

# Synthesis and Structure of a Ni(II)-Cu(II)-Ni(II) Trinuclear Complex With a New Macrocyclic Complex Ligand

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## Abstract

A trinuclear complex,  $[\text{Cu}(\text{NiL})_2(\text{NCS})_2]$ , was prepared by the reaction of a new macrocyclic oxamido complex ligand NiL,  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$  and KNCS. L denotes the doubly deprotonated form of dimethyl 5,6,7,8,15,16-hexahydro-15-methyl-6,7-dioxodibenzo[1,4,8,11]tetraazacyclotetradecine-13,18-dicarboxylate. Excess  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$  is necessary for the formation of the title compound. The structure of the title complex was further characterized by X-ray single-crystal analysis. Cu(II) and each Ni(II) is bridged by the oxamido group from the corresponding macrocyclic ligand. The coordination geometry around each Ni(II) ion is slightly distorted square planar with  $\text{N}_4$  donor set, and the Cu(II) ion has a distorted octahedral coordination geometry of  $\text{O}_4\text{N}_2$  donor set.  $\pi \cdots \pi$  interactions and C–H $\cdots$ O hydrogen bonds link the molecules to form two-dimensional supramolecular layers.

**Key words:** synthesis, crystal structure, macrocyclic compound, complex ligand, Ni(II)-Cu(II)-Ni(II) complex

## Introduction

Macrocyclic complexes have received considerable attention because of their relationship to biomimetic and catalytic systems and the applications in biology, medicine and chemical techniques.<sup>1–4</sup> Polynuclear complexes have also attracted extensive interests due to their significance in catalysis, biochemistry, materials science and etc.<sup>5–7</sup> “Complexes-as-ligands” is an important approach for preparing polynuclear complexes.<sup>6,7</sup> This contribution reports the preparation and crystal structure of a new Ni(II)-Cu(II)-Ni(II) trinuclear macrocyclic complex  $[\text{Cu}(\text{NiL})_2(\text{NCS})_2]$ , in which NiL is a new tetraazamacrocyclic nickel(II) complex ligand (Chart 1). L denotes the dianion of dimethyl 5,6,7,8,15,16-hexahydro-15-methyl-6,7-dioxodibenzo[1,4,8,11]tetraazacyclotetradecine-13,18-dicarboxylate. Two other Ni(II)-Cu(II)-Ni(II) trinuclear complexes, each of which contains two molecules of another NiL like complex ligand, were reported by some of us.<sup>8,9</sup> All the three complex ligands incorporate oxamido and phenyl groups. Oxamido group is a good bridge capable of linking metals to form polynuclear complexes and mediating ferro- and antiferromagnetic coupling between metal centers.<sup>7–11</sup> Complex fragments similar to NiL can take part in normal and special  $\pi \cdots \pi$  interactions controlling molecular packing in crystals and playing a role in molecular recognition events between isomers.<sup>8–12</sup>

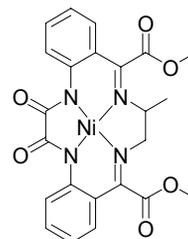


Chart 1. NiL.

## Results and discussion

### Synthesis

The new macrocyclic complex ligand NiL can be easily synthesized by a method similar to that to prepare its analogues.<sup>13</sup> The title complex  $[\text{Cu}(\text{NiL})_2(\text{NCS})_2]$  was prepared by the reaction of NiL,  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$  and KNCS in methanol. It is notable that excessive  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$  was necessary for the formation of the title compound. When the molar ratio of NiL and  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$  was 2:1 (the same ratio of NiL and Cu in the title compound), the reaction mixture could not turned into a solution after being stirred and heated, and the solid separated from the reaction mixture was NiL rather than species containing both NiL and Cu, whether in no existence of  $\text{NCS}^-$  or in the existence of  $\text{NCS}^-$  in more than 2 times excess. When the molar ratio of NiL,  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$  and KNCS was 1:2:6.3, the reaction mixture changed into an orange solution after

being stirred and heated at 65 °C for a few min, and the title compound was obtained in the end. The formerly reported Ni(II)-Cu(II)-Ni(II) trinuclear complexes were also prepared by using NiL like complex ligands in the existence of excess  $\text{Cu}(\text{ClO})_2 \cdot 6\text{H}_2\text{O}$ , which was not discussed in the former contributions.<sup>8,9</sup>

