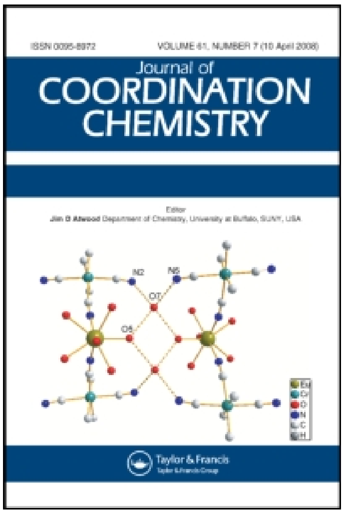

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Syntheses and crystal structures of *cis*- and *trans*-copper(II) complexes of L-arginine

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Two copper(II) complexes of L-arginine, *trans*-$[Cu(l\text{-}Arg)_2(NO_3)]NO_3 \cdot 3H_2O$ (**1**) and $\{$*cis*-$[Cu(l\text{-}Arg)_2](NO_3)_2 \cdot 3H_2O\}_n$ (**2**) (Arg = arginine) were prepared by reaction of $Cu(NO_3)_2 \cdot 3H_2O$ and L-arginine in acetone and aqueous solution, respectively. X-ray analysis reveals **1** crystallizes in a monoclinic system, $P2_1$ with $a = 10.3857(15)$, $b = 16.885(3)$, $c = 15.9586(19)$ Å, $\beta = 15.9586(19)°$, $Z = 4$, $V = 2654.2(6)$ Å^3. The copper(II) centers lie in a distorted N_2O_3 square-pyramidal environment. While **1** adopts a mononuclear structure, and the axial position occupied by a nitrate with Cu1–O9 = 2.535 Å and Cu2–O20 = 2.581 Å, **2** features a 1-D infinite chain structure. In **1**, adjacent monomeric units connect with each other to give a 2-D layer structure of (4, 4) nets through hydrogen bonds between the guanidinium and carboxylic groups of arginine, and 2-D layers further assemble to a 3-D supermolecular structure via a series of inter-layer hydrogen bonds.

Keywords: Copper; L-arginine; Crystal structure

1. Introduction

Amino acids have received much attention as fundamental units of biomacromolecules, important biological ligands in the life process and excellent building blocks for multidimensional coordination materials [1, 2]. Among them, L-arginine involving charged or polar side chain of guanidinium group is intriguing because guanidinium group has the ability to form hydrogen or electrostatic bonds with the carboxylate, phosphate, and other groups in proteins, which play an important role in biological molecular recognition, reactivity of enzymes, stabilization of protein structures and specific interaction with DNA [3]. In addition, copper is an essential trace element in all living organisms. Therefore, the copper(II)-L-arginine species will be models of bioinorganic chemistry, and the corresponding investigation on physicochemical properties and structure of the model system will have significance in exploring the catalysis, storage and transport of trace metallic elements during the life process [4, 5].

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Herein, we report the syntheses and crystal structures of two copper-L-arginine complexes, *trans*-[Cu(l-Arg)$_2$(NO$_3$)]NO$_3\cdot$3H$_2$O (**1**) and {*cis*-[Cu(l-Arg)$_2$] (NO$_3$)$_2\cdot$ 3H$_2$O}$_n$ (**2**) [6].

2. Experimental

2.1. *Materials and general methods*

L-arginine, CuNO$_3\cdot$3H$_2$O, and acetone were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N) of the complexes were performed on a Vario-EL elemental analyzer. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 360 FT-IR spectrometer using KBr pellets.

2.2. *Synthesis*

2.2.1. *trans*-[Cu(l-Arg)$_2$(NO$_3$)]NO$_3\cdot$3H$_2$O (1). To an acetone-aqueous (2 : 1) solution (10 mL) of L-arginine (0.352 g, 2.0 mmol) was added an acetone solution (10 mL) of CuNO$_3\cdot$3H$_2$O (0.242 g, 1.0 mmol). The reaction mixture was refluxed 10 h, and then cooled to room temperature and filtered. The filtrate was left to evaporate for several weeks at room temperature to obtain purple needle-like crystals. Yield, 0.51 g (86%). Anal. Calcd for **1**, $C_{12}H_{34}CuN_{10}O_{13}$ (%): C, 24.43; H, 5.81; N, 23.74. Found (%): C, 24.53; H, 5.81; N, 23.58. IR (KBr pellet): 3365(s), 3199(s), 1697(s), 1635(s), 1595(s), 1385(vs), 1186(m), 814(m).

