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The Crystal and Molecular Structure of Trimeric $[L_2CuCl_2]_3$, L = N,N-diethylnicotinamide

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The complex prepared with a 2:1 molar ratio of L = N,N-diethylnicotinamide to anhydrous copper(II) chloride has been crystallized from ethanol as the trimeric unit $[L_2CuCl_2]_3$. *The crystals are monoclinic, space group* $P2_1/c$ *with* a = *16.618(1),* b = *8.253(2),* c = *28.194(1)* Å, β = *117.3(4)°. The trimeric unit utilizes a crystallographic center of symmetry. Least squares refinement of the structure using 3692 independent intensities has yielded an R factor of 0.059. Each molecule consists of two five-coordinate and one six-coordinate copper center. The* μ,μ*-dichloro bridging system is asymmetric with a Cu···Cu separation of 3.686 Å. The Cu–N distances range from 2.004(4) to 2.027(4) Å and the Cu–Cl distances from 2.264(2) to 2.982(–) Å. The copper coordination spheres are compared to that in* (py_2CuCl_2).

Introduction

Copper(I) halides react with equimolar proportions of N,N-diethylnicotinamide, DENC, in aprotic solvents to form the tetranuclear complexes $[(DENC)CuX]_4$. A crystal structure determination [1] of the air-stable iodide has revealed a tetrameric, 'cubane' structure with molecular core dimensions closely similar to those of $[pyCuI]_4$ [2] and no significant interaction between the amido substituents and the copper(I) centers. The cryoscopic and spectral properties of the air-sensitive complexes $[(DENC)CuX]_4$, X = Cl or Br, are consistent with the same basic core structure [1].

Spectral and kinetic studies of the aprotic oxidation of $[(DENC)CuX]_4$ by dioxygen in the presence of excess DENC indicate that there is little, if any, tendency of the copper(I) centers to increase their 4-coordination or, as a result, to dissociate into dimers, eqns. 1 and 2.

$$[LCuX]_4 + 4L \longrightarrow [L_2CuX]_4 \quad (1)$$

$$[L_2CuX]_4 \longleftrightarrow 2L_4Cu_2X_2 \quad (2)$$

However, when L is ethylnicotinate, ENCA, or pyridine, py, and X = Cl, both reactions 1 and 2 can be established cryoscopically [3]. The species $[L_2CuX]_4$ contain 5-coordinate copper(I) centers. Their existence is favored by high total copper(I) concentrations, $[Cu^I]_T$, and highly polar solvents like nitrobenzene. The dimers $L_4Cu_2X_2$ presumably contain 4-coordinate copper centers linked by μ,μ-di-halo bridges [4]. By contrast, tetrameric $[LCuX]_4$ complexes exhibit little tendency towards dissociation to produce dimers [1, 3].

These results indicate that DENC is a particularly good stabilizer of $[LCuX]_4$ structures in that $[L_2CuX]_4$ formation is not necessary to stabilize tetrameric structures. Since there is no indication of significant interactions between the DENC substituents and the copper(I) centers and no tendency to coordinate additional DENC ligands [1, 3], this preferential stabilization must arise from ligand electronic effects [3].

As mentioned above, the core structures of $[(DENC)CuI]_4$ [1] and $[pyCuI]_4$ [2] are virtually superimposable, so subtle electronic ligand effects are not identifiable for this particular pair of complexes. However, such effects must exist in the tetrameric copper(I) complexes under consideration because despite the fact that reactions 3 (L = DENC or ENCA) have a common, second-order rate law there is a significant difference in the second-order rate constants [3].

$$[LCuCl]_4 + O_2 \longrightarrow [LCuCl]_4O_2 \quad (3)$$

The products in eqn. 3 are discrete, tetranuclear oxocopper(II) complexes, which also result from reactions 4 and 5, (L = ENCA or py) [3].

$$[L_2CuCl]_4 + O_2 \longrightarrow [LCuCl]_4O_2 + 4L \quad (4)$$

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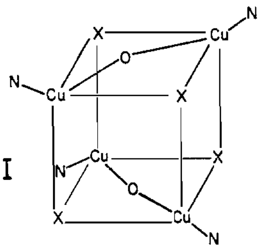
$$2L_4Cu_2Cl_2 + O_2 \longrightarrow [LCuCl]_4O_2 + 4L \qquad (5)$$

