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Copper(II) Complex of a Urea-functionalized Pyridyl Ligand: Synthesis, Crystal Structure, and Acetate Binding Properties

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Abstract. A copper(II) acetate complex with a urea-functionalized pyridyl ligand, $[CuL(OAc)_2]_2 \cdot 2AcOH$ (1) $[L = N \cdot (3 - chlorophenyl) \cdot N' - (3 - pyridyl)$ urea], was synthesized by the reaction of **L** with $Cu(OAc)_2$ in methanol. A zigzag-shaped hydrogen bond chain of **L** is obtained via urea N-H···N_{pyridyl} interactions, and a two-dimensional hydrogen bond network structure is further formed through the C-H···O interaction. In the complex **1**, a paddle-wheel structure is generated by

Introduction

The binding, recognition, and self-assembly of anions has become a fascinating aspect of supramolecular chemistry due to the importance of the anions such as oxyanions and halide anions in physiology, biology and environment.^[1–5] Thus, in recent years, the design and synthesis of simple receptors that can bind anions specifically is the forceful chemical research subject.^[6–8] As one of the most simple and classical hydrogenbond donors, highly polarized N–H fragments are usually contained at the binding site in the neutral synthetic receptors for anions,^[9–11] such as ureas,^[12–15] thioureas,^[16–19] amides,^[20] pyrroles,^[21,22] and benzimidazole.^[23] In these receptors, directional hydrogen bonding interactions make the receptors have the ability to differentiate between anions with different shapes and hydrogen-bonding requirements, which is contrary to the only electrostatic interactions.^[24–28]

The urea groups, possessing two close polarized N–H fragments, have been focused as anion binding sites, owing to their hydrogen-bonding ability that could form quite stable complexes bonded with biologically significant anions such as acetate and halide anion.^[29–32] By introducing pyridyl group, the urea-based pyridyl ligands have become a class of good artificial receptors for ion recognition, in which the urea group can act as hydrogen-bond donor for anions, while the pyridyl moiety can coordinate with metal ions.^[33–35] A series of such ligands have been synthesized and extensively used to recognize ions through cooperative binding of transition metals and anions.^[36,37]

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Ministry of Natural Resources Xi'an 710021, Shaanxi, P. R. China Cu···O_{acetate} interactions and Cu···N_{pyridyl} interactions. Furthermore, hydrogen bonding chain structure is extended through weak C–H···O hydrogen bond interactions. Through ultraviolet-visible (UV/Vis) spectroscopy, the acetate binding properties of L in solution were also evaluated. Variable temperature magnetic susceptibility measurement indicates that the metal complex 1 displays antiferromagnetic coupling property.

Despite the great significant progress of anion binding properties and supramolecular structures for such ligands,^[38–43] the efficient and selective recognition of anions by synthetic promising receptors still remains a challenging subject of anion chemistry. For this purpose, we designed a new ligand, *N*-(3*c*hlorophenyl)-*N'*-(3-pyridyl) urea (**L**) (Scheme 1). Herein we report the synthesis, characterization and the supramolecular structures of the ligand **L** and its Cu^{II} acetate complex [CuL(OAc)₂]₂·2AcOH (1), as well as the investigation of acetate recognition of the ligand **L** including the binding ratio and the association constants (*K*_a) by the method of the UV/Vis spectra titrations.



Scheme 1. Synthesis of the ligand L.

Results and Discussion

Synthesis and Formulation

1

Synthesis and Formulation of Ligand L

The pyridylurea ligand, *N*-(3-chlorophenyl)-*N*'-(3-pyridyl) urea (**L**), was synthesized by the reaction of 3-aminopyridine with 3-chlorophenyl isocyanate (Scheme 1). Characterization of **L** by nuclear magnetic resonance spectroscopy (¹H NMR) and infrared spectroscopy (IR) proved the synthesis of high-purity ligand. The ¹H NMR spectrum of the ligand indicates that the peaks at $\delta = 9.02$ ppm and 8.93 ppm are from two urea hydrogen atoms and 8.61 ppm, 8.21 ppm, 7.94 ppm, and 7.32 ppm are from four groups of hydrogen atoms on the pyridine ring. Besides that, 7.71 ppm, 7.32 ppm, 7.32 ppm, and

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Zeitschrift für anorganische

7.03 ppm belong to the four groups of hydrogen atoms on the benzene ring, respectively. In addition, in the infrared spectrum of the ligand, the stretching vibration of N–H bonds at 3343 cm⁻¹ and 3290 cm⁻¹ and the stretching vibration of carbonyl C=O at 1717 cm⁻¹ also provide direct evidence for the synthesis of the ligand.