### Crystal Structure of the Title Complex $[\text{Cu}(\text{NiL})_2(\text{NCS})_2]$

The title complex has centrosymmetric molecules (Figure 1). The oxamido groups of the two NiL ligands chelate the Cu center in *trans* fashion. Cu resides in a distorted octahedral surrounding formed by four oxamido O atoms and two N atoms from the NCS<sup>-</sup> ligands. The two N atoms and two O atoms occupy the equatorial positions in *trans* fashion. The other two O atoms occupy the apices. The two Cu-N bonds are shorter than the four Cu-O bonds (See Table 1), which presumably reflects that NCS<sup>-</sup> bonds Cu(II) more tightly than the oxamido group due to the negative charge on NCS<sup>-</sup>.

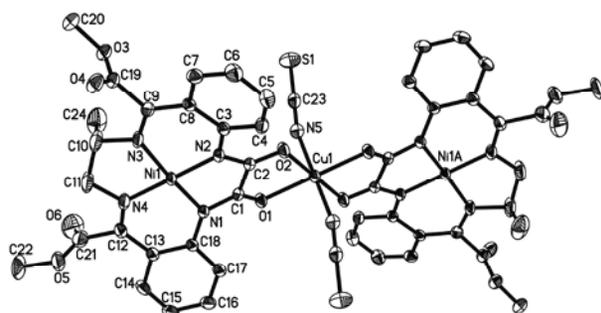


Figure 1. Molecular structure of the title complex.

The two Cu-O bonds (2.389 Å) involving the apical O atoms are considerably longer than the four coordination bonds on the equatorial plane. Jahn-Teller effect is responsible for the remarkable elongation. In the cases of the two formerly reported Ni(II)-Cu(II)-Ni(II) trinuclear complexes with the formulae of  $[\text{Cu}(\text{NiL})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  and  $[\text{Cu}(\text{NiL})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$ , one oxamido O atom of each complex ligand was involved in the shortest Cu-O bond.<sup>8,9</sup> The apices of the Cu(II) coordination octahedron in the former complex are occupied by the other two oxamido O atoms, and those of the later complex are taken by the two  $\text{CH}_3\text{OH}$  ligands.

The intramolecular distance between the Cu atom and the Ni atom is 5.364 Å. The Ni atom resides in a distorted square-planar  $\text{N}_4$  environment. The deviations of the four N atoms from their mean plane are in the range of  $-0.066 \sim 0.066$  Å. The Ni atom is 0.057 Å away from the  $\text{N}_4$  plane. The Ni-N bond lengths (1.858 ~ 1.871 Å) belong to the reported shorter ones<sup>14</sup> and are quite similar to those in the Ag(I)-Ni(II) complex of another NiL like ligand.<sup>11</sup>

Table 1. Selected bond lengths (Å) and angles (°) for the title complex.

