

SYNTHESIS AND CHARACTERIZATION OF NOVEL M(II) (M = Mn(II), Ni(II), Cu(II) OR Zn(II)) COMPLEXES WITH TRIDENTATE N₂,O-DONOR LIGAND (E)-2-AMINO-N'-[1-(PYRIDIN-2-YL)ETHYLIDENE]BENZOHYDRAZIDE

Cheikh Hamidou Kane¹, Daniel Tinguiano¹, Farba Bouyagui Tamboura¹, Ibrahima Elhadj Thiam¹, Aliou Hamady Barry², Mohamed Gaye^{1*} and Pascal Retailleau³

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

²Department of Chemistry, University of Nouakchott, Mauritania, France

³Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS-UPR2301, 1 Avenue la Terrasse, 91198 Gif sur Yvette, France

(Received March 23, 2015; revised January 4, 2016)

ABSTRACT. The coordination chemistry towards the M(II) metal centre (M = Mn, Ni, Cu or Zn) of the hydrazone ligand (*E*)-2-amino-*N'*-[1-(pyridin-2-yl)ethylidene]benzohydrazide (H₃L) has been explored and complexes having formulae [Mn(H₂L)₂] (1), {[Ni(H₂L)₂]:DMF·0.4H₂O} (2), {[Cu₂(H₂L)₂(μ-Cl)₂]:DMF} (3) and [Zn(H₂L)₂] (4) have been isolated and characterized by IR, UV-Visible spectroscopy, elemental analysis and X-ray crystal diffraction. Structural studies reveal that the mononuclear complexes (1), (2) and (4) adopt highly distorted octahedral geometries while the dinuclear complex (3) adopts a square pyramidal geometry around each copper(II) ion.

KEY WORDS: Schiff base, Phenolate, Manganese(II), Nickel(II), Copper(II), Zinc(II), Mononuclear complexes, X-Ray structure

INTRODUCTION

Versatility coordination to metal [1, 2], flexibility in assuming different conformations [3, 4], possibility of tautomerism forms [5, 6] and possibility of reacting in anionic or neutral forms [7, 8], make the study of hydrazones chemistry extremely interesting. The chelating properties of this kind of ligands are diversified by their possible presence in neutral, protonated or deprotonated forms leading of various geometries upon coordination [9-11].

On continuing our work in the field of the synthesis of hydrazide ligand and the studies of their reactivities with transition metal, we describe a simple condensation of 2-aminobenzoylhydrazide and 2-acetylpyridine to yield the title compound (*E*)-2-amino-*N'*-[1-(pyridin-2-yl)ethylidene]benzohydrazide (H₃L). The chelating behaviors of this ligand have been investigated towards several transition metal ions. The synthesis and characterization of three mononuclear (Mn(II), Ni(II) and Zn(II)) and one dinuclear (Cu(II)) metal complexes with the potentially pentadentate Schiff base ligand H₃L, having amine, hydrazone and pyridine moieties with potential atoms donor (Scheme 1). The X-ray crystal structure of Mn(II), Ni(II), Cu(II) and Zn(II) complexes are reported in this present work.

EXPERIMENTAL

Materials and procedures

Methyl anthranilate, hydrazine hydrate, 2-acetylpyridine, MnCl₂·4H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O as well as ZnCl₂ were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyses were performed in a Carlo-Erba EA microanalyser. Infra-red

*Corresponding author. E-mail: mohamedl.gaye@ucad.edu.sn

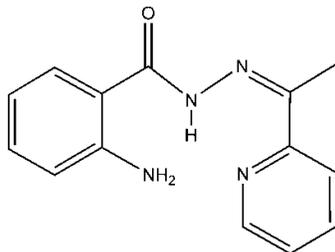
spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. For the ligand, LSI-MS were recorded using a Micromass Autospec spectrometer with 3-nitrobenzyl alcohol as the matrix. The ^1H and ^{13}C NMR spectra of the Schiff base were recorded in CDCl_3 on a Bruker 500 MHz spectrometer at room temperature using TMS as an internal reference. The UV-Vis spectra were run on a Jenway 6505 UV- Spectrophotometer (1100-200 nm) on 10^{-3} M DMF solutions of the complexes. The molar conductance of 10^{-3} M solutions of the metal complexes in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples {calibrant $\text{Hg}[\text{Co}(\text{SCN})_4]$ } were measured using a Johnson Matthey scientific magnetic susceptibility balance. Melting points were recorded on a Büchi apparatus and are uncorrected.

X-ray data collection, structure determination, and refinement

The details of the X-ray crystal data, and the structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. Complex scattering factors were taken from the program package *SHELXTL* [12]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non hydrogen atoms [13]. The hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using *ORTEP-3* [14].