2.2.2. {*cis*-[Cu(L-Arg)$_2$](NO$_3$)$_2\cdot$3H$_2$O}$_n$ (2). To an aqueous solution (10 mL) of L-arginine (0.352 g, 2.0 mmol) was added an aqueous solution (10 mL) of Cu(NO$_3$)$_2\cdot$3H$_2$O (0.242 g, 1.0 mmol). The reaction mixture was heated at 70°C for 10 h, and then treated in a similar way. Blue needle-like crystals were obtained. Yield, 0.42 g (71%). Anal. Calcd for **2**, $C_{12}H_{34}CuN_{10}O_{13}$ (%): C, 24.43; H, 5.81; N, 23.74. Found (%): C, 24.49; H, 5.79; N, 23.53. IR (KBr pellet): 3285(s), 3102(s), 1684(s), 1645(vs), 1605(s), 1561(s), 1328(s), 1188(m), 797(m).

2.3. *X-ray crystallography*

A crystal of dimensions $0.56\times0.52\times0.44\,\text{mm}^3$ was used for data collection on a Siemens P4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda=0.71073$ Å) at 293(2) K. The structure of **2** was solved by direct methods and all calculations were performed with the SHELXL program [7, 8] and refined by full-matrix, least-squares minimizations of $(F_o-F_c)^2$ with anisotropic thermal parameters for all non-hydrogen atoms. The position of the hydrogen atoms were based on difference Fourier synthesis coupled with geometrical analysis. The last successful full-matrix, least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged to $R_1=0.0389$, $wR_2=0.1086$. Crystallographic data are summarized in table 1 and selected bond lengths are listed in table 2, while selected hydrogen bond lengths and angles of **1** are presented in table 3.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{12}H_{34}CuN_{10}O_{13}$	$C_{12}H_{34}CuN_{10}O_{13}$
Formula weight	590.03	590.03
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$C2$
a (Å)	10.3857(15)	26.705(4)
b (Å)	16.885(3)	7.3190(10)
c (Å)	15.9586(19)	12.788(2)
β (°)	108.485(10)	92.090(10)
V (Å^3)	2654.2(6)	2497.8(6)
Z	4	4
μ(Mo-Kα) (mm^{-1})	0.898	0.954
T (K)	296(2)	291(2)
ρ_{Calcd} (g cm^{-3})	1.477	1.569
λ (Å)	0.71073	0.71073
F(000)	1236	1236
θ range for data collection (°)	1.81–25.00	1.53–28.00
Goodness-of-fit on F^2	1.087	1.019
R_1^{a}	0.0389	0.0348
${}_wR_2$^{b}	0.1086	0.0797

$^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $^b{}_wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. For **1**, a = 0.0763, b = 0.0454; for **2**, a = 0.0442, b = 0.0000.

Table 2. Selected bond lengths (Å) for **1** and **2**.

Compound **1**				Compound **2**	
Cu1–O1	1.942(4)	Cu2–O5	1.936(4)	Cu–O3	1.9324(16)
Cu1–O3	1.950(4)	Cu2–O7	1.956(4)	Cu–O1	1.9531(18)
Cu1–N1	1.986(4)	Cu2–N9	1.972(4)	Cu–N1	1.974(2)
Cu1–N5	2.004(4)	Cu2–N13	1.994(4)	Cu–N5	1.980(2)
Cu1–O9#2	2.535	Cu2–O20#1	2.581	Cu–O2#1	2.487(2)

Symmetry transformations used to generate equivalent atoms for **1**: #1: $-x+1$, $y+1/2$, $-z+1$; #2: $-x+1$, $y-1/2$, $-z+1$; for **2**: #1: $-x+3/2$, $y+1/2$, $-z$.