Synthesis and Formulation of Complex 1

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The metal complex $[CuL(OAc)_2]_2 \cdot 2AcOH$ (1) was obtained by crystallization of the reaction product of L with 1 equivalent of Cu(OAc)_2. The formation of 1 can be confirmed by the stretching vibration of N–H bonds at 3360 cm⁻¹ and 3020 cm⁻¹ in the IR spectrum of 1, especially the stretching vibration of acetate at 1620 cm⁻¹.

Crystal Structure

Crystal Structure of Ligand L

The ligand L crystallizes in the orthorhombic space group Pca21, and the detailed crystallogrophic data are shown in Table 1. The space group Pca21 is a non-centrosymmetric polar space group, which is not often encountered. Obviously, this is caused in this case by the orientation of the C=O bond and C–Cl bond of the ligand. Based on the relative orientation of the C=O bond of the urea carbonyl group and the C–Cl bond of the aryl group, the ligand adopts a syn conformation. One N atom of the urea group is connected by the pyridine six-membered ring and chlorophenyl ring, respectively. The structure of L shows that the six-membered ring of Cl phenyl [dihedral

Table 1. Crystallographic data and refinement details for compounds $L \mbox{ and } 1.$

	L	1
Empirical formula	C ₁₂ H ₁₀ ClN ₃ O	C ₃₆ H ₄₀ Cl ₂ Cu ₂ N ₆ O ₁₄
Fw	247.68	978.72
Temperature /K	296(2)	296(2)
Crystal system	orthorhombic	triclinic
Space group	Pca21	$P\bar{1}$
a /Å	13.578(3)	8.0883(18)
b /Å	9.2763(18)	8.691(2)
c /Å	9.2307(18)	15.474(3)
a /°	90	81.979(4)
β /°	90	84.152(4)
γ /°	90	88.326(4)
$V/Å^3$	1162.6(4)	1071.4(4)
Z	4	1
$D_{\rm calc}$ /g·cm ⁻³	1.415	1.517
<i>F</i> (000)	512	502
μ /mm ⁻¹	0.314	1.188
θ range	2.195-25.085	2.367-25.046
Reflections collected	5448	5397
R (int)	0.0206	0.0264
$R_1; wR_2 [I > 2\sigma(I)]$	0.0273; 0.0694	0.0518; 0.1384
R_1 ; wR_2 (all data)	0.0300; 0.0713	0.0722; 0.1652
GOF (F^2)	1.052	1.060
Flack-parameter	0.02(3)	/

angle 17.12°, Figure 1a). The chlorophenyl ring is almost coplanar with the urea carbonyl (torsion angle $C6_{urea}$ –N3–C7–C12_{chlorophenyl} 6.4(4)°]. The C–N bonds of the urea group are 1.362(3) Å and 1.382(3) Å, respectively. The C=O bond length of urea is 1.213(3) Å, which falls within the previously reported C=O bond length of urea (1.20– 1.235Å),^[44,45] indicating the formation of double bonds. In the extended structure of **L**, pyridine N is linked to the urea group of a adjacent ligand **L** by two bifurcated chelating N–H···N hydrogen bonds [N2···N1ⁱ, 3.092(3) Å, N2–H2···N1ⁱ, 156.0°; N3···N1ⁱ, 3.062(3) Å, N3–H3···N1ⁱ, 163.3°, Figure 1b and Table 2]. Through these N–H···N bonding, a zigzag hydrogen bond chain is further formed. The hydrogen bond chain of this N–H···N is different from that of the self-assembly of urea-



Figure 1. Crystal structure of the ligand **L**. (a) ORTEP drawing; (b) Chain obtained by N–H···N hydrogen bonds. (c) 2D hydrogen bond sheet network linked by C–H···O hydrogen bonds. Symmetry codes: ⁱ 1–x, 2–y, z + 0.5; ⁱⁱ x–0.5, 2–y, z.