Synthesis of the (E)-2-amino-N'-[1-(pyridine-2-yl)ethylidene]benzohydrazide ligand

Methylantranilate (3 g, 20 mmol) and excess of hydrazine hydrate (8 mL, 160 mmol) were refluxed during 24 hours and stored overnight in a refrigerator. A white solid was separated, filtered off and recrystallized from ethanol to yield 2-aminobenzohydrazide (2.37 g, 15.69 mmol). The whole solid was dissolved in 40 mL of ethanol and 2-acetylpyridine (1.90 g, 15.69 mmol) was added. The resulting mixture was refluxed during 3 hours to yield a yellow solution. The solution was evaporated to dryness to give yellow solid which was washed with ether and dried in the air. Yield: 53.5% (2.13 g). Anal. calcd (found) for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}$ (H_3L): C, 66.13 (66.15); H, 5.55 (5.54); N, 22.03 (22.01) %. M.p. 170 °C. MS (FAB, m/z): 254 [H_3L] $^+$. IR (KBr, cm^{-1}): 3434m ($\nu_{\text{asym}}(\text{NH}_2)$) and 3317m ($\nu_{\text{sym}}(\text{NH}_2)$); 3284m ($\nu_{\text{N-H}}$); 1651s ($\nu_{\text{C=O}}$); 1615s ($\nu_{\text{C=N}}$); 1583s ($\nu_{\text{C=N}}(\text{py})$); 1567s, 1512m, 1465m ($\nu_{\text{C=C}}(\text{Ar})$). ^1H NMR (CDCl_3) δ 2.40 (s, 3H, $-\text{CH}_3$), 5.54 (s, 2H, NH_2), 6.73-7.27 (m, 4H, H_{Ar}), 7.77-8.60 (m, 4H, H_{Py}), 9.09 (s (broad), 1H, $-\text{NH}$) ppm. ^{13}C NMR (CDCl_3) δ 154.98 ($-\text{C=O}$), 149.40 ($-\text{C=N-}$), 148.68, 136.86, 136.36, 133.14, 124.02, 121.23, 119.31, 117.70, 116.70, 114.39 (C_{Ar}), 10.95 ($-\text{CH}_3$) ppm.



H_3L

Scheme 1

Table 1. Crystallographic data and refinement parameters for (1), (2), (3) and (4).

Identification code	(1)	(2)	(3)	(4)
Empirical formula	C ₂₈ H ₂₆ MnN ₈ O ₂	C ₂₈ H ₂₆ NiN ₈ O ₂ ·C ₃ H ₇ NO·0.4H ₂ O	C ₂₈ H ₂₆ Cl ₂ Cu ₂ N ₈ O ₂ ·C ₃ H ₇ NO	C ₂₈ H ₂₆ ZnN ₈ O ₂
Formula weight	561.51	642.70	777.64	571.94
T (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P $\bar{1}$	C2/c	P2 ₁ /c
a (Å)	21.970 (5)	11.0987 (3)	16.076 (2)	11.0150(10)
b (Å)	10.440 (5)	11.32842 (5)	8.3040 (11)	25.405(2)
c (Å)	12.736 (5)	13.7624 (5)	25.892 (3)	10.3030 (10)
α (°)		102.3972 (16)		
β (°)	117.137 (5)	110.589 (2)	101.887 (2)	117.494 (2)
γ (°)		94.30 (2)		
V (Å ³)	2599.6 (17)	1560.9 (5)	3382.4 (8)	2557.5 (4)
Z	4	2	4	4
D _{calc} (g cm ⁻³)	1.435	1.374	1.527	1.485
μ (mm ⁻¹)	0.55	0.67	1.46	1.00
λ (Å)	0.71073	0.71073	0.71073	0.7173
F(000)	1164	676	1592	1184
Crystal size	0.20 x 0.10 x 0.05	0.2 x 0.10 x 0.05	0.09 x 0.07 x 0.05	0.10 x 0.07 x 0.05
2 θ	2.21 to 27.50	1.6 to 26.4	1.61 to 25.02	4.17 to 25.03
Index ranges	-28→28 ; -12→13 ; -16→16	-13→13 ; -14→13 ; -16→17	-19→19 ; -9→9 ; -30→30	-13→13 ; -30→29 ; -12→12
Reflections collected	5158	9694	12431	7673
Independent refls [R _{int}]	2980 [0.021]	6279 [0.019]	2981 [0.031]	4305 [0.048]
Data/restraints/parameters	2980/0/177	6279/17/456	2981/6/223	4305/0/349
Goodness-of-fit	1.11	1.04	1.04	1.14
R Indices [I > 2 σ (I)] R ₁ , wR ₂	0.043, 0.121	0.049, 0.133	0.033, 0.084	0.070, 0.185
R Indices (all data) R ₁ , wR ₂	0.064, 0.147	0.064, 0.144	0.046, 0.094	0.082, 0.193
Peak and hole (e Å ⁻³)	0.44 and -0.62	0.23 and -0.38	0.43 and -0.42	0.66 and -0.66

Synthesis of metal complexes

Ligand H₃L (1.0 mmol, 254.3 mg) was dissolved under reflux in ethanol (10 mL) to give a clear yellow solution. A solution of metal(II) chlorides (1 mmol) in ethanol (10 mL) was slowly added with stirring. The colored resulting mixture was refluxed for about two hours and the suspension was allowed to cool to room temperature and then filtered off. The precipitate was washed with cold ethanol and acetone and dried in air. The resulting solid was dissolved in dimethylformamide (DMF) solvent and the solution was allowed to concentrate in air. Appropriate crystals of [Mn(H₂L)₂], {[Ni(H₂L)₂]·DMF·0.4H₂O}, {[Cu₂(H₂L)₂(μ -Cl)₂]·(DMF)} and {[Zn(H₂L)₂] suitable to be studied by X-ray diffraction were obtained by slow recrystallization of the solids from DMF.

