



# Unexpected Formation of Copper Dimethylglyoxime Dimer from the Reaction of Cuprous Chloride and Tetradentate Buthylene-Bridged Diiminedioxime Ligand

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## ABSTRACT

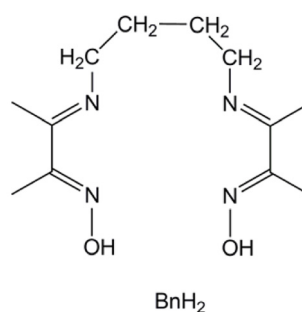
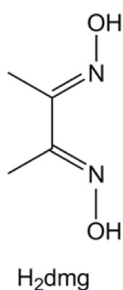
A reaction of a ligand 3,3'-(1,4-butanediyl)dinitrilo)bis(2-butanone)dioxime (BnH<sub>2</sub>) and CuCl yield green [Cu(H<sub>2</sub>dmg)Cl(μ-Cl)]<sub>2</sub>, 1. The dimethylglyoxime (H<sub>2</sub>dmg) and Cu<sup>II</sup> ions in 1 were *in situ* produced during the course of reaction and formed doubly chloro-bridged Cu(II) dimers. The geometry around copper ion is distorted square pyramidal. The weak intermolecular hydrogen bonds are observed in 1 giving 1D structure. The existence of two O-O distances of O2-O1 = 2.922 and O4-O3 = 2.910 Å indicates that these weak intermolecular hydrogen bonds are not equivalent. Hence doublet of the O-H stretching at 3302 and 3216 cm<sup>-1</sup> are observed.

**Keywords:** diiminedioxime, cuprous chloride, dimethylglyoxime, hydrogen bond, doubly chloro-bridged Cu<sup>II</sup> dimers

## 1. INTRODUCTION

Dimethylglyoxime (H<sub>2</sub>dmg) is bidentate ligand and used as chelating agent. Usually H<sub>2</sub>dmg ligand coordinates to metal ions via nitrogen or oxygen donor atoms depending on the chemistry of the central metals. A short intramolecular hydrogen bond between *cis* oxime groups in bis (dimethylglyoximate) complex is typical. In the special category of dimeric halo-bridged adducts of copper(II)

halides with α, β-dionedioxime ligands, some CuCl<sub>2</sub> adducts with a number of glyoxime derivatives have been prepared earlier [1-3], but only one member of this category, di-μ-chlorobis (chlorodimethylglyoxime) copper(II) or di-μ-chlorobis(chloro (2, 3-butanediionedioxime)) copper(II), [CuCl<sub>2</sub>(dmgH)]<sub>2</sub> has been structurally characterized [2-5] so far.



In this study similar dimeric complex, [Cu(H<sub>2</sub>dmg)Cl(μ-Cl)]<sub>2</sub>, is obtained from the reaction between CuCl and tetradentate butylene-bridged diiminedioxime ligand (BnH<sub>2</sub>). The tetradentate methylene-bridged diiminedioxime ligands form complexes with various transition metals. A short intramolecular hydrogen bond between *cis* oxime groups is typical. The number of bridging methylene groups (*n* = 2-4) as well as the effect of metal size play a role on the formation of hydrogen bond in the complexes [6-11]. As part of our ongoing research on the formation of diiminedioxime copper complexes, we plan to prepare monovalent copper complex of BnH<sub>2</sub>. Several attempts had been made to synthesize this complex, but all of the obtained products contain H<sub>2</sub>dmg ligand. The H<sub>2</sub>dmg is *in situ* produced from the cleavage reaction of BnH<sub>2</sub> during the course of reaction. In this article the synthesis, structure, and spectroscopic properties of this complex are the main focus.

## 2. MATERIALS AND METHODS

### 2.1 Materials and Instruments

All chemicals are commercially available (Fluka Co., Scharlau Co., Carlo Erba Co., BHD Co., Fisher Co., Merck Co. and LAB-SCAN Co.) and used without further purification. All X-ray data were collected on a Bruker Smart CCD Diffractometer. The elemental analyses were performed by CHNS/O Analyzer Perkin Elmer Model

PE 2400 Series II. The FTIR spectra were recorded on a Bruker Model Equinox 55 Spectrophotometer using KBr pellets. Absorption spectra of complexes were recorded in a mixed solvent (H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH = 1:5) from the Jasco V-530 spectrophotometer.

