Two Novel Sandwich Copper(II) Complexes [CuLCl]₂[CuCL₄] and [CuLBr]₂[CuBr₄] (L = N,N'-bis(Furaldehyde)diethylenetriamine)[1]

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Abstract—The novel trinuclear copper(II) complexes [CuLCl]₂[CuCl₄] (I) and [CuLBr]₂[CuBr₄] (II) (where L = N,N'-*bis*(furaldehyde)diethylenetriamine) were synthesized and structurally characterized by X-ray diffraction. They consist of sandwich units. Both I and II crystallize isomorphously in the monoclinic space group *P*2/*n* and feature cation/anion/cation geometry. The novel trinuclear copper(II) complexes I and II shown to be stabilized by a number of weak hydrogen bonds and intermolecular π–π stacking interactions.

INTRODUCTION

Schiff-base ligands has play an important role in the development of coordination chemistry since the late 19th century. The finding that metal complexes of these ligands are ubiquitous. As their facile synthesis, wide applications [1] and research in this area have been stimulated by biological modeling applications, catalysis, design of molecular ferromagnets, and materials chemistry [2–6]. To the best of our knowledge, in the past two decades, Schiff base complexes derived from furaldehyde have been reported to a less extent. Recently, we have embarked on the synthesis of ligands N,N'-*bis*(furaldehyde)ethylenediamine (**L¹**) and N,N,N'-*bis*(furaldehyde)diethylenetriamine (**L²**) shown below containing N,O-chelating moieties and have chosen furaldehyde as the common starting material:

(L¹)   (L²)
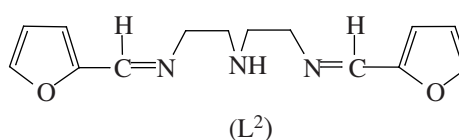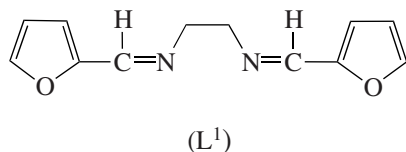
Copper is considered to be an important inorganic element involved in various biological processes. Copper exists in many organs, such as the liver, kidney, brain, and pancreas, plays an important role, and functions within proteins, enzymes, etc.

We have reported ligand L¹ and its complex [7] with zinc. Ligand L² possesses a remarkable capacity for coordination with transition metals. From a chemical point of view, L² is considered to be a good type of chelating ligand with extensive chemical properties. Therefore, this ligand can coordinate to transition metals as a bidentate, tridentate, quadridentate or pentadentate ligand with consequent variable structural properties. In some cases, the O atom of furaldehyde does not coordinate to the metal ion, such as in the title complexes, but it can slightly affect the configuration of the complex and may be a potential coordinating atom. Thus, the complexes of L² with copper were of novel configuration .

EXPERIMENTAL

All reagents were obtained from commercial sources. Ligand L² was synthesized by ourselves from furaldehyde and diethylenetriamine blended in dichloromethane in a ratio of 2 : 1. Then, anhydrous sodium sulfate was added to this mixture in order to remove water produced, the filtered solution was distilled, and then the pure ligand was got.

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[1] The article is published in the original.

Table 1. Crystal data and X-ray experimental details for complexes **I** and **II**

Parameter	Value	
	I	**II**
T, K	298(2)	298(2)
Formula weight	921.93	1188.69
Crystal system	Monoclinic	Monoclinic
Space group	$P2/n$	$P2/n$
a, Å	10.970(4)	11.1019(13)
b, Å	7.546(3)	7.6986(8)
c, Å	22.271(8)	22.782(3)
β, deg	95.993(6)	96.835(2)
V, Å^3	1833.6(12)	1933.3(4)
Z	2	2
$F(000)$	930	1176
ρ_{calcd}, g/cm^3	1.670	2.042
Crystal size, mm	$0.53 \times 0.35 \times 0.31$	$0.20 \times 0.10 \times 0.08$
μ, cm^{-1}	2.203	7.136
Scan mode	ω-2θ	ω-2θ
$\theta_{min}/\theta_{max}$, deg	1.84/25.02	1.96/27.46
Index ranges	$-5 < h < 13$, $-8 < k < 8$, $-25 < l < 26$	$-11 < h < 14$, $-6 < k < 9$, $-28 < l < 29$
Reflection collected	9015	11501
R_{int}	0.0407	0.0312
Observed data, $I > 2\sigma(I)$	3139	4430
Refined parameters	213	213
GOOF on F^2	1.024	0.977
ωR_2 (all data)	0.1024	0.1492
R_1 ($I > 2\sigma(I)$)	0.0443	0.0441

