

## Synthesis, Structure and Properties of the Isomeric Dinuclear Complexes [(DENC)<sub>2</sub>CuX<sub>2</sub>]<sub>2</sub> (DENC = N,N-Diethylnicotinamide; X = Cl or Br) and the Kinetics of their Reactions with DENC in Methylene Chloride

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Received June 9, 1984

### Abstract

Tetrahalo-tetrakis-(N,N-diethylnicotinamide)dinuclear copper(II) species [(DENC)<sub>2</sub>CuX<sub>2</sub>]<sub>2</sub> (X = Cl or Br) differ in that while the chloro complex is bridged by two DENC molecules in the solid but two chloro groups in solution, the bromo complex is always bromo-bridged. These conclusions result from an X-ray structural determination of (DENC)Cl<sub>2</sub>Cu-(DENC,DENC)CuCl<sub>2</sub>(DENC) and from spectroscopic comparisons. The kinetics of conversion of the respective dimers to monomeric (DENC)<sub>3</sub>CuX<sub>2</sub> species have been measured in methylene chloride solution.

### Introduction

Copper(I) halides, CuX, form a series of complexes with L = pyridine, py, ethylnicotinate, ENCA, and N,N-diethylnicotinamide, DENC, which are oxidized by dioxygen to tetranuclear L<sub>n</sub>Cu<sub>4</sub>X<sub>4</sub>O<sub>2</sub> complexes in aprotic solvents [1, 2]. The ligands are coordinated only through N(pyridine) and are not oxidized by dioxygen. These reactions are of interest because they involve the direct, 4-electron reduction of O<sub>2</sub> within single molecular units [2]. However, the core structure of the oxocopper(II) products with py ligands is different from those with ENCA and DENC [2, 3]. The latter two ligands themselves differ in that only DENC stabilizes octahalotetracopper(II) complexes L<sub>4</sub>Cu<sub>4</sub>X<sub>8</sub> [4] and only DENC forms the unusual di(μ-DENC)-bridged complex with ZnCl<sub>2</sub> in which the pyridine nitrogen and the carbonyl oxygen of the amido substituent are used to bridge two, four-coordinate zinc(II) centers [5]. Table I summarizes commonalities and

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TABLE I. Commonalities and Differences in Metal Complexes Obtained with py, ENCA and DENC Ligands (x Denotes Formation of the Designated Complex).

Desired Product	L = py	ENCA	DENC	Ref.
L <sub>n</sub> Cu <sub>4</sub> X <sub>4</sub> (X = halide)	x(n = 3,4, insoluble; <sup>a</sup> n = 8, soluble)	x(n = 4 or 8)	x(n = 4)	1, 2
L <sub>4</sub> Cu <sub>4</sub> X <sub>8</sub> (X = Cl or Br)	b	b	x	4
[L <sub>2</sub> CuCl <sub>2</sub> ] <sub>3</sub>	c	c	x	6
ZnCl <sub>2</sub> (L,L)Cl <sub>2</sub> Zn	c	c	x	5
(μ <sub>4</sub> -oxo)L <sub>4</sub> Cu <sub>4</sub> X <sub>6</sub>	x <sup>d</sup>	x <sup>d</sup>	x <sup>d</sup>	4, 7, 8
L <sub>n</sub> Cu <sub>4</sub> X <sub>4</sub> Y <sub>2</sub> (X = Cl or Br; Y = O or CO <sub>3</sub> )	x(n = 3,4) <sup>d,e</sup>	x(n = 4) <sup>f</sup>	x(n = 4) <sup>f</sup>	1, 2
[LCuNi(H <sub>2</sub> O)X <sub>2</sub> ] <sub>2</sub> Y <sub>2</sub> (Y = O, CO <sub>3</sub> )	g	x <sup>f</sup>	x <sup>f</sup>	4

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>Reaction of CuX<sub>2</sub> with a deficit or excess of L in methylene chloride gives L<sub>2</sub>CuX<sub>2</sub>, not the tetrameric products obtained with a deficit of DENC. <sup>c</sup>Not investigated. <sup>d</sup>EPR active. <sup>e</sup>Not Y = CO<sub>3</sub>; py<sub>n</sub>Cu<sub>4</sub>X<sub>4</sub>O<sub>2</sub> is easily decomposed by excess py; initiates phenolic oxidative coupling by dioxygen. <sup>f</sup>EPR inactive. <sup>g</sup>L = py does not stabilize the transmetalated products shown.

differences between these pyridine ligand/metal systems.

In seeking to explore the special properties of DENC which give rise to a variety of copper(II) complex structures we have determined the crystal and molecular structure and spectroscopic properties of dimeric  $\text{Cl}_2(\text{DENC})\text{Cu}(\text{DENC}, \text{DENC})\text{Cu}(\text{DENC})\text{Cl}_2$ , **1** (Scheme 1), for comparison with those of the corresponding zinc(II) complex. This dimeric complex adopts dihalobridges in aprotic solvents; by contrast, the corresponding bromo complex has bromo bridges both as a solid and in solution. Also reported are the kinetics of conversion of these dimers to monomeric  $(\text{DENC})_3\text{CuX}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) in methylene chloride.

## Experimental

### Materials

DENC and ENCA (Aldrich) were distilled under reduced pressure before use. Methylene chloride and nitrobenzene were distilled from phosphorus(V) oxide and stored over 4 Å molecular sieves. Anhydrous copper(II) halides were obtained from the hydrates (Alfa) by heating overnight at 120 °C under vacuum.

The title complexes  $[(\text{DENC})_2\text{CuX}_2]_2$  were prepared by treating a solution of DENC (0.1 mol) in 50/50% v/v methylene chloride/ethanol (30 ml) with a solution of the anhydrous copper(II)

halide (0.05 mol) in absolute ethanol (20 ml). The mixture was refluxed for one hour on a water-bath. Evaporation of the solvent over a 2–3 day period at room temperature gave turquoise-blue crystals ( $\text{X} = \text{Cl}$ ) of dimensions suitable for structural characterization. Analysis\*: Found: C, 48.65; H, 5.74; N, 11.12; Cu, 12.86; Cl, 14.35%; M. wt,  $970 \pm 20$ ; Calcd. for  $[(\text{DENC})_2\text{CuCl}_2]_2$ : C, 48.83; H, 5.74; N, 11.39; Cu, 12.93; Cl, 14.43%; M. wt, 982; and found for  $[(\text{DENC})_2\text{CuBr}_2]_2$ : C, 41.64; H, 4.77; N, 9.52; Cu, 10.94; Br, 27.43%; M. wt,  $1140 \pm 20$ ; Calcd.: C, 41.41; H, 4.83; N, 9.66; Cu, 10.96; Br, 27.61; M. wt,  $1160 \text{ gm mol}^{-1}$ .

