

# Synthesis and Crystal Structure of a One-Dimensional Coordination Polymer Containing Unusual $\text{Na}_2\text{Cu}_2$ Tetrametallacyclic Units

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A unique coordination polymer,  $\{[\text{CuLNa}(\text{ClO}_4)] \cdot \text{H}_2\text{O}\}_n$  (1), was isolated from the solution containing sodium perchlorate and the neutral macrocyclic oxamidocopper(II) complex  $[\text{CuL}]$  ( $\text{H}_2\text{L} = 2,3\text{-dioxo-}5,6:13,14\text{-dibenzo-}7,12\text{-bis(ethoxycarbonyl)-}1,4,8,11\text{-tetraazacyclotetradeca-}7,11\text{-diene}$ ). The complex is composed of  $[\text{Na}_2\text{Cu}_2]$  tetrametallacycles bridged by perchlorate ions to form infinite one-dimensional chains which are stacked via  $\pi\text{-}\pi$  interactions and weak coordination bonds to result in a two-dimensional supramolecular network. The perchlorate ions were found to coordinate to sodium atoms in the unusual bridging chelating tridentate mode of  $\mu_2\text{-(O:O',O')}$ .

**Keywords** coordination polymer, macrocyclic complex, crystal structure

## Introduction

Self-assembled infinite coordination polymers and supramolecules with specific network topologies have attracted considerable attention due to their potential applications as functional materials as well as fascinating molecular and crystal structures. While the vast majority of publications and reviews have been devoted to the assembly of transition metal complexes,<sup>1-4</sup> less attention has been paid to systems containing main group metal complexes.<sup>5-9</sup> Several heterobimetallic sodium-copper coordination polymers,<sup>7-9</sup> including a three-dimensional architecture which contains sodium perchlorate as a building block,<sup>9</sup> have been reported.

Recently we have reported some macrocyclic oxamidocopper(II) complexes,<sup>10,11</sup> whose structures are exemplified by  $[\text{CuL}]$  in Fig. 1, where  $\text{H}_2\text{L} = 2,3\text{-dioxo-}5,6:13,14\text{-dibenzo-}7,12\text{-bis(ethoxycarbonyl)-}1,4,8,11\text{-tetraazacyclotetradeca-}7,11\text{-diene}$ . The complexes contain uncoordinated carbonyl groups, and recently a number of polynuclear complexes have been designed by using  $[\text{CuL}]$  and its analogues as ligands to another transition metal ion.<sup>12</sup> However, the coordination of these "complex ligands" to main group metal ions has not yet been explored. Here the synthesis and crystal structure of a unusual copper-sodium coordination polymer  $\{[\text{CuLNa}(\text{ClO}_4)] \cdot \text{H}_2\text{O}\}_n$  (1) derived from  $[\text{CuL}]$  are reported.

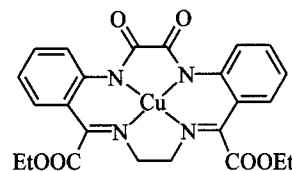


Fig. 1 Mononuclear  $[\text{CuL}]$  precursor.

## Experimental

### Synthesis

The  $[\text{CuL}]$  precursor was prepared as described

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elsewhere.<sup>11</sup>  $\{[\text{CuLNa}(\text{ClO}_4)] \cdot \text{H}_2\text{O}\}_n$  (**1**) was obtained as red crystals by slow evaporation of an acetonitrile solution containing  $[\text{CuL}]$  and  $\text{NaClO}_4$  in a 1:1 molar ratio. Yield 78%. IR (KBr)  $\nu$ : 3350 (br), 1730 (s), 1635 (sh), 1615 (s), 1585 (m), 1545 (m), 1470 (w), 1440 (m), 1370 (m), 1330 (m), 1300 (s), 1270 (m), 1190 (s), 1090 (vs), 740 (m)  $\text{cm}^{-1}$ ; molar conductance (MeCN)  $\Lambda$ : 140  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . Anal. calcd for  $\text{C}_{24}\text{H}_{24}\text{ClCuN}_4\text{NaO}_{11}$ : C 43.25, H 3.63, N 8.41; found C 43.02, H 3.72, N 8.67.