Cu(1)-N(5)	1.927(4)	Ni(1)-N(4)	1.858(3)
Cu(1)-O(1)	2.062(2)	Ni(1)-N(3)	1.862(3)
Cu(1)-O(2)	2.389(3)	Ni(1)-N(1)	1.871(3)
Ni(1)-N(2)	1.858(3)	O(1)-Cu(1)-O(2)	74.5(1)
N(5)#1-Cu(1)-N(5)	180.0(2)	O(2)#1-Cu(1)-O(2)	180.0(1)
N(5)#1-Cu(1)-O(1)	86.9(1)	N(2)-Ni(1)-N(4)	179.3(2)
N(5)-Cu(1)-O(1)	93.2(1)	N(2)-Ni(1)-N(3)	93.1(1)
O(1)-Cu(1)-O(1)#1	180.0(1)	N(4)-Ni(1)-N(3)	86.5(1)
N(5)-Cu(1)-O(2)#1	92.3(1)	N(2)-Ni(1)-N(1)	86.7(1)
O(1)-Cu(1)-O(2)#1	105.5(1)	N(4)-Ni(1)-N(1)	93.8(1)
N(5)-Cu(1)-O(2)	87.7(1)	N(3)-Ni(1)-N(1)	172.4(2)

#1 =  $-x + 1, -y + 2, -z + 1$ .

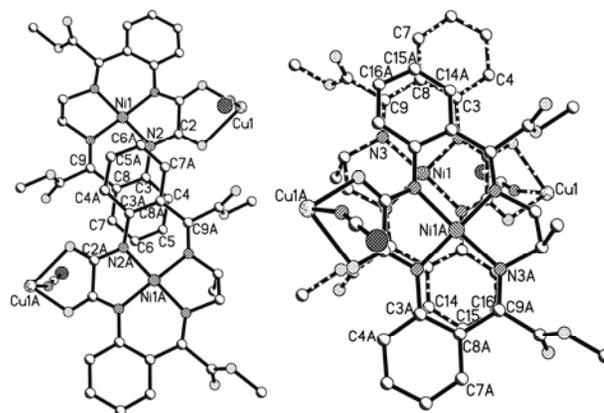


Figure 2. Plots showing the  $\pi \cdots \pi$  interactions. Only one asymmetric unit of each  $[\text{Cu}(\text{NiL})_2(\text{NCS})_2]$  molecule is depicted for the concision of the plots.

Each of the two NiL fragments of a trinuclear molecule overlaps on one side with a NiL fragment of a neighboring trinuclear molecule (Figure 2, left) and overlaps on the other side with a NiL fragment of another neighboring trinuclear molecule (Figure 2, right). Many of the atom-to-atom distances between the overlapping NiL fragments fall into the range of  $\pi \cdots \pi$  interactions ( $< 3.80$  Å).<sup>15</sup> As in some cases reported by us,<sup>11,12</sup> N(2), N(3) and C(2) (Figure 2) belong to non-aromatic  $\pi$ -systems. Non-aromatic  $\pi$ -systems can also be involved in  $\pi \cdots \pi$  interactions, though descriptions on such cases are still rare.<sup>11,12,16–18</sup> The above  $\pi \cdots \pi$  interactions link the complex molecules to form supramolecular layers (Figure 3) in the crystal. The linking in the layers is further strengthened by intermolecular C-H $\cdots$ O bonds.

### IR Spectra of the Title Complex

The bands at *ca* 1740  $\text{cm}^{-1}$  in the IR spectra of the free NiL ligand and the title complex can be assigned to the absorption of C=O (ester).<sup>10,13</sup> The band at 1670  $\text{cm}^{-1}$  for the free NiL ligand is attributed to  $\nu(\text{C}=\text{O})$  (oxamido). Two bands at 1630 and 1600  $\text{cm}^{-1}$