### 2.2 Synthesis of Ligand 3, 3'-(1, 4-butanediyl)dinitrilo)bis(2 butanone)dioxime(BnH<sub>2</sub>)

Ligand (BnH<sub>2</sub>) was prepared using the procedure described in the literature [4] with slight modification. Diacetylmonoxime (20.23 g, 0.20 moles) in 50 cm<sup>3</sup> of methanol was added to 1, 4-diaminobutane (10.00 cm<sup>3</sup>, 0.10 moles). The resulting mixture solution was stirred at room temperature. After 30 minutes, white solid precipitated. It was then separated by vacuum filtration and washed with cold methanol and then diethyl ether, and dried in desiccator. The yield was 76%. The BnH<sub>2</sub> ligand has a melting point of 149-150 °C. This ligand was identified by the infrared spectrum.

### 2.3 Synthesis of Dichlorodi-μ chlorobis(dimethylglyoxime)dicopper(II), 1, [Cu(H<sub>2</sub>dmg)Cl(μ-Cl)]<sub>2</sub>

To 0.508 g (2.0 mmol) BnH<sub>2</sub> dissolved in 30 cm<sup>3</sup> of acetone, 0.269 g (2.0 mmol) of CuCl dissolved in concentrated HCl was added dropwise. While stirring, the yellow product precipitated. The mixture was stirred for 30 minutes and left at room temperature.

After 2 days, the yellow product changed to green crystalline product and was recrystallized from hot acetone. The green parallelepiped crystals are designated as complex 1. *Anal. Calc.* for  $C_8H_{16}N_4Cu_2O_4Cl_4$  (%): C, 19.17; H, 3.22; N, 11.18. Found: C, 19.45; H, 3.86; N, 11.34.

## 2.4 X-ray Crystallographic Analysis

The diffraction data for complex 1 with appropriate size crystal was collected at 298(2) K on a 1 K Bruker Smart CCD Diffractometer using  $\omega$  rotation scans with a scan width of  $0.3^\circ$  and graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). For data collection and data integration, the SMART and SAINT

programs were used [12] and empirical absorption correction was performed with the program SADABS [13]. The structure was solved by direct method using the SHELXTL program system [14] and was refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters. The hydrogen atom positions were calculated based on an "ideal" C-H distance of  $0.96 \text{ \AA}$ , O-H distance of  $0.86 \text{ \AA}$  and with idealized angles agreed with a difference Fourier map. Crystal data and additional details of the data collection and refinement of the structures are presented in Table 1 and the selected bond lengths and angles for  $[Cu(H_2dmg)Cl(\mu-Cl)]_2$  are shown in Table 2.

**Table 1.** Crystal data for  $[Cu(H_2dmg)Cl(\mu-Cl)]_2$ , 1.

Chemical	$Cu_2C_8H_{16}N_4O_4Cl_4$	V ( $\text{\AA}^3$ )	429.24(2)
Formula mass	501.13	$\lambda$ ( $\text{\AA}$ )	MoK $\alpha$ 0.71073
Crystal system	triclinic	$D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.939
Space group	P1	measured reflections	3144
Temperature(K)	298	independent reflections	2668
Z	1	$\mu$ ( $\text{mm}^{-1}$ )	3.118
a, b, c ( $\text{\AA}$ )	7.7161(2), 8.1414(3), 8.1983(2)	Goodness of fit on $F^2$	0.98
$\alpha$ ( $^\circ$ )	108.143(1)	$R[F^2 > 2\sigma(F^2)]$	0.046
$\beta$ ( $^\circ$ )	101.283(2)	wR( $F^2$ )	0.120
$\gamma$ ( $^\circ$ )	110.856(2)		