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urea formed by N–H···O hydrogen bond, which is common in urea-based ligands.^[46,47] It is indicated that the self-assembly of pyridyl-urea by N–H···N hydrogen bond (in the presence of pyridylurea) is more stable than urea-urea self-assembly. Furthermore, the 1D hydrogen bonds structure further self-assembled via C–H···O interactions [C1···O1ⁱⁱ, 3.314(3) Å, C1– H1···O1ⁱⁱ, 140.7°] involving carbonyl oxygen atom of urea functionality (Figure 1c and Table 2), leading to an infinite 2D hydrogen bond sheet network structure.

		-		
	<i>D</i> –H••• <i>A</i>	Н•••А	D····A	<i>D</i> –Н•••А
L	N2–H2•••N1 ⁱ	2.29	3.092(3)	156.0
	N3–H3•••N1 ⁱ	2.23	3.062(3)	163.3
	C1–H1•••O1 ⁱⁱ	2.54	3.314(3)	140.7
1	N2–H2•••O7 ⁱⁱ	2.16	2.953(6)	153.6
	N3–H3•••O7 ⁱⁱ	2.07	2.884(6)	157.3
	C4–H4•••O1 ⁱⁱⁱ	2.56	3.362(6)	144.5

Table 2. Selected hydrogen bond parameters /Å,° for L and 1.

Symmetry codes for L: ⁱ 1–*x*, 2–*y*, z + 0.5; ⁱⁱ x–0.5, 2–*y*, z. Symmetry codes for 1: ⁱⁱ x–1, y, z; ⁱⁱⁱ 1–x, –y, –z.

Crystal Structure of Complex 1

X-ray single crystal diffraction results of complex 1 indicate that 1 crystallizes in the triclinic space group $P\bar{1}$ and the detailed crystallographic data are exhibited in Table 1. In complex 1, the asymmetric unit comprises two acetate ions and one L ligand coordinated to the Cu²⁺ ion, and one CH₃COOH molecule (Figure 2a). Compared with ligand L, the bond length of C=O in urea of complex 1 is 1.215(6) Å, which is slightly longer than that of ligand L, and the selected bond lengths and angles for 1 are listed in Table 3. The Cu^{II} ion is coordinated by two carbonyl oxygen atoms from acetate groups and one pyridine N atom from L [Cu1····O2, 1.970(3) Å, Cu1···O4, 1.968(3) Å, Cu1···N1, 2.193(4) Å, Figure 2a and Table 3]. The Cu-O bond length values are slightly shorter than that (1.980(6) Å] found in $[Cu_2(phend)_2(\mu-OAc)_4]$.^[48] Among them, one carbonyl oxygen atom is on the same plane as L, and the other is distorted [O2-Cu1-O4, 88.61(15)°, Figure 2a and Table 3]. The other O atom of the carboxyl group is linked to the adjacent Cu atom to form a unit (monomer) with two ligands L molecule, two Cu(OAc)₂ molecules and two CH₃COOH molecules (Figure 2b). The urea groups of the two ligands act as hydrogen-bond donors to form two pairs of bifurcated chelating N-H···O hydrogen bonds with the carbonyl oxygen atoms of CH3COOH, respectively [N2···O7ⁱⁱ, 2.953(6) Å, N2-H2-O7ⁱⁱ, 153.6°; and N3-O7ⁱⁱ, 2.884(6) Å, N3-H3···O7ⁱⁱ, 157.3°, Figure 2b and Table 2]. The pyridyl N donors of two ligands are coordinated to a pair of Cu^{II} ions in the axial positions to generate the paddle-wheel units, while two acetate groups from two different Cu(OAc)₂ groups are located in the equatorial plane [Cu1...N1, 2.193(4) Å, Cu1····O2, 1.970(3) Å, Figure 2b and Table 3]. The copper atom (Cu1) is slightly out of the square plane of oxygen atoms (0.207 Å), which is consistent with the theory that the longer the Cu-Cu distance within the dimer, the higher the Cu outof-plane deviation.^[49] In complex 1, the Cu1···Cu1ⁱ distance is 2.6432(11) Å, which falls into the same order of magnitude as described in the literature (2.612–2.713 Å).^[50–54] Adjacent complex **1** units are held together by the C–H···O hydrogen bonds [C4···O1ⁱⁱⁱ, 3.362(6) Å, C4–H4···O1ⁱⁱⁱ, 144.5°, Figure 2c and Table 2], forming a hydrogen bond chain structure including paddle-wheel units. Such Cu₂(COO)₄ paddle-wheel clusters have been used as secondary building units (SBUs) for the construction of porous metal–organic frameworks (MOFs).^[55–57]