[Mn(H₂L)₂](1). Yield: 86% (0.4823 g). Anal. calc for C₂₈H₂₆N₈MnO₂: C, 59.89; H, 4.67; N, 19.96. Found: C, 59.87; H, 4.65; N, 19.93%. IR (KBr, cm⁻¹): 3342 [ν_{NH_2}]; 1626 [$\nu_{\text{C=O}}$]; 1595,

1463 [$\nu_{(\text{C}=\text{N})\text{py}}$ and $\nu_{(\text{C}=\text{C})\text{Ar}}$], 1248 [$\nu_{(\text{C}-\text{O})}$]. μ_{eff} (μ_{B}) 5.88. Λ_{M} (DMF, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 32. UV-Vis (λ , nm) (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$) 345(0.77), 415(0.016). Colour: yellow.

$\{[\text{Ni}(\text{H}_2\text{L})_2] \cdot \text{DMF} \cdot 0.4\text{H}_2\text{O}\}$ (2). Yield: 52% (0.3359 g). Anal. calc for $\text{C}_{31}\text{H}_{33.8}\text{N}_9\text{NiO}_{3.4}$: C, 57.68; H, 5.28; N, 19.53. Found: C, 57.72; H, 5.25; N, 19.49%. IR (KBr, cm^{-1}): 3296 [ν_{NH_2}]; 1622 [$\nu_{\text{C}=\text{O}}$]; 1595, 1467 [$\nu_{(\text{C}=\text{N})\text{py}}$ and $\nu_{(\text{C}=\text{C})\text{Ar}}$], 1256 [$\nu_{(\text{C}-\text{O})}$]. μ_{eff} (μ_{B}) 2.81. Λ_{M} (DMF, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 27. UV-Vis (λ , nm) (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$) 401(3), 555(0.301), 729(0.554), 935(0.745). UV-Vis (λ , nm). Colour: red.

$\{[\text{CuCl}(\text{H}_2\text{L})]_2 \cdot (\text{DMF})\}$ (3). Yield: 92% (0.7154 g). Anal. calc for $\text{C}_{31}\text{H}_{33.8}\text{N}_9\text{Cu}_2\text{Cl}_2\text{O}_3$: C, 47.88; H, 4.28; N, 16.21. Found: C, 47.72; H, 4.37; N, 16.33%. IR (KBr, cm^{-1}): 3284 [ν_{NH_2}]; 1620 [$\nu_{\text{C}=\text{O}}$]; 1592, 1461 [$\nu_{(\text{C}=\text{N})\text{py}}$ and $\nu_{(\text{C}=\text{C})\text{Ar}}$], 1244 [$\nu_{(\text{C}-\text{O})}$]. μ_{eff} (μ_{B}) 1.74. Λ_{M} (DMF, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 30. UV-Vis (λ , nm) (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$) 293(3), 358(3), 461(3), 615(0.19). Colour: green.

$[\text{Zn}(\text{H}_2\text{L})_2]$ (4). Yield : 83% (0.4747 g). Anal. calc for $\text{C}_{28}\text{H}_{26}\text{N}_8\text{ZnO}_2$: C, 58.80; H, 4.58; N, 19.59. Found: C, 58.78; H, 4.57; N, 19.54%. IR (KBr, cm^{-1}): 3342 [ν_{NH_2}]; 1620 [$\nu_{\text{C}=\text{O}}$]; 1591, 1460 [$\nu_{(\text{C}=\text{N})\text{py}}$ and $\nu_{(\text{C}=\text{C})\text{Ar}}$], 1248 [$\nu_{(\text{C}-\text{O})}$]. Λ_{M} (DMF, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 36. Colour: yellow.

RESULTS AND DISCUSSION

General characterization

One-pot synthesis of 1:1 molar ratio of the Schiff base (H_3L) and M(II) metal salts in refluxing ethanol (M = Mn, Ni, Cu or Zn) afforded mononuclear or dinuclear complexes. The complexes gave analytically pure products and were characterized by elemental analysis, IR, UV-Vis spectroscopy and constant temperature magnetic measurements. Colors, magnetic moment, molar conductivity and spectral data of all the prepared Schiff base complexes are given in the experimental section. All complexes are paramagnetic in nature except the Zn(II) complex which is diamagnetic. The observed value of effective magnetic moment of the Mn(II) complex is $5.88 \mu_{\text{B}}$. This value is close to the spin-only value (5.92 at room temperature and typical for high-spin Mn(II) complex with d^5 configuration ($S = 5/2$) and shows an octahedral environment in the vicinity of the manganese atom [15, 16]. For the $\{[\text{Ni}(\text{H}_2\text{L})_2] \cdot \text{DMF} \cdot 0.4\text{H}_2\text{O}\}$ complex, the value of the magnetic moment of $2.81 \mu_{\text{B}}$ is above the expected value of $2.83 \mu_{\text{B}}$ for nickel(II) mononuclear complex in octahedral environment [17]. $\{[\text{CuCl}(\text{H}_2\text{L})]_2 \cdot (\text{DMF})\}$ complex shows μ_{eff} value of $1.74 \mu_{\text{B}}$, which is closer to the spin only value of $1.73 \mu_{\text{B}}$, expected for copper complexes [18] with single unpaired electron located in an $d_{x^2-y^2}$ orbital. In fact no coupling phenomenon exists in this complex at room temperature.