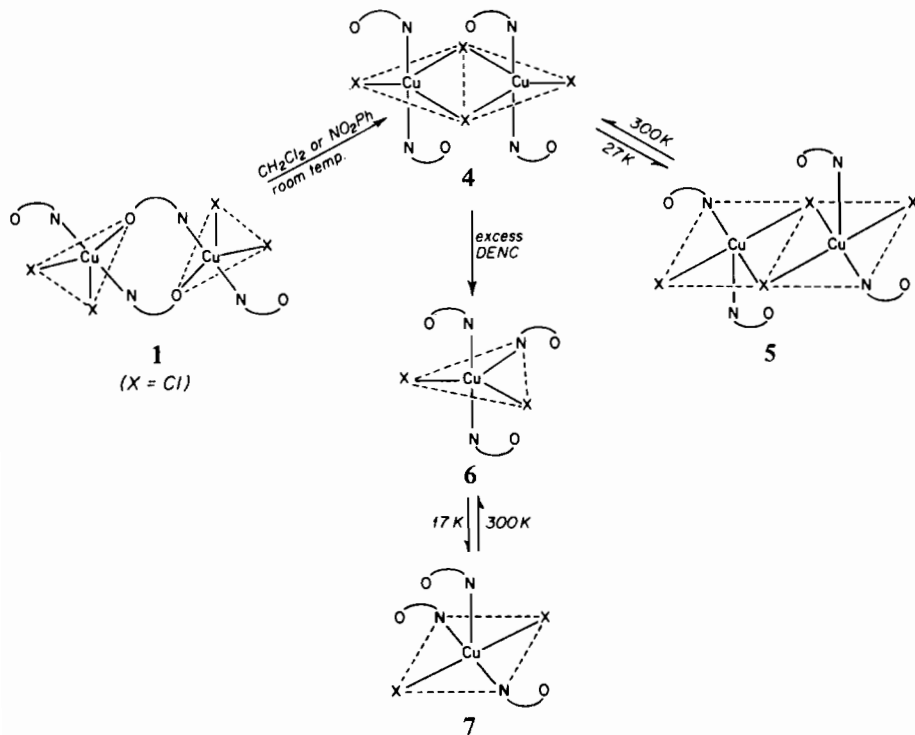
Attempts to prepare the corresponding complexes with ENCA ligands gave light blue insoluble precipitates of  $(\text{ENCA})_2\text{CuX}_2$  [9].

### Molecular Structure Determination

#### Crystal Data

$\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{CuN}_4\text{O}_2$ ,  $M = 490.9$ ; Triclinic,  $a = 10.563(1)$ ,  $b = 13.123(1)$ ,  $c = 9.829(2)$  Å,  $\alpha = 98.77(1)$ ,  $\beta = 116.05(1)$ ,  $\gamma = 100.34(1)^\circ$ ,  $U = 1162 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.403 \text{ g cm}^{-3}$ ,  $F(000) = 510$ . Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ),  $\mu = 36.1 \text{ cm}^{-1}$ . Space group  $P\bar{1}$  ( $C_i^1$ ).

\*Metal and halide analyses were performed in our laboratory; all other elemental analyses were made by Galbraith Laboratories, Knoxville, TN.



Scheme 1.

### Data Collection and Structure Solution

A turquoise-blue crystal of dimensions *ca.* 0.07 × 0.15 × 0.25 mm was attached to a glass fiber and mounted on a Syntex P2<sub>1</sub> automated diffractometer. Unit cell dimensions were obtained by a least-squares fit of 13 reflections well-separated in reciprocal space. One hemisphere of data was collected in the range  $4 \leq 2\theta \leq 130^\circ$  using  $\theta/2\theta$  scans and a variable scan rate. Two standard reflections, monitored after every 98 reflections, showed no variation with time. The data were corrected for Lorentz and polarization effects; an empirical absorption correction, determined from a  $\psi$  scan, was also made. The 3309 statistically significant reflections ( $I > 2\sigma(I)$ ) were used in the structure solution and refinement.

The structure was solved via Patterson and Fourier syntheses. Least squares refinement of positional and isotropic (subsequently anisotropic) thermal parameters of non-hydrogen atoms brought *R* to 0.083. Hydrogen atomic positions were calculated and added to the structure factor calculations. Continued refinement of the positional and thermal (anisotropic non-hydrogen, isotropic hydrogen) parameters led to convergence at *R* 0.047\*\*.

The atomic scattering factors for the non-hydrogen atoms were taken from ref. [10], with those of Cu and Cl corrected for anomalous scattering [11]. The scattering factors for hydrogen were taken from ref. [12].

Final atomic positional coordinates for the non-hydrogen atoms appear in Table II, interatomic distances and angles are in Table III, and mean planes are in Table IV. Tables of anisotropic thermal parameters, interatomic separations <3.5 Å and observed and calculated structure factors may be obtained from the Authors.