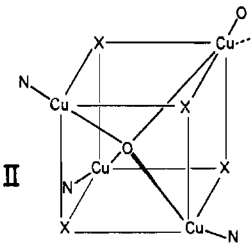
The 5-coordinate copper(II) centers in the products have little tendency to coordinate DENC or ENCA, that is the special stability conferred on copper(I) by DENC or ENCA is not so important for oxocopper(II) centers. Although the products $[LCuX]_4O_2$ do not appear to crystallize without disproportionation, we have concluded that they have structure I, with monodentate coordination of DENC or ENCA through their pyridine nitrogens and no significant interaction with their carbonyl substituents [3].

I



forms stable dicarbonate
L = ENCA
DENC

II



no reaction with CO_2
L = PY

Important ligand electronic effects are operating for pyridine ligand systems because reactions 4 and 5 with L = py give structure II, which now has a high affinity for py and undergoes reactions 6 and 7 [5].

$$[pyCuCl]_4O_2 + 4py \longleftrightarrow py_4Cu_2O_2 + 2py_2CuCl_2 \qquad (6)$$

$$2py_4Cu_2O_2 \xrightarrow{py} [py_mCu_2O_2]_2, \textit{etc.} \qquad (7)$$

We thus observe that coordinated pyridine ligands not only control the rate [3] of aprotic copper(I) halide oxidation by dioxygen but also determine the structure and properties of the product.

One of the driving forces for reaction (6) must be the stabilization achieved by coordination of pyridine at the 5-coordinate copper(II) centers of structure II. By contrast, the 5-coordinate centers of structure I are inert to coordination of DENC or ENCA.

Since it is apparent that electronic ligand effects are operating throughout we decided to examine the structural chemistry of the DENC-copper(II) chloride system via single-crystal x-ray diffraction in order to address the following questions:

(1) Does copper(II) chloride form a *bis*-DENC complex ?

(2) Does the structure of this complex differ significantly from that of py_2CuCl_2 [6]; specifically, are the amido substituents coordinated and do any structural differences arise from the different electronic properties of the coordinated ligands ?

Experimental

(a) Complex Preparation

Synthesis.

The complex $[(DENC)_2CuCl_2]_3$ was prepared by refluxing anhydrous copper(II) chloride (0.05 mol) with DENC (0.10 mol) in 100 ml of anhydrous ethanol. Although only a green powder formed on slowly cooling the product solution, pale blue crystals of dimensions suitable for structural characterization were formed in the closed system after 10 weeks at room temperature.

(b) Crystal Data

$C_{60}H_{84}Cl_6Cu_3N_{12}O_6$, M = 1472.7, monoclinic, a = 16.618(1), b = 8.253(2), c = 28.194(1), β = 117.3(4)°, U = 3436 Å^3, D_m = 1.38 g cm^{-3}, Z = 2, D_c = 1.423 g cm^{-3}, F(000) = 1530. Cu-Kα radiation (λ = 1.5418 Å), μ = 26.5 cm^{-1}. Space group $P2_1/c$ ($C_{2h}{}^5$) from systematic absences $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$.

(c) Intensity Data and Structure Solution

The cell dimensions were initially obtained from film data and later were refined by centering 15 high order reflexion on a Syntex $P2_1$ automated diffractometer. Three dimensional data were collected to θ = 65° using a variable speed, θ–2θ scan technique. Of the 5275 reflections collected, 3692 were considered observed ($I > 3.0\sigma(I)$) and to these were applied the usual Lorentz and polarization factors; an empirical absorption correction, determined from a ψ scan, was also applied.

Having no prior knowledge of the exact composition of the complex, the initial assumption made was that the unit cell would hold four molecules, one at each of the general positions. This approach yielded a poorly defined heavy atom position from the Patterson synthesis which, upon subsequent Fourier calculations, did not yield a chemically reasonable structure.

Next the possibility of a copper atom occupying a special position was explored. The three dimensional Fourier synthesis based on the phases calculated with a copper atom at 000 (Wyckoff position a) allowed elaboration of the coordination sphere. Subsequent Fourier maps permitted location of all non-hydrogen atoms. Least squares refinement of positional and isotropic (subsequently anisotropic) thermal parameters of non-hydrogen atoms brought R to 0.073, at which time hydrogen atoms, at calculated positions and with assigned isotropic thermal parameters, were added to the structure factor calculation. Continued refinement of the non-hydrogen atoms brought the refinement to convergence at R = 0.059 [7].