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	d(D···A)	∠(DHA)	D–H···A	d(D···A)	∠(DHA)
Intra-layer H-bonds			N10–H10···O12	2.866(7)	171.2
N15–H15A···O2	2.804(7)	162.1	N11–H11A···O13	2.973(8)	162.9
N16–H16A···O1	3.087(6)	176.3	N14–H14···O10	2.937(8)	170.7
N11–H11B···O4#1	2.806(7)	166.3	O22–H2OB···O12#2	2.696(6)	165(7)
N12–H12B···O3#1	3.057(6)	170.2	O22–H2OA···O24#2	2.788(7)	171(6)
N3–H3A···O8#2	2.838(7)	165.8	O24–H4OA···O20#5	2.657(6)	157(10)
N4–H4A···O7#2	3.105(6)	168.6	O26–H6OB···O19#1	2.713(8)	167(8)
N7–H7A···O6#3	2.774(7)	154.9	O26–H6OA···O13#6	2.837(7)	167(8)
N8–H8A···O5#3	3.008(6)	176.6			
			H-bonds only for rooting molecules		
Inter-layer H-bonds			N6–H6···O15	2.880(7)	165.4
N1–H1B···O13#4	3.009(6)	157.0	N7–H7B···O16	2.944(8)	158.6
N2–H2···O19	3.022(8)	157.3	O23–H3OA···O21	2.688(8)	162(7)
N3–H3B···O20	2.858(8)	166.1	O21–H1OB···O13#7	2.804(6)	165(7)
N9–H9B···O24	2.959(8)	158.0	O25–H5OA···O10#3	2.696(7)	175(7)

Symmetry transformations used to generate equivalent atoms for **1**: #1: $x-2$, $y+1$, $z-1$; #2: $x+2$, y, $z+1$; #3: x, $y-1$, z; #4: $-x$, $y-1/2$, $-z$; #5: $-x+1$, $y+1/2$, $-z+1$; #6: $-x-2$, $y+1/2$, $-z-1$; #7: $-x-1$, $y-1/2$, $-z$.

3. Results and discussion

3.1. *Preparation and IR spectrum*

Compounds **1** and **2** were prepared by reaction of $Cu(NO_3)_2 \cdot 3H_2O$ and L-arginine in acetone and aqueous solution, respectively. The solvent plays a key role in the formation of **1** and **2**. Considering the solubility of amino acids in water, we started using water as solvent, and blue crystals of $\{cis\text{-}[Cu(L\text{-}Arg)_2](NO_3)_2 \cdot 3H_2O\}_n$ were obtained [6]. Then we carried out the reaction in mixing solvent of acetone and water (2 : 1), *cis*-**2** appeared early but *trans*-**1** was obtained after a longer time, indicating transformation from *cis* to *trans* during the reaction.

In **1** and **2**, the characteristic features of L-arginine dominate the IR spectrum [9]. The absorption bands appearing at 3000–3500 cm^{-1} (3365 and 3199 cm^{-1} for **1**; 3285(s) and 3102(s) for **2**) correspond to N–H stretching vibrations of guanidinium. The sharp bands in the 1700–1600 cm^{-1} region (1697, 1635, and 1595 cm^{-1} for **1**; 1684, 1645, 1605, and 1561 cm^{-1} for **2**) are attributed to the COO– asymmetric stretching modes. The presence of nitrate ions was indicated by the very strong peaks at 1385 cm^{-1} in **1** and 1328 cm^{-1} in **2**, respectively.

3.2. *Crystal structure*

X-ray analysis revealed that the asymmetric unit of **1** consists of two $[Cu(l\text{-}Arg)_2(NO_3)]^+$ cations, two NO_3^- anions and four lattice water molecules. In each $[Cu(l\text{-}Arg)_2(NO_3)]^+$ unit, the copper center coordinates to two carboxylate oxygen atoms, two amino nitrogen atoms of two l-Arg molecules and one nitrate anion in a distorted N_2O_3 square-pyramidal environment (average $Cu–O_{carboxyl}$: 1.946 Å, average Cu–N: 1.989 Å and average $Cu–O_{nitrate}$: 2.563 Å). The configuration around copper is *trans* with respect to the amino groups (figure 1).

As expected, the guanidinium group of arginine forms hydrogen bonds and plays an important role in constructing the 3-D supermolecular network of **1**. In the structure, each $[Cu(l\text{-}Arg)_2(NO_3)]^+$ cation of Cu1 connects to four adjacent monomeric units of Cu2 through eight *intra*-layer hydrogen bonds between the guanidinium and carboxylic groups of arginine, giving rise to a 2-D layer structure of (4, 4) nets in the *bc* plane with the N–O bond length falling in the range 2.774(7) ~ 3.087(6) Å (figure 2). The 2-D layer structure of **1** is different from the 1-D tape structure of *trans*-$[Cu(l\text{-}Arg)_2](X)_2$ complexes reported by Yamauchi [10–12]. The layers adopt two different stacking modes, face to face and back to back, to form a 3-D network (figure 3). Scheme 1 illustrates the hydrogen bonding between two layers in detail. We classify the face to face stacking mode as coordination nitrate in the layers pointed to each other alternately, while in the back to back mode, there is no coordination nitrate. As shown in scheme 1, the coordination nitrate groups (N17O9O10O11 and N20O18O19O20), lattice water molecules (O21, O23 and O24) fill the interlayer space of face to face, and the dissociative nitrate anions of (N18O12O13O14 and N19O15O16O17), lattice water molecules (O22, O25, O26) are present between the layers of back to back. The N17O9O10O11, N20O18O19O20, N18O12O13O14, O22, O24, O26 connect with each other or link to the layer *via* a series of *inter*-layer hydrogen bonds forming a 3-D supermolecular network, further stabilizing the layer structure, but N19O15O16O17, O21, O23, O25 only fix themselves within the interlayer space through intermolecular