### Physical Measurements

Solution electronic spectral measurements were made with Beckman DK-1A and Cary 14 or 2300 spectrophotometers in matched quartz cells at room temperature. Infrared spectra were obtained with a Perkin-Elmer Model 567 spectrometer calibrated with the 906.5 or 3026.3 cm<sup>-1</sup> absorptions of polystyrene. EPR spectra were recorded at 100 KHz modulation and 10 G modulation amplitude on Bruker ER 200 and Varian E-9 spectrometers. 10-mW incident power was used and resonance conditions were at *ca.* 9.75 GHz (X-band) at room temperature and *ca.* 9.1 GHz at 27 K. Spectra at

TABLE II. Fractional Atomic Coordinates ( $\times 10^4$ ) for the Non-hydrogen Atoms, with Standard Deviations in Parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	4082.0(6)	3137.0(4)	1068.5(6)
Cl(1)	6490(1)	3146(1)	2217(1)
Cl(2)	2038(1)	3120(1)	-1078(1)
N(1)	4648(3)	4732(2)	1978(3)
C(2)	5600(4)	5126(3)	3521(4)
C(3)	6100(4)	6210(3)	4259(4)
C(4)	5608(5)	6916(3)	3381(5)
C(5)	4653(5)	6525(3)	1794(5)
C(6)	4185(4)	5430(3)	1124(5)
C(7)	7120(4)	6597(3)	6012(4)
N(8)	8463(4)	6533(4)	6526(4)
C(9)	9126(7)	6310(8)	5503(7)
C(10)	9814(9)	7278(12)	5271(10)
C(11)	9488(7)	6867(7)	8235(6)
C(12)	9894(18)	5934(14)	8840(11)
O(1)	6628(3)	6950(2)	6854(3)
N(13)	3541(3)	1527(3)	463(4)
C(14)	3662(5)	973(3)	1523(5)
C(15)	3462(4)	-128(3)	1229(5)
C(16)	3171(5)	-670(4)	-259(7)
C(17)	3062(5)	-105(4)	-1351(5)
C(18)	3236(5)	985(4)	-974(5)
C(19)	3726(5)	-695(3)	2502(5)
N(20)	2671(4)	-943(3)	2886(4)
C(21)	2947(8)	-1505(5)	4152(7)
C(22)	2309(7)	-2703(5)	3528(7)
C(23)	1240(6)	-731(5)	2129(8)
C(24)	1143(11)	247(8)	3081(15)
O(2)	4907(4)	-896(3)	3132(5)

low temperatures were obtained with an Air Products LTD-3-110 Heli-Tran liquid helium transfer refrigerator. The field was calibrated with a powder sample of DPPH ( $g = 2.0037$ ) [13].

The rates of decomposition of the title complexes by excess DENC were measured in the thermostated cell compartment of the Cary 2300 with an expanded absorption scale and zero suppression to maximize the absorption change during reaction. Decomposition of  $2.0 \times 10^{-3}$  M [(DENC)<sub>2</sub>CuX<sub>2</sub>]<sub>2</sub> was monitored at 850 nm in methylene chloride with [DENC] = 0.4–2.5 M (X = Cl) and 0.3–0.7 M (X = Br). Temperature was maintained at  $(23.0 \pm 0.2)$  °C. Pseudo first-order rate constants  $k_{obsd}$  were calculated from the slopes of linear plots of  $\ln(A_t - A_\infty)$  vs. time, where  $A_t$  is the absorbance at time *t*.

### Results and Discussion

We have previously reported the molecular structure of trimeric [(DENC)CuCl<sub>2</sub>]<sub>3</sub>, which crystallizes from ethanol at molar DENC:CuCl<sub>2</sub> = 2 as blue,

\*\*All crystallographic calculations were carried out on a VAX 11/780 computer. The principal programs used were: The X-RAY system-version of 1976, J. M. Stewart, editor, Technical Report TE-446 of the Computer Science Center, University of Maryland, College Park, Maryland; ORTEP, crystallographic illustration programs, C. K. Johnson, Oak Ridge, ORNL-3794.

TABLE III. Interatomic Separations (Å) and Valency Angles (deg.), with Estimated Standard Deviations in Parentheses.

<b>a) Bond lengths</b>			
Cu—Cl(1)	2.282(1)	C(9)—C(10)	1.447(18)
Cu—Cl(2)	2.254(1)	C(11)—C(12)	1.491(21)
Cu—N(1)	2.012(3)	N(13)—C(14)	1.334(6)
Cu—N(13)	2.007(4)	N(13)—C(18)	1.347(6)
Cu—O(1) <sup>a</sup>	2.475(3)	C(14)—C(15)	1.387(6)
N(1)—C(2)	1.347(5)	C(15)—C(16)	1.395(7)
N(1)—C(6)	1.348(6)	C(15)—C(19)	1.500(7)
C(2)—C(3)	1.381(6)	C(16)—C(17)	1.371(7)
C(3)—C(4)	1.377(6)	C(17)—C(18)	1.380(7)
C(3)—C(7)	1.515(6)	C(19)—N(20)	1.329(7)
C(4)—C(5)	1.380(7)	C(19)—O(2)	1.224(7)
C(5)—C(6)	1.384(7)	N(20)—C(21)	1.488(8)
C(7)—N(8)	1.304(6)	N(20)—C(23)	1.464(8)
C(7)—O(1)	1.232(5)	C(21)—C(22)	1.505(10)
N(8)—C(9)	1.480(8)	C(23)—C(24)	1.515(14)
N(8)—C(11)	1.481(7)		
<b>b) Valency angles</b>			
Cl(1)—Cu—Cl(2)	149.35(5)	C(7)—N(8)—C(11)	119.6(4)
Cl(1)—Cu—N(1)	90.7(1)	C(9)—N(8)—C(11)	115.8(5)
Cl(1)—Cu—N(13)	88.4(1)	N(8)—C(9)—C(10)	112.6(9)
Cl(1)—Cu—O(1) <sup>a</sup>	104.8(1)	N(8)—C(11)—C(12)	111.4(7)
Cl(2)—Cu—N(1)	94.2(1)	Cu—N(13)—C(14)	121.1(3)
Cl(2)—Cu—N(13)	90.7(1)	Cu—N(13)—C(18)	120.5(3)
Cl(2)—Cu—O(1) <sup>a</sup>	105.8(1)	C(14)—N(13)—C(18)	117.8(4)
N(1)—Cu—N(13)	171.7(1)	N(13)—C(14)—C(15)	124.1(4)
N(1)—Cu—O(1) <sup>a</sup>	83.6(1)	C(14)—C(15)—C(16)	117.1(4)
N(13)—Cu—O(1) <sup>a</sup>	88.6(1)	C(14)—C(15)—C(19)	121.6(4)
Cu—N(1)—C(2)	117.6(3)	C(16)—C(15)—C(19)	120.9(4)
Cu—N(1)—C(6)	124.0(3)	C(15)—C(16)—C(17)	119.3(5)
C(2)—N(1)—C(6)	118.3(4)	C(16)—C(17)—C(18)	119.9(5)
N(1)—C(2)—C(3)	122.6(4)	N(13)—C(18)—C(17)	121.8(4)
C(2)—C(3)—C(4)	118.7(4)	C(15)—C(19)—N(20)	118.2(4)
C(2)—C(3)—C(7)	120.0(4)	C(15)—C(19)—O(2)	117.8(5)
C(4)—C(3)—C(7)	121.2(4)	N(20)—C(19)—O(2)	124.0(5)
C(3)—C(4)—C(5)	119.3(4)	C(19)—N(20)—C(21)	117.6(5)
C(4)—C(5)—C(6)	119.3(4)	C(19)—N(20)—C(23)	124.9(5)
N(1)—C(6)—C(5)	121.8(4)	C(21)—N(20)—C(23)	117.4(5)
C(3)—C(7)—N(8)	117.5(4)	N(20)—C(21)—C(22)	112.8(6)
C(3)—C(7)—O(1)	118.0(4)	N(20)—C(23)—C(24)	112.9(7)
N(8)—C(7)—O(1)	124.5(4)	Cu—O(1) <sup>a</sup> —C(7) <sup>a</sup>	151.8(3)
C(7)—N(8)—C(9)	123.9(5)		

