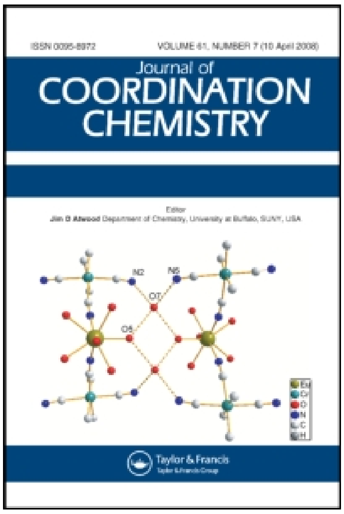

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Ali Morsali[a]; Ali Ramazani[b]; Ali Reza Mahjoub[a]
[a] Department of Chemistry, Tarbiat Modarres University, Tehran, Iran [b] Department of Chemistry, University of Zanjan, Zanjan, Iran

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Ni(II), Pd(II), Cu(II) AND Zn(II) COMPLEXES WITH *N*-(2-PYRIDYL)CARBONYLANILINE (L), SYNTHESES AND X-RAY CRYSTAL STRUCTURES OF $[Cu(L)_2(H_2O)_2](NO_3)_2$, $[Cu(L)_2(H_2O)_2](ClO_4)_2$ AND $[Zn(L)_2(H_2O)_2](ClO_4)_2$

ALI MORSALI[a,]*, ALI RAMAZANI[b] and ALI REZA MAHJOUB[a]

[a]*Department of Chemistry, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran, Iran;*
[b]*Department of Chemistry, University of Zanjan, P.O. Box 45195-313, Zanjan, Iran*

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Reaction of the *N*-(2-pyridyl)carbonylaniline ligand (L) with $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $Zn(ClO_4)_2$, $Ni(NO_3)_2$ and $PdCl_2$ gives complexes with stoichiometry $[Cu(L)_2(H_2O)_2](NO_3)_2$, $[Cu(L)_2(H_2O)_2](ClO_4)_2$, $[Zn(L)_2(H_2O)_2](ClO_4)_2$, $[Ni(L)_2(H_2O)Cl](NO_3)$ and $PdLCl_2$. The new complexes were characterized by elemental analyses and infrared spectra. The crystal structures of $[Cu(L)_2(H_2O)_2](NO_3)_2$, $[Cu(L)_2(H_2O)_2](ClO_4)_2$, and $[Zn(L)_2(H_2O)_2](ClO_4)_2$ were determined by X-ray crystallography. The cation complexes $[M(L)_2(H_2O)_2]$ contain copper(II) and zinc(II) with distorted octahedral geometry with two *N*-(2-pyridyl)carbonylaniline (L) ligands occupying the equatorial sites. The hexa-coordinated metal atoms are bonded to two pyridinic nitrogens, two carbonyl oxygens and two water molecules occupying the axial sites. Both the coordinated water molecules and uncoordinated amide NH groups of the *N*-(2-pyridyl)carbonylaniline (L) ligands are involved in hydrogen bonding, resulting in infinite hydrogen-bonded chains running in one and two-dimensions.

Keywords: Ni(II); Pd(II); Cu(II); Zn(II); Complexes; Crystal structure; *N*-(2-pyridyl)carbonylaniline ligand

INTRODUCTION

Research on the coordination chemistry of carbonylaniline-derived ligands has progressed very rapidly since the early 1980s [1–4]. The incorporation of carbonylaniline groups in the ligands and preparation of new complexes allows electronic and steric control of the properties of metal complexes. A six-membered heterocycle, *e.g.*, pyridine, and an amide, e.g., carbonylaniline, can thus be directly linked in a single ligand system [5–6], such that electronic communication between the two groups can be avoided. The general structure of the ligand can be shown as L.

The presence of a pyridyl nitrogen at the adjacent position to the amide linkage helps the ligand (L) to bind to a metal ion in a bidentate fashion forming a five membered

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*Corresponding author. E-mail: morsal_a@net1cs.modares.ac.ir

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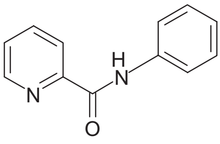
chelate ring either through N-bonding (**1**). or through O-bonding (**2**) from the amide linkage. Both linkage isomers, O-bonded and N-bonded, are known for glycinamide chelated to a metal center [7–9]. This ligand (L) is interesting not only because of the structural chemistry of its multifunction coordination modes but also because of the formation of complexes similar to metal-peptides [10–11]. The palladium, nickel, zinc and copper-containing species play an important role in the catalytic activation of organic carbonyl compounds, for both industrial organic chemistry [12–15] and biological processes [16]. Thus there is ample justification for investigating the coordination chemistry of metals with terminal carbonylaniline-derived ligands. Here, we report the syntheses and characterization of Ni(II), Pd(II), Cu(II) and Zn(II) complexes with *N*-(2-pyridyl)carbonylaniline (L).



