Molecular Crystal Structure of Dichloro(*NNN'N'*-tetraethylethylenediamine)copper(II)

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The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray data collected by counter methods. Crystals are monoclinic, space group *C*2/*c*, with $Z = 4$ in a cell of dimensions: $a = 15{\cdot}302(9)$, $b = 7{\cdot}890(4)$, $c = 11{\cdot}645(8)$ Å, and $\beta = 90{\cdot}19(5)^\circ$. The structure was solved by heavy-atom methods, and refined by full-matrix least-squares to R 0·024 for 938 independent intensities. The copper atom lies on a C_2 axis, which also passes through the teen ligand. The complex is a four-co-ordinated monomer with distorted square-planar geometry at the copper atom, the plane being formed by the two nitrogen atoms from the teen ligand and the two chlorine atoms. The geometry at copper is entirely different from that in the analogous, but dimeric, tetramethylethylenediamine complex, the closest out-of-plane $Cu \cdots Cl$ approach being 5·2 Å and shortest $Cu \cdots Cu$ separation 5·8 Å.

EXTENSIVE correlations have been reported between the structures and magnetic properties of copper(II) dimers where the bridging atoms are oxygen, and the magnetic properties of these complexes have been shown to be largely determined by the bridging angle.[1] In order to extend these correlations to the more complicated case of the halogen-bridged dimers, the structural and magnetic properties of a variety of such systems have been investigated.[2-11]

It has been previously reported [12,13] that *NNN'N'*-tetramethylethylenediamine (tmen) and *NNN'N'*-tetraethylethylenediamine (teen) will react with equimolar amounts of copper(II) chloride and copper(II) bromide in methanol or ethanol to give complexes of formula [$CuLX_2$] (L = tmen or teen, X = Cl or Br).

The crystal structures of [$Cu(tmen)Br_2$] and [$Cu(tmen)Cl_2$] have been reported,[9,11] and both were found to be halogen-bridged dimers with relatively weak out-of-plane Cu–X interactions linking adjacent square-planar CuN_2X_2 chromophores. Presumably, the presence of the methyl groups prevents the formation of a six-co-ordinated chain structure as found [14,15] in the pyridine complexes [$Cu(py)_2X_2$]; a similar stereochemical effect has been observed [3,10] in the 2-methylpyridine complexes [$Cu(pic)_2X_2$], and it is noteworthy that in the 2,3-dimethylpyridine analogues the methyl groups prevent co-ordination from either side and a monomeric structure results.[16] Since it has been established that the in-plane dimers $[\{Cu(tmen)OH\}_2]^{2+}$ and $[\{Cu(teen)OH\}_2]^{2+}$ have similar structures,[17,18] we thought it likely that the structures of the complexes [$Cu(teen)X_2$] may be similar to those of [$Cu(tmen)X_2$] and, hence, be of utility in establishing a magneto-structural correlation. However, since the bulkier ethyl groups would provide greater steric hindrance to out-of- than to in-plane dimer formation, it was also possible that the teen complexes would be monomeric rather than dimeric. We have therefore undertaken a complete three-dimensional structural study of [$Cu(teen)Cl_2$]; the results are presented here.

EXPERIMENTAL

Bright blue crystals of [$Cu(teen)Cl_2$] were prepared by the method of ref. 19; in addition to the crystalline material, a quantity of light green powder was observed in the preparation.

Crystal Data.—$C_{10}H_{24}Cl_2CuN_2$, $M = 306{\cdot}8$, Monoclinic, $a = 15{\cdot}302(9)$, $b = 7{\cdot}890(4)$, $c = 11{\cdot}645(8)$ Å, $\beta = 90{\cdot}19(5)^\circ$, $D_c = 1{\cdot}450$, $Z = 4$, $D_m = 1{\cdot}45$, $U = 1406$ Å^3. Space group *C*2/*c* or *Cc*, the former choice being verified by the successful refinement. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 55{\cdot}0$ cm^{-1}.

