

[Cu(2-Me-imidH)₄Cl]Cl: a conflict between high symmetry and packing efficiency

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$

R factor = 0.041

wR factor = 0.085

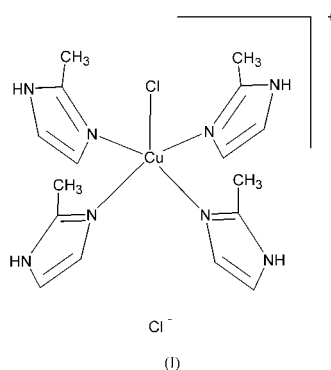
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal and molecular structure of the monomeric title compound, chlorotetrakis(2-methylimidazole)copper(II) chloride, $[\text{CuCl}(\text{C}_4\text{H}_6\text{N}_2)_4]\text{Cl}$, is presented, and compared with those of two other closely related monomeric structures. The monomers are similar, but the supramolecular structures are very different. The influence that steric effects might have in determining crystal properties, such as space group symmetry or packing efficiency, is analysed.

Comment

Fig. 1 presents a molecular diagram of the title compound, $\text{Cu}(\text{2-Me-imidH})_4\text{Cl}\cdot\text{Cl}$ (2-Me-imidH is 2-methylimidazole), (I), which lies on a fourfold symmetry axis; the copper environment takes the form of a square pyramid, with four N-coordinating methylimidazole groups defining the square base and a chloride anion in the apical position. As both the cation and the anion lie on the fourfold rotation axis, the whole array is very symmetric, having only one independent methylimidazole group. The C_{4v} point symmetry displayed by the polyhedron means that only one angle, for example, $\text{Cl1}-\text{Cu}-\text{N1} = 99.06(12)^\circ$, is needed to fully define the coordination geometry, all other angles being simply derived. There is a chloride counter-ion balancing the charge and stabilizing the structure; it lies on the $\text{Cl}-\text{Cu}$ vector, but in the opposite hemisphere at a (presumably) non-bonding distance from copper ($> 4 \text{ \AA}$; see, however, the discussion below).



We shall now compare the results found for (I) with those of two closely related structures, *viz.* hexa- μ_2 -chloro- μ_4 -oxo-tetrakis(*N*-methylimidazole-*N'*)tetracopper(II) chlorotetrakis(*N*-methylimidazole-*N'*)copper(II) chloride, (II) (Clegg *et al.*, 1988), where exactly the same molecular group $[\text{Cu}(\text{Me-imid})_4\text{Cl}]\cdot\text{Cl}$ is present as a cocrystallization product, and $[\text{Cu}(\text{imid})_4\text{Cl}]\cdot\text{Cl}$, (III) (Otieno *et al.*, 2001), a non-methylated homologue of the compound reported here. The overall geometries of all three molecules (as represented by the copper coordination polyhedron) are quite similar, and

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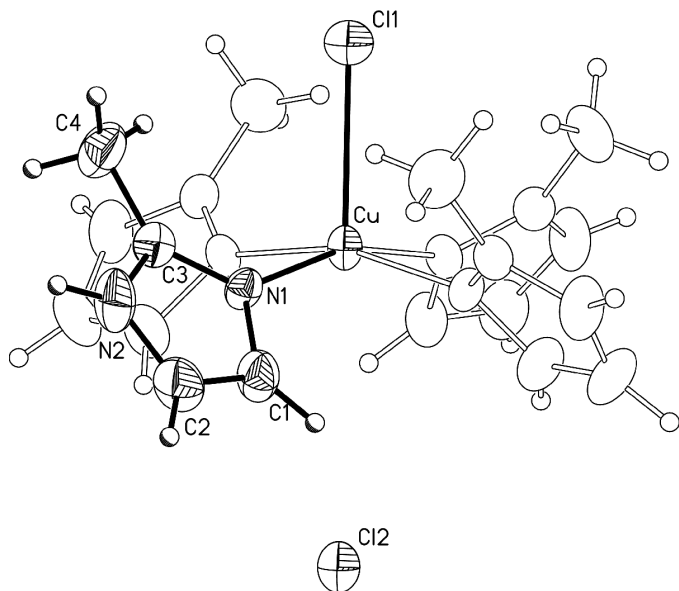


Figure 1
The molecular structure of the monomer in (I). The independent part of the molecule is indicated by solid bonds and segmented ellipsoids; ellipsoids are drawn at the 40% probability level.

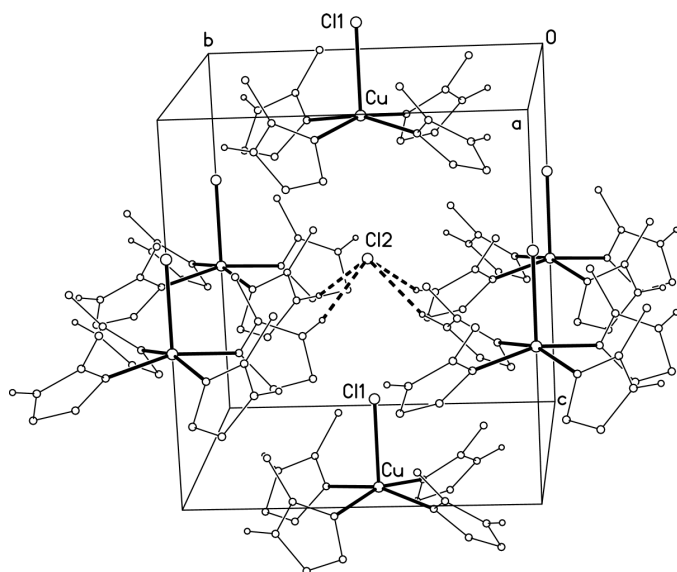


Figure 2
Packing view of (I), showing the hydrogen-bonding scheme leading to an open two-dimensional structure.

mean values for bond lengths and angles are comparable: Cu—Cl = 2.627 (3)/2.542 (1)/2.615 (1) Å, Cu—N = 2.027 (3)/2.015 (13)/2.005 (8) Å and Cl—Cu—N = 99.06 (12)/97.3 (27)/96.7 (53)° for (I), (II) and (III), respectively.