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

Atom	x/*a*	y/*b*	z/*c*
Cu(1)	0(–)	0(–)	0(–)
Cu(2)	–1291.3(4)	477(1)	760.8(3)
Cl(1)	–1296(1)	–1267(1)	–88.3(4)
Cl(2)	1(1)	1875(2)	904.5(4)
Cl(3)	–2534(1)	–664(2)	757(1)
N(1)	–789(2)	1693(5)	–526(1)
C(2)	–1420(3)	1265(5)	–1010(2)
C(3)	–2031(3)	2329(6)	–1366(2)
C(4)	–1969(4)	3967(6)	–1211(2)
C(5)	–1324(4)	4400(6)	–717(2)
C(6)	–734(3)	3249(6)	–380(2)
C(7)	–2732(3)	1917(6)	–1928(2)
N(8)	–3256(3)	598(5)	–2005(1)
C(9)	–3961(4)	287(7)	–2554(2)
C(10)	–4832(4)	1206(9)	–2692(2)
C(11)	–3302(3)	–361(7)	–1588(2)
C(12)	–2922(4)	–2062(7)	–1549(3)
O(13)	–2786(3)	2789(5)	–2294(1)
N(14)	–512(3)	–1117(5)	1320(2)
C(15)	–36(3)	–625(6)	1828(2)
C(16)	535(3)	–1652(6)	2229(2)
C(17)	612(3)	–3257(6)	2096(2)
C(18)	119(4)	–3761(7)	1581(2)
C(19)	–434(3)	–2655(6)	1195(2)
C(20)	1052(3)	–1188(6)	2806(2)
N(21)	1628(3)	79(5)	2940(2)
C(22)	2187(4)	382(7)	3512(2)
C(23)	2987(4)	–752(11)	3755(3)
C(24)	1863(3)	993(7)	2582(2)
C(25)	–1531(4)	–2271(8)	2503(3)
O(26)	945(3)	–1985(5)	3139(1)
N(27)	–2079(3)	2229(5)	259(1)
C(28)	–2834(3)	1831(6)	–182(2)
C(29)	–3452(3)	2984(6)	–503(2)
C(30)	–3270(4)	4600(7)	–371(2)
C(31)	–2503(4)	5021(7)	77(2)
C(32)	–1909(4)	3812(6)	387(2)
C(33)	–4290(4)	2533(8)	–1002(2)
N(34)	–4921(3)	1695(8)	–945(2)
C(35)	–4918(4)	1398(9)	–430(2)
C(36)	–5231(6)	2816(11)	–212(3)
C(37)	–5783(6)	1311(12)	–1415(3)
C(38)	–5863(7)	–378(14)	–1530(4)
O(39)	–4370(3)	2990(6)	–1431(2)

Atomic scattering factors for all atoms except hydrogen were from reference 8, those for hydrogen were from reference 9. Atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms are given in Tables I and II. Tables of hydrogen atomic positions and isotropic thermal parameters, of observed and calculated structure factors, and of torsion angles may be obtained from the Authors.

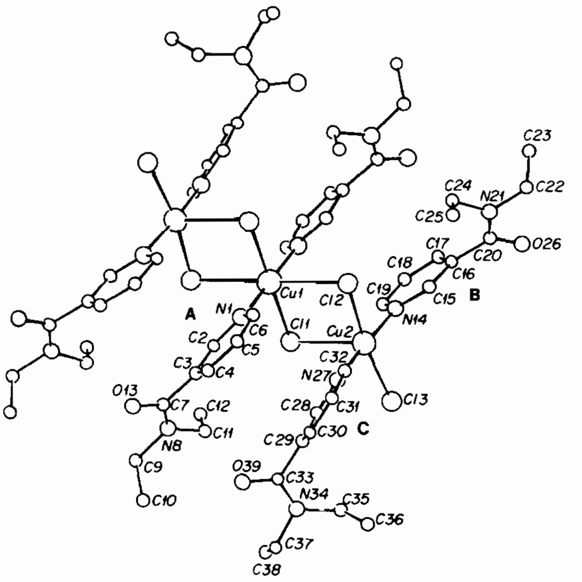


Fig. 1. Perspective view of the non-hydrogen atoms of the trimer showing the numbering scheme.

