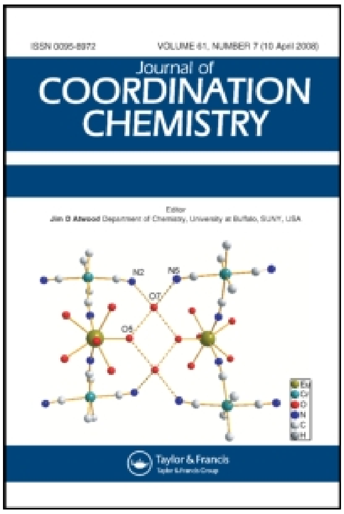

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Synthesis and crystal structures of Cu(II) and Pb(II) aroylhydrazone complexes and magnetic properties of $[Cu_2(L)_2(Cl)_2(HO)_6]_n$ (HL = 2-pyridylaldehyde isonicotinoylhydrazone)

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Two novel aroylhydrazones complexes $\{[Cu_2(L)_2(Cl)_2](H_2O)_6\}_n$ (**1**), $[Pb(L)(CH_3COO)]$ (**2**), (HL = 2-pyridylaldehyde isonicotinoylhydrazone), were synthesized and structurally characterized by means of X-ray single-crystal diffraction. In complex **1**, HL coordinates to Cu(II) using the normal coordination of aroylhydrazone, and also two pyridyl nitrogens forming a coordination polymer. There are strong intermolecular π–π stacking interactions in **2**. Magnetism of complex **1** was studied in the temperature range 5–300 K. The results reveal the occurrence of a weak ferromagnetic coupling with $J = 0.29\,\text{cm}^{-1}$.

Keywords: 2-Pyridylaldehyde isonicotinoylhydrazone (HL); Cu(II) complex; Pb(II) complex; Crystal structure; Magnetic property

1. Introduction

Coordination polymers have attracted much attention from chemists in recent years because of their structure diversity and potential as functional materials [1–3]. Of these polymers, the mumber, type and spatial disposition of ligands are crucial to the construction of a specific supramolecular structure or topology [4–6]; polyfunctional ligands such as polypyridine are frequently used as linkers between adjacent metal ions [6, 7]. Weaker intermolecular forces have been used in deliberate strategies for connecting metal complexes into a wide variety of extended networks [8, 9].

Aroylhydrazones are important polydentate ligands with biologically activity and strong tendency to chelate metals [10–12], coordinating in the enolic, keto form with the carbonyl oxygen and azomethine nitrogen atoms of the aroylhydrazone group, forming a five-membered chelate ring [13–15]. Here, we present a new tetradentate ligand 2-pyridylaldehyde isonicotinoylhydrazone (HL) and its complexes. Although both Cu(II) complex **1** and Pb(II) complex **2** coordinated with HL, the coordination geometries of **1** and **2** are different. Magnetism of complex **1** was also studied.

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2. Experimental

2.1. *Materials and measurement*

Isonicotinoylhydrazine, and 2-pyridylaldehyde of analytical reagent grade were purchased from Alfa Aesar and used without further purification. Melting points were taken on a XT-5 microscope melting point apparatus. IR spectra were recorded on a Nicolet IR-470 spectrometer from KBr pellets between 4000–400 cm^{-1}. Elemental analyses were performed with a Carlo-Erba 1106 elemental analyzer. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 5–300 K with an applied field of 500 G. All data have been corrected for diamagnetism by using Pascal's constants.

2.2. *Synthesis of 2-pyridylaldehyde isonicotinoylhydrazone (HL)*

Four drops of acetic acid were added to a mixture of isonicotinoylhydrazine (1.37 g, 10 mmol) and 2-pyridylaldehyde (1.16 g, 1 mL) in anhydrous ethanol (20 mL). The resultant solution was heated to reflux for 3 h and after cooling a solid was collected by filtration, washed three times with cold ethanol and dried in vacuum. Yield 70%, m.p. 168–170°C. Anal. Calcd for $C_{12}H_{10}N_4O$: C, 63.7; H, 4.4; N, 24.8%. Found: C, 63.5; H, 4.5; N, 24.6%. IR (KBr cm^{-1}): 3448, 3294, 1686, 1668, 1544, 1463, 1403, 1276, 1146, 685. The ligand (HL) is readily soluble in methanol, and ethanol.