However, and in spite of these similarities, there is a marked difference between the structures, arising from the lower point symmetry in (II) and (III). This results in a greater flexibility of orientation for the planar groups in the latter compounds, through the unrestrained rotation around the N—Cu bonds. This seems to facilitate the filling of voids and allows for a diverse array of contacts in which both coordinated and free chloride ions participate in the formation of a three-dimensional hydrogen-bonded structure.

This is in contrast to what happens to (I) where, due to the C_{4v} symmetry, its four equivalent N—CH₃ groups are forced to point in the same direction (in this particular case, towards the apical site). This different geometrical disposition of H-atom donors in (I) results in a quite different hydrogen-bonding scheme: an open two-dimensional supramolecular structure parallel to (001) is built up, with the chloride counter-ion (the only acceptor for hydrogen bonds) acting as the link between monomers (see Table 2 and Fig. 2). The markedly open character of the structure suggested in Fig. 2 is confirmed by the rather low density of (I), 1.471 Mg m⁻³, compared with 1.649 Mg m⁻³ for (II) and 1.668 Mg m⁻³ for (III); it seems that the molecular point symmetry is raised from C_1 to C_{4v} at the expense of the ability of the molecules to pack in an efficient way.

As a final remark, we would like to comment on the intriguing fact that in these three structures the chloride counter-ion is located at distances greater than 3.8 Å from Cu [4.106 (3) Å in (I)], far beyond commonly accepted Cu···Cl bonding distances but, nonetheless, occupying a perfectly 'apical' position (on the extension of the Cl_{coord}—Cu vector) of an imaginary, extremely elongated octahedron. To analyse how common this puzzling situation is, we made a search for copper compounds with a similar square-pyramidal coordination, *viz.* four N atoms at the base, a normally coordinated chloride at an apical position and a free chloride counter-ion occupying a (virtual) second 'apical' site, completing the elongated octahedron, at a distance large enough to discount any conventional coordination (*viz.* > 3.25 Å) (CSD, November 2002 version; Allen, 2002). Besides, it was imposed as an extra restriction, the 'inter-apical' angle should be in the range 170–180°. We found nine such cases, with a continuous range of Cu···Cl distances to an upper limit of 4.83 Å; in very few of them could some steric argument be found in support of such a symmetric disposition of the chloride counter-ion.

Experimental

The copper(II) complex was synthesized as reported by Atria *et al.* (1999). A methanol solution of 2-methylimidazole (1 mmol) was added with stirring to a solution containing copper(II) chloride (1 mmol) in the same solvent. The resulting solution was refluxed for 30 min. Crystals suitable for structure determination were obtained by slow evaporation. HPLC-quality methanol was stored over CaSO₄ for several days and freshly distilled before use. All other reagents and solvents were of commercially available reagent quality. Elemental analysis for (I), required: C 41.52, H 5.23, N 24.21, Cl 15.32, Cu 13.73%; measured: C 41.3, H 5.2, N 24.4%. The C, H, N elemental analyses were performed on a Fison—Carlo Erba EA 1108 model analyser at CEPEDeq (University of Chile).

Crystal data

[CuCl(C₄H₆N₂)₄]Cl
 $M_r = 462.87$
 Tetragonal, $P4nc$
 $a = 9.8106$ (12) Å
 $c = 10.8547$ (19) Å
 $V = 1044.7$ (3) Å³
 $Z = 2$
 $D_x = 1.471$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 134 reflections
 $\theta = 3.1$ –22.9°
 $\mu = 1.32$ mm⁻¹
 $T = 293$ (2) K
 Plate, blue
 0.16 × 0.12 × 0.06 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan [SADABS (Sheldrick, 1996) in SAINNT-NT (Bruker, 2002)]
 $T_{\min} = 0.83$, $T_{\max} = 0.92$
 3889 measured reflections

896 independent reflections
 670 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -8 \rightarrow 11$
 $l = -12 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.085$
 $S = 0.93$
 896 reflections
 64 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.57 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983);
 402 Friedel pairs
 Flack parameter = $-0.03(3)$

Table 1Selected geometric parameters (\AA , $^\circ$).

Cu—N1	2.027 (3)	C1—C2	1.337 (7)
Cu—Cl1	2.627 (3)	C2—N2	1.351 (7)
N1—C3	1.322 (5)	N2—C3	1.337 (6)
N1—C1	1.374 (6)	C3—C4	1.480 (7)
N1 ⁱ —Cu—N1	88.58 (4)	N1—Cu—Cl1	99.06 (12)

Symmetry code: (i) $-y, 1+x, z$.**Table 2**Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2B \cdots Cl2 ⁱⁱ	0.86	2.43	3.258 (5)	162

Symmetry code: (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

H atoms were placed at their expected positions ($N-H = 0.90 \text{ \AA}$, $Csp^2-H = 0.93 \text{ \AA}$ and $Csp^3-H = 0.96 \text{ \AA}$) and allowed to ride on their host atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{host})$.

Data collection: SMART-NT (Bruker, 2001); cell refinement: SMART-NT; data reduction: SAINNT-NT (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL/PC (Sheldrick, 1994); software used to prepare material for publication: SHELXL97.

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