 60 min and the resulting solution was filtered-off and the filtrate was kept at 298 K. Upon keeping ethanol solutions for three days, colored crystals suitable for X-ray diffraction was afforded.

Complex 1 [Mn(HL¹)(Cl₂)(H₂O)]. Green crystals Yield: 75%. Anal. calc. for C₁₁H₁₂Cl₂MnN₄O: C, 38.6; H, 3.6; N, 16.4%. Found: C, 38.6; H, 3.5; N, 16.4%.

Complex 2 [Zn(HL¹)(OAc)₂](H₂O)₃. Yellow crystals Yield: 60%. Anal. calc. for C₁₅H₂₂N₄O₇Zn: C, 41.3; H, 5.1; N, 12.8%. Found: C, 41.4; H, 5.0; N, 12.9%.

Complex 3 [Mn(HL²)₂](ClO₄)₂. Orange crystals Yield: 80%. Anal. calc. for C₂₄H₂₄Cl₂MnN₈O₈: C, 42.5; H, 3.6; N, 16.5%. Found: C, 42.6; H, 3.6; N, 16.5%.

Complex 4 [Cu(HL²)(NO₃)₂]. Green crystals Yield: 45%. Anal. calc. for C₁₂H₁₄CuN₆O₄: C, 38.9; H, 3.8; N, 22.8%. Found: C, 39.0; H, 3.8; N, 22.7%.

X-ray crystallography

Diffractometer: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright Mo-K α rotating anode generator ($\lambda = 0.71075 \text{ \AA}$) with VHF Varimax optics (100 μm focus). Powder X-ray diffraction was carried out using a Bruker D2 Phaser with a Lynxeye detector and Cu-K α radiation (1.5405 \AA). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrysAlisPro 1.171.39.34b. [29]. Gaussian absorption correction was applied. Structure solution and refinement were performed using SHELXT [30] and SHELXL-2014/7 [31]. All hydrogen atoms were added in calculated positions and refined in riding mode on the parent atom. Molecular graphics were generated using ORTEP-3 [32]. The crystal and refinement data are summarized in Table 1. Crystallographic data for the structures reported in this paper have been deposited within the Cambridge Crystallographic Data Centre with the CCDC numbers: 1889247-1889250. The data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

[INSERT TABLE 1]

Results and discussions

General studies

The intention of the reported work was to study the coordination chemistry of ligands isolated from condensation of 2-hydrazino pyridine and 2-formylpyridine (HL¹) or 2-acetylpyridine (HL²) which can act as strong chelating ligand, to produce complexes with metals transition (Scheme 1). Accordingly, the ethanolic solution of organic ligand was treated with transition metal salts in 1:1 molar ratio. The resulting solution was filtered-off and left under slow evaporation for yielding crystals suitable for X-ray diffraction.

[INSERT SCHEME 1]