The IR spectrum of the H_3L ligand display two sharp bands around $3450\text{-}3310 \text{ cm}^{-1}$ assignable to ν_{sym} and ν_{asym} vibrations of the $-\text{NH}_2$ group and a band around 3285 cm^{-1} due to $\nu(\text{N}-\text{H})$ of the amide moiety. Strong bands at 1651 and 1615 cm^{-1} assignable to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ respectively, and bands of medium intensity at 1583 , 1567 , 1512 and 1461 cm^{-1} attributable to $\nu(\text{C}=\text{C})$ are also pointed. On complexation the values of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ stretching vibrations are found to be lower ($1626\text{-}1620 \text{ cm}^{-1}$ and $1569\text{-}1467 \text{ cm}^{-1}$, respectively) than the values observed in spectrum of the ligand. This lower values of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ stretching may be explained by the involvement of the carbonyl oxygen atom and the azomethine nitrogen atom in the coordination to the metal ions [19, 20]. The bands due to $\nu(\text{NH}_2)$ and $\nu(\text{N}-\text{H})$ remain in the spectra of the complexes **1-4**. All the complexes are soluble in DMF. The measurement of molar conductance gives Λ_{M} values of 32, 30 and $36 \text{ S cm}^2 \text{ mol}^{-1}$ for

complex **1**, **3** and **4** respectively and 27 for complex **2** confirming that the three mononuclear (**1**, **2** and **4**) complexes and the dinuclear complex **3** are neutral and non-electrolyte [21]. The electronic spectra in DMF are recorded in the range 200-1000 nm. The intense absorption bands at short wavelengths, between 290 and 405 nm, may be assigned to ligand-metal ion charge transfer bands (LMCT). The octahedral geometry of the manganese(II) complex cannot be supported by the electronic spectrum of the complex. As expected, spin-forbidden d-d bands were not observed in the spectra of the high-spin d^5 Mn(II) complex studied in this work. The absorptions in the range 550-1000 nm may be assigned to d-d transitions of the nickel(II) complex. The octahedral geometry can be supported by the d-d transition bands revealed in electronic spectrum of the nickel(II) complex at 935, 729 and 401 nm. These three bands are assigned to ν_1 ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, ν_2 ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and ν_3 ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$, in octahedral geometry of nickel(II) [22] complex. Electronic spectrum of Cu(II) complexes gave transitions, $A_{1g} \leftarrow B_{1g}$, $B_{2g} \leftarrow B_{1g}$ and $E_g \leftarrow B_{1g}$ [22-25], but it is very difficult to resolve them into separate bands due to the very low energy difference between these bands. The observed band at 615 nm can be assigned to d-d transition [26].

Crystal structures of $[Mn(H_2L)_2]$, $\{[Ni(H_2L)_2] \cdot DMF \cdot 0.4H_2O\}$, $\{[CuCl(H_2L)]_2 \cdot (DMF)\}$ and $[Zn(H_2L)_2]$ complexes, have been also determined by X-ray diffraction.

Crystal structures of complexes

Crystals of **1-4** suitable for X-ray diffraction were obtained by slow recrystallization of the compound from dimethylformamide. The crystals structures of **1-4** are respectively shown in Figures 1-4 together with the atomic numbering scheme adopted and selected bond lengths and angles. Crystal data and structure refinement are given in Table 1.

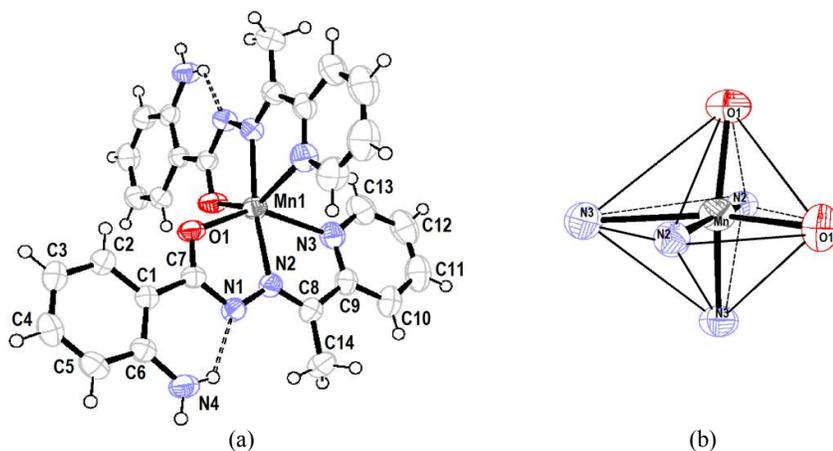


Figure 1. (a) Molecular structure of $[Mn(H_2L)_2]$ and selected bond lengths /Å and angles $^\circ$: Mn1–O1 2.1351(16), Mn1–O1 2.1350(16), Mn1–N2 2.2054(18), Mn1–N2 2.2054(18), Mn1–N3 2.332(2), Mn1–N3 2.332(2), O1–Mn1–O1 99.30(10), O1–Mn1–N2 114.68(6), O1–Mn1–N2 71.48(6), O1–Mn1–N2 71.48(6), O1–Mn1–N2 114.68(6), N2–Mn1–N2 171.16(9), O1–Mn1–N3 141.24(6), O1–Mn1–N3 98.53(7), N2–Mn1–N3 103.55(7), N2–Mn1–N3 69.83(7), O1–Mn1–N3 98.53(7), O1–Mn1–N3 141.24(6), N2–Mn1–N3 69.83(7), N2–Mn1–N3 103.55(7), N3–Mn1–N3 88.42(11). Symmetry transformations used to generate equivalent atoms: (i) $-x+1, y, -z+2$. (b) A view of the coordination environment around the Mn(II) ion in complex **1**.