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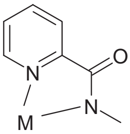

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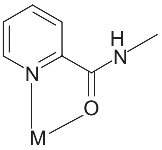

2

EXPERIMENTAL

Physical Measurement

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer.

Synthesis of Ligand

The compound *N*-(2-pyridyl)carbonylaniline (L) was synthesized as previously reported [1].

Synthesis of Pd(*N*-(2-pyridyl)carbonylaniline)Cl$_2$

The complex was prepared by dissolving PdCl$_2$ (0.266 g, 1.5 mmol) and LiCl in distillation methanol (15 cm^3) and adding an alcoholic solution of L (0.297 g, 1.5 mmol). The resulting solution was stirred for 5 h at room temperature, and allowed to stand for 2–3 days in a refrigerator (*ca.* 6°C). A red powder of the desired product precipitated, which was filtered, washed with acetone and ether and air dried (yield 0.394 g, 70%), m.p. 205°C.

Anal. Calcd. for $C_{12}H_9Cl_2N_2O_2Pd$ (%): C, 38.5; H, 2.67; N, 7.48. Found: C, 38.84; H, 3.1 N, 7.69.

IR (KBr, cm^{-1}) ν(N–H) 3210; ν(C–H)$_{ar}$ 3010; ν(C=C), ν(C=N) 1610, 1580; ν(C=O) 1640.

Synthesis of Ni(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)Cl](NO$_3$)

The complex was prepared by dissolving $NiCl_2$ (0.13 g, 1 mmol) in distilled water and adding an alcoholic solution of (0.396 g, 2 mmol) and excess potassium nitrate. The resulting solution was stirred for 2 h at room temperature, and then allowed to stand for 3–4 days in a refrigerator. A blue powder of the desired product precipitated, filtered which was washed with acetone and ether and air dried (yield 0.3 g, 55%), m.p. 215°C.

Anal. Calcd. for $C_{24}H_{22}ClN_5NiO_6$ (%): C, 50.04; H, 3.82; N, 12.16. Found: C, 49.28; H, 3.48; N, 11.93.

IR (KBr, cm^{-1}) ν(N–H) 3216; $\nu(C\text{–}H)_{ar}$ 3030; ν(C=C), ν(C=N) 1615, 1570; ν(C=O) 1650; $\nu(NO_3)$ 1380.

Synthesis of [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$

The complex was prepared by mixing a solution of (0.396 g, 2 mmol) in hot acetonitrile (5 cm^3) and a hot aqueous solution of copper(II) nitrate (0.188 g, 1 mmol). The mixed solution was brought to the boil and allowed to cool slowly overnight, depositing green crystals (yield 0.372 g, 60%), m.p. 290°C.

Anal. Calcd. for $C_{24}H_{24}CuN_6O_{10}$ (%): C, 46.45; H, 3.87; N, 13.54. Found: C, 45.38; H, 3.75; N, 13.41.

IR (KBr, cm^{-1}) ν(N–H) 3205; $\nu(C\text{–}H)_{ar}$ 3020; ν(C=C), ν(C=N) 1610, 1550; ν(C=O) 1655; $\nu(NO_3)$ 1376.

Synthesis of Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$

The complex was prepared using the same procedure as for Cu(*N*-2-pyridyl) carboxylaniline)$_2$(H_2O_2)$_2$(NO_3)$_2$ from L (0.2 g, 2 mmol) and $Cu(ClO_4) \cdot 5H_2O$ (0.307 g, 1 mmol) in acetonitrile (15 cm^3).

Green crystals of Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](ClO_4)$_2$ were obtained by slow diffusion of diethyl ether into the methanol solution (yield 0.46 g, 75%), m.p. 225°C.

Anal. Calcd. for $C_{24}H_{24}Cl_2CuN_4O_{12}$ (%): C, 41.44; H, 3.45; N, 8.5. Found: C, 41.38; H, 3.75; N, 8.41.

IR (KBr, cm^{-1}) ν(N–H) 3205; $\nu(C\text{–}H)_{ar}$ 3030; ν(C=C), ν(C=N) 1610, 1560; ν(C=O) 1655; $\nu(ClO_4)$ 1040.