Synthesis of [CuL$_2$Cl]$_2$[CuCl$_4$] (I). Ligand L^2 (0.259 g, 1 mmol) was dissolved in 10 ml of methanol, and a solution of CuCl$_2$ · 2H$_2$O (0.1705 g, 1.0 mmol) in 20 ml of methanol was added. The mixture was stirred for 20 min at room temperature, and then the solution color turned to dark blue. After several days, the black single crystal suitable for X-ray analysis was obtained from the solution.

IR spectrum (ν, cm^{-1}): 3233 s ν(RN–H); 1637, 1569, 1381, 1254, 1212 s, ν(C=C), ν(C=N), ν(C–C), ν(C–O), ν(C–N).

For Cu$_3$(C$_{14}$H$_{17}$N$_3$O$_2$)$_2$Cl$_6$
anal. calcd, %: C, 36.40; H, 4.00; N, 9.10.
Found, %: C, 36.09; H, 3.427; N, 9.114.

Synthesis of [CuL$_2$Br]$_2$[CuBr$_4$] (II). Ligand L^2 (0.259 g, 1 mmol) was dissolved in 10 ml of methanol, and a solution of CuBr$_2$ (0.2234 g, 1.0 mmol) in 20 ml of methanol was added. The mixture was stirred for 20 min at room temperature, and then the solution color turned to dark blue. Similarly, the black single crystal suitable for X-ray analysis was obtained.

IR spectrum (ν, cm^{-1}): 3226 s ν(RN–H); 1644, 1564, 1363, 1275, 1216 s ν(C=C), ν(C=N), ν(C–C), ν(C–O), ν(C–N).

For Cu$_3$(C$_{14}$H$_{17}$N$_3$O$_2$)$_2$ Br$_6$
anal. calcd, %: C, 28.28; H, 2.86; N, 7.07.
Found, %: C, 28.57; H, 2.91; N, 7.10.

The IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with an EQUINOX55 spectrometer. The C, H, and N microanalyses were carried out with a Vario EL III CHNOS elemental analyzer.

X-ray diffraction analysis. The crystal data and details of the data collections and refinements for structures **I**, **II** are listed in Table 1. Measurements were made with a SMART CCD area detector using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS program package [8] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97 [9] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The functions minimized were $\Sigma w (Fo^2 - Fc^2)$ with $w = (\sigma^2(F_o^2) + aP^2 - bP)^{-1}$, where $P = (\max F_o^2 + 2F_c^2)/3$.

Full tables of atom coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (nos. 256770–256771; deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reactions of L^2 with copper(II) chloride and copper(II) bromide afforded crystalline products in good yields. Each of these complexes crystallizes in the monoclinc space group $P2/n$ and is trinuclear with L^2 : CuX$_2$ = 2 : 3 stoichiometry. Figure 1 shows perspective views of the structure **I**. Selected interatomic
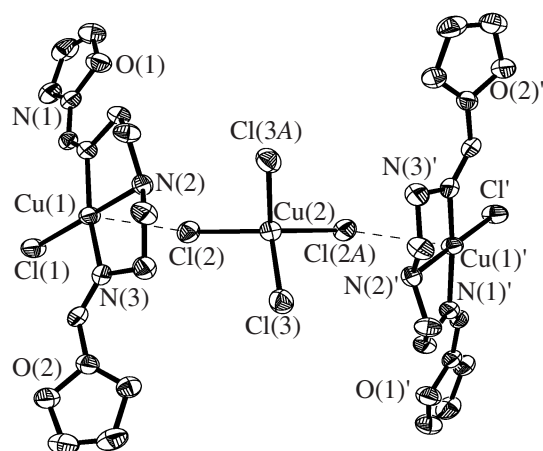
Fig. 1. Perspective view of the X-ray crystal structure of **I**.