**Table 2.** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[Cu(H_2dmg)Cl(\mu-Cl)]_2$ , 1.

Cu1-N1	1.973(11)	N1-O1	1.411(16)	N1-Cu1-N2	77.1(4)	N3-Cu2-N4	76.2(4)
Cu1-N2	2.049(11)	N2-O2	1.355(15)	N1-Cu1-Cl1	91.7(4)	N3-Cu2-Cl2	90.1(4)
Cu1-Cl1	2.228(4)	N3-O3	1.347(14)	N2-Cu1-Cl3	91.5(3)	N4-Cu2-Cl4	94.0(4)
Cu1-Cl3	2.263(3)	N4-O4	1.407(13)	Cl1-Cu1-Cl3	98.5(1)	Cl2-Cu2-Cl4	98.5(1)
Cu1-Cl4	2.729(4)	N1-C1	1.295(17)	Cl1-Cu1-Cl4	95.8(2)	Cl2-Cu2-Cl3	95.7(2)
Cu2-N3	2.019(9)	N2-C2	1.269(17)	N1-Cu1-Cl4	96.5(4)	N3-Cu2-Cl3	95.9(4)
Cu2-N4	2.000(12)	N3-C5	1.292(17)	N2-Cu1-Cl4	92.7(3)	N4-Cu2-Cl3	92.8(4)
Cu2-Cl2	2.268(4)	N4-C6	1.297(16)	Cl3-Cu1-Cl4	92.0(1)	Cl4-Cu2-Cl3	92.8(1)
Cu2-Cl3	2.712(4)	C1-C2	1.46(2)	N1-Cu1-Cl3	166.0(3)	N3-Cu2-Cl4	167.1(4)
Cu2-Cl4	2.247(3)	C5-C6	1.512(17)	N2-Cu1-Cl1	166.6(3)	N4-Cu2-Cl2	164.5(3)
				Cu1-Cl3-Cu2	87.7(1)	Cu2-Cl4-Cu1	87.6(1)

### 3. RESULTS AND DISCUSSION

#### 3.1 Crystal Structure of $[\text{Cu}(\text{H}_2\text{dmg})\text{Cl}(\mu\text{-Cl})_2]$ (Complex 1).

The crystal structure of 1 consists of two square planar  $[\text{Cu}(\text{H}_2\text{dmg})\text{Cl}_2]$  units located in such a way that one chloro ligand of an adjacent unit forms weak bond with copper ion at apical position resulting in a distorted square pyramidal geometry as shown in Figure 1. Thus one chloro ligand in each unit presumably acts as bridging ligand. The Cu-Cl bond length is longer for the bridged chloride than the unbridged ones. The plane of five-membered ring formed by  $\text{H}_2\text{dmg}$  group in each unit is perpendicular to the parallelogram formed by two coppers and two bridging chloride ions. Such  $\text{Cu}_2\text{Cl}_2$  rings pack parallelly making a square hole along

one direction as shown in Figure 2. There are very weak intermolecular hydrogen bonds between oxime hydroxyl groups giving one dimensional polymeric structure along axis  $a$ . The existence of two O-O distances of  $\text{O}2\text{-O}1 = 2.922$  and  $\text{O}4\text{-O}3 = 2.910$  Å indicates that the intermolecular hydrogen bonds formed by two oxime groups are not equivalent. Only one H atom of the two OH groups on  $\text{H}_2\text{dmg}$  ligand participates in an *interdimer* O-H-O bridge. In the dimeric lattice the two OH groups of each dimethylglyoxime occupy slightly different crystallographic positions. Hence, the doublet of the O-H stretching at  $3302$  and  $3216$   $\text{cm}^{-1}$  are observed. These hydrogen bonds are so weak that no broadening of the O-H stretching peaks is observed.

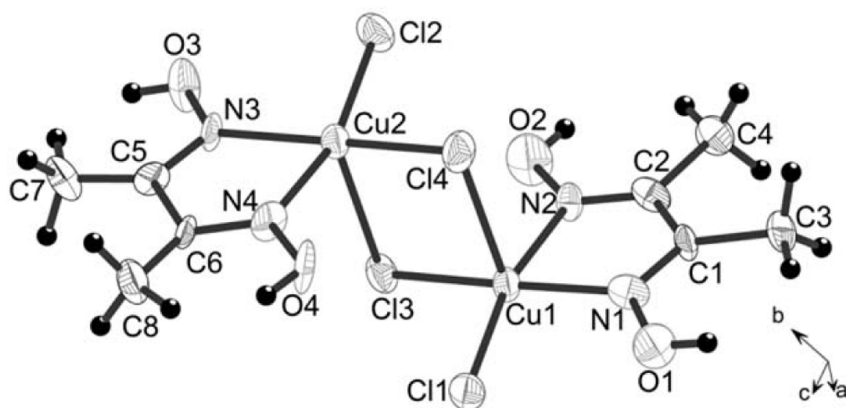


Figure 1. Perspective view of  $[\text{Cu}(\text{H}_2\text{dmg})\text{Cl}(\mu\text{-Cl})_2]$ , 1, showing thermal ellipsoids (50% probability) and atom labeling.