Synthesis of Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$

Colorless crystals of the complex were obtained from reaction of hydrated $Zn(NO_3)_2$ with *N*-(2-pyridyl)carbonylaniline in a molar ratio of 1:2 in aqueous solution with excess $NaClO_4$. The resulting colorless solution was heated and stirred for about 1 h and left to evaporate at room temperature. After a few days, colorless crystals were isolated (yield 0.310 g, 50%), m.p. 300°C.

Anal. Calcd. for $C_{24}H_{24}Cl_2N_4O_{12}Zn$ (%): C, 41.3; H, 3.4; N, 8.04. Found: C, 40.8; H, 3.3; N, 8.19.

IR (KBr, cm^{-1}) ν(N–H) 3202; $\nu(C\text{–}H)_{ar}$ 3010; ν(C=C), ν(C=N) 1620, 1550; ν(C=O) 1658; $\nu(ClO_4)$ 1030.

Crystallography

Crystal Data and Refinement Details

Cu(N-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ $C_{24}H_{24}CuN_6O_{10}$, $M = 620.03$, monoclinic, space group $P2_1/c$, $a = 7.4413(16)$, $b = 11.458(2)$, $c = 14.850(3)$ Å, $\beta = 95.941(5)°$, $V = 1259.3(5)$ Å^3, D_c ($Z = 2$ f.u.) 1.635 Mg/m^3, $F(000)$ 638. Specimen: $0.30 \times 0.40 \times 0.60$ mm; $T_{\max, \min}$ 0.802, 0.558, N 14185, N_0 3521, R 0.0485, R_w 0.1169.

[Cu(N-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ $C_{24}H_{24}Cl_2CuN_4O_{12}$, $M = 694.91$, monoclinic, space group $P2_1/n$, $a = 8.2448(17)$, $b = 11.852(2)$, $c = 14.882(3)$ Å, $\beta = 104.927(4)°$, $V = 1405.1(5)$ Å^3, D_c ($Z = 2$ f.u.) 1.642 Mg/m^3, $F(000)$ 710. Specimen: $0.40 \times 0.50 \times 0.60$ mm; $T_{\max, \min}$ 0.862, 0.558, N 10223, N_0 3691, R 0.0508, R_w 0.1148.

[Zn(N-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ $C_{24}H_{24}Cl_2N_4O_{12}Zn$ $M = 694.74$, monoclinic, space group $P2_1/n$, $a = 8.262(1)$, $b = 11.847(2)$, $c = 14.885(2)$ Å, $\beta = 103.368(6)$, $V = 1417.4(5)$ Å^3, D_c ($Z = 2$ f.u.) 1.635 Mg/m^3, $F(000)$, 712. Specimen: $0.30 \times 0.40 \times 0.50$ mm; $T_{\max, \min}$ 0.952, 0.536, N 11968, N_0 3437, R 0.062, R_w 0.169.

Structure Determination

Crystallographic measurements were made at 393(2) K for Cu(*N*-(2-pyridyl)-carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ and Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and 110(2) K for Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ using a Siemens R3m/V diffractometer. The intensity data were collected within the range $2.23 \leq \theta \leq 29.00°$ for Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ and $2.25 \leq \theta \leq 29.58°$ for Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and $2.27 \leq \theta \leq 28.88°$ for Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ using graphite monochromataed Mo Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 10223 and 14185 and 11968 unique reflections were measured, from which 3691 and 3521 and 3437 with $I > 2\sigma(I)$ were used in the refinement for Cu(*N*-(2-pyridyl)-carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$,Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, respectively. The structures have been solved by direct methods and refined by full-matrix least-squares techniques on F^2.

Positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. R, R_w, with goodness-of-fit on F^2 are 0.864, 1.086 and 1.034; 0.0508, 0.1148 and 0.0485; 0.1169 0.062 and 0.169 for Cu(*N*-(2-pyridyl)-carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, respectively. The final difference density map showed a maximum peak and hole of 1.464, -0.425 e Å^{-3} for Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, 1.870, -0.307 e Å^{-3} for Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ and 1.690, -0.456 for Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$. Corrections were applied for Lorentz and polarization effects as well as the empirical correction for absorption using the Sadabs programs. All structural calculations were carried out with a PDP–11/23+ computer using the SDP–PLUS program package [17,18].

Selected bond lengths and angles are given in Tables I, II and III. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and perspective views of the packing in the unit cells are shown in Figs. 1–6.