2.3. *Synthesis of* $[Cu_2(L)_2(Cl)_2(H_2O)_6]_n$

Five drops of pyridine were added to a methanol solution (15 mL) of HL (0.045 g, 0.2 mmol), then, a methanol solution (15 mL) of $CuCl_2$ (0.034 g, 0.02 mmol) was added dropwise. Dark green single crystals suitable for X-ray structure analyses were obtained after two days by slow evaporation of solvent at room temperature. Yield 45%, m.p. 281–283°C. Anal. Calcd for $C_{24}H_{30}Cl_2Cu_2N_8O_8$: C, 38.0; H, 3.9; N, 14.8%. Found: C, 38.1; H, 4.0; N, 14.6%. IR (KBr cm^{-1}): 3421, 1613, 1567, 1489, 1457, 1371, 1153, 1077, 759, 713.

2.4. *Synthesis of* $[Pb(L)(CH_3COO)]$

Preparation of complex **2** was identical with complex **1**, using $Pb(CH_3COO)_2$ instead of $CuCl_2$ and acetic acid instead of pyridine. A yellow single crystal suitable for X-ray structure analysis was obtained by slow evaporation of solvent at room temperature after a month. Yield 42%, Found: C, 34.1; H, 2.2; N, 13.1%. Calcd for $Pb(L_1)(CH_3COO)$: C, 34.2; H, 2.4; N, 13.2%. IR (cm^{-1}, KBr disk), 3435, 3074, 1644, 1604, 1570, 1349, 1285, 1048, 776, 695.

2.5. *Crystal structure determination*

Intensity data for **1** and **2** were measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K.

Table 1. Crystallographic data and structure refinement for complexes **1** and **2**.

Structural parameter	**1**	**2**
Empirical formula	$C_{24}H_{30}Cl_2Cu_2N_8O_8$	$C_{14}H_{12}N_4O_3Pb$
M	756.54	491.47
Crystal system	Triclinic	Monoclinic
Space group	$p-1$	$P2_1/c$
a (Å)	10.159(2)	7.2718(15)
b (Å)	12.008(2)	12.539(3)
c (Å)	14.168(3)	16.295(3)
α (°)	72.34(3)	90
β (°)	80.93(3)	97.80(3)
γ (°)	70.56(3)	90
V (Å^3)	1549.9(5)	1472.0(5)
D_c (g cm^{-3})	1.621	2.218
Z	2	4
μ (mm^{-1})	1.604	11.480
Crystal size (mm^3)	0.20 × 0.20 × 0.18	0.20 × 0.18 × 0.16
Reflns collected/unique	4322/4322	5436/3076
R_1, wR_2 [$I > 2\sigma(I)$]	0.0453^a, 0.1237^b	0.0370^a, 0.0818^b

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR_2 = [\Sigma(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$.

4322 reflections were measured over the ranges $1.51 \le 2\theta \le 25.00$, $-12 \le h \le 11$, $-14 \le k \le 0$, $-16 \le l \le 15$, yielding 4322 unique reflections for complex **1**; 5436 reflections were measured over the ranges, yielding 3076 unique reflections for complex **2**. Raw data were corrected and the structures were solved using the SHELX-97 program; non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full-matrix least-squares calculations on F^2 were applied on the final refinement. The refinement converged at $R_1 = 0.0453$ and $wR_2 = 0.1237$ for reflections with $I > 2\sigma(I)$ for complex **1**; $R_1 = 0.0370$ and $wR_2 = 0.0818$ for complex **2**. Details of crystal structure determination of the complexes **1** and **2** are summarized in table 1.