### Physical measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. Conductivities in acetonitrile were measured using a DDS-11A conductometer. The IR spectrum was recorded on a Shimadzu IR-408 spectrometer, and the electronic spectrum on a Shimadzu UV-240 recording spectrophotometer.

### X-ray structure determination

The intensity data of **1** using a single crystal of dimensions 0.15 mm  $\times$  0.1 mm  $\times$  0.05 mm were collected at room temperature on a Bruker Smart 1000 CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071073$  nm). A total of 4801 independent reflections was measured in the range of  $2.63 < \theta < 25.03$ . The structure was solved by the direct method and refined by the full-matrix least-squares method on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms.<sup>13</sup> The hydrogen atoms were located geometrically and refined isotropically. The final difference map showed the largest residual peaks of 387 and  $-451 \text{ e} \cdot \text{nm}^{-3}$ . Crystal data and structure refinement are summarized in Table 1.

## Results and discussion

### General characterization

The IR spectrum of complex **1** exhibits a broad medium band ( $3350 \text{ cm}^{-1}$ ) and a broad strong band ( $1090 \text{ cm}^{-1}$ ), indicative of the presence of water molecules and perchlorate ions, respectively. The other features of the spectrum are very similar to those of  $[\text{CuL}]$ .<sup>11</sup> The bands attributable to the  $\nu(\text{C}=\text{O})$  (ester carbonyl) and  $\nu(\text{C}=\text{N})$  vibrations show no significant

shift in comparison with  $[\text{CuL}]$  and appear at  $1730 \text{ cm}^{-1}$  and  $1620 \text{ cm}^{-1}$ , respectively. However, the  $\nu(\text{C}=\text{O})$  (oxamido carbonyl) band observed at  $1650 \text{ cm}^{-1}$  for  $[\text{CuL}]$  is shifted to *ca.*  $1635 \text{ cm}^{-1}$ . The red shift suggests the coordination of the  $[\text{CuL}]$  precursor to another metal ion through the oxamido carbonyl oxygen atoms and reflects the decrease in the  $\text{C}=\text{O}$  bond strength upon coordination. The electronic spectrum of **1** in acetonitrile is almost identical with that of  $[\text{CuL}]$ .<sup>10</sup> The intense band at 375 nm and its shoulder at 420 nm have been attributed to intraligand and/or charge-transfer transitions, and the much weak shoulder absorption at *ca.* 540 nm to the d-d transitions of Cu(II) in a square-planar geometry. The molar conductance value falls within the range expected for 1:1 electrolytes,<sup>14</sup> indicating that the complex dissociates into  $\text{Na}^+$ ,  $\text{ClO}_4^-$  and  $[\text{CuL}]$  and that the perchlorate ion is non-coordinated in the acetonitrile solution.

**Table 1** Crystal data and structure refinement summary for complex **1**

Empirical formula	$\text{C}_{24}\text{H}_{24}\text{ClCuN}_4\text{NaO}_{11}$
$M_r$	666.45
$T$ (K)	298(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ (nm)	0.90213(19)
$b$ (nm)	1.2612(3)
$c$ (nm)	1.4182(3)
$\alpha$ ( $^\circ$ )	115.358(4)
$\beta$ ( $^\circ$ )	101.782(6)
$\gamma$ ( $^\circ$ )	97.325(5)
$V$ ( $\text{nm}^3$ )	1.3846(5)
$D_c$ ( $\text{g} \cdot \text{cm}^{-3}$ )	1.599
$F(000)$	682
$Z$	2
$\mu$ (Mo K $\alpha$ ) ( $\text{mm}^{-1}$ )	0.968
$R_1 [I > 2\sigma(I)]$	0.0698
$wR_2$ (all data)	0.1202
$\rho_{\text{max}}, \rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	387, $-451$