Cell constants were determined by the least-squares method of Busing and Levy.[20] With $Z = 4$ the copper atoms and teen ligands are constrained to lie on a crystallographic inversion centre or a two-fold axis. For any reasonable ligand geometry, the two-fold axis is the only possibility.

Diffraction data were collected from a parallelepiped crystal mounted on a glass fibre roughly normal to the (001) planes, by use of a Picker automatic four-circle diffractometer with nickel-filtered Cu-K_α radiation. The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique and was judged acceptable.[21]

Intensity data were collected at a take-off angle of 1·0° by the θ—2θ scan technique at a scan rate of 1° min^{-1}. Peaks were scanned from 0·6° in 2θ below the calculated

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$K_{\alpha 1}$ peak position to 0·6° above the calculated $K_{\alpha 2}$ peak position. Stationary-counter–stationary-crystal background counts of 10 s were taken at the ends of each scan. Data were collected to 2θ 122°, 1216 independent intensities being recorded. The intensities of three standard reflections, monitored every 100 reflections, showed only the deviations from the mean predicted from counting statistics.

Data were processed by the method of Ibers.[22] After correction for background, the intensities were assigned standard deviations according to the formula: $\sigma(I) = [C + 0{\cdot}25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$, and p was chosen as 0·045. Values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption factors. Of the 1216 independent reflections, only 938, having $I > 3\sigma(I)$, were considered observed and were used in the refinement of the structure. Programs used are described in ref. 18.

Solution and Refinement.—The positions of the copper and chlorine atoms were determined from a three-dimensional Patterson function, and as expected the copper atom was found to lie on the two-fold axis. Two cycles of least-squares refinement were run on these positions. All least-squares refinements were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for copper, chlorine, and nitrogen were taken from ref. 23, for carbon from ref. 24, and for hydrogen from ref. 25. The effects of the anomalous dispersion of copper and chlorine were included,[26] the values of $\Delta f'$ and $\Delta f''$ being taken from ref. 27.

TABLE 1

Positional parameters

Atom	X	Y	Z
Cu	0·0	−0·01043(5)	0·25
Cl	0·08538(4)	0·18704(8)	0·16835(6)
N	0·0827(1)	0·2040(2)	−0·3017(2)
C(1)	0·0488(2)	0·3617(3)	−0·2486(2)
C(2)	0·0733(2)	0·2087(4)	−0·4296(2)
C(3)	0·1190(3)	0·3519(5)	−0·4926(3)
C(4)	0·1760(2)	0·1789(4)	−0·2680(3)
C(5)	0·1881(2)	0·1257(6)	−0·1450(3)
H(1A)	0·067(1)	0·368(3)	−0·174(2)
H(1B)	0·0703(2)	0·455(3)	−0·281(2)
H(2A)	−0·018(2)	0·211(3)	−0·066(2)
H(2B)	0·095(2)	0·109(4)	−0·459(2)
H(3A)	0·099(2)	0·463(5)	−0·468(3)
H(3B)	0·177(2)	0·355(4)	−0·478(3)
H(3C)	0·104(2)	0·338(4)	0·433(3)
H(4A)	0·204(2)	0·282(4)	−0·276(3)
H(4B)	0·199(2)	0·108(4)	−0·319(3)
H(5A)	0·165(2)	0·016(4)	−0·134(3)
H(5B)	0·163(3)	0·189(5)	−0·092(4)
H(5C)	0·247(2)	0·106(4)	−0·133(3)

A difference-Fourier synthesis revealed the positions of the remaining non-hydrogen atoms. The absorption correction was then applied, and four cycles of least-squares refinement with anisotropic thermal parameters assigned to all atoms yielded R 0·061 and R' 0·098. The twelve hydrogen atoms were located in a difference-Fourier map, and two further least-squares cycles were run in which non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters. This reduced R to 0·029, and R' to 0·038. An examination of the final values of $|F_o|$ and $|F_c|$ suggested that the data were suffering from secondary extinction since for strong low-order data $|F_o|$ was uniformly less than $|F_c|$, and a correction of the type described by Zachariasen [28] was applied. In the last cycle of least-squares refinement, the greatest shift in any parameter was 0·9σ, R was 0·024 and R' 0·033. A final difference-Fourier was featureless, with no peak $>$0·31 eA^{-3}. The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables 1 and 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21287 (8 pp., 1 microfiche).*

