

Chloro(diethylenetriamine)copper(II) chloride: a disordered quasi-one-dimensional structure

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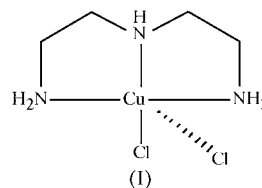
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The title structure, $[\text{CuCl}(\text{C}_4\text{H}_{13}\text{N}_3)]\text{Cl}$, consists of alternating $[\text{CuCl}(\text{dien})]^+$ (dien is diethylenetriamine) and Cl^- ions arranged in quasi-one-dimensional stacks along the crystallographic a axis and forming tetragonally elongated octahedral coordination shells around each Cu atom [equatorial $\text{Cu}-\text{Cl} = 2.2552(8)$ Å, and axial $\text{Cu}-\text{Cl} = 2.831(1)$ and $3.341(1)$ Å]. Crystallographic mirror planes bisect each stack vertically through the Cu, Cl and central N atoms, and horizontally through the $[\text{CuCl}(\text{dien})]^+$ cation. The horizontal mirrors lead to each atom in the puckered $[\text{CuCl}(\text{dien})]^+$ cations being disordered over two crystallographically equivalent sites. Comparison of the title structure with its Br and I analogues shows a growing influence of hydrogen bonding relative to coordination bonds on traversing the series $\text{I} < \text{Br} < \text{Cl}$.

Comment

The title structure, (I), is a member of an approximately isostructural series, the other members being $[\text{CuBr}(\text{dien})]\text{Br}$ (Boeyens *et al.*, 1991) and the polymeric polymorph of $[\text{CuI}_2(\text{dien})]_n$ (Hodgson *et al.*, 1991). The bromide and iodide crystal structures are almost identical, despite the bromide being described as ionic and the iodide as molecular. Both compounds crystallize in the orthorhombic space group $Pmn2_1$ [Br: $a = 8.716(1)$, $b = 8.588(1)$ and $c = 6.337(1)$ Å; I: $a = 8.873(2)$, $b = 8.890(3)$ and $c = 6.658(1)$ Å]. In both cases, alternating $[\text{CuX}(\text{dien})]$ and capping X form quasi-one-dimensional stacks along c , which are bisected vertically by crystallographic mirror planes through the Cu, X and central N atoms. In contrast, the Cl analogue crystallizes in orthorhombic space group $Pmmn$, with $a = 6.0925(4)$, $b = 8.6440(4)$ and $c = 8.3575(4)$ Å. However, resolution of the disorder clearly shows a chemically sensible $P2_1mn$ system (Fig. 1), isomorphous with the Br and I analogues, with an added mirror plane associated with the disordered $[\text{CuCl}(\text{dien})]^+$ group. The $\text{Cu}\cdots\text{Cu}$ separation along the stack corresponds to

the shortest lattice repeat and, along with the geometry around the bridging halide, shows a steady progression from I to Cl (Table 3).



The increasing asymmetry of the two capping $\text{Cu}\cdots X$ distances arises because an $\text{N}-\text{H}\cdots X$ hydrogen bond (Fig. 1 and Table 2) replaces one of the direct $\text{Cu}\cdots X$ interactions. Accompanying these changes, the flattened five-membered rings of the iodide relax to a more typical puckered envelope shape in the Br and Cl structures. This ring conformation, in which the CH_2 adjacent to NH represents the flap of the envelope, is also the norm for the dimeric cations $[\text{CuCl}(\text{dien})]_2^{2+}$ (Draper *et al.*, 2004; Urriaga *et al.*, 1996; Utz *et al.*, 2003) and is even retained when additional capping ligands interact with the Cu atoms, *e.g.* H_2O (Willett, 2001; Zhu *et al.*, 2003) and ClO_4^- in the Br analogue (Towle *et al.*, 1985). Ironically, this is also the conformation seen in the monomeric polymorph of $\text{CuI}_2(\text{dien})$ (Hodgson *et al.*, 1991).

The nature of the disorder is not clear from the current work. Weak interstitial reflections suggest that the determination may well be a subcell. However, attempts at working with larger and lower-symmetry unit cells did not reduce the disorder, and neither did refining the crystals as pseudo-tetragonal twins. It is also unclear whether the disorder is static or dynamic. The asymmetry introduced by the $\text{Cu}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{Cl}$ interactions suggests a static system. However, it is worth noting that the direction of the central NH bond does not, in the case of the above dimeric cations, dictate on

