



Feature article

Structural diversity in Cu(II) and Cd(II) coordination complexes with 4-amino-1,2,4-triazole ligand

Pin-Ning Wang^a, Chun-Wei Yeh^b, Chi-Hui Tsou^c, Yuh-Wen Ho^a, Hsun-Tsing Lee^d, Maw-Cherng Suen^{a,*}^a Department of Creative Fashion Design, Taoyuan Innovation Institute of Technology, Jhongli 32091, Taiwan, ROC^b Department of Chemistry, Chung-Yuan Christian University, Jhongli 32023, Taiwan, ROC^c R&D Center for Membrane Technology, Chung-Yuan University, Jhongli 32023, Taiwan, ROC^d Department of Materials Science and Engineering, Vanung University, Jhongli 32061, Taiwan, ROC

ARTICLE INFO

Article history:

Received 28 August 2013

Accepted 1 February 2014

Available online 12 February 2014

Keywords:

Tridentate ligands

Supramolecular

Trans conformation

4-Amino-1,2,4-triazole

ABSTRACT

The syntheses and structures of the series of metal complexes, namely $[\text{CuCl}_2(\text{L})_2 \cdot \text{H}_2\text{O}]_n$ ($\text{L} = 4\text{-amino-1,2,4-triazole}$), **1**; $\{[\text{Cu}(\text{L})_4][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}\}_n$, **2**; and $[\text{Cd}_2\text{Cl}_4(\text{L})_2 \cdot 2\text{H}_2\text{O}]_n$, **3** are reported. These were prepared by the self-assembly of Cu(II) and Cd(II) salts with **L** in MeOH/H₂O system. All these complexes have been characterized by elemental analysis, IR spectrum, and single crystal X-ray diffraction. Complexes **1–2** show 1-D polymeric infinite chains, while complex **3** shows 2D pleated net. The anions Cl[−] in complexes **1** and **3** act as bridging or terminal ligands to the metal atoms while the ClO₄[−] anions in **2** are not coordinated to the metal centers.

© 2014 Elsevier B.V. All rights reserved.

Contents

Acknowledgment	72
Appendix A. Supplementary material	72
References	72

The design and synthesis of functional coordination polymer have been of interest during recent years [1,2]. Among the various types of interactions employed to create larger molecular arrays, covalent and hydrogen bonds are most widely used. In addition to the nature of the metal atoms and the ligands, counterion-based interaction is one of the common factors that can be modulated to determine the structural type. This is largely due to the range of potential applications in electrical, magnetic, and optical devices [3] and porous zeolite mimics [4]. The various types of polymeric structures include 1-D, 2-D and 3-D network structures [5]. We have recently reported the self-assembly of molecules through N–H–X (X = Cl and Br) interactions and self-complementary double N–H–O hydrogen bonds [6]. Bidentate ligands, such as bpa (bpa = 1,2-bis(4-pyridyl)ethane) [7] and bpen (bpen = *trans*-bis(4-pyridyl) ethane) [8], are able to generate polymetallic coordination networks with interesting supramolecular solid-state architectures. While major

efforts were devoted to the directing roles of these ligands which are covalently coordinated to the metal centers, less attention was paid to the weak interactions.

During our investigation on the coordination chemistry of Cu(II) and Cd(II) metal with 4-amino-1,2,4-triazole (**L**) ligands, we have found that the di- or tridentate ligands and the anions play important roles in 1-D structures. The synthesis and structures of the three new coordination polymers of $[\text{CuCl}_2(\text{L})_2 \cdot \text{H}_2\text{O}]_n$ ($\text{L} = 4\text{-amino-1,2,4-triazole}$), **1**; $\{[\text{Cu}(\text{L})_4][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}\}_n$, **2**; and $[\text{Cd}_2\text{Cl}_4(\text{L})_2 \cdot 2\text{H}_2\text{O}]_n$, **3** form the subject of this report.

Complexes of the type $[\text{CuCl}_2(\text{L})_2 \cdot \text{H}_2\text{O}]_n$ ($\text{L} = 4\text{-amino-1,2,4-triazole}$), **1**; $\{[\text{Cu}(\text{L})_4][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}\}_n$, **2**; and $[\text{Cd}_2\text{Cl}_4(\text{L})_2 \cdot 2\text{H}_2\text{O}]_n$, **3** were prepared by the reacting of CuX_2 (X = Cl, **1** and ClO₄, **2**) and CdCl₂ with **L** in CH₃OH/H₂O [9]. All these complexes have been characterized by elemental analysis and IR spectrum (see Fig. S1 in the Supplementary data) and structurally characterized by an X-ray crystallography. Complexes **1–3** were insoluble in most organic solvents; the suitable crystals for X-ray diffraction studies were obtained from layering **L** in methanolic solution onto a solution of Cu(II) and Cd(II) salts in H₂O [10].

* Corresponding author.