### Description of the structure

The structure of **1** consists of  $[\text{CuL}]$ ,  $\text{Na}^+$ ,  $\text{ClO}_4^-$  and non-coordinated water molecules. A perspective view of the asymmetric unit is depicted in Fig. 2. The atomic coordinates of non-hydrogen atoms are given in Table 2, and the selected bond lengths and angles are listed in Table 3. The Cu atom is in the macrocyclic cavity, and is

coordinated by the four nitrogen atoms of the macrocyclic oxamide (average Cu—N, 0.1931 nm). The deviations of the nitrogen atoms from the N<sub>4</sub> mean plane are less than 0.009 nm and the deviation of the Cu(II) atom is only 0.00098(28) nm, indicating an essentially planar coordination environment that is similar to that in [CuL].<sup>10</sup> The

dihedral angles between the CuN<sub>4</sub> plane and the two phenyl rings are 3.28° and 3.32°, much smaller than those in [CuL] (9.5° and 17.5°),<sup>10</sup> so the [CuL] moiety in **1** is also essentially planar. The planarity implies an extended  $\pi$ -conjugating system in the the [CuL] moiety.

**Table 2** Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $10^{-5}$  nm<sup>2</sup>) of non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu(1)	2775(1)	914(1)	692(1)	47(1)	C(11)	207(8)	960(7)	-974(6)	44(2)
Na(1)	890(3)	-3196(3)	-3345(2)	73(1)	C(12)	-897(8)	430(7)	-2015(7)	57(2)
N(1)	3281(6)	-624(5)	121(5)	41(2)	C(13)	-1906(8)	1057(8)	-2302(7)	61(2)
N(2)	1189(6)	327(6)	-689(5)	44(2)	C(14)	-1864(8)	2219(8)	-1584(8)	63(2)
N(3)	4183(6)	1481(5)	2134(4)	44(2)	C(15)	-786(9)	2738(7)	-595(7)	58(2)
N(4)	2431(7)	2520(5)	1255(5)	49(2)	C(16)	265(8)	2162(7)	-256(6)	43(2)
O(1)	2584(5)	-2285(5)	-1586(4)	70(2)	C(17)	1380(8)	2885(6)	829(6)	43(2)
O(2)	213(6)	-1529(5)	-2235(5)	88(2)	C(18)	1382(9)	4222(8)	1381(7)	57(2)
O(3)	447(5)	4411(4)	2024(4)	59(1)	C(19)	236(10)	5616(7)	2555(7)	82(3)
O(4)	2124(6)	4968(5)	1265(5)	78(2)	C(20)	-1332(10)	5674(8)	1978(7)	109(3)
O(5)	5269(6)	1422(5)	4245(4)	71(2)	C(21)	4407(8)	-1013(7)	656(6)	42(2)
O(6)	7335(6)	2206(5)	3952(4)	72(2)	C(22)	4695(9)	-2174(7)	147(6)	57(2)
O(7)	-1778(8)	-4651(6)	-4425(5)	134(3)	C(23)	5831(11)	-2517(8)	708(8)	69(3)
O(8)	-3793(7)	-4214(7)	-5342(6)	146(3)	C(24)	6641(9)	-1797(9)	1744(8)	68(2)
O(9)	-1280(7)	-3265(6)	-5013(5)	124(2)	C(25)	6411(9)	-676(8)	2275(7)	67(2)
O(10)	-2301(6)	-5302(5)	-6280(5)	102(2)	C(26)	5319(8)	-222(7)	1791(6)	49(2)
O(11)	-22(15)	-779(11)	-5115(12)	307(6)	C(27)	5108(8)	946(7)	2445(6)	41(2)
C(1)	2456(8)	-1339(7)	-922(6)	47(2)	C(28)	6049(10)	1568(7)	3633(7)	55(2)
C(2)	1131(9)	-848(8)	-1369(7)	50(2)	C(29)	5959(10)	2124(9)	5430(7)	104(3)
C(3)	4002(8)	2643(7)	2903(6)	60(2)	C(30)	4795(13)	1952(10)	5964(7)	145(5)
C(4)	3585(8)	3344(7)	2318(6)	59(2)	Cl(1)	-2283(3)	-4364(2)	-5275(2)	71(1)