The elemental analysis results are in good agreement with the calculated values for the four synthesized mononuclear complexes which are non-hygroscopic and stable in air. The electrolytic nature of the complexes was measured in DMF at 10⁻³ M. The molar conductivities Λ of the complexes of HL¹ are 26 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for manganese (II) complex (**1**) and 5 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for Zn(II) complex (**2**) indicating that they are non-electrolytic in DMF solutions, while the values of complexes of HL² are 190 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for Mn(II) complex (**3**) and 180 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for Cu(II) complex (**4**) which are 2:1 electrolytes in DMF solutions [33]. The copper complex probably dissociate in DMF solution. The values of the magnetic moment at room temperature for the three diamagnetic complexes are indicative of the presence of one metal atom per molecule. In fact for manganese (II) complexes the magnetic moment values of 5.69 μ_B and 5.54 μ_B for complex (**1**) and complex (**3**) respectively are in accordance with the presence of one manganese (II) atom per molecule [34]. For the complex (**4**) of copper (II) the magnetic moment values of 1.66 μ_B is in the range expected for a mononuclear copper (II) complex [35]. The infrared spectra of the various synthesized compounds were used to determine the different coordination modes of organic ligands and transition metal anions. In all infrared spectra of the complexes a strong shift to low frequencies of the bands attributed to $\nu_{\text{C=N}}$ of the free ligands is observed. Indeed for HL¹ the frequency which was located at 1635 cm^{-1} has strongly shifted to 1605 cm^{-1} for the complex **1**. In the infrared spectrum of complex (**2**), a strong and broad band centered at 1586 cm^{-1} which has obscured the band attributable to C=N is observed. In the case of ligand HL², the band centered at 1652 cm^{-1} is shifted to 1614 cm^{-1} and 1619 cm^{-1} respectively for complexes (**3**) and (**4**). For all complexes the infrared spectra reveal several bands of variable intensities in the ranges 1600-1450 cm^{-1} and 900-700 cm^{-1} which are characteristic of the pyridine fragments of the organic ligands. In the IR spectrum of complex **1**, additional bands at 3223 cm^{-1} and 907 cm^{-1} are noted which indicate the presence of coordinated water molecules. For compound **2** other characteristic bands at 3370, 1586 and 1388 cm^{-1} respectively attributable to free water molecule, asymmetric vibration and symmetrical vibration of CH₃COO⁻ acetate group are observed. In 1980 Deacon and Phillips [36] established criteria on the basis of $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ for assignment of chelation modes of carboxylate ions : $\Delta\nu$ for monodentate bonding increases compared to the free anion; $\Delta\nu$ decreases for bidentate chelating; and $\Delta\nu$ remains similar to the free anion for bidentate bridging. In 1985 [37] they restated these modes of coordination and it seems that only the unidentate criterion

is valid : $\nu_{as}(\text{CO}_2)$ higher and $\nu_s(\text{CO}_2)$ lower. In the case of the complex (2) the values of $\nu_{as}(\text{CO}_2) = 1587 \text{ cm}^{-1}$ and $\nu_s(\text{CO}_2) = 1388 \text{ cm}^{-1}$ indicate presence of acetate group acting as monodentate fashion [38]. In the case of complex (3), the additional bands at 1070 and 619 cm^{-1} clearly reveal non-coordinated perchlorate anion playing role of counter-ion [39]. In the spectrum of the copper complex (4) bands attributable to coordinated and uncoordinated nitrate groups are observed. The sharp and intense band at 1394 cm^{-1} is attributed to the ionic nitrate group while the two bands at 1245 and 1061 cm^{-1} are assigned to ν_5 and ν_2 , respectively. The difference $\Delta\nu = \nu_5 - \nu_2$ is a criterion for evaluating the coordination mode of the nitrate group. The $\Delta\nu$ value increases from monodentate mode to bidentate mode. In the case of this copper complex the value $\Delta\nu = 184 \text{ cm}^{-1}$ indicates presence of unidentate nitrate group in the complex (4) [40]. The UV-Vis spectra of both compounds are recorded in methanol solution in the range of 200–1000 nm. The UV-Vis spectra of the ligands HL² and HL¹ shows one absorption band attributable to the $\pi \rightarrow \pi^*$ transition of the pyridine rings in the range 280–295 nm. Additional band in the range 310–330 nm which can be attributed to the $n \rightarrow \pi^*$ transitions of the C=N chromophore is also observed. For complexes (1), (2) and (4) high intensity bands due to LMCT appeared in the range 300–450 nm. The spectrum of the copper (II) complex (4) shows one absorption band at 546 nm which may be due to $dxz, dyz \rightarrow dx^2-y^2$ transition. This transition band is indicative of copper (II) atom with distorted square pyramidal geometry as reported in the literature [41].

Crystal structure descriptions

Suitable single-crystals for X-ray diffraction of the complexes 1, 2, 3 and 4 were obtained by slow solvent evaporation at room temperature. Crystal data, collection and refinement parameters are listed in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bond data for complex and are gathered in Table 3. Figure 1–4 displays the asymmetric unit of all compounds with main atom numbering.