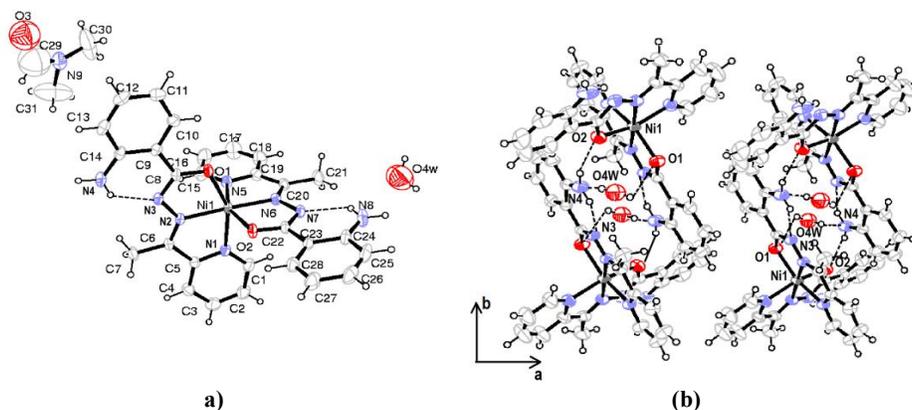


Figure 2. (a) Molecular structure of $\{[Ni(H_2L)_2] \cdot DMF \cdot 0.4H_2O\}$ and selected bond lengths /Å and angles /°: Ni1–N6 1.985(2), Ni1–N2 1.989(2), Ni1–O2 2.093(2), Ni1–N5 2.104(3), Ni1–O1 2.113(2), Ni1–N1 2.119(2), N6–Ni1–N2 175.91(9), N6–Ni1–O2 76.20(9), N2–Ni1–O2 105.34(9), N6–Ni1–N5 78.31(10), N2–Ni1–N5 100.17(10), O2–Ni1–N5 154.49(9), N6–Ni1–O1 107.31(9), N2–Ni1–O1 76.49(9), O2–Ni1–O1 93.30(9), N5–Ni1–O1 93.06(10), N6–Ni1–N1 98.22(10), N2–Ni1–N1 78.02(10), O2–Ni1–N1 91.77(9), N5–Ni1–N1 93.05(10), O1–Ni1–N1 154.45(9). (b) Complex molecules linked by the hydrogen bonds through the water molecule yielding dimers units, and selected bond lengths /Å and angles /°: N4–H4NA···O2i 2.996(2), 153.3; N4–H4NB···N3 2.682(3), 130.6; N8–H8NA···O1ii 3.107(3), 175; N8–H8NB···N7 2.708(3), 126.6. Symmetry codes: (i) $-x+2, -y+2, -z+2$; (ii) $-x+2, -y+2, -z+1$.

Compound 1, $[Mn(H_2L)_2]$ crystallizes in the centrosymmetric space group $C2/c$. The geometry around the manganese ion can be described as slightly distorted octahedral, with a N_4O_2 core comprised by six donor atoms of two ligand molecules. Each ligand acts with two nitrogen and one oxygen atoms. The equatorial plane of the octahedron is formed by one hydrazone and two pyridine N atoms and one O atom from the carbonyl moiety, (rms mean deviation 0.043) with the Mn center 0.079 Å out of this plane. The axial positions are occupied by one oxygen atom and one hydrazino N atom, 141.24(6) [O1–Mn–N3]. The Mn–O1, 2.135(2) Å and Mn–N3, 2.332(2) Å distances correspond to the shortest and the longest bond distance to the manganese center respectively. The hydrazone N distances, Mn1–N2, 2.205(2) Å is smaller than those found in a similar complex [27]. The coordination of each hydrazone to Mn results in the formation of two five membered chelating rings (MnNNCO and MnNCCN). The Mn–O is, thus, stronger than the Mn–N bond and correlates with the slightly less strained five-member ring defined by the MnN2N1C7O1 atoms, which has the N2–Mn–O1 angle of 71.48(6)°. The ring formed by MnN3C9C8N2 is slightly more rigid and has a N2–Mn–N3 angle of 69.83(7)°.

