

1D-Coordination Polymer Formed by Structural Conversion of an Oxazolidine Ligand in Reaction with the Copper(II) Halides

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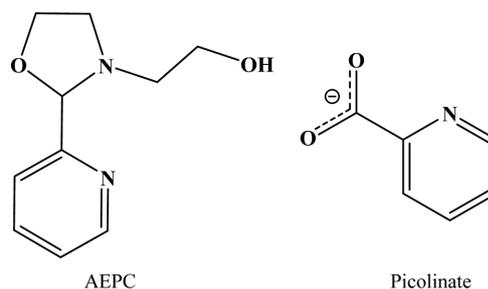
(Received May 20, 2018; Accepted July 12, 2018)

ABSTRACT. A 1D-coordination polymer of 1D- $\{\text{Cu}(\mu\text{-picolinato})_2\}_n$ (1), was prepared by the reactions between 2-(2-(pyridin-2-yl)oxazolidin-3-yl)ethanol (AEPC) ligand and CuCl_2 or CuBr_2 . The product was characterized by elemental analysis, UV-Vis, FT-IR spectroscopy and single-crystal X-ray diffraction. The X-ray analysis results revealed that the AEPC ligand, after reactions with the copper(II) chloride or bromide, gives the same product - 1D- $\{\text{Cu}(\mu\text{-picolinato})_2\}_n$ (1). The coordination modes for various picolinate-based ligands were extracted from the Cambridge Structural Database (CSD). In the crystal structure of 1, the copper atom has a CuN_2O_4 environment and octahedral geometry, which is distorted by elongation of the axial bond lengths due to the Jahn-Teller effect.

Key words: Copper complex, Coordination polymer, Picolinate, Oxazolidine, X-Ray crystal structure

INTRODUCTION

Ring opening reactions of heterocyclic compounds are one of the common structural conversions. One example of this would be the conversion of oxazolines and 1,3-dioxanes in the presence of other reagents to esters.¹ Another example would be the conversion of furan derivatives to the 1,4-dicarbonyls by hydrolysis.² Oxazolidinones can produce carboxylic amides by ring-opening reactions in presence of the Grignard reagents, and³ the hydrolysis of 2-oxazolines produce their corresponding carboxylic acids.^{3,4} Oxazolidine-based compounds can be decomposed to produce the aldehyde and amino alcohol precursors, by treatment with water.⁵ One example of this particular structural conversion is observed in the reaction between 2-(2-(pyridin-2-yl)oxazolidin-3-yl)ethanol (AEPC, Scheme 1) and CuCl_2 or CuBr_2 . Recently we have reported two complexes of cadmium and mercury with AEPC.⁶ In these complexes, the AEPC maintains its structure, whilst our new studies show that this ligand converts to the picolinate ligand (Scheme 1) when coordinating to copper halides. In this work, preparation, characterization and the crystal structure of a 1D-coordination polymer, copper(II), $\{\text{Cu}(\mu\text{-picolinato})_2\}_n$ (1), obtained in the reaction between AEPC and CuCl_2 or CuBr_2 is described. Also all coordination modes of the picolinate ligand and its derivatives extracted from the



Scheme 1. Structures of the AEPC and picolinate.

CSD database are presented and discussed in the context of this work.

EXPERIMENTAL

All starting chemicals and solvents were obtained from Merck and were used as received. The AEPC ligand was synthesized according to the literature.⁶ Infrared spectra (from KBr pellets) in the range $4000\text{-}400\text{ cm}^{-1}$ were recorded with an FT-IR 8400-Shimadzu spectrophotometer. The carbon, hydrogen and nitrogen contents were determined using a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The melting point was measured with a Barnsted Electrothermal 9200 electrically heated apparatus. The electronic spectrum was recorded in H_2O using

a Shimadzu model 2550 UV-Vis spectrophotometer (190–900 nm).

