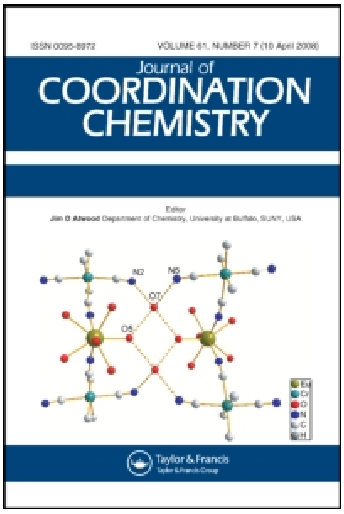

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The structure of di-µ-chloro-<i>bis</i>- {chloro(<i>N</i>,<i>N</i>-diethylethane-1,2-diamine-κ^2)copper(II)}

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The structure of di-μ-chloro-*bis*-{chloro(*N*,*N*-diethylethane-1,2-diamine-κ^2)copper(II)}

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Dichloro(*N*,*N*-diethyl-ethane-1,2-diamine)copper(II) has copper(II) ions in square pyramidal coordination. The two nitrogen atoms of the diamine {Cu–$N_{primary} = 1.979(3)$, Cu–$N_{tertiary} = 2.108(2)$ Å} and two chloride ions are in the basal plane {Cu–Cl1 = 2.2680(9), Cu–Cl2 = 2.2989(8) Å}. A centrosymmetrical dimer di-μ-chloro-*bis*{chloro(*N*,*N*-diethylethane-1,2-diamine-κ^2)copper(II)}, $C_6H1_6Cl_2CuN_2$, is formed by axial coordination by Cl2, *trans* to the tertiary nitrogen, to a second copper(II) ion, with $Cu \cdots Cu^i = 3.4855(9)$ and $Cl2–Cu^i = 2.7860(8)$ Å. The dimer is also linked by H-bond $N1–H \cdots Cl1^i$.

Keywords: Copper compound; Amine compound, *N*,*N*-diethyl-ethane-1,2-diamine; Dimeric compound; Dinuclear compound; Crystal structure

1. Introduction

Dihalide-mono(diamine) compounds of copper(II) can, in principle, exist with discrete [Cu(N-N)X_2] groups, with [Cu(N-N)$_2$][CuX_4] ionic structures, or with a variety of chloro-bridged structures.

The ethane-1,2-diamine compound [Cu(en)Cl_2]$_n$ has a structure with the two nitrogen atoms of the diamine and the two chloride ions in square-planar primary coordination [1]. These units are linked into stair-like chains by bridging by one of the chloride ions, with symmetrical tetragonal coordination of the copper(II). In contrast the compounds of *N*,*N*-dimethyl-ethane-1,2-diamine, [Cu(dmeen)Cl_2] and [Cu(dmeen)Br_2] [2], of *N*,*N*,*N*′-trimethyl-ethane-1,2-diamine, [Cu(tmeen)Cl_2], and *N*,*N*,*N*′-trimethyl-*N*′-iso-propyl-ethane-1,2-diamine, [Cu(itmeen)Cl_2] [3], crystallise as symmetrical dimers, with offset square planar Cu(N-N)Cl_2 units linked by weaker axial coordination by one of the halide ions.

A blue compound [Cu(deten)Cl_2] is formed by reaction of equimolar amounts of $CuCl_2$ and *N*,*N*-diethyl-ethane-1,2-diamine (3-ethyl-3-azapentane-1-amine, deten) [4]. The structure of this compound has been determined by X-ray diffraction, to see how the diethyl substituted tertiary amine group affects the structure adopted.

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Dinuclear, di-anion-bridged, structures are present for the *N*,*N*-diethyl-ethane-1,2-diamine compounds: $[Cu(deten)(N_3)_2]_2$ [5], $[Cu(deten)(NCO)_2]_2$ [6] and $[Cu(deten)(N_3)(NCO)]_2$ (with bridging azide ions) [7]. Oxalato-bridged dinuclear structures are present for $[Cu_2(deten)_2(\mu\text{-}C_2O_4)(H_2O)_2](ClO_4)_2$ and $[\{Cu_2(deten)_2(\mu\text{-}C_2O_4)(\mu\text{-}N_3)_2\}_n](ClO_4)_n$ (which has the oxalato-bridged dimers linked into a chain by bridging azide ions) [8] and with dicarboxalato-bridged structures for $[Cu(deten)(adipate)]_2$ [9] and $[Cu(deten)(succinate)]_2$ [10]. The only reported mono-nuclear structure of a mono-deten copper(II) compound is for $[Cu(deten)(NO_2)_2]$ [11]. Structures have been reported for $[Cu(deten)_2](BF_4)_2$ [12] and $[Cu(deten)_2(ReO_2)]Cl \cdot 3H_2O$ [13].