The complex 2, $\{[Ni(H_2L)_2] \cdot DMF \cdot 0.4H_2O\}$ crystallizes in the triclinic space group $P\bar{1}$. The structure is of a mononuclear nickel complex with the metal ion bound to two nitrogen and one oxygen atoms from each of the two molecules ligand in an octahedral environment. The arrangement around the nickel ion can be described as distorted octahedral, being the main distortion due to the tense five members ring [O1–Ni1–N2 76.44(7)°; N1–Ni1–N2 77.94(7)°; O2–Ni1–N6 76.25(7)°; N6–Ni1–N5 78.20(7)°]. The axial positions of the distorted octahedral environment can be considered that occupied by one hydrazone nitrogen atom and one oxygen of the carbonyl, [O1–Ni–N1 154.32(6)°] and the equatorial plane is thus formed by one oxygen atom, two pyridyl nitrogen atoms and one nitrogen atom of the hydrazonic moiety. Interestingly,

the distorted octahedral polyhedron can be viewed in two ways: firstly, the plane with axial position O1-Ni-N1 154.42(6)° and equatorial plane N2N5N6O2 (rms mean deviation of 0.034 and Ni1 0.025 away from that plane), secondly, the plane with axial position O2-Ni-N5 154.42(6)° and equatorial plane N2N1N6O1 (rms mean deviation of 0.023 and Ni1 0.002 away from that plane). These equatorial planes are roughly perpendicular (89.67(6)°). The asymmetric unit of **2** contains one molecule of the complex with two lattice disordered solvent molecules, which occupies each partially its site (16 and 26% respectively). Thus, the title complex is 0.4 water solvated. Intramolecular hydrogen bond involving the free amino group, and the uncoordinated nitrogen atom of the hydrazone moieties lead to the formation of six membered rings. No intermolecular hydrogen bonds were observed.

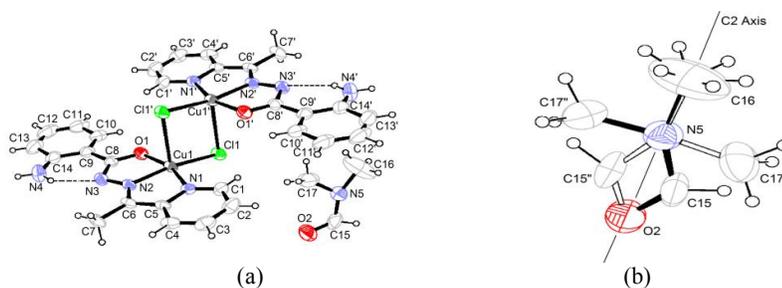


Figure 3. (a) : Molecular structure of $\{[\text{CuCl}(\text{H}_2\text{L})]_2(\text{DMF})\}$ and selected bond lengths /Å and angles /°: Cu1–N2 1.928(3), Cu1–O1 1.945(3), Cu1–N1 2.004(3), Cu1–Cl1 2.2315(10), N2–Cu1–O1 79.71(13), N2–Cu1–N1 80.78(14), O1–Cu1–N1 160.36(13), N2–Cu1–Cl1 168.47(10), O1–Cu1–Cl1 99.29(9), N1–Cu1–Cl1 99.39(10). N4–H4NA···N3 2.697(4), 131.8; N4–H4NB···O2i 3.035(4), 176.3. Symmetry codes: (i) $-x+1, -y+1, -z+1$. (b) : Representation showing the disordered DMF solvent molecule around the twofold axis.

The structure of $\{[\text{CuCl}(\text{H}_2\text{L})]_2\text{DMF}\}$ **3** is centrosymmetric with space group $C2/c$ and is consistent with dinuclear neutral units in which the two metal centers are linked by two ligand molecules and two chloride. The two copper atoms are pentacoordinated with a $\{\text{N}_2\text{OCl}_2\}$ core formed by one monoanionic tridentated ligand molecule coordinated through the pyridine and the hydrazone nitrogen atoms and the oxygen of the carbonyl group. Two chloride ions shared by the two copper atoms complete the coordination sphere around each metal ion. The two chloride anions acts as bidentate bridging mode. The coordination of the hydrazone to Cu results in the formation of two five membered chelating rings (CuOCNN and two CuNCCN). The distortion of the coordination polyhedron from the square pyramid to the trigonal bipyramid is calculated by the Addison parameter $\tau = (\beta - \alpha)/60$ where β and α are the two largest donor–metal–donor angles [28]. A value of $\tau = 0$ indicates an ideal square pyramid and when $\tau = 1$, the geometry around the metal center is a perfect trigonal bipyramid.

The geometry around each copper(II) ion can be best described as a square pyramidal arrangement as indicated by the Addison's parameter: $\tau = 0.135$ [28] [O1–Cu–N1, 160.35(9); N2–Cu–Cl1, 168.50(7); O1–Cu–Cl1, 99.28(6); N1–Cu–Cl1, 99.42(7); N2–Cu–O1, 79.74(10); N2–Cu–N1, 80.72(10)°]. The equatorial plane of the distorted square pyramidal environment around each Cu can be defined by one of the bridging chloride atom, the oxygen atom from one molecule ligand and the two nitrogen atoms (equatorial plane: Cl1, N1, N2, O1; rms mean deviation of 0.082 and Cu 0.1121(8) away from that plane). The apical position is occupied by

the other Cl with Cu–Cl distance of 2.775 Å. The longer bond length in the equatorial plane correspond to the chloride and the nitrogen pyridine atoms respectively, Cu–Cl1 2.2314(8) Å and Cu–N1 2.003(2) Å. The shorter bond length corresponds to the hydrazino nitrogen atom of the Schiff base, Cu–N2 1.927(2) Å. The Cu···Cu separation is 3.415 Å, not showing interaction between the metal ions. This distance is similar to those found for the chloride dinuclear complexes prepared by Mukherjee *et al.* [29] (3.523 Å) and (4.499 Å) [30]. The DMF solvent molecule was found to be disordered around the twofold axis, in two positions with equal site occupancy (Figure 3b).