Results and Discussion

The results of the X-ray diffraction study show that DENC forms a *bis*-complex with copper(II) chloride and that this complex consists of discrete trimeric $[(DENC)_2CuCl_2]_3$ units (*1*) in which Cu(1) lies on an inversion center. Each pair of copper atoms is asymmetrically linked by di(μ-chloro) bridges and each copper coordinates two DENC ligands. A view of a single trimer is shown in Fig. 1 and a projection of the unit cell contents in Fig. 2. Bond distances and angles for the inner coordination spheres of the copper atoms are listed in Table III and bond distances and intramolecular angles of the DENC ligands are in Table IV.

Figure 1 shows the trimer to possess two distinctly different environments for its copper atoms. The central copper atom, which lies on an inversion center, adopts a distorted octahedral geometry. This distortion is of a Jahn–Teller nature and results in a *trans* planar array of two Cu–N(pyridine) and two Cu–Cl bonds of normal length (2.021 and 2.301 Å, respectively) and long, *trans* Cu–Cl bonds (2.982 Å). The former Cu–Cl lengths correspond well to lengths observed in di(μ-chloro) copper(II) complexes [10]. The 2.982 Å bond also lies within the range of previously observed lengths [10].

This coordination sphere is quite similar to that observed for py_2CuCl_2 [6], *2*, in which two Cu–Cl and two Cu–N bonds form a *trans*-square planar array and two weaker Cu–Cl interactions normal to this plane complete a distorted octahedron. The Cu–N, Cu–Cl (equatorial) and Cu•••Cl (axial)

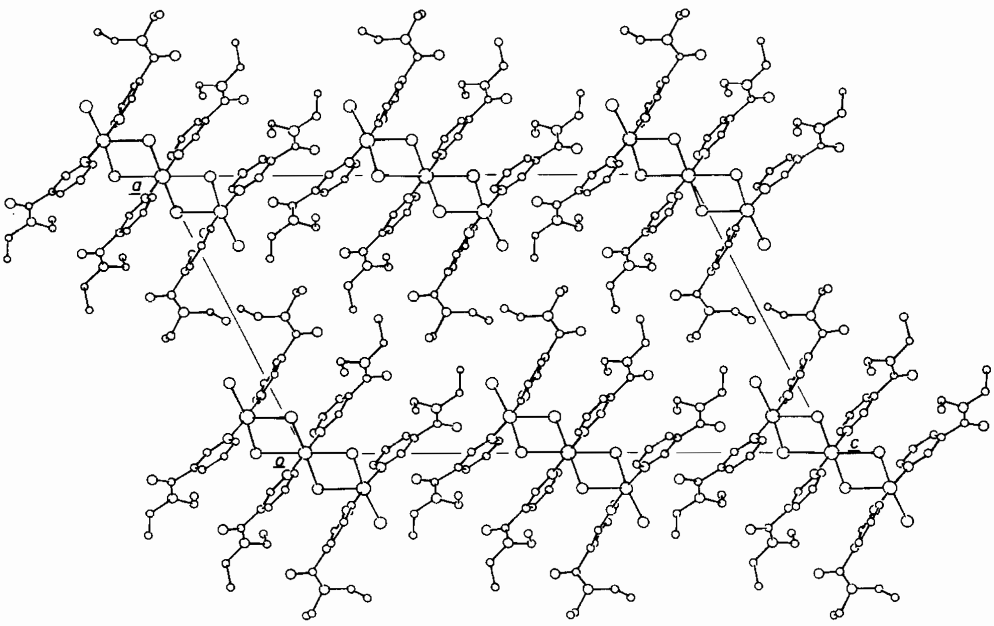


Fig. 2. A projection of the unit cell contents as viewed along the crystallographic *b* axis.