TABLE I Selected bond lengths and angles for $[Cu(L)_2(H_2O)_2](NO_3)_2$

Bond lengths (Å)		*Bond angles* (°)	
Cu(1)–O(1)	1.9650(14)	O(1)–Cu(1)–O(1)#1	180.00(9)
Cu(1)–O(1)#1	1.9650(14)	O(1)–Cu(1)–N(2)	82.06(7)
Cu(1)–N(2)	1.9769(17)	O(1)#1–Cu(1)–N(2)	97.94(7)
Cu(1)–N(2)#1	1.9769(17)	O(1) –Cu(1)–N(2)#1	97.94(7)
Cu(1)–O(1W)#1	2.4053(17)	O(1)#1 –Cu(1)–N(2)#1	82.06(7)
Cu(1)–O(1W)	2.4053(17)	N(2) –Cu(1)–N(2)#1	180.00(10)
		O(1)–Cu(1)–O(1W)#1	88.01(6)
		O(1)#1–Cu(1)–O(1W)#1	91.99(6)
		N(2)–Cu(1)–O(1W)#1	92.07(6)
		N(2)#1–Cu(1)–O(1W)#1	87.93(6)
		O(1)–Cu(1)–O(1W)	91.99(6)
		O(1)#1–Cu(1)–O(1W)	88.01(6)
		N(2)–Cu(1)–O(1W)	87.93(6)
		N(2)#1–Cu(1)–O(1W)	92.07(6)
		O(1 W)#1–Cu(1)–O(1W)	180.00(11)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z$.

TABLE II Selected bond lengths and angles for $[Cu(L)_2(H_2O)_2](ClO_4)_2$

Bond lengths (Å)		*Bond angles* (°)	
Cu(1)–O(1)	1.9700(17)	O(1)–Cu(1)–O(1)#1	180.00(9)
Cu(1)–O(1)#1	1.9700(17)	O(1)–Cu(1)–N(2)	82.51(8)
Cu(1)–N(2)	1.961(2)	O(1)#1–Cu(1)–N(2)	97.49(8)
Cu(1)–N(2)#1	1.961(2)	O(1)–Cu(1)–N(2)#1	97.50(8)
Cu(1)–O(1W)#1	2.389(2)	O(1)#1 –Cu(1)–N(2)#1	82.51(8)
Cu(1)–O(1W)	2.389(2)	N(2)–Cu(1)–N(2)#1	180.00(14)
		O(1)–Cu(1)–O(1W)#1	94.21(8)
		O(1)#1–Cu(1)–O(1W)#1	85.79(8)
		N(2)–Cu(1)–O(1W)#1	84.28(8)
		N(2)#1–Cu(1)–O(1W)#1	95.72(9)
		O(1)–Cu(1)–O(1W)	85.79(8)
		O(1)#1–Cu(1)–O(1W)	94.21(8)
		N(2)–Cu(1)–O(1W)	95.72(9)
		N(2)#1–Cu(1)–O(1W)	84.28(9)
		O(1W)#1–Cu(1)–O(1W)	180.00(1)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+2$, $-z$.

TABLE III Selected bond lengths and angles for $[Zn(L)_2(H_2O)_2](ClO_4)_2$

Bond lengths (Å)		*Bond angles* (°)	
Zn(1)–O(8)	2.078(2)	O(8)–Zn (1)–N(1)	78.80(1)
Zn(1)–O(1S)	2.154(3)	O(8A)–Zn(1)–N(1)	101.2(1)
Zn(1)–N(1)	2.086(3)	N(1)–Zn (1)–N(1A)	180.00(1)
		O(1)–Zn(1)–O(1A)	180.00(1)
		O(8)–Zn(1)–O(8A)	180.00(1)