Fig. 2. Space-filling illustration of the sandwiched structure of **I**.

distances and angles for **I** and **II** are listed in Table 2. Although the two structures appear to be very similar, there is some intriguing subtle difference. In the two structures, L^2 adopts very similar conformation, wherein the plane of each furan ring is almost parallel to the new plane, which derived from three N atoms of L^2, Cu^{2+}, and Cl^-.

The crystals of compounds **I** and **II** are isostructural, both containing a basic unit in which a tetrahedral $[CuCl_4]^{2-}$ or $[CuBr_4]^{2-}$ anion [10–14] is sandwich between a pair of the $[CuL^2Cl]^+$ or $[CuL^2Br]^+$ units. As shown for **I** in Fig. 1 the central CuX_4^{2-} anion (X = Cl) completes its typical elongated tetrahedral geometry by the formation of μ-Cu(1)···X(2)–Cu(2) linkages [15] to the cations and anions, where the semicoordinate Cu(1)···Cl(2) distance is 3.0062(16) Å and the bridging angle is 122.26(6)° (**I**), the semicoordinate Cu(1)···Br(2) distance is 3.099(16) Å and the bridging angle is 119.63(6)° (**II**). In the copper(II) chloride complex (**I**), the $[CuL_2Cl]^+$ cation has approximate square four-coordinate geometry, and in this arrangement the atoms N(1), N(2), N(3), Cl(1), and Cu(1) define the basal plane, as defined by a coplanar error value of 0.0264 Å [16], whereas Cl(2) occupies the apical position and semicoordinate [15] to Cu(1), whose bond to the copper atom is longer. Similarly, in the copper(II) bromide complex (**II**), the $[CuL^2Br]^+$ cation has approximate square four-coordinate geometry. In this arrangement, the atoms N(1), N(2), N(3), Br(1), and Cu(1) define the basal plane, as defined by a coplanar error value of 0.0322 Å [16], whereas Br(2) occupies the apical position and semicoordinate to Cu(1), whose bond to the copper atom is longer. This geometry allows for a weak interaction [15] between the metal and the formally noncoordinated X(2) (shown as a space-filling illustration in Fig. 2 for **I**).
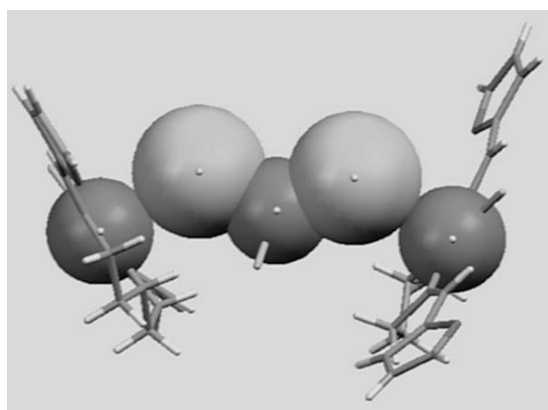
It is clear that three copper ions are linked by two μ-Cl (or μ-Br) bridge forming a slightly distorted "M" configuration. An intramolecular hydrogen bond formed by L^2 (N(2)), which is always coordinated to Cu(1), and the semicoordinate X atom of the distorted tetrahedral $[CuX_4]^{2-}$ anion leads to further stabilization. The N–H···X hydrogen bonding provides stability to the lattice [17], leading to the formation of cation/anion/cation geometry. There is also a further stabilizing factor operating in these complexes: the intermolecular π–π stacking interactions between the furan rings of L^2. All of these interactions of complex **I** involve furan rings separated by about 3.912 Å, which is shown in Fig. 3, and the angle between these furan rings was 25.9°. In complex **II**, there are also intermo-

Table 2. Selected bond lengths (Å) and bond angles (deg) with standard deviations in parentheses for complex **I** (X = Cl) and **II** (X = Br)