Compound 1 crystallizes in the orthorhombic system with the space group Pbca. An ORTEP view of the structure is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. In the asymmetric unit there is a single molecule of complex formed by a manganese (II) atom which is bounded to one organic ligand HL¹, one water molecule and two chloride anions. The ligand acts in tridentate fashion through one azomethine and two nitrogen atoms from pyridine rings. The manganese (II) atom is hexacoordinated and the geometry around the manganese (II) center is best described as an octahedral polyhedron. The basal plan is occupied by O1, N3, C11 and Cl2 atoms, the apical positions being occupied by the two nitrogen atoms from the pyridine rings. The sum value of the angles in the basal plan is 359.008° while the angle subtended by the atoms in apical position (N1-Mn-N4 = 141.22(6)°) is considerably different of the ideal value of 180°. The octahedral geometry is severely distorted. The distances Mn-N are in the range 2.2461(16)-2.2781(15) Å and are

comparable with the values found for analogous complex dichlorido(2,4,6-tri-2-pyridyl-1,3,5-triazine)manganese(II) [42]. The Mn-Cl (Mn-Cl1 = 2.5294(5) and Mn-Cl2=2.4132(5) Å) are the longest distances while the shortest distance is Mn-O_{water} with 2.2356(14) Å. In this compound, there is intermolecular hydrogen bonds involving respectively the OH of one of the coordinated water molecule as donors and the coordinated chloride atoms as acceptor (O2-H1A...Cl1 and O2-H1B...Cl2) (Table 3).

Fig. 1 ORTEP plot (30% probability ellipsoids) showing the molecule structure of the manganese (II) complex of HL¹

The X-ray structural determination of compound **2** derived from HL¹ reveals a mononuclear neutral zinc (II) complex which crystallizes in the triclinic system with the space group P-1. An ORTEP view of the compound formulated as [Zn(HL¹)(CH₃COO)₂](H₂O)₃ is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. The complex is built up as a mononuclear zinc (II) where the metal atom is linked to three nitrogen atom from the organic ligand molecule and to two acetate groups which act in monodentate fashion. The coordination geometry around the zinc (II) atom is best discussed with the trigonality index. In fact the Addison index [43] $\tau = (\beta - \alpha)/60$ where β and α are the largest values of the bond angles around zinc (II) atom can be used to attributed the geometry of a penta-coordinated metal complex. When the geometry is a perfect square-pyramidal $\tau = 0$ and when $\tau = 1$ a perfect trigonal bipyramidal geometry is obtained. In the pentacoordinated environment of the zinc (II) atom in our complex, the τ value of 0.352 is indicative of a distorted square pyramidal geometry around the metal center. However when the modified index suggested by Konno et al. [44], $\chi = (\beta + \gamma + \delta - 2\alpha)/180$ (which takes in account the others angles β et α are the largest angles, γ and δ being the other angles around the metal centers without the donors atoms defining β) is used, the χ value of 0.750 suggests that the geometry around the zinc (II) atom is a distorted trigonal bipyramid. The equatorial plan is occupied by N3, O21 and O31 with angle values in close proximity of the ideal value of 120° (N3-Zn-O31 = 120.74(5)°, N3-Zn-O21 = 122.96(4)° and O21-Zn-O31 = 116.14(5)°). The value of the sum of the subtended angles is 359.84°. The apical positions are occupied by N1 and N4 with an angle N1-Zn-N4 = 147.08(5)° severely deviated from the ideal value of 180°. The oxygen atom of the acetate groups are strongly linked to the zinc (II) atom as shown by the short distance values of Zn1-O21 = 1.9714(10) Å and Zn-O31 = 1.9684(10) Å. These values are in accordance with those found for similar complexes in which the acetate group acts in unidentate fashion [45]. The distance Zn-N fall in the range 2.1276(12) - 2.1931(12) Å and are comparable with the values found for the complex [Zn(CH₃COO)₂(4-pyao)₂] (4-pyao = pyridine-4-aldoxime; 4-pyamo = pyridine-4-amidoxime [27]). In this compound, there is intermolecular hydrogen bonds involving respectively the NH of the hydrazino moiety of the ligand molecule and OH of one of the uncoordinated water molecule as donors and the oxygen