TABLE II. Anisotropic Temperature Factor Parameters* (×10^4) for the Non-Hydrogen Atoms, with Estimated Standard Deviations in Parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	306(4)	328(5)	429(3)	–29(4)	27(3)	104(4)
Cu(2)	372(3)	402(4)	439(3)	15(3)	83(3)	95(3)
Cl(1)	359(4)	361(6)	404(3)	–53(5)	90(4)	17(4)
Cl(2)	394(6)	387(6)	490(6)	–22(5)	131(4)	15(5)
Cl(3)	472(7)	750(9)	773(6)	11(7)	219(5)	308(6)
N(1)	307(17)	311(19)	426(16)	–21(16)	73(13)	42(16)
C(2)	355(21)	303(22)	436(19)	–11(19)	94(15)	19(18)
C(3)	373(21)	378(24)	436(19)	12(20)	106(15)	89(19)
C(4)	534(27)	353(25)	560(25)	59(23)	119(20)	97(23)
C(5)	566(28)	248(24)	655(29)	28(22)	102(22)	–8(22)
C(6)	476(25)	402(26)	439(22)	–14(23)	57(19)	29(21)
C(7)	404(23)	444(27)	448(22)	82(21)	61(18)	50(21)
N(8)	371(19)	424(22)	388(16)	26(18)	49(14)	–39(17)
C(9)	432(25)	664(33)	474(25)	58(26)	0(20)	–189(24)
C(10)	505(30)	923(44)	630(32)	228(31)	32(24)	–114(33)
C(11)	391(23)	471(27)	541(22)	3(23)	103(18)	45(23)
C(12)	589(33)	452(31)	830(35)	–70(27)	74(27)	7(29)
O(13)	728(24)	744(26)	439(16)	–90(21)	41(16)	214(18)
N(14)	403(19)	405(21)	467(19)	–25(18)	122(14)	81(17)
C(15)	483(23)	368(26)	477(19)	53(20)	193(15)	13(19)
C(16)	423(21)	356(24)	420(19)	–7(20)	159(14)	22(18)
C(17)	536(25)	387(26)	487(22)	0(22)	155(18)	48(20)
C(18)	625(28)	456(29)	557(22)	–72(25)	196(20)	–34(23)
C(19)	488(24)	343(24)	442(19)	–26(21)	92(17)	42(20)
C(20)	485(23)	429(26)	429(19)	58(22)	157(16)	64(20)
N(21)	435(19)	465(23)	420(16)	–21(18)	144(13)	–40(17)
C(22)	665(31)	592(33)	474(22)	–76(28)	146(21)	–103(24)
C(23)	576(33)	1162(56)	614(32)	75(38)	91(25)	–66(38)

(continued on facing page)

TABLE II. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(24)	528(24)	477(29)	598(22)	−28(24)	249(17)	−26(23)
C(25)	723(32)	478(32)	938(32)	−89(28)	366(23)	−139(28)
O(26)	750(21)	557(22)	448(16)	−92(19)	209(13)	79(16)
N(27)	389(19)	408(22)	433(16)	5(17)	109(13)	14(17)
C(28)	420(23)	472(27)	439(22)	6(22)	94(17)	28(21)
C(29)	503(24)	487(28)	404(19)	14(22)	149(16)	72(20)
C(30)	643(31)	505(31)	677(29)	119(27)	202(22)	159(26)
C(31)	567(29)	398(29)	763(32)	74(24)	195(23)	64(25)
C(32)	528(27)	403(27)	626(25)	−15(23)	179(20)	−96(23)
C(33)	580(28)	668(34)	429(22)	129(27)	125(19)	123(24)
N(34)	579(28)	1078(41)	487(22)	−211(29)	−3(21)	136(27)
C(35)	675(34)	951(47)	614(29)	−71(36)	170(24)	90(33)
C(36)	1252(49)	969(57)	1355(48)	102(45)	717(34)	−189(45)
C(37)	850(48)	1227(64)	649(38)	−237(48)	−116(37)	−44(45)
C(38)	1436(69)	1511(75)	1008(45)	−294(64)	433(43)	−618(46)
O(39)	8326(27)	980(32)	458(16)	−27(25)	129(15)	203(20)

*In the form: $B\sin^2\theta/\lambda^2 = 2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

TABLE III. Internuclear Distances (Å) and Angles (Deg.) in the Coordination Spheres, with Estimated Standard Deviations in Parentheses.