TABLE 2

Thermal parameters

(*a*) Anisotropic * (×10^4; for Cu and Cl ×10)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	330(3)	780(9)	526(5)	0	−5(2)	0
Cl	518(4)	1046(12)	913(7)	−152(5)	115(4)	93(6)
N	36(1)	97(3)	60(2)	−4(1)	3(1)	−2(2)
C(1)	55(1)	87(4)	55(2)	−17(2)	2(1)	−6(3)
C(2)	46(2)	122(5)	50(2)	−07(2)	4(1)	1(3)
C(3)	71(2)	173(6)	63(3)	−17(3)	5(2)	26(3)
C(4)	34(1)	166(6)	71(2)	−15(2)	0(1)	11(3)
C(5)	43(2)	259(8)	78(3)	−6(3)	−12(2)	25(4)

(*b*) Isotropic

	B		B		B
H(1A)	2·8(5)	H(3A)	6·9(10)	H(4B)	4·5(7)
H(1B)	3·8(6)	H(3B)	5·7(9)	H(5A)	6·0(9)
H(2A)	2·9(6)	H(3C)	5·8(8)	H(5B)	7·2(12)
H(2B)	3·8(6)	H(4A)	4·6(7)	H(5C)	6·6(9)

* In the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

DISCUSSION

The complex consists of monomeric four-co-ordinate units (Figure 1). The co-ordination around the Cu^{II} ion is roughly square-planar, although there is a small distortion towards tetrahedral geometry since two *trans*-atoms lie 0·14 Å above and the other pair 0·14 Å below the best least-squares plane through the five atoms.

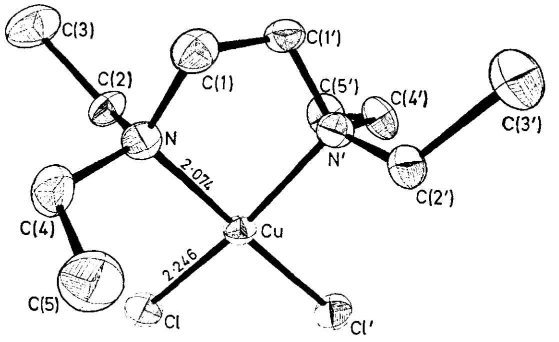

FIGURE 1 The co-ordination around the copper centres

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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Thus, while square-planar copper(II) complexes are relatively uncommon, this structure may be compared to those of bis[2-(2-aminoethyl)pyridine]copper(II) iodide,[29] bis[*p*-nitrophenylacetylglycine]copper(II),[30] and several other complexes.[31]

Intramolecular distances and angles, along with their estimated standard deviations, are presented in Tables 3 and 4. The Cu–Cl distance [2·246(1) Å] is normal as expected for such terminal bonds.[2,3,7-9] The Cu–N bond length [2·074(2) Å] is outside of the range [1·98(2)—2·04(1) Å] found in precise crystallographic measurements of a variety of complexes of formula $[Cu(en)_2X_2]$,[32,33] and is also longer than those found in most other copper–amine complexes;[17,18,34-36] it is, however, similar to the distances [2·054(4) and 2·081(3) Å] in the corresponding $[\{Cu(tmen)Cl_2\}_2]$ complex.[9] The bond lengths and angles associated with the teen ligand are as expected;[13,17,18] the presence of an inversion centre in the unit cell constrains half of the monomeric units in the cell to contain δ and half to contain λ rings.