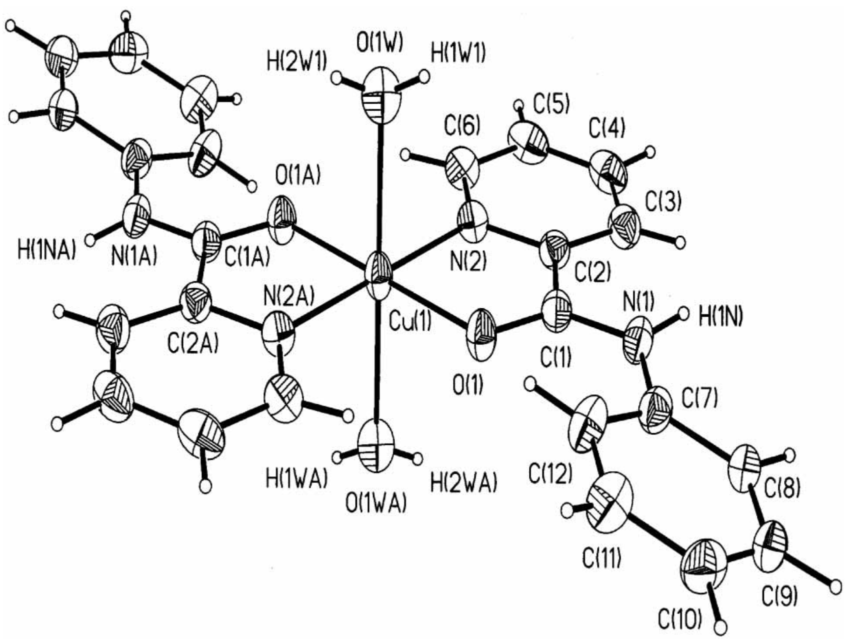

FIGURE 1 ORTEP diagram of $[Cu(L)_2(H_2O)_2](NO_3)_2$.

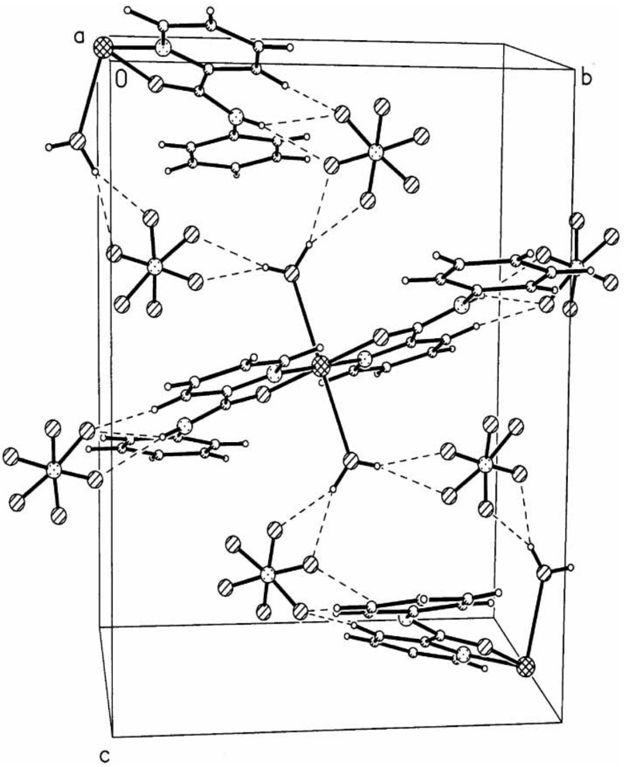

FIGURE 2 The unit cell of $[Cu(L)_2(H_2O)_2](NO_3)_2$ showing hydrogen bonding interactions.

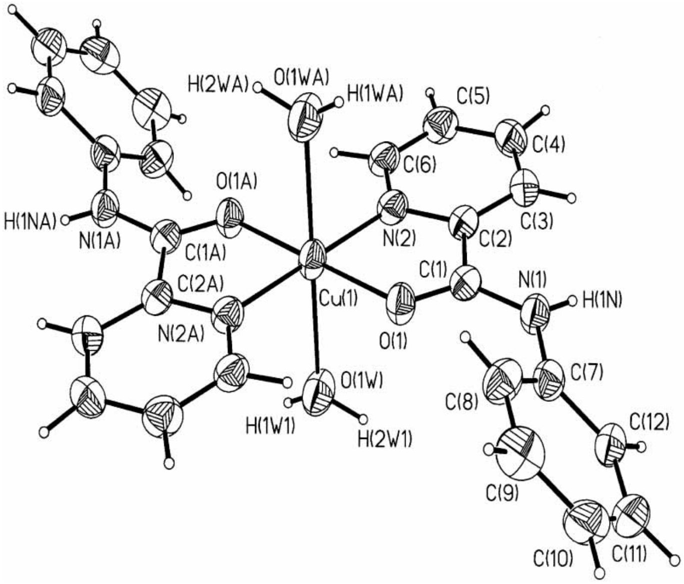

FIGURE 3 ORTEP diagram of $[Cu(L)_2(H_2O)_2](C10_4)_2$.