Synthesis of catena-{bis(μ -picolinato)copper(II)}, {Cu(μ -picolinato)₂}_n(1)

A solution of AEPC (0.19 g, 1 mmol), dissolved in ethanol (15 mL), was added to a stirring solution containing CuCl₂·2H₂O (0.24 g, 1 mmol) in the same solvent (5 mL). The reaction mixture was stirred for six hours at 50 °C and then filtered. The main part of the solution was rotary evaporated and the rest was filtrated. The remaining solution was left to slow evaporate and formed an oily product. Acetone (15 mL) was added to the resultant oil and stirred for a day before filtering. After evaporation of the acetone, an oily compound was formed. By adding distilled water (15 mL) and stirring for one hour before filtering, the final solution was obtained. After a few days purple crystal prisms, suitable for single crystal X-ray diffraction analysis, had formed. Yield: 0.03 g, 7%; m.p. 210 °C. Anal. Calcd for C₁₂H₈CuN₂O₄ (%): C, 46.83; H, 2.62; N, 9.10. Found: C, 46.89; H, 2.60; N, 9.06. IR (KBr disk): 3076 (ν CH_{ar}), 1646 (ν_{as} COO), 1476 (ν C=C), 1349 (ν_s COO), 662 (δ OCO) cm⁻¹. UV-Vis (H₂O, λ_{max} (nm)/ ϵ): 687/46 (d→d).

Similar crystals were also obtained from a reaction between AEPC (0.54 g, 2.8 mmol) and CuBr₂ (0.63 g, 2.8 mmol) using the same method as that discussed above. The reaction mixture was then filtrated. After evaporation of the solvent, an oily compound was formed and acetone (15 mL) was added to the product and stirred for one day before filtering. After evaporation of the acetone, another oily product was formed. By adding distilled water (15 mL) and stirring for one hour, before filtering, the final solution was obtained. After a few days suitable crystals were obtained. Yield: 0.04 g, 5%.

Crystal structure determination and refinement

Compound **1** was analyzed at 173 K using a Rigaku SCX-mini CCD diffractometer with a SHINE monochromator. Mo K α radiation ($\lambda = 0.71075$ Å) was used for all the compounds and intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using CrystalClear⁷ or CrysalisPro.⁸ Structures were solved by dual space methods (SHELXT)⁹ and refined by full-matrix least-squares against F² (SHELXL-2013).¹⁰ Non-hydrogen atoms were refined anisotropically, and N-H and O-H hydrogen atoms were refined freely with DFIX restraints, whilst all other hydro-

Table 1. Crystal data and structure refinement for complexes **1**

Complex 1	
Empirical formula	C ₁₂ H ₈ CuN ₂ O ₄
Formula weight, g mol ⁻¹	307.75
Crystal size, mm ³	0.12 × 0.11 × 0.03
Temperature, K	173
Crystal system	triclinic
Space group	P $\bar{1}$
Unit cell dimensions (Å, °)	
a	5.1544(11)
b	7.619(2)
c	8.093(3)
α	66.79(3)
β	73.86(2)
γ	71.63(2)
Volume, Å ³	272.87(15)
Z	1
Calculated density, g cm ⁻³	1.873
Absorption coefficient, mm ⁻¹	2.01
F(000), e	155
2 θ range for data collection (°)	5.4–62.2
h, k, l ranges	-7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11
Reflections collected / independent / R _{int}	3276 / 1662 / 0.069
Data / ref. parameters	1662 / 88
Goodness-of-fit on F ²	1.02
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0896, wR ₂ = 0.2146
Final R indexes [all data]	R ₁ = 0.1490, wR ₂ = 0.2625
Largest diff. peak / hole, e Å ⁻³	2.16 / -1.56

gen atoms were refined geometrically using a riding model. All calculations were performed using the CrystalStructure interface.¹¹ Selected crystallographic data are presented in Table 1. Diagrams of the molecular structure and unit cell were created using Ortep-III¹² and Diamond.¹³ Selected bond lengths and angles are displayed in Fig. 1.