<sup>a</sup>Coordinates from Table II transformed by  $1 - x, 1 - y, 1 - z$ .

needle crystals [6]. When the solvent is changed to 30% v/v methylene chloride/ethanol and allowed to evaporate for two days at room temperature, larger, chunky, turquoise crystals of a DENC-bridged dimer are obtained. Unlike the case with [(DENC)-CuCl]<sub>4</sub>Cl<sub>4</sub> species, which oxidize ethanol and crystallize as (μ<sub>4</sub>-oxo)(DENC)<sub>4</sub>Cu<sub>4</sub>Cl<sub>6</sub> [4], the complexes with DENC:CuX<sub>2</sub> = 2 do not oxidize ethanol.

#### Description of the Solid State Structure of [(DENC)<sub>2</sub>-CuCl<sub>2</sub>]<sub>2</sub>

In the solid state the (DENC)<sub>2</sub>CuCl<sub>2</sub> units of the chloro complex 1 associate as DENC-bridged dimers

around centers of symmetry, resulting in five-coordinate copper (Fig. 1). The metal centers, which are coordinated by two pyridinic nitrogen atoms, two terminal chlorine atoms and an amide oxygen atom from the centrosymmetrically related unit, display an irregular coordination. This coordination may best be described as trigonal bipyramidal (see below), with pyridinic nitrogen atoms occupying the axial sites, distorted toward square pyramidal geometry by the opening of the Cl—Cu—Cl angle to 149.35(5)°.

The pyridine rings are very nearly planar (Table IV) and are inclined at an angle of 29.1° to one another. The copper lies close to these ring planes

TABLE IV. Distances (Å) of Atoms from Least-Squares Planes through Various Groups of Atoms; Atoms Defining the Plane are Italicized.

Plane 1			
<i>N(1)</i>	-0.006	<i>C(5)</i>	0.007
<i>C(2)</i>	0.005	<i>C(6)</i>	0.000
<i>C(3)</i>	0.003	Cu	0.063
<i>C(4)</i>	-0.008		
Plane 2			
<i>N(13)</i>	0.001	<i>C(17)</i>	-0.007
<i>C(14)</i>	-0.011	<i>C(18)</i>	0.008
<i>C(15)</i>	0.012	Cu	-0.254
<i>C(16)</i>	-0.003		
Plane 3			
<i>C(3)<sup>a</sup></i>	0.000	<i>O(1)<sup>a</sup></i>	0.000
<i>C(7)<sup>a</sup></i>	0.000	Cu	1.060
<i>N(8)<sup>a</sup></i>	0.000		

<sup>a</sup>Coordinates from Table II are transformed by  $1 - x$ ,  $1 - y$ ,  $1 - z$ .

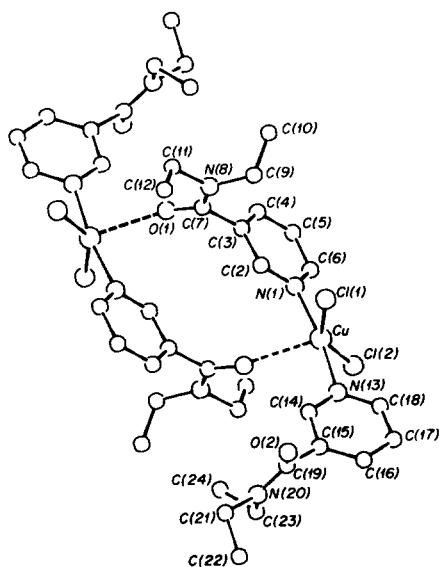


Fig. 1. Perspective view of the non-hydrogen atoms of the dimer **1** showing the numbering scheme.

(displaced 0.063 and 0.254 Å, respectively) but lies 1.060 Å out of the plane defined by C(3), C(7), N(8) and O(1). Also, the copper is slightly displaced (0.025 Å) toward N(1) from the plane defined by the chlorine atoms and the amide oxygen atom.

Though in square pyramidal copper(II) complexes the Cu–O(apical) bonds are generally longer than the Cu–O(eq) bonds, e.g. 2.200 Å (av.) vs. 1.979 Å (av.) for carboxyl oxygens in  $Cu_4(OH)_2(CF_3CO_2)_6(quinoline)_4$  [14], the Cu···O separation in **1** is extremely long, 2.475(3) Å, indicative of a weak interaction. This distance is even longer than the apical Cu···O (carboxyl) separation of 2.351 Å

holding together chelate molecules of the product of reaction of formaldehyde with bis(serinato)-copper(II) [15]. It is however, similar to one of the Cu···O separations (2.45 Å) found in bis(bipyridyl)copper(II) perchlorate, where perchlorate ions link metal centers [16]. However, a Cu···O = C-bridge interaction is evident in the ir spectrum (see below).