3. Discussion and results

3.1. *IR spectra*

Aroylhydrazones can exhibit keto-enol tautomerism. In IR spectra of the ligand HL, the ν(C=O) and the ν(N–H) of HL appeared at 1686 and 3294 cm^{-1}, respectively, which indicated free HL exists in the ketoform. In IR spectra of **1** and **2** ν(C=O) and ν(N–H) of HL disappeared with two new bands at 1077 cm^{-1}, 1048 cm^{-1} and, 1613 cm^{-1}, 1604 cm^{-1} are assigned to ν(C–O), ν(C=N), indicating that HL coordinates to Cu(II) and Pb(II) through the azomethine nitrogen and oxygen of depronated amide in the enolform.

3.2. *Structure of complex 1*

The structure consists of $Cu_2(L)_2(Cl)_2$ units and water molecules. The selected bond lengths and bond angles are listed in table 2. Figure 1 shows an ORTEP drawing of the Cu(II) complex with the atom numbering, figure 2 is a perspective view of the

Table 2. Selected bond distances (Å) and angles (°) for **1**–**2**.

Complex **1**			
Cu(1)–N(2)	1.949(4)	Cu(1)–O(1)	2.009(3)
Cu(1)–N(1)	2.041(4)	Cu(1)–Cl(1)	2.2251(18)
Cu(1)–N(8)	2.246(4)	Cu(2)–N(6)	1.936(5)
Cu(2)–O(2)	2.030(4)	Cu(2)–N(5)	2.037(5)
N(2)–Cu(1)–O(1)	78.01(16)	N(2)–Cu(1)–N(1)	79.34(18)
O(1)–Cu(1)–N(1)	156.94(17)	N(2)–Cu(1)–Cl(1)	163.37(13)
Complex **2**			
Pb(1)–O(2)	2.299(5)	Pb(1)–O(1)	2.416(5)
Pb(1)–N(2)	2.477(6)	Pb(1)–N(1)	2.675(6)
C(6)–N(2)	1.283(9)	C(7)–N(3)	1.332(9)
O(2)–Pb(1)–O(1)	82.2(2)	O(2)–Pb(1)–N(2)	82.0(2)
O(1)–Pb(1)–N(2)	64.06(18)	O(2)–Pb(1)–N(1)	81.57(19)
O(1)–Pb(1)–N(1)	126.16(19)	N(2)–Pb(1)–N(1)	63.03(18)

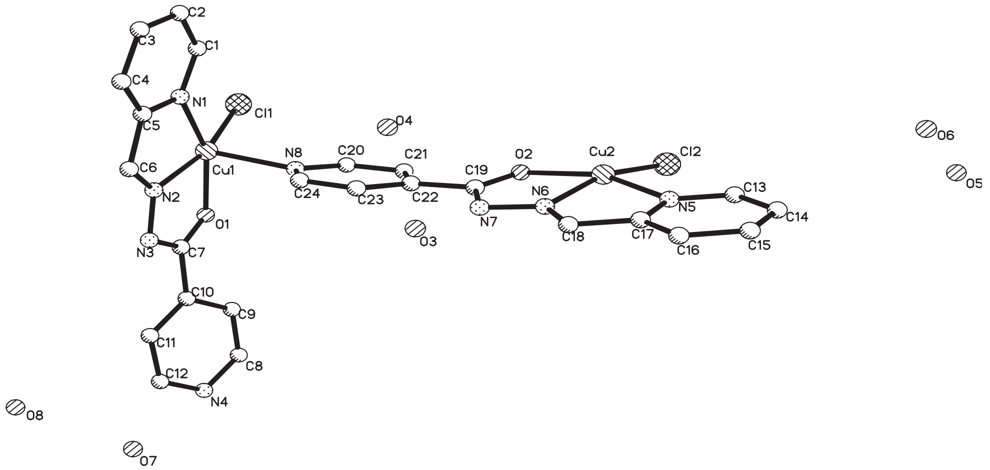

Figure 1. Crystal structure of complex **1**.