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-1814319 (**1**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

2,2'-Azanediylbis(ethan-1-ol) in the reaction with picolinaldehyde under solvent free conditions gave AEPC via an oxazolidination reaction.⁶ Reaction of AEPC with an ethanolic solutions of CuCl₂ in a molar ratio of 1:1 resulted in

the formation of complex **1**. The same compound was formed in the reaction of AEPC with copper(II) bromide (Table 1). The complex is air-stable, and soluble in DMSO. Study of the literature revealed that similar structures to that complex **1**¹⁴ have been reported previously from different precursors than those used in this study. Also the temperature of the data collection in our report (173 K) is different than the previous works (100 K for structure similar to **1**). In addition, this paper has demonstrated a novel and rare structural conversion reaction during the complexation process. In all CSD searches which have been presented, for more precise results, the structures containing any error or disorder have been omitted.

Spectroscopic characterization

In the FT-IR spectrum of **1**, three bands at 1646, 1349 and 662 cm^{-1} were assigned to the ν_{as} (COO), ν_{s} (COO) and δ (OCO) respectively, confirming the presence of the acetate unit in **1**. The differences between asymmetric (ν_{as}) and symmetric (ν_{s}) stretching of the acetate group (Δ) can reveal its coordination type. In monodentate complexes, Δ values are much greater than the acetate salt (164 cm^{-1}) while in bidentate complexes these values are significantly less than the acetate salt.¹⁵ The Δ value for **1** is calculated to be 297 cm^{-1} and can be viewed as a pseudo-monodentate coordination, which is consistent with the literature structure.¹⁴ Thus the acetate ion here acts as a monodentate ligand.

Description of the crystal structure

X-ray analysis of **1** (Fig. 1) revealed a 1D-coordination polymer,¹⁶ extending by the formation of Cu-O-C-O-Cu bridges (Fig. 2). In this way, two picolinato ligands link two copper(II) centers by their carboxylato groups. The copper atoms in the polymeric backbone are coordinated by two nitrogen and two oxygen atoms of two picolinato ligands and two oxygen atoms belonging to two other picolinates, giving a CuN_2O_4 environment with distorted octahedral geometry. The complex has a center of inversion in the center of the $\text{Cu1/O3/Cu1}^i/\text{O3}^i$ plane and C_i symmetry. The axial Cu1-O3 bond lengths (2.735(5) Å) are much longer than those of equatorial ones (Cu1-N1, 1.960(5) Å and Cu1-O2, 1.948(4) Å) due to Jahn-Teller effect¹⁷ so the structure of **1** must be distorted. Each picolinato ligand acts as a bridging NO_2 -donor to form a planar, five-membered chelate ring (with r.m.s value of 0.052(7) Å for the C2 atom). Is this coordination mode for picolinate-based ligand common or unusual? To answer this question, a search for all complexes containing the picolinate unit in the

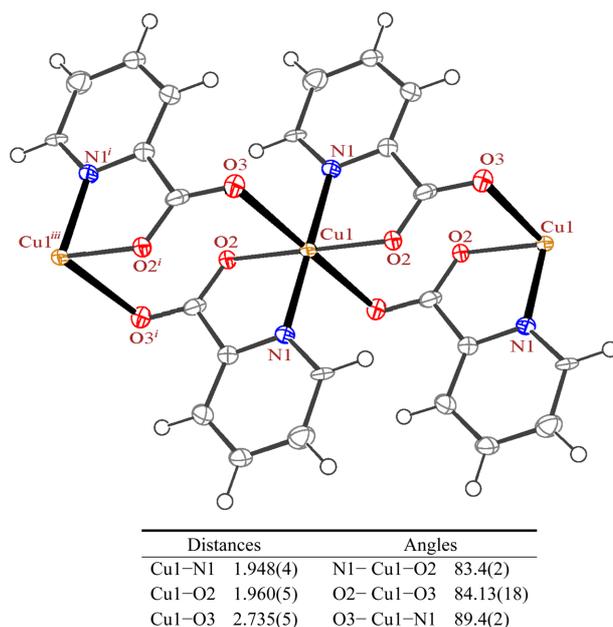


Figure 1. The ortep diagram of the molecular structure of the complex **1**. The ellipsoids are drawn at the 50% probability level. The caption is the selected bond lengths (Å) and angles ($^\circ$) with estimated standard deviations in parentheses.