The most interesting fact about structure **1** is that it has dimerized using bridging DENC ligands. This ligand has been observed to act in this capacity in two other crystallographically studied complexes but in each instance the metals being bridged are zinc– $Zn_2(DENC)_2Cl_4$  (**2**) [5] and  $Zn_2(DENC)_2(NCS)_4$  (**3**) [17]. The zinc centers display nearly tetrahedral geometry in both **2** and **3**.

The molecular parameters of the two unique DENC ligands in **1** are remarkably similar, the only major difference being the torsion angle about the C(3)–C(7) bond. In the bridging DENC the C(2)–C(3)–C(7)–O(1) angle is very large,  $-108.7(4)^\circ$ ; in the terminal DENC it is significantly smaller but still large,  $-97.9(5)^\circ$ . In the Zn dimers the C(2)–C(3)–C(7)–O(1) angles are much smaller,  $74.6^\circ$  (**2**) and  $82.8^\circ$  (**3**). This larger torsion angle in **1** leads to a greater separation between the N and O donor atoms in an individual bridging DENC ligand. The N···O separation in **1** is 4.54 Å compared to 4.35 Å in **2** [5] and 4.40 Å in **3** [17]. The separation in **1** corresponds more closely to that observed when the two coordinating sites of DENC contribute to different coordination spheres [18].

The large C(3)–C(7) torsion angle, combined with the weak Cu···O interaction, allows the centrosymmetrically related pyridine rings to lie quite far apart. The closest ring···ring approach in **1** is 3.68 Å, between C(2) atoms. This compares with a closest approach of 3.23 Å in **2** (between C(2) atoms) and of 3.37 Å in **3** (between N(1) and C(2)'). This also results in the intra-dimer coppers being 7.70 Å apart in **1**.

Except for the Cu···O separation, the bond lengths in the copper coordination sphere lie well within accepted values. The mean Cu–N bond length of 2.010 Å corresponds to Cu–N(ax) distances in similar complexes [19] and the Cu–Cl distances, 2.282(1) and 2.254(1) Å, correspond to those found in  $CuCl_4^{2-}$  ions. The N–Cu–Cl angles range from  $88.4(1)$ – $94.2(1)$  (mean  $91.0^\circ$ ), while the N–Cu–O angles are smaller,  $83.6(1)$  and  $88.6(1)^\circ$ . This distortion of the N(1)–Cu–N(13) angle ( $171.7(1)^\circ$ ) places N(1) and N(13) approximately equidistant from the chlorine atoms and the amide oxygen atom.

The packing is as discrete dimers with the shortest inter-dimer separations all involving the oxygen of the terminal DENC ligand.

We do not know why the molecular structures

of solid  $(\text{DENC})_2\text{CuCl}_2$  complexes depend on the crystallizing solvent, although the spectra discussed below indicate strong solvent structural effects on coordination of DENC ligands by copper(II). The carbonyl groups of *trans*-terminal DENC ligands in solid  $[(\text{DENC})_2\text{CuCl}_2]_3$  are actually oriented for bridge formation, but this does not occur in pure ethanol [6].

#### Spectral Properties of $[(\text{DENC})_2\text{CuX}_2]_2$ Complexes

Electronic and ir spectral characteristics of dimeric  $[(\text{DENC})\text{CuX}_2]_2$  ( $\text{X} = \text{Cl}$  and  $\text{Br}$ ) as solid samples and in various solvents are summarized in Table V and illustrated in Figs. 2 and 3.

Analysis of the X-ray data for the chloro complex leads to 5-coordinate copper(II) centers, each of which coordinates two terminal chloro ligands in a DENC-bridged, solid dimeric structure (Fig. 1). The Nujol mull visible spectrum of the solid has a single, broad absorption maximum at 700 nm (Fig. 2). The existence of bridging and terminal DENC ligands in the solid chloro complex leads to splitting of  $\nu_{\text{C}=\text{O}}$  into two components, the one at lower energy ( $1610\text{ cm}^{-1}$ ) corresponding to the effect of copper coordination on bridging carbonyl group stretching. Bands assigned to  $\nu_{\text{Cu}-\text{O}}$  and  $\nu_{\text{Cu}-\text{Cl}}$  are observed at 510 and  $370\text{ cm}^{-1}$ , respectively (Fig. 3).

On the other hand, the visible spectrum of the solid bromo complex  $(\text{DENC})_2\text{CuBr}_2$  consists of two bands, and the IR spectrum contains a single  $\nu_{\text{C}=\text{O}}$  band and no  $\nu_{\text{Cu}-\text{O}}$  band. We have recently concluded that at least 3 halides coordinated in 5-coordinate copper(II) geometries are necessary for the appearance of two maxima in the 700–1100 nm region [9]. For the complexes described here, this requirement can only be satisfied by a  $\mu,\mu$ -dihalobridged structure which is a trigonal bipyramid (see below).

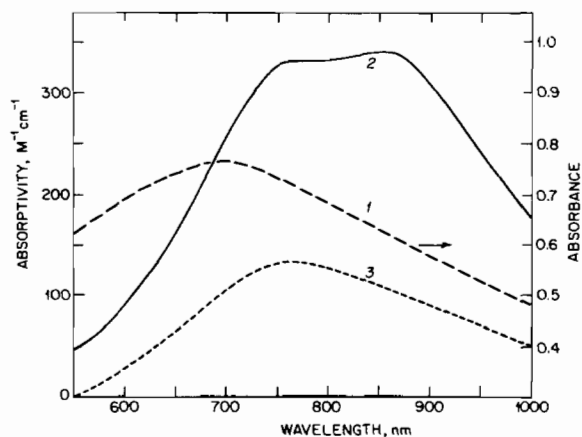


Fig. 2. Room temperature electronic spectra of  $[(\text{DENC})_2\text{CuCl}_2]_2$ : 1, (Nujol mull); 2, 4 (methylene chloride solution); 3, 6 in methylene chloride.