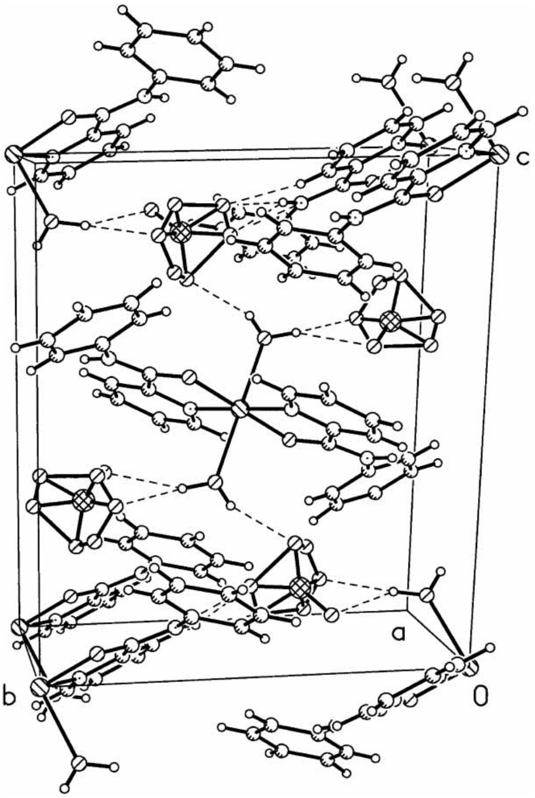

FIGURE 4 The unit cell of $[Cu(L)_2(H_2O)_2](ClO_4)_2$ showing hydrogen bonding interactions.

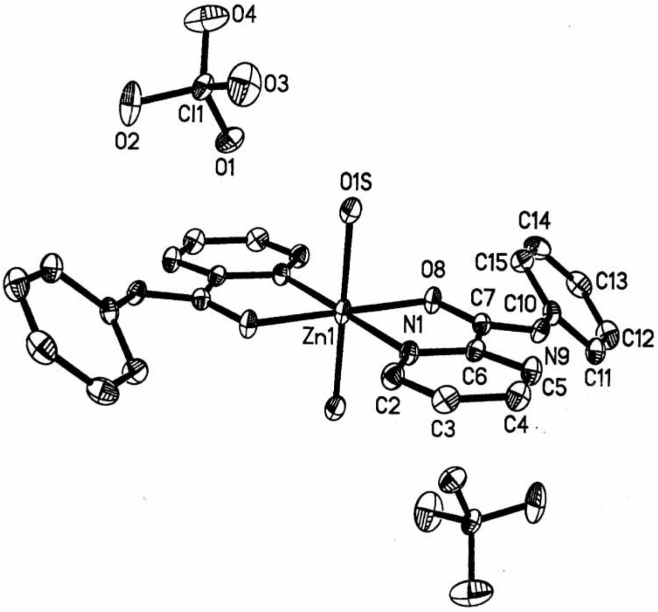

FIGURE 5 ORTEP diagram of $[Zn(L)_2(H_2O)_2](ClO_4)_2$.

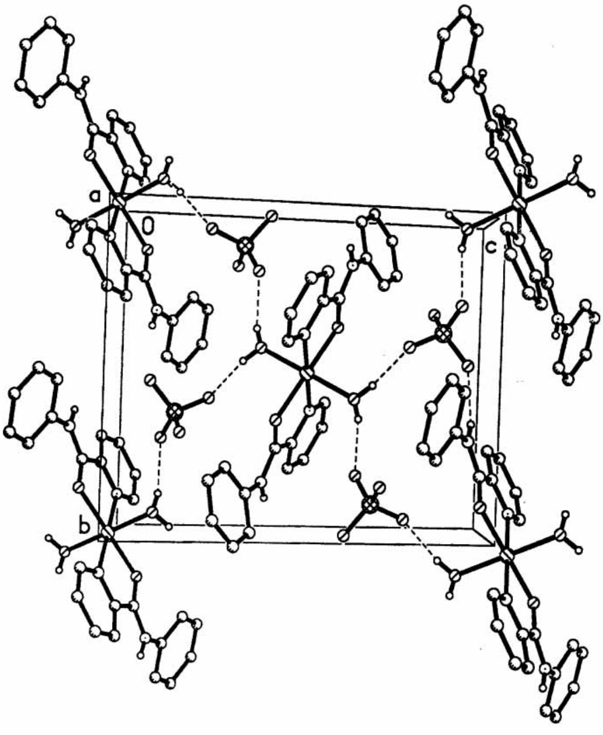

FIGURE 6 The unit cell of $[Zn(L)_2(H_2O)_2](ClO_4)_2$ showing hydrogen bonding interactions.