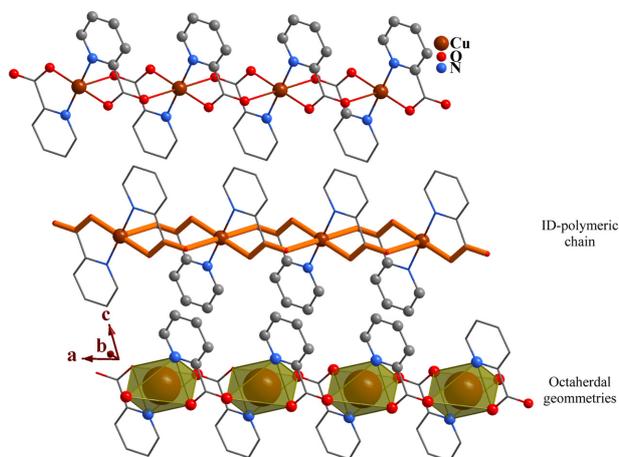


Figure 2. A packing plot of complex **1**, showing the hydrogen bonds and 1D-polymeric chain. Only the hydrogen atoms involved in hydrogen bonding are shown. Each CuO_4N_2 unit is shown as octahedral.

CSD was performed. This study revealed that there are 33 coordination modes (Fig. 3) for this class of compounds which can be divided up into four groups including: “NO-Chelate Modes”, “Two Chelates Modes”, “ O_2 -Chelate Modes” and “Non-Chelate Modes”. 92% of all the structures contain an NO-chelate ring (Fig. 4) and “(N, O^{alc})” mode is the most frequently observed coordination mode (56%, Fig. 5) in which the picolinate unit acts as an NO-

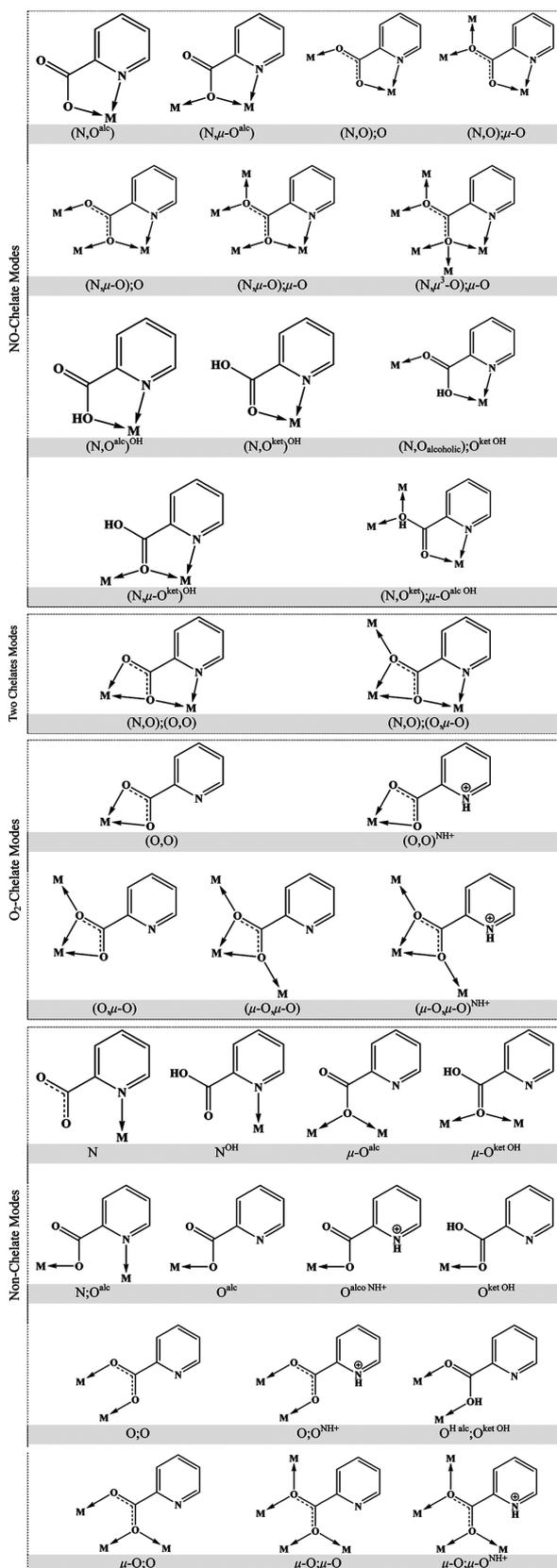


Figure 3. All coordination modes of the picolinate-based ligands.