**Table 3** Selected bond distances (nm) and angles (°) \*

Cu(1)—N(1)	0.1913(5)	Cu(1)—N(2)	0.1943(6)
Cu(1)—N(3)	0.1939(5)	Cu(1)—N(4)	0.1927(6)
O(1)—Na(1)	0.2327(6)	O(2)—Na(1)	0.2271(6)
O(7)—Na(1)	0.2543(7)	Na(1)—O(10a)	0.2349(6)
O(9)—Na(1)	0.2707(7)	Na(1)—O(6b)	0.2417(6)
N(1)-Cu(1)-N(4)	175.1(2)	N(1)-Cu(1)-N(3)	93.5(3)
N(4)-Cu(1)-N(3)	85.5(3)	N(1)-Cu(1)-N(2)	88.2(3)
N(4)-Cu(1)-N(2)	93.3(3)	N(3)-Cu(1)-N(2)	174.0(2)
O(2)-Na(1)-O(1)	69.06(19)	O(2)-Na(1)-O(10a)	154.3(2)
O(1)-Na(1)-O(10a)	85.5(2)	O(2)-Na(1)-O(6b)	97.6(2)
O(1)-Na(1)-O(6b)	92.0(2)	O(10a)-Na(1)-O(6b)	87.0(2)
O(2)-Na(1)-O(7)	101.0(2)	O(1)-Na(1)-O(7)	139.2(2)
O(10b)-Na(1)-O(7)	95.6(2)	O(6a)-Na(1)-O(7)	128.8(2)
O(2)-Na(1)-O(9)	86.9(2)	O(1)-Na(1)-O(9)	154.7(2)
O(10a)-Na(1)-O(9)	118.8(2)	O(6b)-Na(1)-O(9)	83.1(2)
O(7)-Na(1)-O(9)	51.1(2)		

\* Symmetry codes, a:  $-x, -y-1, -z-1$ ; b:  $-x+1, -y, -z$ .

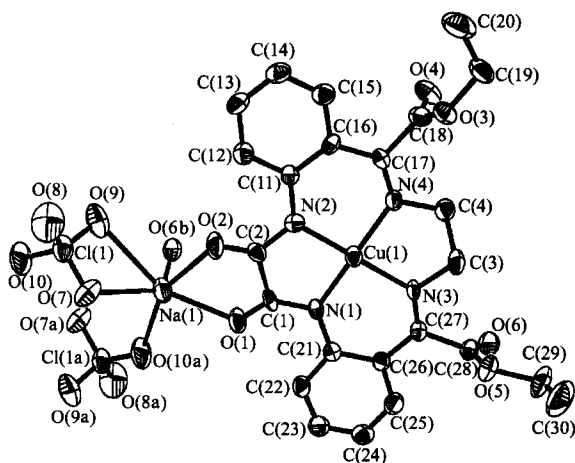


Fig. 2 A view of the asymmetric unit in complex 1 with 30% thermal ellipsoids.