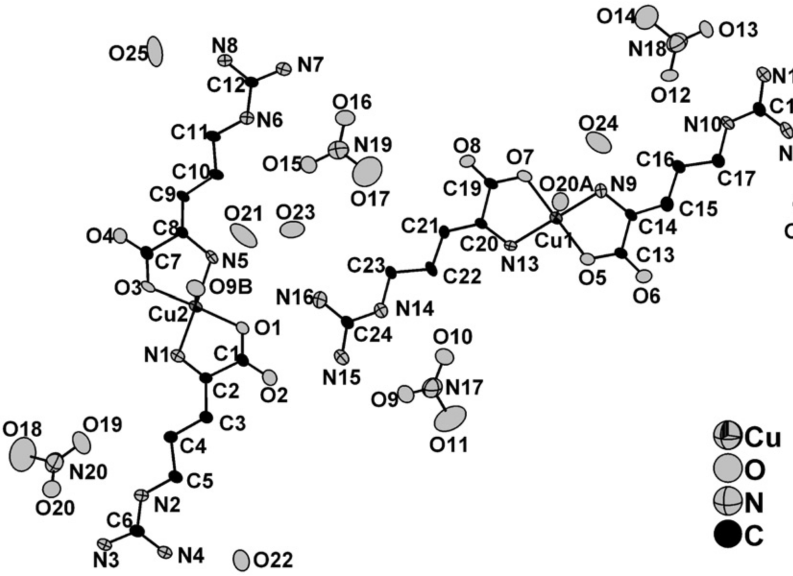


Figure 1. ORTEP drawing (ellipsoids at 50% probability) with the atom-labeling scheme for **1**. A: $-x+1$, $y+1/2$, $-z+1$; B: $-x+1$, $y-1/2$.

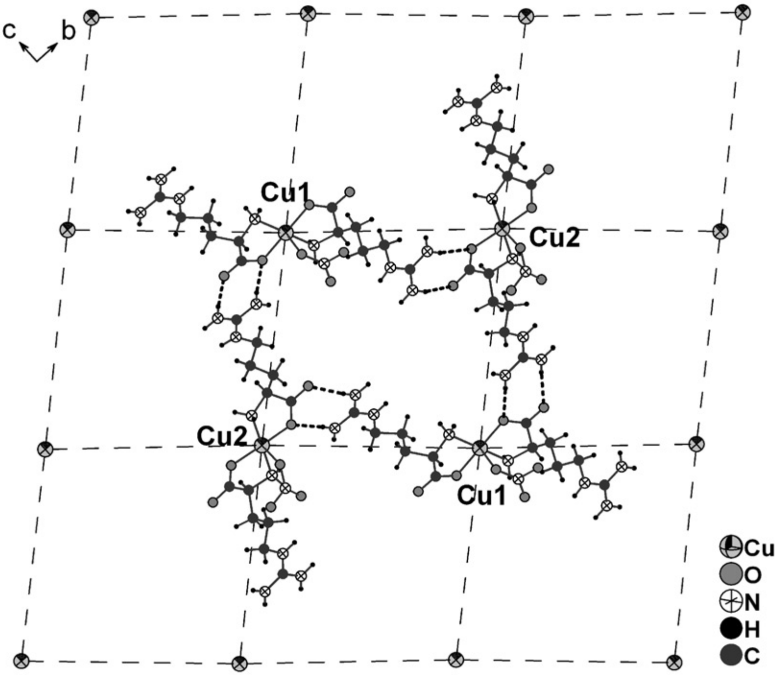


Figure 2. View of the (4, 4) nets formed by the hydrogen bonds consisting of the guanidinium and carboxylate group of arginine in **1**.

