

Tetrakis(2-methylimidazo)bis(trifluoromethylsulfonato)copper(II)

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å
 R factor = 0.058
 wR factor = 0.126
Data-to-parameter ratio = 13.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4(\text{CF}_3\text{SO}_3)_2]$, was prepared by reaction of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-methylimidazole in acetonitrile. The central Cu atom is coordinated by four 2-methylimidazole ligands forming an equatorial plane (average Cu–N 2.007 Å) and two trifluoromethylsulfonate anions at the axial sites, with long Cu–O bonds of 2.651 (4) and 3.069 (6) Å; thus, the Cu atom has the octahedral environment typical for Cu^{II} complexes, with a tetragonal distortion. All four 2-methylimidazole rings are tilted out of the CuN_4 plane by about 50° .

Comment

The coordination chemistry of copper complexes has been the focus of numerous studies, since it can provide important clues for better understanding the structures and probable mechanisms of reactions involving copper-containing metalloproteins (Kaim & Schewederski, 1994). The structures of copper complexes are affected by various factors (Hathaway, 1987), such as ligand field stabilization energies, the Pauling electroneutrality principle, Jahn–Teller effect, counter-ion effects, steric effects, *etc.* Considerable research effort has been focused on low molecular weight Cu^{II} –imidazole complexes in order to understand their stereochemistry and the interactions of histidyl residues with copper ions (Ohtsu *et al.*, 2001; Wang *et al.*, 1999; Jian *et al.*, 1999). The structures and bonding properties of Cu^{II} –imidazole chromophores have been studied by X-ray diffraction and electronic spectra in our earlier work (Liu & Su, 1995; Su *et al.*, 1995). The study of the title complex, (I), was undertaken in order to compare its structure with that of its analogue, $[\text{Cu}(\text{Him})_4(\text{CF}_3\text{SO}_3)_2]$ (where Him = imidazole), and thus consider the effect of substitution at the imidazole ligands on the structure of the complex.

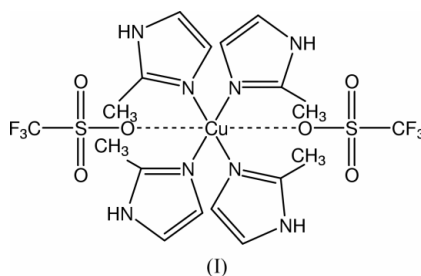


Fig. 1 shows an *ORTEP* (Johnson, 1965) drawing of the title complex and Table 1 lists the distances and angles involving the Cu atom. The Cu atom has an octahedral coordination, with bond angles indicating relatively slight distortions (12 angles in the range 82.96 – 99.05° and three angles, 175.0 –

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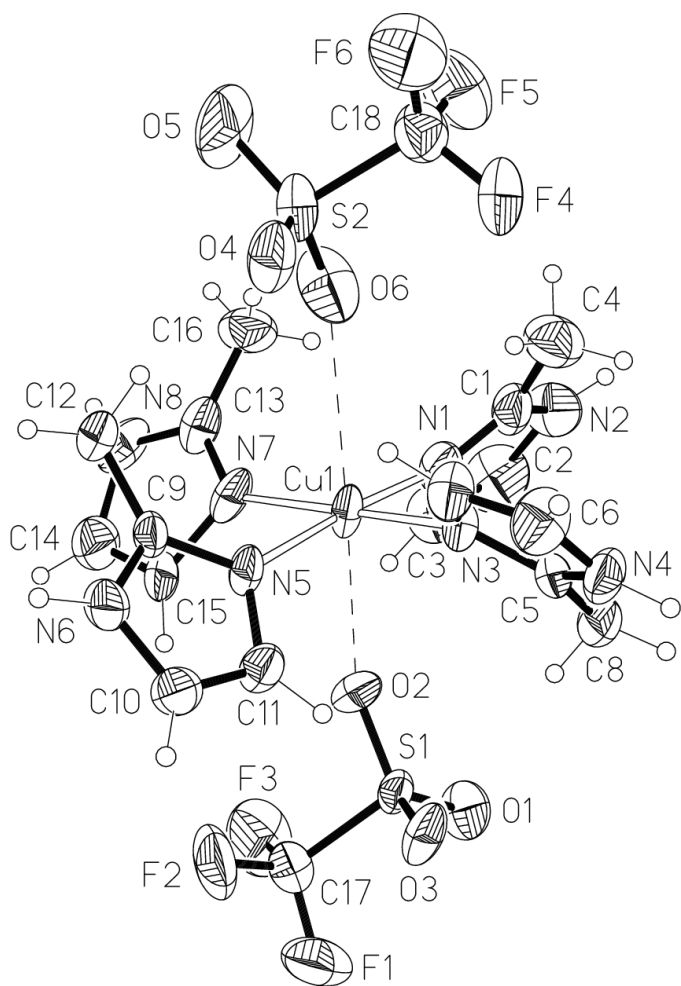


Figure 1
ORTEP (Johnson, 1965) drawing of the structure of tetrakis(2-methylimidazolo)bis(trifluoromethylsulfonato)copper(II), with 35% probability displacement ellipsoids, showing the atom-numbering scheme.