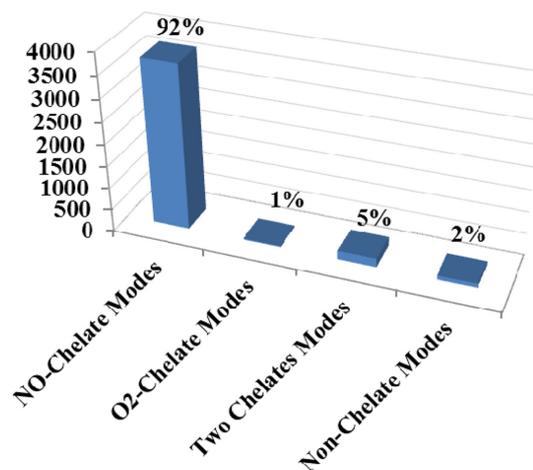


Figure 4. Statistical analysis all of the coordination modes of the picolinate-based ligands based on the chelate formation.

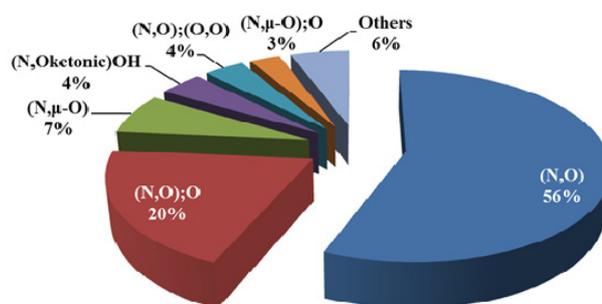


Figure 5. Statistical analysis all of the coordination modes of the picolinate-based ligands.

donor and forms one chelate ring. The observed mode in complex **1** is “(N,O);O” which is the second most common mode of the CSD analogues (20%). In another comparison, the percentage of bridged and non-bridged structures was calculated. The data revealed that the picolinate unit commonly forms a non-bridged structure (87%). Further consultation of the CSD revealed that there is no example of the “(N,O);O” coordination mode with a Cu center, that would allow a comparison of the geometric parameters with complex **1**. In this complex the Cu-O bond length in the chelate ring (1.948(5) Å) is significantly shorter than the axial Cu-O bond (2.735(5) Å), the direction in which the 1D coordination polymer extends. The angle between the mean planes running through the pyridine ring and COO unit is 8.5(4)°, confirming the molecule is almost planar. This angle was calculated to be 7.76° for all complexes with the “(N,O);O” mode.

In the crystal network of **1** (Fig. 2), there are N...O and O...O interactions which more stabilized the network and have important role in the extending of the network into three directions.

CONCLUSION

In this work, a new coordination polymer, 1D- $\{\text{Cu}(\mu\text{-picolinato})_2\}_n$ (**1**), was synthesized in a reaction between AEPC and copper(II) halides and its spectral (IR, UV-Vis, ^1H NMR) and structural (single crystal X-ray diffraction) properties were investigated. These structural analyses revealed that the AEPC ligand can convert to the other structures during the complexation process. In complex **1**, the picolinato ligands form a CuN_2O_4 environment around the copper atom. The octahedral geometry in this structure is distorted by elongation of the axial bonds due to the Jahn-Teller effect. Studying the coordination modes of the picolinate-based ligands revealed that these types of ligands have 33 coordination modes which can be divided into 4 main modes, of which the “(NO)” mode is the most common (56%). Also these ligands tend to form NO-chelate rings (92%) and non-bridged structures (87%).

Acknowledgments. We are grateful to Urmia University of I. R. Iran. Publication cost of this paper was supported by the Korean Chemical Society.

Supporting Information. Additional supporting information is available in the online version of this article.

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