The sodium atom is six-coordinated by two oxamido oxygens from one [CuL] molecule, an ester carbonyl oxygen from another [CuL] molecule, and three oxygens from two perchlorate ions, with a coordination geometry intermediate between octahedron and pentagonal pyramid (with O(6b) at the apex). As a result of the above coordination modes, two [CuL] molecules are linked by two Na atoms to give a unusual cyclic tetranuclear  $\text{Na}_2\text{Cu}_2$  unit (18-membered tetrametallacycle), as shown in Fig. 3 (above). In such a unit, the extended  $\pi$ -conjugating systems in the two [CuL] moiety are parallel and separated by 0.350 nm (interplane distance), suggesting the presence of  $\pi$ - $\pi$  interactions. The metal-to-metal separations within the unit are 0.556 nm (Cu $\cdots$ Na), 0.519 nm (Cu $\cdots$ Cu) and 1.002 nm (Na $\cdots$ Na). The tetrametallacyclic units are linked by perchlorate ions to result in an infinite 1D chain along the [111] direction (Fig. 3, middle). The perchlorate ion behaves as a simultaneously bridging and chelating tridentate ligand. This coordination mode [denoted as  $\mu_2$ -(O:O', O'')] of perchlorate ions is unusual and has only been identified in the high temperature form of  $\text{Ln}(\text{ClO}_4)_3$  (Ln = Yb, Tm and Lu).<sup>15</sup> The sodium atoms in the  $[\text{Na}_2(\text{ClO}_4)_2]$  moiety are separated by 0.470 nm.

The above chains are stacked along the *a* axis in such a fashion that the neighboring [CuL] molecules arising from neighboring chains are also parallel and their extended  $\pi$ -conjugating systems are separated by 0.354 nm (Fig. 3, bottom), suggesting the presence of interchain  $\pi$ - $\pi$  interactions. The interchain Cu $\cdots$ Cu separation is 0.484 nm. On the other hand, one of the ethoxycar-

bonyl groups of the macrocyclic ligand is oriented in such a way that the ethoxy oxygen [O(3)] is located at the "vacant" coordinative site (assuming a pentagonal pyramidal geometry) of the Na ( $-x, -y, -z$ ) atom that belongs to an adjacent chain, with the Na $\cdots$ O distance being 0.3197(7) nm, indicating a weak coordinative interaction. The interchain  $\pi$ - $\pi$  and Na $\cdots$ O interactions organize the chains in space to form a 2D supramolecular network extended along the  $\langle 0\bar{1}1 \rangle$  plane.

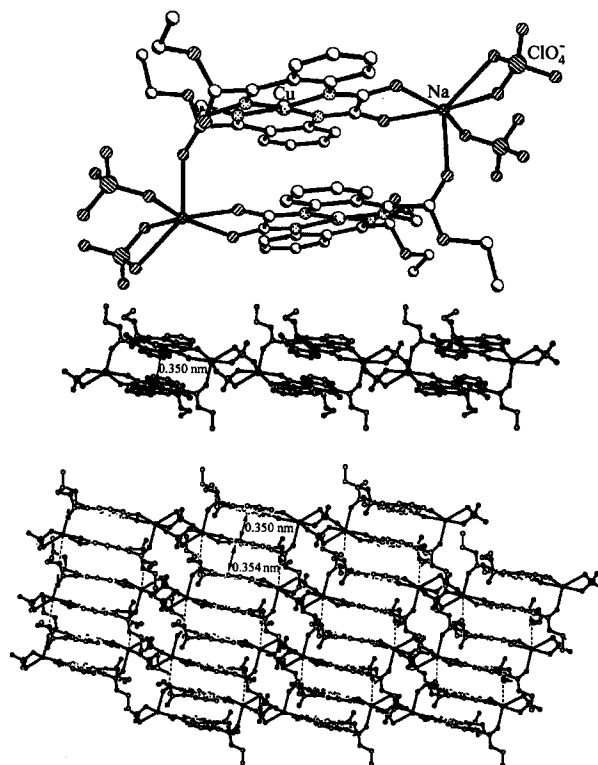


Fig. 3 Views of the tetranuclear cyclic unit (above), the 1D chain (middle) and the quasi-2D network showing the weak intra- and interchain interactions (bottom).

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