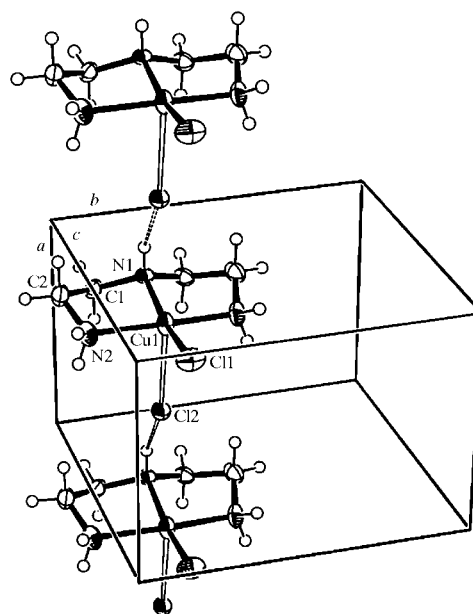


Figure 1

A view of the $[\text{CuCl}(\text{dien})]\text{Cl}$ stack in (I), with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

which side of the $[\text{CuCl}(\text{dien})]^+$ system the capping halide approaches the Cu atom. It is therefore possible to envisage the capping halide hopping from Cu to Cu with minimal conformational disturbance, so that at least part of the disorder may be dynamic.

Experimental

Crystals suitable for crystallographic study were prepared by mixing equal volumes of 0.02 M methanol solutions of CuCl_2 and dien. The resulting solution was then subjected to vapour diffusion using diethyl ether as the anti-solvent.

Crystal data

$[\text{CuCl}(\text{C}_4\text{H}_{13}\text{N}_3)]\text{Cl}$	$Z = 2$
$M_r = 237.61$	$D_x = 1.793 \text{ Mg m}^{-3}$
Orthorhombic, $Pmmm$	Mo $K\alpha$ radiation
$a = 6.0925(4) \text{ \AA}$	$\mu = 3.02 \text{ mm}^{-1}$
$b = 8.6440(4) \text{ \AA}$	$T = 133(2) \text{ K}$
$c = 8.3575(4) \text{ \AA}$	Plate, blue
$V = 440.14(4) \text{ \AA}^3$	$0.25 \times 0.25 \times 0.05 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	1086 measured reflections
φ and ω scans	579 independent reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	576 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.519$, $T_{\max} = 0.864$	$R_{\text{int}} = 0.023$
	$\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.2888P]$
$R[F^2 > 2\sigma(F^2)] = 0.03$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.21$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
579 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
77 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
All H-atom parameters refined	Extinction coefficient: 0.045 (5)

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—N1	1.459 (3)	N1—Cu1	2.014 (3)
C1—C2	1.523 (4)	N2—Cu1	2.016 (2)
C2—N2	1.489 (4)	Cl1—Cu1	2.2552 (8)
N1—C1—C2	106.75 (19)	C2—N2—Cu1	109.86 (16)
N2—C2—C1	106.6 (2)	N1—Cu1—N2	83.76 (7)
C1—N1—Cu1	108.27 (14)		
Cu1—N2—C2—C1	35.6 (3)	C1—N1—Cu1—N2	-21.3 (2)
N2—C2—C1—N1	-53.7 (3)	N1—Cu1—N2—C2	-8.8 (2)
C2—C1—N1—Cu1	46.2 (2)		

The final refinement was carried out in the space group $Pmmm$, which resulted in each atom of the $[\text{CuCl}(\text{dien})]^+$ cation semi-occupying two sites on either side of the bc mirror plane. Decisions regarding which atoms constituted a molecular fragment were made by selecting a combination that generated bond lengths and angles which matched those in similar previously published structures. Also, H atoms were subjected to DFIX rather than AFIX constraints, so that angles involving H atoms could also be used to avoid incorrect assignments. Although dihedral angles did not form part of the above selection process, their final values showed excellent agreement with those in similar structures.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1C \cdots Cl2 ⁱ	0.83 (2)	2.48 (5)	3.188 (3)	144 (7)
N2—H2C \cdots Cl1 ⁱⁱ	0.85 (2)	2.69 (3)	3.437 (2)	147 (4)
N2—H2D \cdots Cl2 ⁱⁱ	0.83 (2)	2.68 (2)	3.429 (2)	150.8 (14)

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, -y, -z + 1$.

Table 3

Comparison of geometric parameters (\AA , $^\circ$) for $[\text{CuX}_2(\text{dien})]$ complexes.

X	Cu \cdots X	Cu \cdots X	Cu \cdots Cu	Cu \cdots X \cdots Cu
I \ddagger	3.328 (1)	3.368 (1)	6.658 (1)	167.7 (1)
Br \ddagger	3.139 (4)	3.298 (4)	6.377 (1)	164.3 (1)
Cl \S	2.831 (1)	3.341 (1)	6.092 (1)	161.6 (1)

\ddagger Hodgson *et al.* (1991). \ddagger Boeyens *et al.* (1991). \S This work.

Data collection: *KappaCCD Server Software* (Nonius, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3036). Services for accessing these data are described at the back of the journal.

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