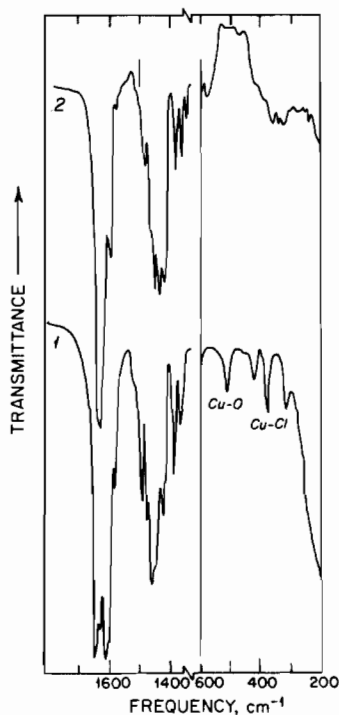


Fig. 3. Partial infra-red spectra of  $[(\text{DENC})_2\text{CuCl}_2]_2$ : 1, KBr disk; 2, methylene chloride solution.

Cryoscopic data (Experimental Section) indicate that dihalo-bis-(DENC)copper(II) species are dimeric in nitrobenzene. The electronic spectra of both complexes in methylene chloride and nitrobenzene contain two absorption bands (Table V and Fig. 2), corresponding to structure 4 (Scheme I). As found for the solid bromo complex, a single  $\nu_{\text{C}=\text{O}}$  band and no  $\nu_{\text{Cu}-\text{O}}$  band are observed in the IR spectra of methylene chloride solutions of both halo complexes (Fig. 3), indicating terminal DENC ligands and halo bridging in solution.

These dihalo-bis-(DENC)copper(II) complexes differ from the corresponding pyridine and ENCA complexes in being soluble in a wide range of solvents. The solutions have different spectra, those in water having only one absorption maximum which is very similar to that of monomeric  $(\text{DENC})_3\text{CuX}_2$  species (see below) obtained by treatment of  $(\text{DENC})_2\text{XCu}(\text{X},\text{X})\text{CuX}(\text{DENC})_2$ , 4, with excess DENC (Fig. 2). In methanol, the very broad absorption maximum is centered approximately midway between the discrete maxima in methylene chloride, but with much lower molar absorptivity. It could correspond to the presence of dihalo-bridged dimers but the two bands expected for structure 4 are not discernible and the absorptivity seems very low in comparison to absorptivities for other dimers with structure 4.

TABLE V. Electronic and Infrared Spectral Data for [(DENC)<sub>2</sub>CuX<sub>2</sub>]<sub>2</sub> Complexes (X = Cl or Br).

Complex	Solvent	Color	Band maxima, nm ( $\epsilon, M^{-1} cm^{-1}$ )	$\nu_{C=O}$	$\nu_{Cu-O}$
[(DENC) <sub>2</sub> CuCl <sub>2</sub> ] <sub>2</sub>	solid	blue	700	1640,1610	510
	CH <sub>2</sub> Cl <sub>2</sub>	green	775(328), 850(338)	1635	—
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	green	775(360), 850(370)		
	CH <sub>3</sub> OH	bluish green	830(180)		
	H <sub>2</sub> O <sup>a</sup>	blue	700(17)		
	CH <sub>2</sub> Cl <sub>2</sub> /DENC <sup>a</sup>	blue	760(125)		
[(DENC) <sub>2</sub> CuBr <sub>2</sub> ] <sub>2</sub>	solid	green	700, 850(sh)	1630	—
	CH <sub>2</sub> Cl <sub>2</sub>	brown	790(790), 850(845)	1630	—
	CH <sub>3</sub> OH	green	820(370)		
	H <sub>2</sub> O <sup>a</sup>	blue	765(18)		
	CH <sub>2</sub> Cl <sub>2</sub> /DENC <sup>a</sup>	green	750(330)		

<sup>a</sup>Monomeric copper(II) species are assumed in H<sub>2</sub>O and known to be predominant in CH<sub>2</sub>Cl<sub>2</sub> in the presence of excess DENC (Table VI and text).

### EPR Spectra

We have used EPR spectroscopy 1) to confirm the differences between [(DENC)<sub>2</sub>CuX<sub>2</sub>]<sub>2</sub> (X = Cl or Br) structures in the solid state, 2) to establish the dimeric structures of these complexes in methylene chloride at room and at liquid helium temperatures for comparison with the solids and 3) to confirm that the products of reaction of these dimers with excess DENC in methylene chloride solution are monomeric (DENC)<sub>3</sub>CuX<sub>2</sub> complexes. All the EPR data are collected in Table VI, particular spectra are shown in Fig. 4 and the geometrical conclusions we have drawn are shown in Scheme I.

The room temperature X-band EPR spectrum

of a powder sample of **1** is shown in Fig. 4a. Three signals are seen in the  $\Delta M_s = 1$  region which indicates an elongated rhombic symmetry of the *g*-tensor, Table VI, and can be taken to show that the ground state is  $d_{z^2}$  [20]. The geometry around each copper(II) ion is thus trigonal bipyramidal, as established by the molecular structure, Fig. 1. A half-field  $\Delta M_s = 2$  transition ( $g = 4.34$ ) is also observed, implying the presence of an exchange interaction between the two copper(II) centers of **1**. The EPR parameters of the powder spectrum of **1** are essentially temperature independent.

By contrast, we observe marked temperature dependences of the *g*-values, and hence copper(II)

TABLE VI. EPR Data<sup>a</sup>.