Figure 2. Crystal structure of the complex 1. (a) ORTEP drawing of asymmetric unit of 1. (b) Monomer of 1 with a paddle-wheel structure. (c) Chain structure held together by the C–H···O hydrogen bonds including paddle-wheel units in 1. Symmetry code for 1: i -x, -y, 1-z; $i^{i} x-1$, y, z; $i^{ii} 1-x$, -y, -z.

Table 3. Selected bond lengths /Å and angles /° for L and 1.

	Bond	Dist.	Bond	Angle	
L	C6-O1 C6-N2 C6-N3	1.213(3) 1.382(3) 1.362(3)	O1-C6-N2 O1-C6-N3 N2-C6-N3	123.7(2) 125.5(2) 110.8(2)	
1	Cu1-O2 Cu1-O3 ⁱ Cu1-O4 Cu1-O5 ⁱ Cu1-N1 Cu1-Cu1 ⁱ C6- O1 C6-N2 C6-N3	$\begin{array}{c} 1.970(3) \\ 1.969(3) \\ 1.968(3) \\ 1.963(3) \\ 2.193(4) \\ 2.6432(11) \\ 1.215(6) \\ 1.370(6) \\ 1.362(6) \end{array}$	O2-Cu1-N1 O3- Cu1-N1 ⁱ O4-Cu1-N1 O5-Cu1-N1 ⁱ O2-Cu1-O4 O2-Cu1-O3 ⁱ O1-C6-N2 O1-C6-N3 N2-C6-N3	96.92(13) 95.13(13) 95.37(13) 96.81(13) 88.61(15) 167.92(13) 122.9(4) 124.0(4) 113.2(4)	

Symmetry code for 1: i -x, -y, 1-z.

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Acetate Binding Properties of L

Binding Mode of the Ligand L to AcO⁻ Anion

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The binding mode of **L** with AcO⁻ anion was studied in CH₃CN by UV/Vis spectra. Keeping the total concentration of **L** with AcO⁻ is 1×10^{-5} mol·L⁻¹, and the molar ratio of host to guest was changed in the following turn : 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10. All the UV/Vis spectra of molar ratio of host to guest were acquired (Figure 3a), and Job's plot^[58–60] of molar fraction $x_{\rm L}$ of **L** vs. the concentration of the corresponding complex ([HG]) were obtained. The absorbances at the wavelength of 266 nm were used to calculate the complex concentration, [HG] = $(A_0 - A) / A_0 \times$ [H], where A_0 stood for the absorbance of the free ligand, A was the absorbance of the solution after adding AcO⁻ anion, [H] represented the total concentration of the corresponding ligand **L**. Job's plot analysis revealed a 1:1 complexation mode between the ligand **L** and AcO⁻ anion (Figure 3b).