TABLE 3

Intramolecular distances (Å)

Atoms		Atoms	
Cu–N	2·074(2)	C(2)–H(2A)	0·84(2)
Cu–Cl	2·246(1)	C(2)–H(2B)	0·92(3)
N–C(1)	1·484(3)	C(3)–H(3A)	0·97(4)
N–C(2)	1·496(4)	C(3)–H(3B)	0·91(4)
N–C(4)	1·494(3)	C(3)–H(3C)	0·90(4)
C(2)–C(3)	1·519(4)	C(4)–H(4A)	0·92(3)
C(4)–C(5)	1·503(5)	C(4)–H(4B)	0·89(3)
C(1)–C(1′)	1·493(6)	C(5)–H(5A)	0·94(4)
C(1)–H(1A)	0·92(3)	C(5)–H(5B)	0·88(5)
C(1)–H(1B)	0·89(3)	C(5)–H(5C)	0·93(4)

TABLE 4

Intramolecular angles (°)

N–Cu–N′	85·1(1)	C(1)–N–C(2)	111·2(2)
N–Cu–Cl	91·8(1)	C(2)–N–C(4)	110·7(2)
Cl–Cu–Cl′	92·2(1)	C(2)–N–Cu	104·5(2)
N–Cu–Cl′	171·8(1)	C(4)–N–Cu	114·2(2)
N–C(1)–C(1′)	110·0(2)	N–C(2)–C(3)	117·2(2)
C(1)–N–Cu	106·4(2)	N–C(4)–C(5)	113·7(2)
C(1)–N–C(4)	109·7(2)		

The closest Cu ··· Cu separation [5·825(4) Å] and the out-of-plane Cu–Cl distance [5·229(4) Å] are too long to allow any magnetic interaction through the chlorine atoms. Figure 2 shows a view of two unit cells viewed normal to the *ac*-plane. It is apparent from this Figure that the terminal carbon atoms of the ethyl groups (and their associated hydrogen atoms, which are not shown) effectively block approach of the out-of-plane chlorine atoms from either side. Thus, there is an intermolecular Cl ··· H(5C) interaction of 3·07 Å which is only slightly larger than the sum of the van der Waals radii of these atoms.[37] It appears, therefore, that while the presence of four methyl groups on the ethylenediamine ligands allows dimer formation,[9,11] the presence of four ethyl groups prevents it in complexes of this general type. Presumably, the wide variety of geometries observed for complexes $[CuLCl_2]$ where L is a bidentate ligand (or $[CuL_2Cl_2]$ where L is unidentate)[3,9-11,14-16,29,38-43] is largely the result of these stereochemical interactions.

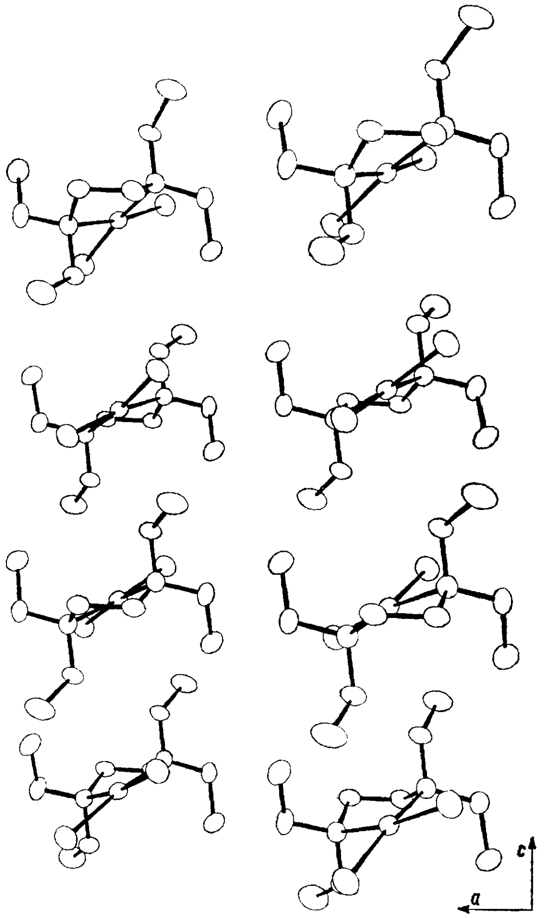

FIGURE 2 View of the crystal packing; molecules in the right-hand column are located near $y = \frac{1}{2}$, those on the left near $y = 0$

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