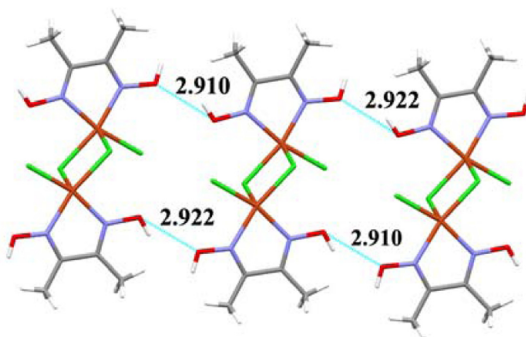


Figure 2. Packing of complex 1 showing hydrogen bondings along axis  $a$  and  $\text{Cu}_2\text{Cl}_2$  parallelogram.

### 3.2 Infrared Spectrum

The vibrational frequencies for particular bonds in free ligand and complex are summarized in Table 3. The doublet splitting of the O-H stretching band at 3302 and 3216  $\text{cm}^{-1}$  for the dimeric complex is consistent with the existence of two O-O distances of O2-O1 = 2.922 Å and O4-O3 = 2.910 Å. The spectrum of the “free ligand”,

by contrast, shows no obvious evidence for such splitting. One  $\nu(\text{C}=\text{N})$  is observed at lower frequencies than that in free ligand supporting the coordination at oxime and imine nitrogens. When the complex is formed, two N-O bonds are distinguishable. Two  $\nu(\text{N}-\text{O})$  stretching bands appear at 1089 and 1064  $\text{cm}^{-1}$ .

**Table 3.** Vibrational frequencies ( $\text{cm}^{-1}$ ) for the particular bonds in the free ligand and complex 1.

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )	$\nu(\text{N}-\text{O})$	Reference
$\text{H}_2\text{dmg}$	3208b	1446s	981s 906s	3
$[\text{Cu}(\text{H}_2\text{dmg})\text{Cl}(\mu\text{-Cl})_2]$	3302s 3216s	1394s	1089s 1064s	This work
$[\text{Cu}(\text{H}_2\text{dmg})\text{Cl}_2]$	3310s 3220s	1390s	1105s 1080s	3
$[\text{CuCl}_2(\text{dmgH})_2]$	3283s 3238s	1390s	1085s 1047s	5
$[\text{Cu}_2(\mu\text{-Hdmg})_2(\text{Hdmg})]\text{ClO}_4$	not report	1532	1214	15

Crystal structure of **1** is similar to that synthesized by direct reaction between  $\text{CuCl}_2$  and dimethylglyoxime [3]. The reaction between divalent copper chloride and  $\text{BnH}_2$  was also performed in order to confirm that only monovalent copper ion catalyzes cleavage reaction of  $\text{BnH}_2$  ligand. The reaction of  $\text{CuCl}_2$  and  $\text{BnH}_2$  results in a binuclear complex  $[\text{Cu}(\mu\text{-BnH})_2(\text{ClO}_4)_2]$  whose structure is similar to that obtained from literature[10].

### 3.3 Supplementary Data

CCDC 966183 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK, fax: +44 1223 336 033; or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk> on request.

### 4. CONCLUSION

The reaction between  $\text{CuCl}$  and  $\text{BnH}_2$  yields green doubly chloro-bridged  $\text{Cu}(\text{II})$  dimers containing dimethylglyoxime ligand. The dimethylglyoxime ( $\text{H}_2\text{dmg}$ ) and  $\text{Cu}(\text{II})$

ions were *in situ* produced during the course of reaction. The  $\text{BnH}_2$  ligands are probably hydrolyzed into diaminobutane and diacetylmonoxime. Some diacetylmonoxime are further hydrolyzed giving butadione and hydroxylamine which then reacts with the unhydrolyzed diacetylmonoxime to form dimethylglyoxime. One chloro ligand of an adjacent unit forms weak bond with copper ion at apical position resulting in a distorted square pyramidal geometry.

### ACKNOWLEDGEMENTS

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