2-D lamellar structure. The Cu(II) has a coordination geometry that approximates square pyramidal, each Cu(II) ion in the complex is five-coordinate with a pyridyl nitrogen, an azomethine nitrogen, an oxygen from one HL, a chloride atom and a pyridyl nitrogen atom of isonicotinoylhydrazine from the other ligand (HL). It can be seen from table 2 and figure 1 that the N1, N2, O1, Cl1, Cu1 form the basal plane (only deviate 0.099 Å). The apical Cu(1)–N(8) distance of 2.246(4) Å is greater than the Cu(1)–N distances in plane which are in the range 1.949(4) Å to 2.041(4) Å.

The pyridine plane of 2-pyridylaldehyde and the pyridine plane of isonicotinoylhydrazine are not coplanar (dihedral angle is 28°). The C–O bond length of 1.269(6) Å is longer than that of some complexes [11, 12] [1.220(7) Å, 1.245(9) Å], however it is nearly equivalent to those of other complexes [14, 15] [1.274(5) Å, 1.265(3) Å, 1.263(3) Å], indicating that it coordinates to the Cu(II) ion in the enolic form. Pyridyl nitrogen N(8) of isonicotinoylhydrazine moiety coordinates to Cu(II) forming a 1-D zigzag chain.The two pyridine plane of neighboring molecules are parallel

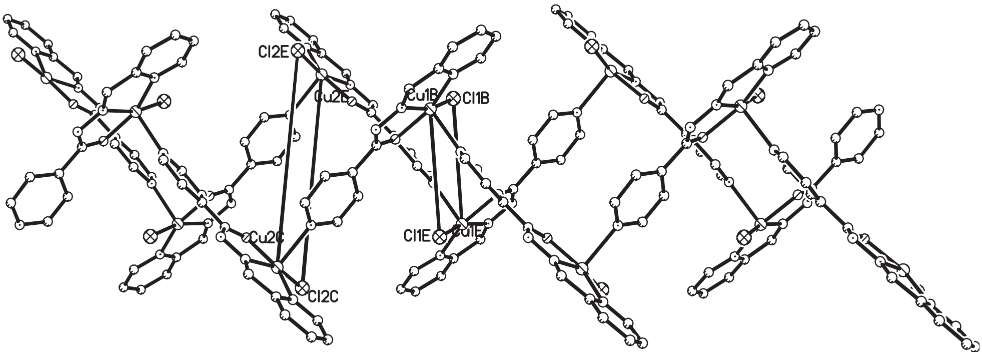

Figure 2. View of the 2-D lamellar structure in complex **1**.

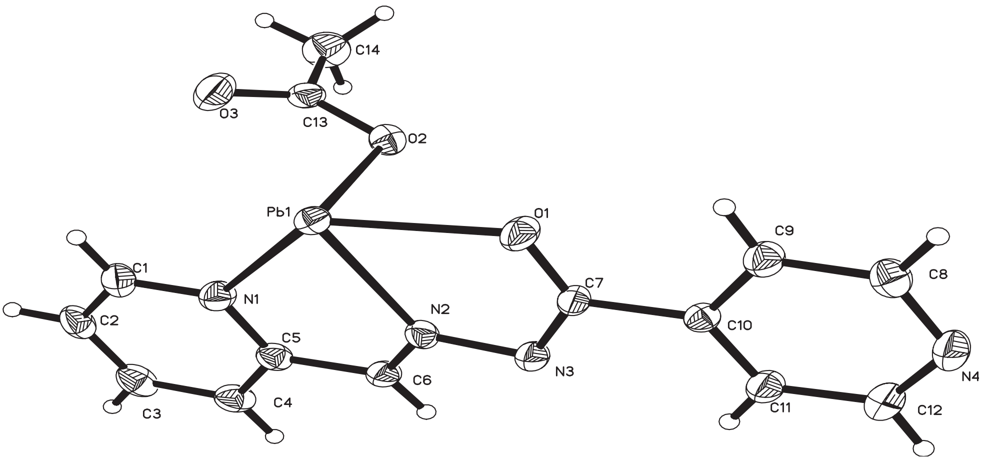

Figure 3. Crystal structure of complex **2**.