Intramolecular hydrogen bond involving the free amino group, and the uncoordinated nitrogen atom of the hydrazone moieties lead to the formation of six membered ring. In the crystal structure, a weak intermolecular H bond (N4 ...O2) is also observed, involving the free amino group, and the O atom of the DMF solvent molecule.

Compound 4, [Zn(H₂L)₂] crystallizes in the centrosymmetric space group *P2₁/c*. The geometry around the zinc ion can be described as slightly distorted octahedral, with a N₄O₂ core comprised by six donor atoms of two ligand molecules. Each ligand acts with two nitrogen and one oxygen atom. The axial positions of the distorted octahedral environment can be considered that formed by one hydrazone nitrogen atom and one oxygen atom and the equatorial plane formed by one oxygen atom, one nitrogen atom from the hydrazone moiety and two pyridyl nitrogen atoms. Interestingly, the distorted octahedral polyhedron can be viewed in two ways: firstly, the plane with axial position O1–Ni–N7 148.84(16)° and equatorial plane N3N6N8O2 (rms mean deviation of 0.054 and Zn -0.047 away from that plane), secondly, the plane with axial position O2–Ni–N6 147.93(15)° and equatorial plane N8N7N3O1 (rms mean deviation of 0.035 and Zn -0.052 away from that plane). Two intramolecular hydrogen bond involving the free amino group and the uncoordinated nitrogen atom of the hydrazone moieties and one weak intermolecular H bond (N4 ...O2) are observed.

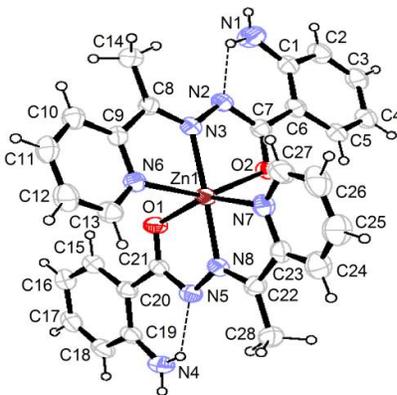


Figure 4. Molecular structure of {[Zn(H₂L)₂]} and selected bond lengths /Å and angles /°: Zn1–N8 = 2.069(4), Zn1–N3 = 2.070(4), Zn1–O1 = 2.103(4), Zn1–O2 = 2.142(3), Zn1–N7 = 2.187(5), Zn1–N6 = 2.235(4), N8–Zn1–N3 = 177.76(17), N8–Zn1–O1 = 74.17(15), N3–Zn1–O1 = 106.12(15), N8–Zn1–O2 = 107.67(15), N3–Zn1–O2 = 74.53(15), O1–Zn1–O2 = 98.26(16), N8–Zn1–N7 = 75.00(17), N3–Zn1–N7 = 104.52(17), O1–Zn1–N7 = 148.84(16), O2–Zn1–N7 = 95.21(16), N8–Zn1–N6 = 103.76(16), N3–Zn1–N6 = 74.01(16), O1–Zn1–N6 = 96.22(16), O2–Zn1–N6 = 147.93(15), N7–Zn1–N6 = 86.76(16). N4 H4NB... N5 0.86 2.06 2.707(6) 131.0, N4 H4NA... O2i 0.86 2.28 3.057(6) 151.0, N1 H1NB N2 0.86 2.03 2.668(7) 130.5. Symmetry codes: (i) -x+1, -y, -z+1.

CONCLUSION

The potentially pentadentate hydrazone ligands reported here, obtained by condensation of 2-acetyl pyridine with 2-aminobenzohydrazide, form mononuclear octahedral manganese(II) and nickel(II) complexes or dichloro bridged binuclear copper(II) complex with square pyramidal geometry. Though the ligand is potentially pentadentate, it acts as tridentate donors with the metal ions used in this work. The oxygen atom and the imino nitrogen atom of the hydrazone moiety and the pyridine nitrogen of the ligand are involved in coordination, while the amino moiety remains uncoordinated. According to the data of elemental analysis, molar conductivity, FT-IR and UV-Vis spectra, and X-ray crystallographic structure determination, these complexes have a metal to hydrazone stoichiometry of 1:2 in mononuclear species and 1:1 in dinuclear complex.