RESULTS AND DISCUSSION

Syntheses and Spectroscopic Properties of the Complexes

Reaction between $PdCl_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ with *N*-(2-pyridyl)carbonylaniline ligand provided powdery materials that analyzed as Pd(*N*-(2-pyridyl)carbonylaniline)Cl_2], Ni(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)Cl] (NO_3), [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](NO_3)$_2$, [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$ (H_2O)$_2$](ClO_4)$_2$, and [Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](ClO_4)$_2$, respectively. The comparison of the IR spectrum of the free ligand with those of the complexes shows a negative shift in ν(C=O) of the amide linkage in the complexes, [1675 (L) compared with 1640 {Pd(*N*-(2-pyridyl)carbonylaniline)Cl_2}, 1650 {Ni(*N*-(2-pyridyl) carbonylaniline)$_2$(H_2O)$_2$](NO_3)$_2$}, 1655 {Cu(*N*-(2-pyridyl)carbonylaniline)$_2$ (H_2O)$_2$] (NO_3)$_2$}, 1655 {Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](ClO_4)$_2$}, and 1658 Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](ClO_4)$_2$], indicating [19] that the oxygen atom of the amide linkage is coordinated to the metal. The IR spectra of the [Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](ClO_4)$_2$ and Cu(*N*-(2-pyridyl)carbonylaniline)$_2$ (H_2O)$_2$](ClO_4)$_2$ complexes show ν(ClO_4) at 1050–1110 cm^{-1} and Cu(*N*-(2-pyridyl)carbonylaniline)$_2$ (H_2O)$_2$](NO_3)$_2$, Ni(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)Cl](NO_3) complex shows ν(NO_3) at *ca.* 1380 cm^{-1}. An attempt to isolate [Pd(L)$_2$]Cl_2 was not successful; each time a 1:1 adduct was isolated and attempts to isolate single crystals of Ni(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)Cl](NO_3) and Pd(*N*-(2-pyridyl)carbonylaniline)Cl_2 for X-ray crystallography were similarly unsuccessful.

Crystal Structure of [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H_2O)$_2$](NO_3)$_2$

The molecular structure (Fig. 1) consists of discrete [Cu(*N*-(2-pyridyl) carbonylaniline)$_2$ (H_2O)$_2$]$^+$ cations and NO_3^- anions. The cation complex is mononuclear occupying special positions in the inversion centers. Table I lists selected bond distances and angles. In the cation, the coordination around Cu is distorted octahedral and molecules have an inversion center and approximate C_{2h} symmetry. The Cu is chelated by two bidentate L ligands, through their O and N atoms, and two water molecules forming a five-membered metallocycle. Two oxygen atoms from amide and two nitrogen atoms from pyridyl are in trans positions [the angles O(amide)–Cu–O(amide) and N(pyridyl)–Cu–O(pyridyl) are 180°], and also the two coordinated water molecules are trans [O(water)–Cu–O(water) is 180°]. The bond distances Cu–N (1.9769 Å), Cu–O_{amide} (1.9650 Å) and Cu–O_{water} (2.4053 Å) are consistent with previously described values [19–20]. The bite angles of O(1)–Cu(1)–N(2) and O(1)#1–Cu(1)–N(2)#1), 82.06 and 82.06°, are similar to those reported [21–23]. The nitrate anions in this compound show rotational disorder over two positions with unequal occupancies. Cations are linked by hydrogen bonding (Fig. 2). The coordinated L molecules and the two coordinated water molecules are involved in hydrogen bonding acting as hydrogen-bond donors with coordinated O and N atoms as potential hydrogen-bond acceptors (Table IV). As shown in Fig. 2, the hydrogen bonding yields infinite chains parallel to the crystallographic vectors *a* and *b*. Each cation is bonded to four neighbors assembling the molecules into a two-dimensional chain.

TABLE IV Hydrogen bond distances (Å) and angles (°) for $[Cu(L)_2(H_2O)_2](NO_3)_2$

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*<(DHA)*	*A*
O(1W)–H(1W1)	0.843	1.972	2.770	157.52	O(4)$[-x+1/2, y-1/2, -z+1/2]$
O(1W)–H(1W1)	0.843	2.062	2.877	162.36	O(2)$[-x+1, y-1/2, 1-z+1/2]$
O(1W)–H(2W1)	0.748	1.905	2.593	152.71	O(2)$[x, y-1, z]$
O(1W)–H(2W1)	0.748	2.176	2.916	170.36	O(2)$[x, y-1, z]$
N(1)–H(1N)	0.804	2.097	2.857	157.63	O(2)
N(1)–H(1N)	0.804	2.232	2.982	155.45	O(3)

TABLE V Hydrogen bonds distances (Å) and angles (°) for $[Cu(L)_2(H_2O)_2](ClO_4)_2$