to each other [figure 2], but the interplanar separation is very long (7.826 Å). Crystals of **1** contain water, but hydrogen bonding is not observed. The Cl1E–Cu1B distance (5.556 Å) being shorter than Cl2C–Cu2E (9.662 Å), and the Cu2C–Cu2E distance (6.216 Å) being shorter than Cu1B–Cu1E (9.753 Å), a 2-D lamellar structure is formed by weak intermolecular forces between Cu(II) ions and chlorides.

3.3. *Crystal structure of complex 2*

Although **1** and **2** are coordinated with HL, the coordination geometries of **1** and **2** (figures 3 and 4) are different. The coordination number of similar Pb(II) compounds in the literature [16–18] is five with acetate coordinated as bidentate ligand. However, the coordination number of **2** is four (a pyridyl nitrogen, an azomethine nitrogen and an amide oxygen from one HL and an oxygen from acetate) and acetate ions are monodentate, Pb (II) has triangular pyramidal geometry. N1, N2, O1, Pb1 are

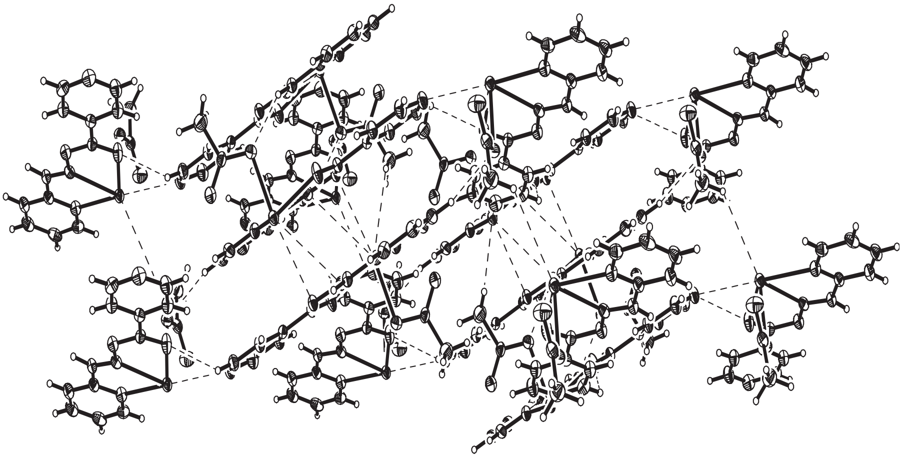

Figure 4. Crystal packing of complex **2**.

co-planar constituting the basal plane and O2 is the apical ligand with a Pb1–O2 distance (2.299 Å) shorter than Pb1–O1 (2.416 Å). In complex **2**, pyridyl rings are parallel between neighboring HL's with center to center separation of 3.4567 Å, indicating the strong intermolecular π–π stacking interactions. Main group metal ions easily coordinate oxygen, so oxygen atom of acetate coordinates to Pb(II) while the pyridyl nitrogen of isonicotinoylhydrazine is free.

3.4. *Magnetic properties of* $\{[Cu_2(L)_2(Cl)_2](H_2O)_6\}_n$

The temperature dependent magnetic susceptibilities of **1** have been studied in the range 5 to 300 K. The magnetic moment at 300 K ($\mu_{eff} = 2.36\mu_B$) per copper(II) center is higher than expected for an isolated paramagnetic system with $S = 1/2$ ($\mu_{eff} = 1.73\mu_B$). By the value of magnetic moment measured at 300 K, the 2^+ oxidation state of copper in **1** could be confirmed with a calculation of spin-only magnetic moment. The increase in χ_M with decreasing temperature at very low temperatures is due to the presence of traces of a monomeric paramagnetic impurity.