atoms of the coordinated acetate group as acceptor (N2-H...O22 and O51-H...O32). Intramolecular hydrogen bonds involving uncoordinated water molecule are also observed (Table 3).

Fig. 2 ORTEP plot (30% probability ellipsoids) showing the molecule structure of the zinc (II) complex of HL¹

The compound **3** which is formulated as [Mn(HL²)₂](ClO₄)₂ crystallizes in the monoclinic crystal system with Cc space group. In the asymmetric unit one discrete mononuclear complex is present with two perchlorate anions. The Fig. 3 depicts the perspective view of the complex. Selected bond lengths and angles are listed in Table 2. The coordination polyhedron around the manganese atom ion is constructed by two neutral ligand molecule HL¹ which acts in tridentate fashion. The manganese (II) atom is coordinated to each of the two HL¹ ligand through three nitrogen donor atoms. The two nitrogen pyridine atoms and the azomethine atom are coordinated to the manganese (II) while the N-H atom of the hydrazino moiety remains uncoordinated. The basal plan is occupied by N1, N4, N21 and N24 while the apical positions are occupied by N3 and N23. The angles in the basal plan N1–Mn–N4 = 142.44(12), N21–Mn–N24 = 139.9(4) and the angles between the apical atoms N3–Mn–N23 = 173.2(3) are indicative of a severely distorted octahedral polyhedron around the Mn atom center. This strongly distortion can be explained by the formation of five membered ring which deviate the angle N–Mn–N from 90° to 71°. One of the perchlorate anion (ClO₄⁻) is disordered and was constrained to be tetrahedral with three sites having occupancies of 0.236(3); 0.221(3) and 0.543(2). Both atoms of one of the ligand molecule are disordered with two sites having occupancies of 0.419(4) and 0.581(4). The chain bridging the two pyridine rings in the ligand is disordered. The bonds lengths in the bridging chain C-CH=N-NH-C are respectively 1.405(12) and 1.44(3) Å for C-C, 1.328(14) and 1.24(4) Å for C=N, 1.37(2) and 1.36(2) Å for N-N and 1.316(9) and 1.326 (18) Å for N-C. These bonds are slightly longer than those observed for this ligand in other complexes [27]. This may be related to the disorder detected for this chain.

Fig. 3 ORTEP plot (30% probability ellipsoids) showing the molecule structure of the manganese (II) complex of HL²

X-ray diffraction of the copper (II) complex **4** reveals that the compound crystallizes in the monoclinic system with space group of P2₁/n. Selected bond lengths and angles are listed in Table 2. The fig. 4 shows the asymmetric unit which is composed by one copper (II) atom linked in tridentate fashion to the organic ligand via one azomethine and two nitrogen atoms from pyridine rings, one coordinated water molecule and two coordinated nitrate acting as unidentate units a. The metal center is hexacoordinated and the copper (II) atom is in a distorted octahedral environment. The basal plane is