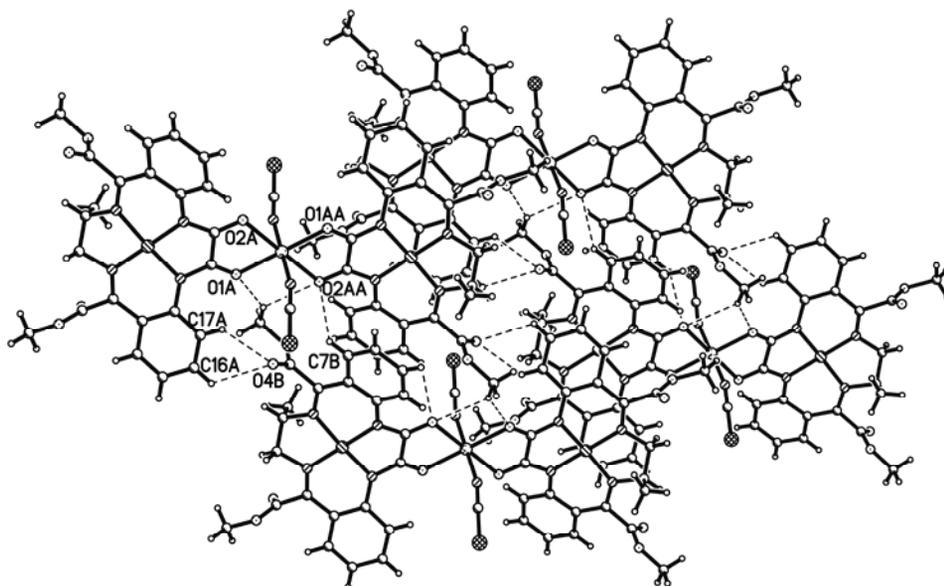


Figure 3. A portion of a supramolecular layer interlinked by  $\pi\cdots\pi$  interactions and C-H $\cdots$ O hydrogen bonds.

for the title complex can be ascribed to the absorption of  $\nu(\text{C}=\text{O})$  (oxamido), which shows red-shift compared to the corresponding band for the free ligand due to the Cu-O coordination and shows splitting due to the two obviously different Cu-O bond lengths. The band at *ca* 2080  $\text{cm}^{-1}$  in the IR spectra of the title complex is attributed to the absorption of  $\text{NCS}^-$ .

## Conclusions

A Ni(II)-Cu(II)-Ni(II) trinuclear complex was synthesized by “complex-as-ligand” approach using a new mononuclear macrocyclic complex ligand. The synthesis unfolded that excess  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  is necessary to form the title compound. This observation may be of meaning in directing assembly processes of like systems. The crystal structure of the title complex was determined by X-ray single crystal analysis.

## Experimental

**General.** All the starting materials were of analytical grade and were used as purchased without further purification. Analyses of C, H and N were carried out on a Perkin-Elmer 240 elemental analyzer. The i.r. spectra were recorded on a BIO-RAD FTS 3000 infrared spectrophotometer.

**Synthesis.** Dimethyl 2,2'-(oxalyldiimino)bis(phenylglyoxylate) was prepared by a literature method.<sup>13</sup>

NiL: The mixture of dimethyl 2,2'-(oxalyldiimino)bis(phenylglyoxylate) (0.8184 g, 1.987 mmol),  $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  (0.4944 g, 1.987 mmol), triethylamine (1.2 mL), 1,2-propanediamine (0.1474 g, 1.987 mmol) and

MeOH (25 mL) was stirred and heated at about 65 °C for 6 h and then cooled to room temperature. The red solid was collected by filtration, washed with MeOH and dried in vacuum to afford NiL as a red powder (0.6848 g, yield 68.0%). Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{N}_4\text{NiO}_6$ : C 54.47, H 3.98, N 11.05. Found: C 54.35, H 4.03, N 11.00. IR (KBr)  $\nu$  1741, 1670, 1595, 1549, 1442, 1389, 1347, 1215, 1168, 1045, 748  $\text{cm}^{-1}$ .

$[\text{Cu}(\text{NiL})_2(\text{NCS})_2]$ : The mixture of NiL (0.0507 g, 0.1 mmol),  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.0741 g, 0.2 mmol), KNCS (0.048 g, 0.63 mmol) and MeOH (70 mL) was stirred and heated at 65 °C for 15 minutes and then cooled to room temperature. The filtrate of the mixture was evaporated at room temperature for 17 days, and orange crystals suitable for X-ray single-crystal analysis were obtained (0.0269g, yield 45.0%). Anal. Calcd for  $\text{C}_{48}\text{H}_{40}\text{CuN}_{10}\text{Ni}_2\text{O}_{12}\text{S}_2$ : C 48.60, H 3.45, N 12.00. Found: C 48.29, H 3.38, N 11.73. IR (KBr)  $\nu$  2083, 1740, 1630, 1600, 1580, 1550, 1435, 1410, 1340, 1215, 1165, 1040, 750  $\text{cm}^{-1}$ .