Binding Constant K of the Ligand L to AcO⁻ Anion

The binding constant of L with AcO⁻ anion was analyzed in CH₃CN by UV/Vis titration at room temperature. The solution of AcO⁻ in CH₃CN solution of ligands (0.01 mM) was prepared for the UV/Vis titration (Figure 4a). Small portions $(3 \,\mu L)$ of the AcO⁻ solutions were added to the solution of L (3 mL, 0.01 mM). UV/Vis titration spectra reveal that upon addition of AcO⁻ to L, the high absorption peak at 256 nm undergoes a red shift to 266 nm. An isosbestic point at 260 nm suggests that the appearance of the stable complex. With the addition of AcO-, the absorbance at 266 nm increases gradually. The binding constant K of L with AcO^{-} was fitted by Origin nonlinear least-squares through the following formula:^[61–63] $X = X_0 + (X_{\text{lim}} - X_0)/2c_H \{c_H + c_G + 1/K - [(c_H + C_G)/2c_H \}$ $c_{\rm G} + 1/K)^2 - 4c_{\rm H}c_{\rm G}]^{1/2}$, where the X_0 represented the absorbance of L at 266 nm, X and X_{lim} stood for the absorbance of L at 266 nm in the presence of an anion and its limit value,



Figure 3. (a) UV/Vis spectra of L with AcO⁻ in CH₃CN, H = L, G = AcO⁻ (in the form of tetrabutylammonium acetate (TBAOAc), [10H] = $[10G] = 1 \times 10^{-5}$ mol·L⁻¹. (b) Job's plot analysis for the L with AcO⁻ in CH₃CN at the wavelength of 266 nm in CH₃CN.



Figure 4. (a) UV/Vis spectra of L before and after titration with various amount of AcO^{-} (0–10 equiv.) in CH₃CN. (b) The fitting curve of the titration at 266 nm in CH₃CN.

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Figure 5. Thermal dependence of the magnetic susceptibility (x_M) and $(x_M T)$ vs. T for the metal complex 1 at 0.1 T applied field in the temperature range 2–400 K.

respectively, *K* is the binding constant of **L** with AcO⁻, c_H is the initial concentration of **L** and c_G is the concentration of AcO⁻ during titration. The fitting curve reveals that the binding constant *K* of **L** with AcO⁻ is $K = 1.505 \times 10^4 \text{ m}^{-1} (R^2 = 0.9906)$ (Figure 4b).

The stoichiometric 1:1 complex formation between receptor L and AcO⁻ anion is consistent with that of receptors consisting of urea binding site.^[31,43] Such hydrogen bonding interactions between urea groups and acetate anions have been used to make the ion-selective electrode for acetate based on a porphyrin ionophore,^[64] to operate the translational isomerism of the interlocked molecular switch reversibly through the sequential addition and removal of acetate anions,^[65] and to construct the colorimetric chemosensor for naked-eye detection of acetate anion.^[66,32] The study of acetate anion binding properties may facilitate to understand the mechanism of acetate cell-metabolism in physiology.^[67–69]

Magnetic Measurement of 1

Variable temperature magnetic susceptibility measurement of the metal complex [CuL(OAc)₂]₂·2AcOH (1) was carried out and the result is shown in Figure 5. Upon lowering the temperature, the magnetic susceptibility (x_M) first increases very smoothly and then decreases rapidly, with a broad maximum around 300 K (Figure 5a). This behavior is characteristic for antiferromagnetic coupling within the carboxylato-bridged pairs of Cu^{II} forming the copper complex.^[70] As shown in Figure 5b, the decreasing x_MT value from 0.33 to 0.01 cm³·K·mol⁻¹ upon lowering the temperature from 300 to 60 K also indicates the existence of antiferromagnetic coupling when the spins become more and more constrained.^[71] This behavior is consistent with the *syn-syn*, equatorial-equatorial arrangement of the carboxylato-bridges around copper centers.^[72]

Conclusions

In summary, we have demonstrated that a copper(II) acetate complex [CuL(OAc)₂]₂·2AcOH (1) can be synthesized via the

reaction of N-(3-chlorophenyl)-N'-(3-pyridyl) urea (L) with Cu(OAc)₂. Unlike the two-dimensional infinite hydrogen bond network formed by the interaction of the ligand L through Nurea-H-Npyridyl interactions and C-H-O interactions, complex 1 forms a special paddle-wheel-like structure through the interaction of Cu-Npyridyl interactions and Cu-Oacetate interactions, which further forms an infinite hydrogen bonding chain extended by C-H···Ourea hydrogen bonds. In addition, the binding ratio of the ligand to acetate anion 1:1 and the binding constant of $K = 1.505 \times 10^4 \text{ m}^{-1}$ are obtained by Job's plot experiments and UV/Vis spectroscopy titration. Variable temperature magnetic measurement of complex 1 exhibits an antiferromagnetic interaction between the carboxylato-bridged dinuclear Cu^{II} ions. The investigation of structure and related properties of the acetate-bridged dinuclear Cu^{II} complex provides useful information for its applications in anion chemistry and physiology.