Between 300 and 5 K, the data follow the Curie–Weiss law, leading to the parameters $C_M = 0.69\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ and $\theta = +2.89$ K (figure 5). The positive and small θ value suggests a weak ferromagnetic interaction between the Cu(II) centers, which is confirmed by the continuous increase of $\chi_m T$ upon cooling to about 5 K. The very weak ferromagnetic interaction is propagated through the isonicotinoylhydrazine bridge within the zigzag chain. Upon cooling from room temperature, the $\chi_m T$ value increases continuously from $0.695\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ at 300 K to a maximum of $0.741\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ at 10 K. This behavior is characteristic of ferromagnetic coupling between the Cu(II) ions. Further cooling below 10 K causes the $\chi_m T$ to decrease, reaching a value of $0.734\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ at 5 K. In addition, the variation of magnetic susceptibility with temperature for the complex can be satisfactorily fitted to an empirical function (see equation (2); J is the exchange coupling constant; N, g, μ_B, k have their usual meanings; adjustable parameters $A = 0.178$, $B = -0.930$, $C = -1.710$, $D = -4.974$, $E = -9.115$, $F = 0.1852$) introduced by Hall [19]. This empirical function represents

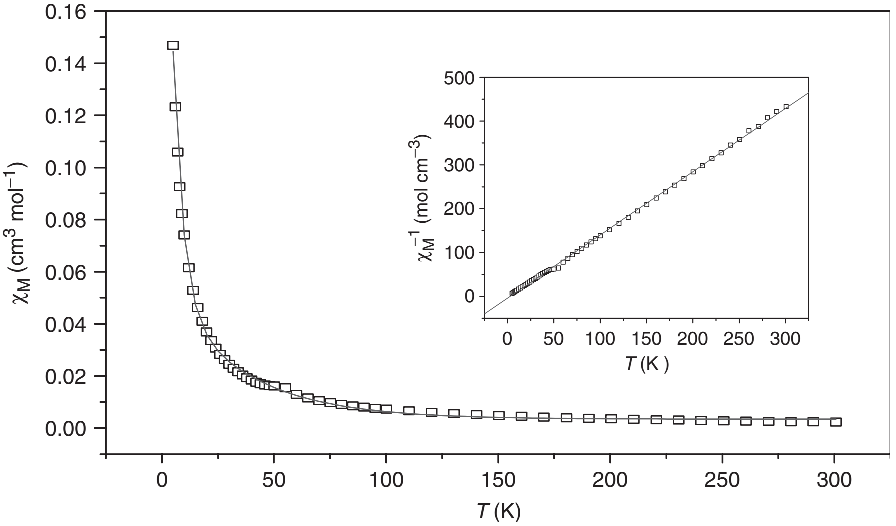

Figure 5. Thermal variation of χ_M and $\chi_M{}^{-1}$ for complex **1**.

the numerical calculations performed by Fisher [20] to describe a uniformly spaced chain with spin of $S=1/2$.

$$\chi_M = \frac{Ng^2\mu B^2}{kT}\left(\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}\right) \tag{1}$$

where $x = |J|/\mathrm{k}T$. The best fit parameters are $g = 2.03$, $J = 0.29\,\mathrm{cm}^{-1}$. The discrepancy factor $\sigma = [\Sigma(\chi_{\mathrm{obs}} - \chi_{\mathrm{calc}})^2/\Sigma\chi_{\mathrm{obs}}]^{1/2}$ in the least-squares fits was 1.03×10^{-5}. Obviously, the positive and small J value also suggests the ferromagnetic interaction between the copper(II) ions is very weak.

Supplementary data

Full atomic data are available as a file in CIF format, deposited with the CCDC No. 222128 for **1**; 237172 for **2**.

Acknowledgements

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