**X-Ray structure analysis.** Diffraction data for the single crystals of the title complex were collected by  $\omega$ -scans technique on a Bruker Smart-1000-CCD area detector with Mo  $K\alpha$  radiation and graphite monochromator. Further details of crystal data, data collection and refinement are listed in Table 2. The structure was solved by direct method and subsequent Fourier difference techniques and refined using full-matrix least-squares procedure on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97 and SHELXL-97).<sup>19</sup> Hydrogen atoms were added geometrically and refined with the riding model position parameters and fixed isotropic thermal parameters.

Further details of the crystal structure investigation are available from the Cambridge Crystallographic Center with quotation number CCDC 266794.<sup>20</sup>

**Table 2.** Data collection and processing parameters for the title complex.

Empirical formula	C <sub>48</sub> H <sub>40</sub> CuN <sub>10</sub> Ni <sub>2</sub> O <sub>12</sub> S <sub>2</sub>
Formula weight	1193.98
Temperature	293(2) K
Wavelength	0.71073 Å
Monochromator	Graphite
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	$a = 9.507(4)$ Å, $\alpha = 117.312(6)^\circ$ $b = 11.921(4)$ Å, $\beta = 96.829(6)^\circ$ $c = 12.536(4)$ Å, $\gamma = 99.523(6)^\circ$
Volume, Z	1213.8(8) Å <sup>3</sup> , 1
Calculated density	1.633 g/cm <sup>3</sup>
Absorption coefficient	1.363 mm <sup>-1</sup>
F(000)	611
Crystal size	0.30 × 0.20 × 0.10 mm
$\theta$ Range for data collection	1.88° to 25.02°
Limiting indices	-11 ≤ h ≤ 11, -14 ≤ k ≤ 7, -12 ≤ l ≤ 14
Reflections collected / unique	4844 / 4240 [ $R_{\text{int}} = 0.0198$ ]
Completeness to $\theta = 25.02^\circ$	98.6 %
Max. and min. transmission	0.8757 and 0.6852
Observed reflections	3071 [ $I > 2\sigma(I)$ ]
Data / restraints / parameters	4240 / 1 / 341
Goodness-of-fit on $F^2$	1.018
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0423$ , $wR2 = 0.0943$
R indices (all data)	$R1 = 0.0692$ , $wR2 = 0.1050$
Largest diff. peak and hole	0.629 and -0.377 e <sup>-</sup> Å <sup>-3</sup>

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## Povzetek

Trijedrni kompleks [Cu(NiL)<sub>2</sub>(NCS)<sub>2</sub>] smo pripravili z reakcijo novega makrocikličnega oksamido liganda NiL, Cu(CIO)<sub>2</sub>·6H<sub>2</sub>O in KNCS (L je oznaka za dvakrat deprotonirano obliko dimetil 5,6,7,8,15,16-heksahidro-15-metil-6,7-dioksodibenzo[1,4,8,11]tetraazaciklotetradecin-13,18-dicarboksilata). Spojini smo določili strukturo z rentgensko strukturno analizo. Bakrovi in nikljevi atomi so povezani z oksamidno skupino. Geometrija štirih dušikovih atomov, koordiniranih na Ni(II), je kvadratno planarna, na Cu(II) pa so oktaedrično koordinirani štirje kisikovi in dva dušikova atoma.  $\pi \cdots \pi$  interakcije in C–H $\cdots$ O vodikove vezi povezujejo molekule v dvodimenzionalne supramolekularne plasti.