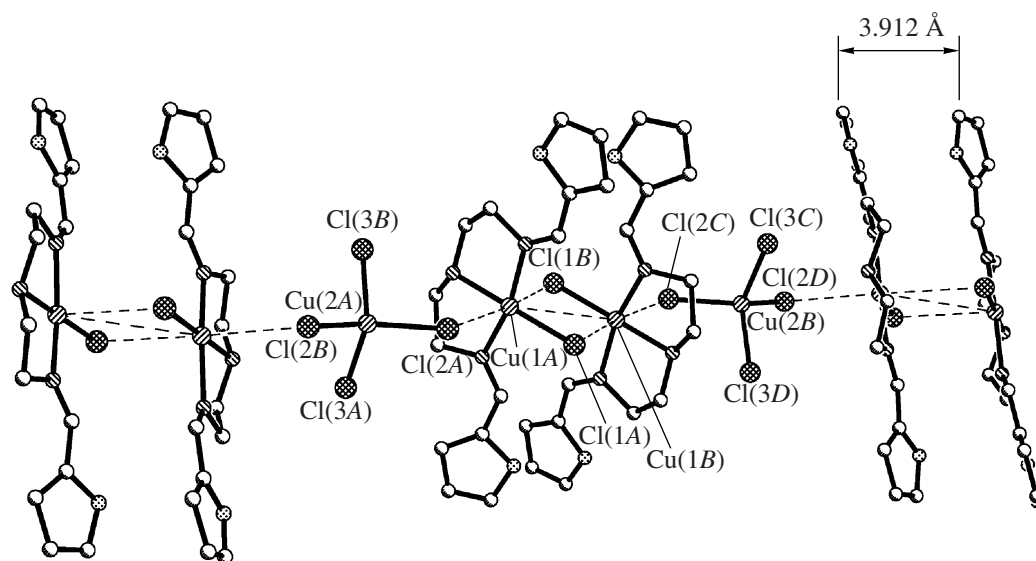| Bond	I	II
	d, Å	
Cu(1)–N(3)	1.995(3)	2.023(4)
Cu(1)–N(2)	2.004(3)	2.011(4)
Cu(1)–N(1)	2.025(4)	1.992(4)
Cu(1)–X(1)	2.2527(14)	2.4032(8)
Cu(2)–X(2)	2.2487(14)	2.3750(7)
Cu(2)–X(3)	2.2796(16)	2.3977(8)
Angle	ω, deg	
N(3)Cu(1)N(2)	82.87(14)	82.63(17)
N(3)Cu(1)X(1)	97.24(11)	96.92(12)
N(2)Cu(1)N(1)	82.74(14)	83.12(17)
N(1)Cu(1)X(1)	97.13(11)	97.41(12)
X(2A)Cu(2)X(2)	130.32(8)	129.07(5)
X(2)Cu(2)X(3)	105.03(5)	103.93(2)
X(2)Cu(2)X(3A)	98.86(5)	99.87(2)
X(3)Cu(2)X(3A)	121.07(10)	122.74(5)

Fig. 3. The intermolecular π–π stacking interaction in **I** involving furan rings forming the 1D chain.

lecular similar π–π stacking interactions, the distances of furan rings were 3.523 Å, and the angle of the inter-related furan rings was 27.3°. Although these are weak interactions, the combined influence of all stacking interactions is likely to be significant [18, 19].

Complexes **I** and **II** formed the 1D chain through intermolecular π–π stacking interactions (Fig. 3). In addition, the sandwich units interact weakly [20] and include Cu···Cl 3.279, Cu···Cu 3.917 Å in complex **I** (shown as a dashed line in Fig. 3) and Cu···Br 3.295, Cu···Cu 4.004 Å in complex **II**.

Thus, we synthesized two similar copper(II) complexes, which show trinuclear structural units as the formation of μ-Cu(1)···X(2)–Cu(2) linkages. The molecular configuration of complexes **I** and **II** is the novel sandwiched structure linked by two μ-Cl or μ-Br bridges and formed a slightly distorted "M" configuration. It was found that intramolecular hydrogen bonds and intermolecular π–π hyphen stacking interactions provided stability of the lattice and formed the 1D chain.

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