occupied by N1, N3, N4 and O41 atoms, the apical positions being occupied by O21 and O31 from the monodentate nitrate ligands. The angles in the basal plan $N1-Cu-N3 = 79.87(5)^\circ$, $N3-Cu-N4 = 79.86(5)^\circ$, $N4-Cu-O41 = 101.56(5)^\circ$, $N1-Cu-O41 = 96.66(4)^\circ$, $N3-Cu-O41 = 165.50(5)^\circ$, $N1-Cu-N4 = 159.13(5)^\circ$ and the angles between the apical atoms $O21-Cu-O31 = 168.96(4)^\circ$ are indicative of a severely distorted octahedral polyhedron around the Cu atom center. The two apical Cu-ONO₂ distances are significantly different (Cu-O21 = 2.2721(10) Å and Cu-O31 = 2.6265(11) Å while the equatorial Cu-N and Cu-OH₂ distances are in the range [1.9513 Å - 2.0096 Å]. The axial elongation is due to the Jahn-Teller distortion of the degenerated d⁹ electronic ground state. The hard donor site O31-NO₂ is weakly coordinated to the soft copper (II), and can be easily dissociated as observed with the conductance measurement and the infrared spectroscopy. Intramolecular hydrogen bond involving the OH of the coordinated water molecule as donors and an oxygen atoms of the coordinated nitrate group as acceptor (O41-H41A...O32) is observed. Intermolecular hydrogen bonds involving the NH of the hydrazine moiety of the ligand as donor and an oxygen atoms of the coordinated nitrate group as acceptor (N2-H2A...O31) and the OH of the coordinated water molecule as donors and an oxygen atoms of the nitrate group as acceptor (O41-H41B...O22) are also observed (Table 3).

Fig. 4 ORTEP plot (30% probability ellipsoids) showing the molecule structure of the copper (II) complex of HL²

[INSERT TABLE 2]

[INSERT TABLE 3]

Conclusion

The mononuclear complexes of the ligand HL¹ and HL² derived from 2-hydrazinopyridine are synthesized and characterized. The complexes are characterized by elemental analysis, IR and UV-Visible spectroscopies, magnetic measurements, conductivity study and X-ray diffraction analysis. Both ligands coordinated to transition metal center as tridentate fashion to generated mononuclear complex in each case.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Vigato PA, Tamburini S (2004) Coord Chem Rev 248:1717–2128

- [2] Guricová M, Pižl M, Smékal Z, Nádherný L, Čejka J, Eigner V, Hoskovicová I (2018) *Inorg Chim Acta* 477:248–256
- [3] Cao W, Liu Y, Zhang T, Jia J (2018) *Polyhedron* 147:62–68
- [4] Zaltariov M-F, Cazacu M, Avadanei M, Shova S, Balan M, Vornicu N, Vlad A, Dobrov A, Varganici C-D (2015) *Polyhedron* 100:121–131
- [5] Shabbir M, Akhter Z, Ashraf AR, Ismail H, Habib A, Mirza B (2017) *J Mol Struct* 1149:720–726
- [6] Upadhyay KK, Kumar A, Upadhyay S, Mishra PC (2008) *J Mol Struct* 873:5–16
- [7] Yahsi Y, Kara H (2014) *Spectrochim Acta A Mol Biomol Spectrosc* 127:25–31
- [8] Singh DP, Allam BK, Singh KN, Singh VP (2015) *J Mol Catal Chem* 398:158–163
- [9] Valentová J, Varényi S, Herich P, Baran P, Bilková A, Kožíšek J, Habala L (2018) *Inorg Chim Acta* 480:16–26
- [10] Iftikhar B, Javed K, Khan MSU, Akhter Z, Mirza B, Mckee V (2018) *J Mol Struct* 1155:337–348
- [11] Mahmoud WH, Mahmoud NF, Mohamed GG (2017) *J Organomet Chem* 848:288–301
- [12] Fouda MFR, Abd-Elzaher MM, Abdelsamaia RA, Labib AA (2007) *App Organomet Chem* 21:613–625
- [13] Ceyhan G, Köse M, McKee V, Uruş S, Gölcü A, Tümer M (2012) *Spectrochim Acta A Mol Biomol Spectrosc* 95:382–398
- [14] Neary MC, Parkin G (2016) *Polyhedron* 116:189–196
- [15] Golbedaghi R, Fausto R, Salehzadeh S, Tofani M, Safaraabadi S (2018) *Inorg Chim Acta* 480:27–32
- [16] Abou-Hussein AAA, Linert W (2012) *Spectrochim Acta A Mol Biomol Spectrosc* 95:596–609
- [17] Egekenze RN, Gultneh Y, Butcher R (2018) *Inorg Chim Acta* 478:232–242
- [18] Carmona-Vargas CC, Aristizábal SL, Belalcázar MI, D’Vries RF, Chaur MN (2019) *Inorg Chim Acta* 487:275–280
- [19] Ly HN, Brook DJR, Oliverio O (2011) *Inorg Chim Acta* 378:115–120
- [20] Lions F, Dance IG, Lewis J (1967) *J Chem Soc A Inorg Phys Theor* 565-572
- [21] Vecchio-Sadus AM (1995) *Transit Met Chem* 20:38–45
- [22] Chaur MN, Collado D, Lehn J-M (2011) *Chem Eur J* 17:248–258
- [23] Kosobokov MD, Xue T, Vicic DA (2018) *Polyhedron* 155:366–369
- [24] Dunn JG, Edwards DA (1971) *J Chem Soc A Inorg Phys Theor* 988–994
- [25] Ndiaye-Gueye M, Dieng M, Thiam IE, Sow MM, Gueye-Sylla R, Barry AH, Gaye M, Retailleau P (2017) *Rev Roum chim* 62:35–41
- [26] Ndiaye-Gueye M, Dieng M, Thiam EI, Lo D, Barry AH, Gaye M, Retailleau P (2017) *South Afr J Chem* 70 8–15
- [27] Gueye NdM, Moussa D, Thiam EI, Barry AH, Gaye M, Retailleau P (2017) *Acta Crystallogr E* 73:1121–1124
- [28] Sarr M, Diop M, Thiam EI, Barry AH, Gaye M, Retailleau P (2018) *Acta Crystallogr E* 74:450–453