Supplementary data. CCDC 988200, 988201, 988202 and 998022 contain the supplementary crystallographic data for $\{[\text{Cu}_2(\text{H}_2\text{L})_2(\mu\text{-Cl})_2]\cdot((\text{CH}_3)_2\text{CO})\cdot(\text{H}_2\text{O})\}$, $[\text{Mn}(\text{H}_2\text{L})_2]$, $\{[\text{Ni}(\text{H}_2\text{L})_2]\cdot\text{DMF}\cdot 0.4\text{H}_2\text{O}\}$ and $[\text{Zn}(\text{H}_2\text{L})_2]$, respectively. 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 CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

REFERENCES

1. Pal, S. *J. Chem. Crystallogr.* **2000**, 30, 329.
2. Saghatforoush, L.A.; Chalabian, F.; Aminkhani, A.; Karimnezhad, G.; Ershad, S. *Eur. J. Med. Chem.* **2009**, 44, 4490.
3. Maiti, A.; Ghosh, S. *J. Inorg. Biochem.* **1989**, 36, 131.
4. Gudasi, K.B.; Shenoy, R.V.; Vadavi, R.S.; Patil, S.A.; Nethaji, M. *J. Mol. Struct.* **2006**, 788, 22.
5. Knoepfel, D.W.; Liu, J.; Meyers, E.A.; Shore, S.G. *Inorg. Chem.* **1998**, 37, 4828.
6. Sy, A.; Dieng, M.; Thiam, I.E.; Gaye, M.; Retailleau, P. *Acta Cryst.* **2013**, E69m, 108.
7. Iskander, M.F.; El-Sayed, L.; Salem, N.M.H.; Haase, W.; Linder, H.J.; Foro, S. *Polyhedron* **23**, **2004**, 23.
8. Gudasi, K.B.; Patil, S.A.; Vadavi, R.S.; Shenoy, R.V.; Patil, M.S. *Trans. Met. Chem.* **2005**, 30, 726.
9. Ainscough, E.W.; Brodie, A.M.; Dobbs, A.J.; Ranford, J.D.; Waters, J.M. *Inorg. Chim. Acta* **1998**, 267, 27.
10. Gudasi, K.B.; Patil, S.A.; Vadavi, R.S.; Shenoy, R.V.; Patil, M.S. *Trans. Met. Chem.* **2005**, 30, 1014.
11. Gudasi, K.B.; Patil, S.A.; Bakale, R.P.; Nethaji, M. *J. Mol. Struct.* **2014**, 1065-1066, 179.
12. SHELXTL version *An Integrated System for Solving and Refining Crystal Structures from Diffraction Data (Revision 5.1)*, Bruker AXS Ltd.: WI, USA; **1997**.
13. Sheldrick, G.M. *SHELXTL-97 Program for the Refinement of Crystal Structures*, University of Göttingen: Germany; **1997**.
14. Farrugia, L.J. *J. Appl. Crystallogr.* **1997**, 30, 565.
15. Mandal, S.; Karmakar, T.K.; Ghosh, A.; Fleck, M.; Bandyopadhyay, D. *Polyhedron* **2011**, 30, 790.
16. Shelke, V.A.; Jadhav, S.M.; Shankarwar, S.G.; Munde, A.S.; Chondhekar, T.K. *Bull. Chem. Soc. Ethiop.* **2011**, 25, 381.
17. Sahoo, S.C.; Dubey, M.; Alam, Md.A.; Ray, M. *Inorg. Chim. Acta* **2010**, 363, 3055.
18. Bhowmik, P.; Chattopadhyay, S.; Drew, M.G.B.; Ghosh, A. *Inorg. Chim. Acta* **2013**, 395, 24.

19. Lodeiro, C.; Basitida, R.; Bertolo, E.; Macias, A.R. *Trans. Metal Chem.* **2003**, 28, 388.
20. Alhadi, A.A.; Shaker, S.A.; Yehye, W.A.; Ali, H.M.; Abdullah, M.A. *Bull. Chem. Soc. Ethiop.* **2012**, 26, 95. Chandra, S.; Sharma, A.K. *Spectrochim. Acta A* **2009**, 72, 851.
21. Geary, W.J. *Coord. Chem. Rev.* **1971**, 7, 81.
22. Kala, U.L.; Suma, S.; Kurup, M.R.P.; Krishnan, S.; John, R.P. *Polyhedron* **2007**, 26, 1427.
23. Bhaumik, P.K.; Harms, K.; Chattopadhyay, S. *Polyhedron* **2013**, 62, 179.
24. John, R.P.; Sreekanth, A.; Rajakannan, V.; Ajith, T.A.; Kurup, M.R.P. *Polyhedron* **2004**, 23, 2549.
25. Siji, V.L.; Sudarsanakumar, M.R.; Suma, S.; Kurup, M.R.P. *Spectrochim. Acta A* **2010**, 76, 22.
26. Kurup, M.R.P.; Varghese, B.; Sithambaresan, M.; Krishnan, S.; Sheeja, S.R.; Suresh, E. *Polyhedron* **2011**, 30, 70.
27. Pouralimardan, O.; Chamayou, A.-C.; Janiak, C.; Hosseini-Monfared, H. *Inorg. Chim. Acta* **2007**, 360, 1599.
28. Addison, A.W.; Rao, T.N.; Reedijk, J.; van Rijn, J.; Verschoor, G.C. *J. Chem. Soc. Dalton Trans.* **1984**, 1349.
29. Mukherjee, S.; Basu, C.; Chowdhury, S.; Chattopadhyay, A.P.; Ghorai, A.; Ghosh, U.; Stoeckli-Evans, H. *Inorg. Chim. Acta* **2010**, 363, 2752.
30. Song, Y.; Massera, C.; Roubeau, O.; Lanfredi, A.M.M.; Reedijk, J. *Polyhedron* **2005**, 24, 1599.