E-mail address: sun@tiit.edu.tw (M.-C. Suen).

The crystal structures of complex **1** belong to the space group $P2_1/c$. Fig. 1(a) shows the geometry of Cu(II) atom in **1**, which is coordinated and bridged by four nitrogen atoms from four **L** ligands in the equatorial plane and two chloride anions in the axial position with the bond angles significantly deviated from 90° or 180° . The Cu(II) atom is coordinated

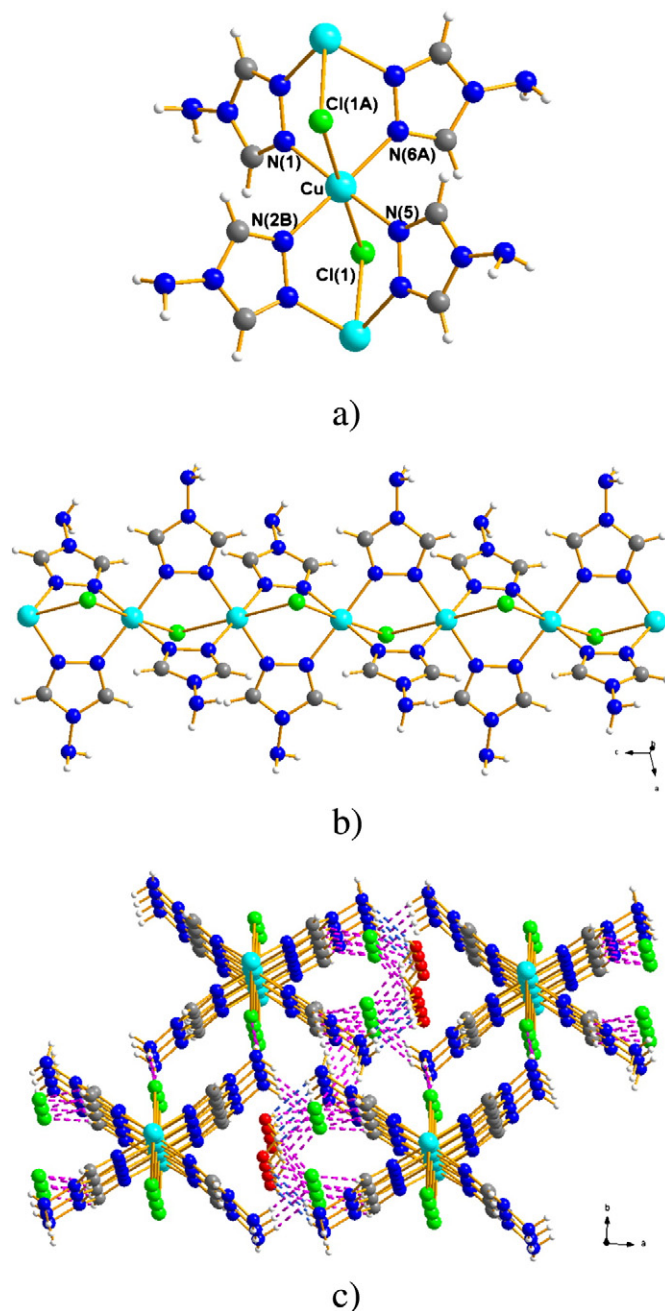


Fig. 1. (a) Coordination environment of Cu(II) in **1**. Selected bond distances and angles (\AA , $^\circ$): Cu–N(1) = 2.0091(15), Cu–N(5) = 2.0168(15), Cu–N(6A) = 2.0098(15), Cu–N(2B) = 2.0259(15), Cu–Cl(1) = 2.7065(5), Cu–Cl(1A) = 2.7915(5), N(1)–Cu–N(6A) = 88.28(6), N(1)–Cu–N(5) = 178.51(5), N(6A)–Cu–N(5) = 90.33(6), N(1)–Cu–N(2B) = 91.83(6), N(6A)–Cu–N(2B) = 177.43(6), N(5)–Cu–N(2B) = 89.53(6), N(1)–Cu–Cl(1) = 95.08(5), N(6A)–Cu–Cl(1) = 93.75(4), N(5)–Cu–Cl(1) = 85.55(4), N(2B)–Cu–Cl(1) = 88.80(4), N(1)–Cu–Cl(1A) = 86.87(4), N(6A)–Cu–Cl(1A) = 86.31(4), N(5)–Cu–Cl(1A) = 92.49(4), N(2B)–Cu–Cl(1A) = 91.13(4). Symmetry transformations used to generate equivalent atoms: (A) $x, -y + 3/2, z + 1/2$, (B) $x, -y + 3/2, z - 1/2$. (b) A diagram showing the 1D zigzag chain of **1**. (c) Packing diagram for **1** showing the interactions between the chains.

by nitrogen atoms from four different **L** ligands and two *trans* chloride atoms. The metal–ligand bonding is characterized by the Cu–N bond lengths in the range from 2.0091(15) to 2.0259(15) \AA with the N–Cu–N bond angles in the range from $88.28(6)$ to $178.51(5)^\circ$. The calculated T value for the Cu(II) center in **1** is 0.72, indicating a distorted tetragonal bipyramidal geometry as shown by Hathaway and Hodgson [13]. The long Cu–Cl distances in the axial positions are presumably due to the weak coordination ability of the Cl^- anion and the d^9 electronic configuration of the Cu(II) ion that result in strong Jahn–Teller distortion.