a) Bond lengths			
Cu(1)–Cl(1)	2.302(–)	Cu(2)–Cl(2)	2.304(1)
Cu(1)–Cl(2)	2.982(–)	Cu(2)–Cl(3)	2.264(2)
Cu(1)–N(1)	2.021(–)	Cu(2)–N(14)	2.004(4)
Cu(2)–Cl(1)	2.790(1)	Cu(2)–N(27)	2.027(4)
b) Valency angles			
Cl(1)–Cu(1)–Cl(2)	87.8(–)	Cl(2)–Cu(2)–N(14)	88.6(1)
Cl(1)–Cu(1)–N(1)	88.6(–)	Cl(2)–Cu(2)–N(27)	91.0(1)
Cl(2)–Cu(1)–N(1)	90.8(–)	Cl(3)–Cu(2)–N(14)	89.5(1)
Cl(1)–Cu(2)–Cl(2)	92.56(5)	Cl(3)–Cu(2)–N(27)	89.8(1)
Cl(1)–Cu(2)–Cl(3)	97.92(5)	N(14)–Cu(2)–N(27)	174.0(2)
Cl(1)–Cu(2)–N(14)	94.7(1)	Cu(1)–Cl(1)–Cu(2)	92.2(–)
Cl(1)–Cu(2)–N(27)	91.3(1)	Cu(1)–Cl(2)–Cu(2)	87.4(–)
Cl(2)–Cu(2)–Cl(3)	169.5(1)		

TABLE IV. Internuclear Distances (Å) and Valency Angles (Deg.) of the DENC Ligands, with Estimated Standard Deviations in Parentheses.

	A	B	C
a) Bond lengths			
N(1)–C(2)	1.333(6)	1.343(6)	1.340(7)
N(1)–C(6)	1.339(6)	1.339(7)	1.351(7)
C(2)–C(3)	1.369(7)	1.383(7)	1.389(7)
C(3)–C(4)	1.410(7)	1.398(7)	1.380(8)
C(3)–C(7)	1.514(7)	1.499(7)	1.503(8)
C(4)–C(5)	1.359(8)	1.366(8)	1.366(9)

(continued overleaf)

TABLE IV. *(continued)*

	A	B	C
C(5)–C(6)	1.382(8)	1.394(8)	1.394(8)
C(7)–N(8)	1.348(7)	1.349(7)	1.326(9)
C(7)–O(13)	1.226(7)	1.225(6)	1.215(7)
N(8)–C(9)	1.473(7)	1.467(7)	1.470(9)
N(8)–C(11)	1.447(7)	1.450(7)	1.471(10)
C(9)–C(10)	1.519(9)	1.509(10)	1.520(12)
C(11)–C(12)	1.522(8)	1.514(9)	1.424(15)
b) Valency angles			
Cu–N(1)–C(2)	120.6(–)	119.5(3)	120.2(3)
Cu–N(1)–C(6)	120.6(–)	121.4(3)	120.9(4)
C(2)–N(1)–C(6)	118.6(4)	119.1(4)	118.5(5)
N(1)–C(2)–C(3)	123.5(4)	122.3(4)	122.3(5)
C(2)–C(3)–C(4)	117.6(5)	118.4(4)	118.8(5)
C(2)–C(3)–C(7)	125.4(4)	124.6(4)	122.1(5)
C(4)–C(3)–C(7)	116.9(4)	117.0(4)	119.1(5)
C(3)–C(4)–C(5)	118.8(5)	119.3(5)	119.4(5)
C(4)–C(5)–C(6)	120.0(5)	119.3(5)	119.3(5)
N(1)–C(6)–C(5)	121.5(5)	121.7(5)	121.6(5)
C(3)–C(7)–N(8)	118.6(4)	118.8(4)	117.4(5)
C(3)–C(7)–O(13)	118.2(5)	118.8(5)	119.1(5)
N(8)–C(7)–O(13)	123.2(5)	122.3(5)	123.4(6)
C(7)–N(8)–C(9)	116.9(4)	116.8(4)	124.1(5)
C(7)–N(8)–C(11)	125.6(4)	126.2(4)	120.1(6)
C(9)–N(8)–C(11)	116.4(4)	116.1(4)	114.4(6)
N(8)–C(9)–C(10)	112.8(5)	112.0(5)	115.1(7)
N(8)–C(11)–C(12)	112.9(5)	114.0(5)	111.5(8)

separations in *2* are 2.02, 2.28 and 3.05 Å, respectively [6].