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*<(DHA)*	*A*
O(1W)–H(1W1)	0.778	2.055	2.767	152.22	O(4)$[x+1/2, -y+3/2, z-1/2]$
O(1W)–H(1W1)	0.778	2.373	3.116	160.23	O(5)$[x+1/2, -y+3/2, z-1/2]$
O(1W)–H(1W1)	0.778	2.546	3.248	150.84	O(4A)$[x-1/2, -y+3/2, z-1/2]$
O(1W)–H(2W1)	0.937	2.147	3.046	160.65	O(3)$[-x, -y+1, -z]$
O(1W)–H(2W1)	0.937	2.405	3.163	137.97	O(2)$[-x, -y+1, -z]$
O(1W)–H(2W1)	0.937	2.622	3.492	154.81	O(3A)$[-x, -y+1, -z]$
N(1)–H(1N)	0.790	2.129	2.850	151.57	O(5A)
N(1)–H(1N)	0.790	2.182	2.963	169.91	O(5)

Crystal Structure of [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$

The molecular structure of the complex (Fig. 3) consists of discrete [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$]$^+$ cations and ClO$_4^-$ anions. The cation complex is mononuclear and occupies special positions in the inversion centers. Table II lists selected bond distances and angles. In the cation, the coordination around Cu is a distorted octahedron with an inversion center and approximate C_{2h} symmetry. The Cu is chelated by two bidentate L ligands, through their O and N atoms, and two water molecules forming a five-membered metallocycle. Two oxygen atoms from amide and two nitrogen atoms from pyridyl are in trans positions [the angles O(amide)–Cu–O(amide) and N(pyridyl)–Cu–O(pyridyl) are 180°], and also the two coordinated water molecules are trans [O(water)–Cu–O(water) is 180°]. The bond distances Cu–N (1.961 Å), Cu–O$_{\text{amide}}$ (1.9700 Å) and Cu–O$_{\text{water}}$ (2.389Å) are consistent with previously described values [20–23]. The bite angles of O(1)–Cu(1)–N(2) and O(1)#1–Cu(1)–N(2)#1), 82.51 and 82.51° are similar to those reported [21–23]. The perchlorate anions in this compound show rotational disorder over two positions with unequal occupancies. Cations are linked by hydrogen bonding (Fig. 4). The coordinated L molecules and the two coordinated water molecules are involved in hydrogen bonding acting as hydrogen-bond donors with coordinated O and N atoms as potential hydrogen-bond acceptors (Table V). As shown in Fig. 3, the hydrogen bonding yields infinite chains parallel to the crystallgraphic vectors *a* and *b*. Each cation is bonded to four neighbors assembling the molecules into a two-dimensional chain.

ORTEP and unit cell diagrams of Zn(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ are given in Figs. 5 and 6. The structure is similar to the two other compounds.

General Observation

The striking similarity of the three compounds, [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](NO$_3$)$_2$, [Cu(*N*-(2-pyridyl)carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ and Zn(*N*-(2-pyridyl) carbonylaniline)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, is that all have the same geometry, distorted octahedral and approximate C_{2h} symmetry, and hydrogen bonding interaction acting as hydrogen-bond donors with coordinated O and N atoms as potential hydrogen-bond acceptors.

The different feature is that, of the three compounds, the $[Cu(N\text{-}(2\text{-pyridyl})carbonylaniline)_2(H_2O)_2](NO_3)_2$, $[Cu(N\text{-}(2\text{-pyridyl})carbonylaniline)_2(H_2O)_2](ClO_4)_2$ complexes are two-dimensional chains but $Zn(N\text{-}(2\text{-pyridyl})carbonylaniline)_2(H_2O)_2](ClO_4)_2$ is a one-dimensional chain. The other difference is that there is an elongation of the axial bonds in the two copper complexes (Tables I and II) more than in the zinc complex. The reason for this is the Jahn–Teller effect [24–25] arising from the unequal occupation of the e_g pair of orbitals (d_{z^2} and $d_{x^2-y^2}$) when a d^9 ion is subjected to an octahedral crystal field.

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Supplementary Data

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers 182763 for $[Cu(N\text{-}(2\text{-pyridyl})carbonylaniline)_2(H_2O)_2](NO_3)_2$, 182762 for $Cu(N\text{-}(2\text{-pyridyl})carbonylaniline)_2(H_2O)_2](ClO_4)_2$ and 181400 for $Zn(N\text{-}(2\text{-pyridyl})carbonylaniline)_2(H_2O)_2](ClO_4)_2$.

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