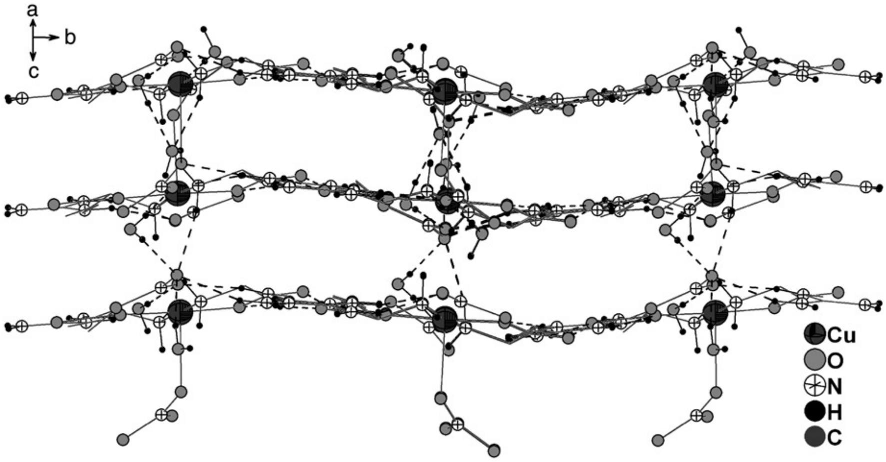
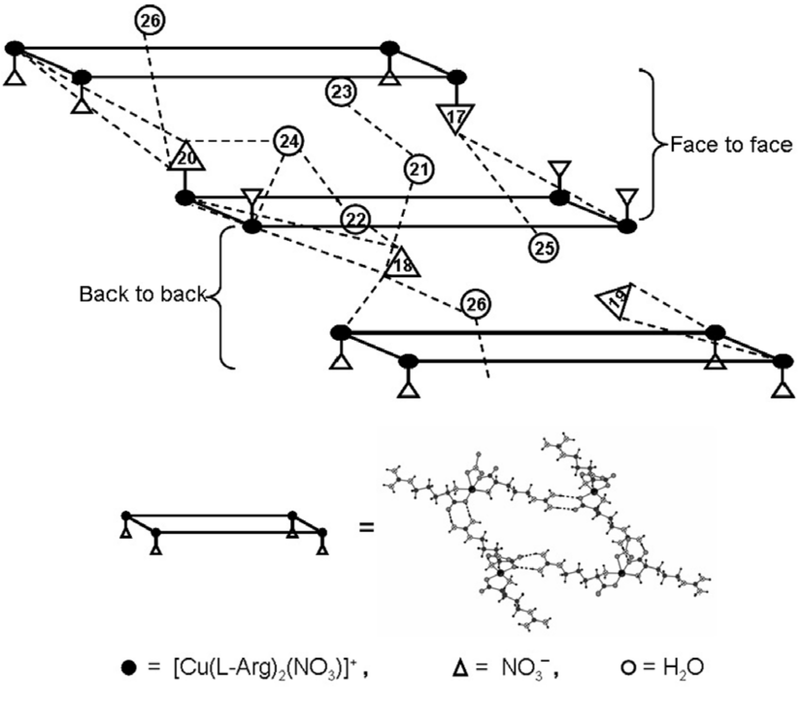


Figure 3. 3-D supermolecular structure stacked by (4, 4) nets via a series of *inter*-layer H-bonds.



Scheme 1. Schematic illustration for the H-bonding linkage between layers.

hydrogen bonds which have no contribution to the formation of the supermolecular network of **1**.

In summary, we have synthesized two isomeric compounds *trans*-$[Cu(l\text{-}Arg)_2(NO_3)]NO_3 \cdot 3H_2O$ and $\{$*cis*-$[Cu(l\text{-}Arg)_2](NO_3)_2 \cdot 3H_2O\}_n$ in acetone and aqueous solution, respectively. Compound **1** is mononuclear with three types of hydrogen bonding interactions: *intra*-layer interactions between the guanidinium and carboxylate groups for forming 2-D layer structure, inter-layer interactions for constructing the resultant 3-D network, and intermolecular interaction for fixing dissociative molecules of interlayer. Compound **2** has a one-dimensional infinite chain structure. The acetone transformation from *cis*-**2** to *trans*-**1** during the reaction indicates *trans*-**1**'s intermediate has higher thermodynamic stability than *cis*-**2**, offering an effective synthetic route for similar isomeric compounds.

Supplementary material

Full lists of crystallographic data are available from the Cambridge Crystallographic Data Centre with deposition number CCDC 641753 for **1** and CCDC 641752 for **2**. Copies of this information can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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