In the trimer, *1*, the geometry about the five coordinate Cu(2) is best described as a slightly distorted tetragonal pyramid. The basal plane consists of Cl(2), Cl(3), N(14), and N(27) and the apical site is occupied by Cl(1). The angles Cl(1) makes with atoms in the basal plane are all greater than 90°, ranging from 91.3 to 97.9°. This distortion is also manifest in the Cl(2)–Cu(2)–Cl(3) and N(14)–Cu(2)–N(27) angles which are less than 180° (169.5 and 174.0°, respectively). The basal plane atoms show little deviation from the best least squares plane through them, ±0.05 Å, and Cu is displaced only slightly toward the apical chloride, 0.16 Å. The axial and equatorial Cu–Cl distances differ considerably; those in the basal plane are 2.264(4) and 2.304(4) Å with the former involving the terminal chloride and the latter being part of a μ-chloro bridge. The dimer di(μ-chloro)-*bis*[chloro*bis*(4-methyloxazole)copper(II)] also contains different basal plane Cu–Cl distances (2.272(1), 2.381(1) Å) for a distorted tetragonal pyramidal geometry [11a]. Here, too, the bond to the bridging chloride is longer than that to the terminal chloride. In contrast to this, di(μ-chloro)-*bis*[chloro-(N,N,N′-triethylethylenediamine)copper(II)] [10] displays a terminal Cu–Cl bond which is *longer* than the Cu–Cl bond in the bridge (2.307(1) and 2.284(1) Å, respectively). In *1* the axial Cu–Cl bond, which is also involved in a μ-chloro bridge, is 2.790(1) Å, much longer than either of the others in this coordination sphere but significantly shorter than the axially elongated bond in the octahedral coordination sphere of Cu(1).

The chloride bridges are asymmetrical and lead to a Cu···Cu separation of 3.686 Å; this value lies approximately mid-range for the Cu···Cu separation reported in di(μ-chloro) copper(II) dimers [10]. The Cu–Cl–Cu bridging angles are 92.2 and 87.4° with the latter being associated with the more asymmetrical of the bridges.

The geometrical and structural parameters of each DENC ligand are normal. The Cu–N distances observed [2.004(4), 2.021(–), 2.027(4) Å] are indistinguishable from those exhibited by pyridine-copper(II) complexes [12] and allow no distinction to be made between the electronic character of pyridine and that of DENC. The torsion angles about the C(3)–C(7), C(16)–C(20) and C(29)–C(33) bonds indicate the lack of interaction between the π electrons in the carbonyl group and those of the pyridine ring [C(4)–C(3)–C(7)–O(13) 45.7°, C(30)–C(29)–C(33)–O(39) 62.1°, C(17)–C(16)–C(20)–O(29) –53.9°]. This lack of interaction perhaps explains the pyridine-like Cu–N distances observed in *1*.

Why *1* crystallizes as discrete trimers and does not adopt an extended 4 plus 2 structure as observed for *2* is not obvious since the only difference between py_2CuCl_2 and $[(DENC)_2CuCl_2]_3$ is that the ligands in *1* are substituted pyridines. The isomorphous complexes di-μ-halo-*bis*[halobis(4-methyloxazole)copper-(II)] (halo = Cl [11a], Br [11b]) exists as discrete dimers but in these molecules steric factors associated with the C(4) methyl substitution of the oxazole dictate the lack of extended coordination. Were *1* to pack in an extended fashion the only change to the inner coordination sphere would be a lengthening of the Cu(2)–Cl(1) distance. The relative orientations of the DENC ligands would also require slight modification but this could be accomplished by small rotations about single bonds. This would seem to indicate that extended coordination of the copper-(II) centers does not represent a substantially lower energy packing arrangement than does the observed packing arrangement. There are no intermolecular separations less than the sums of van der Waals radii.

Subtle electronic differences between DENC and py as ligands for copper(II) chloride are not evident in the solid state, although it is again clear that the substituent in DENC is not coordinated. We conclude that ligand electronic effects are more obivous in halo–(oxo)copper(II) complexes than they are in common copper(II) halide species, although on the basis of the evidence presented we should not expect large differences in Cu–DENC and Cu–py bond distances with a given halide ligand for oxocopper-(II) centers.

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