Complex	State	Temperature K	EPR Parameters								Ground state	
			$g_1$	$g_2$	$g_3$	$g_{11(A_{11})}^b$	$g_{\perp}$	$g_{av}$	$g(\Delta M_s = 2)$	<i>G</i>		<i>R</i>
[(DENC) <sub>2</sub> CuCl <sub>2</sub> ] <sub>2</sub>	solid	300	2.24	2.05	2.02			2.1	4.34		6.3	$d_z^2$
		11	2.31	1.95	1.90			2.05	4.64		7.2	$d_z^2$
	CH <sub>2</sub> Cl <sub>2</sub>	298	2.20	2.11	2.06			2.12	4.58		1.8	$d_z^2$
		27				2.31(150)	2.1	2.17	4.64	3.10		$d_{x^2-y^2}$
[(DENC) <sub>2</sub> CuBr <sub>2</sub> ] <sub>2</sub>	solid	300						2.06	4.33			$d_z^2$
		11						(165)				
	CH <sub>2</sub> Cl <sub>2</sub>	298						2.07	4.10			$d_z^2$
		27				2.32(85)	2.09	2.16	4.57	3.55		$d_{x^2-y^2}$
(DENC) <sub>3</sub> CuCl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	298	2.19	2.11	2.06			2.12			1.7	$d_z^2$
		11				2.34(168)	2.07	2.16		5.0		$d_{x^2-y^2}$
(DENC) <sub>3</sub> CuBr <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	298						2.02				$d_z^2$
		11				2.27(172)	2.06	2.13		4.5		$d_{x^2-y^2}$

<sup>a</sup>See reference 22 for parameter definitions. <sup>b</sup>Units are  $10^{-4} cm^{-1}$ .

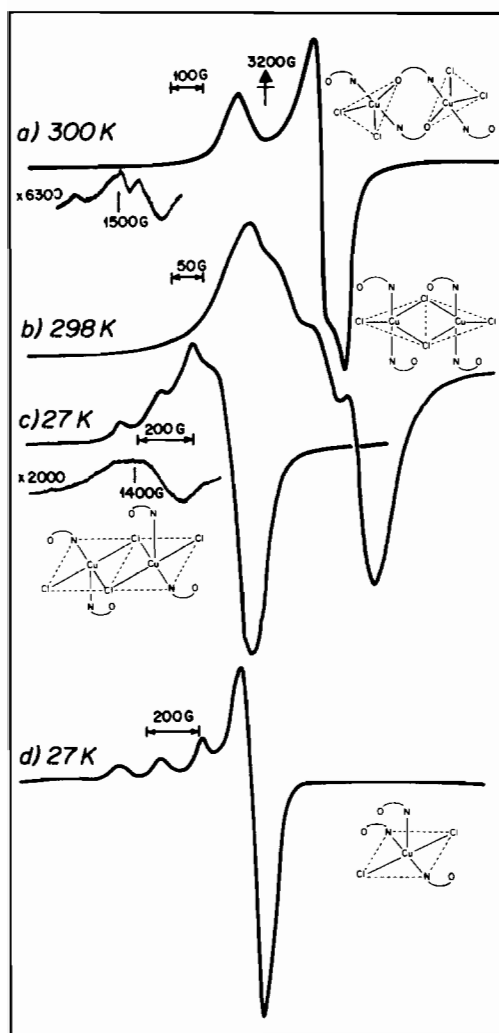


Fig. 4. EPR spectra. (a) 1, powder, 300 K; (b) 4, methylene chloride solution, 298 K; (c) 5, methylene chloride glass, 27 K; (d) 7, methylene chloride glass, 11 K.

geometries, for solutions of 1, of the bromo dimer and of monomeric  $(\text{DENC})_3\text{CuX}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) complexes in methylene chloride.

The room temperature spectrum of 1 in methylene chloride, Fig. 4b, is typical of elongated rhombic copper(II) complexes with  $d_{z^2}$  ground states, indicating trigonal bipyramidal geometry around each copper(II) center, structure 4. At 27 K we observe (Table VI and Fig. 4c) axial symmetry, with  $g_{11} > g_{\perp}$  ( $d_{x^2-y^2}$  ground state, square pyramidal geometry 5). A  $\Delta M_s = 2$  transition ( $g = 4.64$ ) is observed, demonstrating that there are two copper centers, each with an unpaired electron, and that the electrons are interacting to populate a triplet state with low zero field splitting. The presence of this EPR signal also indicates that the exchange interaction is not large enough to make the singlet state so

energetically favored as to leave the triplet state unpopulated [21].

The room temperature powder and methylene chloride solution spectra of dimeric  $[(\text{DENC})_2\text{CuBr}_2]_2$ , 4, as well as the solution spectrum of monomeric  $(\text{DENC})_3\text{CuBr}_2$ , 6, are nearly isotropic. As in other bromocopper(II) complexes [22], the breadth and shape of the EPR spectra are presumably due to dipolar broadening and enhanced spin lattice relaxation of the bromide ion. On the other hand, the EPR solution spectrum of  $[(\text{DENC})_2\text{CuBr}_2]_2$  at 27 K shows axial symmetry with a  $d_{x^2-y^2}$  ground state, indicating square pyramidal geometry around each copper(II) center, 5 ( $\text{X} = \text{Br}$ ).

Although the room temperature EPR spectrum of the product of reaction of 1 with excess DENC in methylene chloride is the result of rhombic symmetry with  $d_{z^2}$  ground state 6, the spectra of this product and of the corresponding bromo complex at 11 K exhibit axial symmetry. Four hyperfine lines are observed, with  $A_{11} \sim 170 \times 10^{-4} \text{ cm}^{-1}$ , indicative of an electron interacting with only one copper nucleus. Also, there are no observable  $\Delta M_s = 2$  transitions, which means that the products are monomeric, consistent with their simple absorption spectra (Fig. 2). Close examination of the EPR spectra reveals nitrogen hyperfine interactions (7 lines) in the perpendicular region (especially in the bromo complex) indicating that the product solutions contain  $[\text{CuN}_3\text{X}_2]$  chromophores. The effective axial symmetry of the electronic field, as well as the fact that the ground state of both complexes is  $d_{x^2-y^2}$ , shows that the copper(II) ion is in an environment with two *trans*-halogen atoms and two *trans*-nitrogen atoms coordinated in the basal plane [23]. Thus, the effective symmetry is appropriate to a square pyramid with the third pyridinic nitrogen of DENC occupying the apical site in 7. We note that the hyperfine coupling constants  $A_{11}$  in dimeric structures 5 are smaller than those of monomeric structures 7 (Table VI), because of spin delocalization over the bridging halide ligands. Delocalization in 5 is greater for  $\text{X} = \text{Br}$  than for  $\text{X} = \text{Cl}$ .