2. Results and discussion

2.1. *Structural study*

The structure of $[Cu(deten)Cl_2]$ has been determined by X-ray diffraction, see section 3.2 for crystallographic details.

The compound has copper(II) ions coordinated by the two nitrogen atoms of a deten chelate (which has an approximately symmetrical gauche conformation) and two chloride ions. Centrosymmetrical dimeric units are formed by bridging axial coordination by chloride ion Cl2 to a second copper(II) ion, Cu^i (symmetry operation $i = 1 - x,\ 1 - y,\ -z$i), see figure 1. The non-bridging chloride ion Cl1 is coordinated *trans* to the primary amine nitrogen atom N1 with the CuN_2Cl_2 group appreciably folded along the N1–Cu1–Cl1 axis. The Cu–N distance (see table 1) is appreciably shorter for the primary amine nitrogen atom N1 than for the tertiary amine nitrogen atom N3 while the Cu–Cl distances for the non-bridging chloride ion Cl1 is only marginally shorter than that for the bridging chloride ion Cl2, with a longer axial link $Cl2\text{–}Cu^i$. The dimer components are further linked by a hydrogen bond $[H1 \cdots Cl1^i = 2.62;\ N1 \cdots Cl1^i = 3.527(2)\,\text{Å},\ N1\text{–}H1A \cdots Cl1^i = 169^\circ]$ and the dimer units are linked into a chain (base vector 1 0 0) by a hydrogen bond

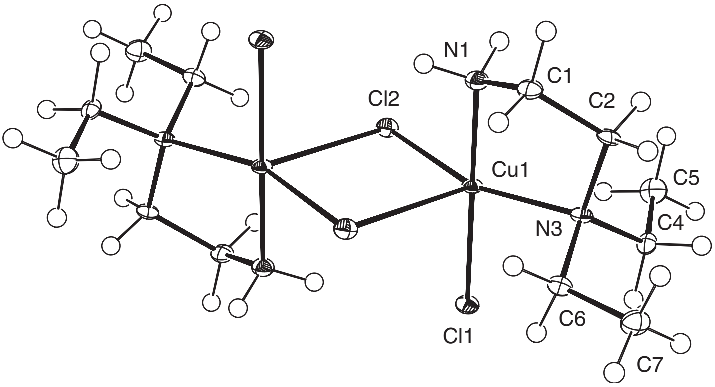

Figure 1. $[Cu(deten)Cl_2]_2$, drawn [14] at the 50% confidence level, with H-atoms shown as circles of arbitrary radii.

Table 1. Geometric parameters (Å, °) for [Cu(deten)Cl$_2$]$_2$.

Atoms	Parameter	Atoms	Parameter
Cu1–N1	1.979(3)	N1–Cu1–Cl2$^{\mathrm{i}}$	84.20(7)
Cu1–N3	2.108(2)	N3–Cu1–Cl1	93.92(7)
Cu1–Cl1	2.2680(9)	N3–Cu1–Cl2$^{\mathrm{i}}$	101.82(6)
Cu1–Cl2	2.2989(8)	N1–Cu1–Cl2	88.85(7)
Cu1–Cl2$^{\mathrm{i}}$	2.7860(8)	Cl1–Cu1–Cl2$^{\mathrm{i}}$	93.33(3)
Cu–Cu$^{\mathrm{i}}$	3.4855(9)	N3–Cu1–Cl2	161.83(6)
		Cl2–Cu1–Cl2$^{\mathrm{i}}$	94.02(2)
N1–Cu1–N3	84.0(1)	Cu1–Cl1–Cu1$^{\mathrm{i}}$	85.97(3)
Cl1–Cu1–Cl2	93.99(3)		
N1–Cu1–Cl1	176.37(6)		

Symmetry operation $\mathrm{i} = 1 - x,\ 1 - y,\ -z$.

Table 2. Comparison of dimensions of [Cu(diamine)Cl$_2$] compounds (Å, °).