- [29] CrysAlisPro 11713934b Rigaku Oxford Diffraction 2017
- [30] Sheldrick GM (2015) *Acta Crystallogr A* 71:3–8
- [31] Sheldrick GM (2015) *Acta Crystallogr C* 71:3–8
- [32] Farrugia LJ (1997) *J Appl Crystallogr* 30:565
- [33] Geary WJ (1971) *Coord Chem Rev* 7:81–122
- [34] Chioma F, Ekennia AC, Ibeji CU, Okafor SN, Onwudiwe DC, Osowole AA, Ujam OT (2018) *J Mol Struct* 1163:455–464
- [35] Puchoňová M, Matejová S, Jorík V, Šalitraš I, Švorc L, Mazúr M, Moncol' J, Valigura D (2018) *Polyhedron* 151:152–159
- [36] Deacon GB, Phillips (1980) *Coord Chem Rev* 33:227–250
- [37] Deacon GB, Huber F, Phillips RJ (1985) *Inorg Chim Acta* 104:41–45
- [38] Sangeetha S, Murali M (2015) *Inorg Chem Commun* 59:46–49
- [39] Pratihari JL, Mandal P, Brandão P, Mal D, Felix V (2018) *Inorg Chim Acta* 479:221–228
- [40] Diouf O, Sall DG, Gaye ML, Sall AS (2007) *Comptes Rendus Chim* 10:473–481
- [41] Sadhu MH, Kumar SB, Saini JK, Purani SS, Khanna TR (2017) *Inorg Chim Acta* 466:219–227
- [42] Ha K (2010) *Acta Crystallogr E* 66:m262
- [43] Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC (1984) *J Chem Soc Dalton Trans* 1349–1356
- [44] Konno T, Tokuda K, Sakurai J, Okamoto K (2000) *Bull Chem Soc Jpn* 73:2767–2773
- [45] Coropceanu EB, Croitor L, Siminel AV, Fonari MS (2014) *Polyhedron* 75:73–80