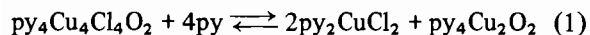
#### *Kinetics of Dissociation of $(\mu, \mu)$ -Dihalobridged Dimers 4 by Reaction with DENC in Methylene Chloride*

The two  $\mu_2$ -oxogroups in the symmetrical tetramers  $[(\text{DENC})\text{CuX}]_4\text{O}_2$  [1-3] are not required to hold the dimeric halves together because  $[(\text{DENC})\text{CuX}]_4\text{X}_4$  complexes, which contain the same  $[(\text{DENC})\text{CuX}]_4$  core but terminal halo ligands, are quite stable in aprotic solvents and can be stoichiometrically transmetalated with core structure retention [4]. On the other hand, the species that crystallize from methylene chloride containing  $\text{L} = \text{ENCA}$  or  $\text{py}$  and large excesses of  $\text{CuX}_2$  are  $\text{L}_2\text{CuX}_2$



species (Experimental Section), showing that such [LCuX]<sub>4</sub>X<sub>4</sub> tetramers are unstable under conditions in which [(DENC)CuX]<sub>4</sub>X<sub>4</sub> exist. In other words, [LCuX]<sub>4</sub>X<sub>4</sub> species, if they exist at all, have a high affinity for their respective ligands, whereas [(DENC)CuX]<sub>4</sub>X<sub>4</sub> do not.

The titration of py<sub>4</sub>Cu<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub> with py is quite straightforward in aprotic solvents, with  $K = 2.1 \times 10^8 \text{ M}^{-4}$  in methylene chloride at 25 °C in eqn. (1) [24]. However, the species [LCuX]<sub>4</sub>O<sub>2</sub>, L = ENCA and especially



DENC, need to be treated with large excesses of their respective ligands to bring about significant changes in their absorption spectra. Available evidence thus indicates that DENC is particularly effective in stabilizing tetrameric halocopper(II) structures.

We have first attempted to account for the individual steps of decomposition of [(DENC)CuX]<sub>4</sub>X<sub>4</sub> by excess DENC because such tetramers are constructed with only halobridges. Unfortunately, because the observed decreases in absorbance at the characteristic maxima [4] of the tetramers can result from both DENC coordination and Cu–X bond breaking, we have been unable to assign the data to discrete steps. However, at particular stages of the titrations the spectra approximate those of 4 (Fig. 2) and so we have investigated the kinetics of reaction of 4 with excess DENC in methylene chloride.

The EPR results presented earlier indicate that the overall reaction is given by eqn. (2).



At fixed temperature and wavelength, the disappearance of dimers 4 is strictly first-order in the presence of a large excess of DENC, and the observed first-order rate constant,  $k_{\text{obsd}}$ , is proportional to  $[\text{DENC}]^2$ , Fig. 5. The rate law is thus eqn. (3), with  $k = (7.1 \pm 0.5) \times 10^{-4}$  and  $(31 \pm 2)$

$$\text{rate} = \frac{-d[4]}{dt} = k[4][\text{DENC}]^2 \quad (3)$$

$\times 10^{-4} \text{ M}^{-2} \text{ sec}^{-1}$  for X = Cl and X = Br, respectively, in methylene chloride at 23 °C. A mechanism consisting of reactions (4) and (5) leads to rate law (6). Eqn. (6) reduces to eqn. (3) if  $K[\text{DENC}]^2 \lesssim 0.1$

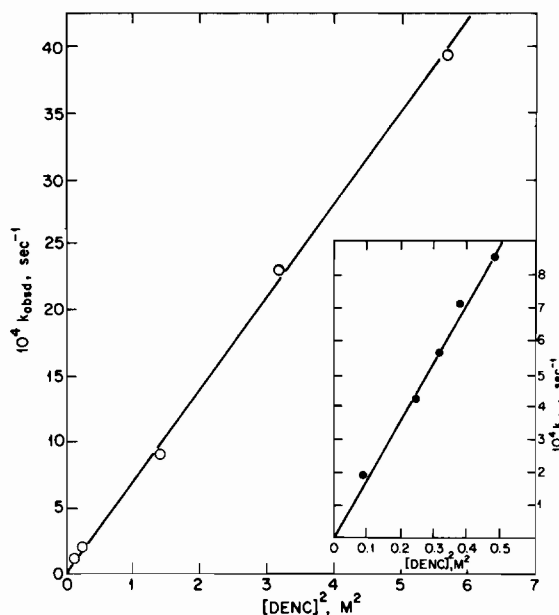
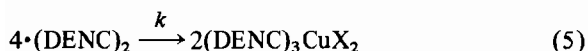
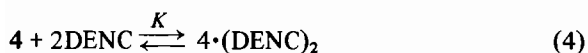


Fig. 5. Plots of  $k_{\text{obsd}}$  ( $\text{sec}^{-1}$ ) vs.  $[\text{DENC}]^2$  for reaction of 4 (o, X = Cl; •, X = Br) with DENC in methylene chloride at 23 °C.

$$\text{rate} = \frac{kK[4][\text{DENC}]^2}{1 + K[\text{DENC}]^2} \quad (6)$$

at the highest  $[\text{DENC}]^2$  employed, which gives  $K \lesssim 0.02 \text{ M}^{-1}$  and  $k \geq 3.5 \times 10^{-2} \text{ sec}^{-1}$  (X = Cl) and  $K \lesssim 0.2 \text{ M}^{-1}$  and  $k \geq 1.5 \times 10^{-2} \text{ sec}^{-1}$  (X = Br) in methylene chloride at 23 °C.

These data, especially when compared with the results of equilibrium (1), confirm that structures 4, L = DENC, have a low affinity for DENC.

#### Acknowledgements

This work was generously supported by Biomedical Research Support Grant RR07143 from the Department of Health and Human Services and Faculty Research and Development Grant 7590 from Northeastern University. A. E. thanks Alexandria University for study leave and the Egyptian Government for financial support. The National Science Foundation contributed towards the purchase of the diffractometer. Thanks are also extended to Dr. Mark Nelson and Professor David Wharton for experimental assistance in obtaining EPR spectra, and to Dr. Mohamed A. El-Sayed for useful discussions.

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