Compound	Cu–N most subs.	Cu–N least subs.	Cu–Cl non-bridge	Cu–Cl bridge	Cu $\cdots$ Cl axial	Cu $\cdots$ Cu	N–Cu–N
[Cu(en)Cl$_2$]$_n$	2.010(5)	2.017(5)	2.286(2)	2.301(2)	2.887(2)	5.77	172.8(1)
[Cu(dmeen)Cl$_2$]	1.991(5)	2.074(6)	2.253(2)	2.309(2)	2.734(3)	3.458(3)	167.7(2)
[Cu(deten)Cl$_2$]	1.979(3)	2.108(2)	2.268(1)	2.299(1)	2.876(1)	3.486(1)	161.8(1)
[Cu(tmeen)Cl$_2$]	2.063(2)	2.008(2)	2.237(1)	2.288(1)	2.949(1)	3.549(1)	163.4(1)
[Cu(itmeen)Cl$_2$]	2.057(2)	2.089(2)	2.247(1)	2.253(1)	3.066(1)	4.002(1)	155.4(1)

[H1B $\cdots$ Cl1$^{\mathrm{ii}}$ = 2.63, N1 $\cdots$ Cl1$^{\mathrm{ii}}$ = 3.523(2) Å, N1–H1B $\cdots$ Cl1$^{\mathrm{ii}}$ = 165°; symmetry operation $\mathrm{ii} = 1 - x,\ 1 - y,\ -z$].

The compound [Cu(en)Cl$_2$]$_n$ has a square-planar primary coordination arrangement, with the square-planar units linked into chains by symmetrical axial bridging by one chloride ion [1]. Steric interactions by the substituent groups apparently prevent adoption of similar chain structures by the compounds of the N-substituted diamines [Cu(deten)Cl$_2$]$_2$, [Cu(dmeen)Cl$_2$]$_2$ (and [Cu(dmeen)Br$_2$]$_2$), [Cu(tmeen)Cl$_2$]$_2$ and [Cu(itmeen)Cl$_2$]$_2$, which have similar di-nuclear di-chloride-bridged structures, with the bridging chloride *trans* to the most substituted nitrogen. For these compounds the extent of nitrogen substitution has little effect on the in-plane Cu–Cl distances (see table 2). The mean Cu–N distances increase with increasing substitution in the sequence en < deen < deten < tmeen < itmeen, with the greatest difference between the values for the two nitrogen atoms for deten. The axial Cu–Cl and Cu $\cdots$ Cu distances and the extent of the folding of the primary coordination N$_2$Cl$_2$ group {along the N$_{\text{most substituted}}$–Cu–Cl$_{\text{bridging}}$} axis generally increase in the same sequence.

3. Experimental

3.1. *Preparation of compound [4]*

Ethanol solutions containing equimolar amounts of Cu(II)Cl2 and *N*,*N*-diethylethane-1,2-diamine, were mixed. The resulting blue crystals were filtered off and recrystallised from hot methanol. The crystal studied was grown by evaporation of a methanol solution.

3.2. *Crystallography*

Di-μ-chloro-*bis*{chloro(*N*,*N*-diethyl-ethane-1,2-diamine-κ^2)copper(II)} $C_{12}H_{32}Cl_4Cu_2N_4$, $M_r = 470.97$, $Z = 1$, triclinic, space group $P\bar{1}$, cell dimensions a, 6.105(1); b, 7.593(2); c, 11.183(2) Å; α, 94.687(3); β, 94.577(3); γ, 110.696(3)°; (cell parameters from 851 reflections at 98(2) K, θ, 2.9–26.3°).

Diffraction data was collected [14] for a block ($0.28 \times 0.26 \times 0.15\,\mathrm{mm}^3$) by using a Bruker SMART CCD diffractometer, with Mo-Kα radiation (fine focus sealed tube, graphite monochromator) at 98(2) K, with h, $-6 \rightarrow 7$; k, $-9 \rightarrow 9$; l, $-13 \rightarrow 10$; θ, $2.89 \rightarrow 26.3°$. 2084 Reflections were measured ($R_{\mathrm{int}} = 0.013$) with 1548 independent reflections and 1400 reflections with $I > 2\sigma(I)$. Absorption corrections (multi-scan [15]) were applied $T_{\min}/T_{\max} = 0.849$.

The structure was solved and refined on F^2 using SHELXTL [16], with H-atoms in calculated positions and riding. Final R_1 (all) = 0.0338, R_1 ($I > 2\sigma(I)$) = 0.0290, wR (all) = 0.0756, wR ($I > 2\sigma(I)$) = 0.0734; $\{w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.3893P]$ where $P = (F_o^2 + 2F_c^2)/3\}$.

Supplementary data

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre; CCDC 289568. Copies may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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