Fig. 1(b) shows that complex **1** is a coordination polymer of $[\text{CuCl}(\text{L})_2]_n$, forming a 1-D linear chain. The **L** ligands act as the $\mu_2\text{-}\eta^1:\eta^1$ -bridging coordination mode to bridge the two Cu(II) atoms to form a $[\text{Cu}_2\text{N}_4]$ six-membered metallocycle. The Cu(II) centers form 1D core-shared beaded chain along c -axis. The Cu–Cu separation is 3.658(2) \AA . Fig. 1(c) shows a representative packing diagram for **1**. The 1D cationic chains and uncoordinated Cl^- anions are linked through various N–H–Cl and C–H–Cl hydrogen bonds and the cocrystallized water molecules also interact with 1D cationic chains and uncoordinated Cl^- anions through O–H–Cl and N–H–O hydrogen bonds (see Table S2 in the Supplementary data).

The structure of **2** was solved in the space group $C2/c$. Fig. 2(a) shows the local coordination of the copper center in **2**. The single crystal X-ray structure shows its coordination polymer consisting of copper ions, **L** ligands, and H_2O . The copper metal center adopts a slightly distorted octahedral coordination geometry with the bond angles only deviating slightly from 90° to 180° . The Cu(II) atom is bonded to six nitrogen atoms from six different **L** ligands. Fig. 2(b) shows its infinite 1-D chains consisting of $\text{Cu}_2(\text{L})_3$. The **L** ligands adopt the $\mu_2\text{-}\eta^1:\eta^1$ -bridging coordination mode to bridge the two Cu(II) atoms. The Cu–Cu separation is 3.873(2) or 3.896(3) \AA in the $\text{Cu}_2(\text{L})_3$ core. The DA: AD self-complementary interaction involves two strong N–H–N hydrogen bonds forming a waving 2D hydrogen bonded net in Fig. 2(c) (see Table S2 in the Supplementary data). In complex **2**, the 1-D chains are further linked by the anions and lattice water molecules through N–H–O and O–H–O hydrogen bonds to form 3-D supramolecular structures. Fig. 2(d) shows a representative packing diagram for **2**.

The crystal structure of **3** was solved in the space group $P2_1/c$ and the building block is shown in Fig. 3(a). There are two independent Cd(II) atoms in complex **3**. The Cd(1) ion is coordinated by four nitrogen atoms in the equatorial plane and two *trans* chloride anions in the axial position with the bond angles significantly deviated from 90° or 180° , while the Cd(2) atom is bonded to five chloride atoms from four bridging and a terminal Cl^- anions and one amino nitrogen atom of the **L** ligand to complete a distorted octahedral geometry. Complex **3** forms a 2-D waving net as shown in Fig. 3(c), which is composed of bis four-connected nodes, which adopts $(3^2, 5^2, 6^2)(3, 5^3, 6^2)$ net. The **L** ligands in 2D net adopt $\mu_2\text{-}\eta^1:\eta^1$ - and $\mu_3\text{-}\eta^1:\eta^1$ -bridging coordination mode to bridge the Cd(II) atoms, and the Cd–Cd separation distances are 3.8331(2), 3.8511(2), and 7.2336(3) \AA , respectively.

The extended structure contains layers of 2D pleated nets based on the *sql* topology with rectangular grid-like corrugated sheets showing dimensions of $17.19 \times 17.96 \text{ \AA}^2$, Fig. 3(b), which are positioned in an ABAB manner, Fig. 3(c). All the 2D nets are equivalent and are composed of 60-membered metallocycles. The distortion from a perfect square is due to the presence of two independent L^2 ligands which adopts the same GAG *trans* conformation, but different in torsional angles. The 2D nets are interlinked by the Cl^- anions and co-crystallize water molecules through N–H–Cl, O–H–Cl, and weaker C–H–Cl interactions, Fig. 3(d) (see Table S2 in the Supplementary data).

In this study, the coordination chemistry of Cu(II) and Cd(II) salts with the rigid ligand **L** was investigated. Three polymeric complexes involving 1-D and 2-D frameworks were obtained. It was shown that the self-assembly frameworks of these divalent metal coordination

Download English Version:

<https://daneshyari.com/en/article/7749335>

Download Persian Version:

<https://daneshyari.com/article/7749335>

[Daneshyari.com](https://daneshyari.com)