Experimental Section

Materials and Instruments: All solvents for the syntheses (analytical grade) were used without further purification, and the metal salt Cu(OAc)₂, 3-chloro-phenylisocyanate, and 3-pyridyl-amine were commercially available. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. IR spectra were measured with an IR spectrometer equipped with a Smart Omni-Transmission accessory (Thermo Scientific). The UV/Vis spectra were measured in acetonitrile solution by PERSEE TU-1950 Ultraviolet-Visible Spectrophotometer. Magnetic measurement was carried out with a physical property measurement system (PPMS-9, Quantum Design).

Synthesis of the Ligand L: An acetonitrile solution (50 mL) of 3chloro-phenylisocyanate (1.32 g, 8.6 mmol) was dropped into an acetonitrile solution (50 mL) of 3-pyridyl-amine (0.81 g,8.6 mmol). The mixture was refluxed for 2 h and the precipitate thus obtained was filtered off and washed with diethyl ether, and then dried under vacuum to yield L as a white solid (1.88 g, 88%). The ligand L was dissolved into the methanol and then filtered. The clear solution was volatilized and concentrated at room temperature for several days to obtain single-crystals suitable for X-ray diffraction. M.p.: 184–185 °C. IR (KBr): $\tilde{v} = 3343$ (N–H), 3290 (N–H), 3055, 1717 (C=O), 1596, 1541, 1475, 1295, 1268, 1190, 704 cm⁻¹. ¹H NMR ([D₆]DMSO, Zeitschrift für anorganische und allgemeine Chemie

400 MHz, ppm): δ = 9.02 (s, 1 H, NH), 8.93 (s, 1 H, NH), 8.61 (s, 1 H, Py-H1), 8.21 (m, 1 H, Py-H5), 7.94 (m, 1 H, Py-H3), 7.71 (s, 1 H, Ar-H12), 7.32 (m, 3 H, Ar-H8, Py-H4, Ar-H9), 7.03 (m, 1 H, Ar-H10).

Synthesis of the Acetate Complex [CuL(OAc)₂]₂·2AcOH (1): L (70 mg, 0.28 mmol) and the metal salt Cu(OAc)₂ (51.3 mg, 0.28 mmol) were added to the methanol (50 mL). After refluxing for about 2 h, the reaction solution was cooled down to the room temperature and then filtered. The clear solution was volatilized and concentrated at room temperature for several days to obtain single-crystals suitable for X-ray diffraction. Yield: 52 %. M.p.: 208–209°C. IR (KBr): $\tilde{v} = 3360$ (N–H), 3020 (N–H), 1730 (C=O), 1620 (acetate), 1590, 1480, 1200, 702 cm⁻¹.

X-ray Crystallography: The Bruker intelligent APEX II graphite monochromatic Mo- K_{α} ray diffractometer ($\lambda = 0.71073$ Å) was used to collect the diffraction data of L and 1. This structure is directly solved using the SHELXTL package.^[73] Using the SHELXL-2018 program, all non-hydrogen atoms are anisotropically refined by full-matrix least-squares on $|F|^2$. The hydrogen atoms are contained in the ideal position, and their thermal parameters are equivalent to 1.2 times their attached atoms. The crystallographic data of L and 1 are listed in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1974254 for L and CCDC-1974255 for 1 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

Magnetic Measurement: Magnetic susceptibility measurement was carried out in the temperature range 2–400 K at 0.1 T applied field with a physical property measurement system (PPMS-9, Quantum Design).

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Zeitschrift für anorganische und allgemeine Chemie

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Copper(II) Complex of a Urea-functionalized Pyridyl Ligand: Synthesis, Crystal Structure, and Acetate Binding Properties