175.6°), and equatorial Cu–N bonds in the normal range for Cu–N coordination (1.994–2.026 Å). Both axial Cu–O bonds are much longer than one would expect for normal Cu–O coordination bonds; in addition, one of the Cu–O distances (Cu1–O6 3.069 (6) Å) is significantly longer than the other (Cu1–O2 2.651 (4) Å), which is very different from the geometry of other Cu^{II}–imidazole complexes, which have long but almost identical axial bonds, *e.g.* 2.593 Å in [Cu(Him)₄(CF₃SO₃)₂] (Liu & Su, 1995), 2.625 Å in [Cu(Him)₄(ClO₄)₂] (Ivarsson, 1973), 2.574 Å in [Cu(Him)₄(SO₄)₂] (Fransson & Lundberg, 1972) and 2.566 Å in [Cu(Him)₄(NO₃)₂] (McFadden *et al.*, 1976).

It was found that the conformations of the imidazole ligands in tetrakis-imidazole and tetrakis-monosubstituted imidazole copper(II) complexes are mainly affected by the donor abilities of both the imidazole ligands and the counter ions. For the title complex, the dihedral angles between the imidazole rings and the equatorial CuN₄ plane are 47.2 (2), 47.8 (3), 51.9 (3) and 51.3 (2)°, respectively. The dihedral angles for the analogue with unsubstituted imidazole and the same anion, [Cu(Him)₄(CF₃SO₃)₂], fall into two categories; one pair of

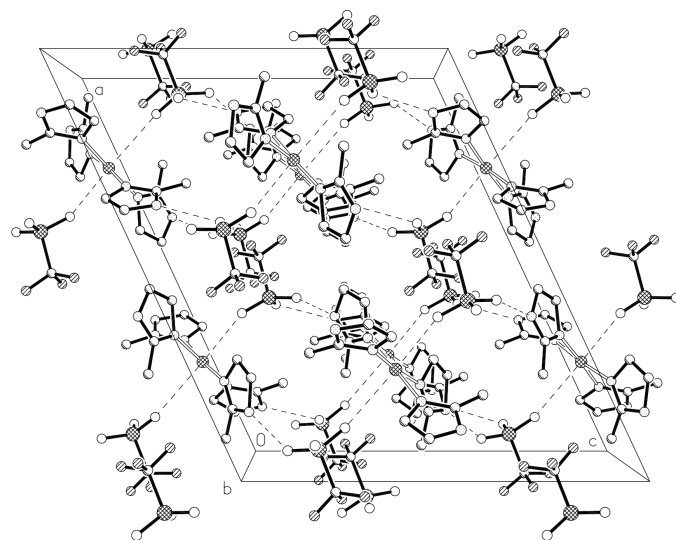


Figure 2
A view of the packing along the *b* direction. Dashed lines denote weak Cu–O bonds and hydrogen bonds.

trans imidazole rings is almost perpendicular to the equatorial plane (88.2°) and another is tilted by 59.4° (Liu & Su, 1995). Complexes with very weak σ -donor anions such as [Cu(Him)₄(ClO₄)₂] (Ivarsson, 1973), tend to have a perpendicular and a parallel pair of imidazole ligands, forming dihedral angles of 94.3 and 18.7° with the metal coordination plane, respectively. Corresponding complexes with stronger σ -donor anions have all four imidazole rings perpendicular to the equatorial plane, *e.g.*, 98.6 and 94.6° in [Cu(Him)₄(NO₃)₂] (McFadden *et al.*, 1976).

A view of the packing is shown in Fig. 2. The discrete complexes are connected by hydrogen bonding between N atoms of imidazole ligands and O atoms of trifluoromethylsulfonate to form layers parallel to the *bc* plane.

Experimental

2-Methylimidazole (Merck), 2,2'-dimethoxypropane (Aldrich), cupric oxide (Merck), trifluoromethylsulfonic acid (Aldrich) and organic solvents of reagent grade were used as received. Cu(CF₃SO₃)₂·6H₂O was prepared from CuO and CF₃SO₃H. Tetrakis(2-methylimidazolo)bis(trifluoromethylsulfonato)copper(II), [Cu(2-CH₃-Him)₄(CF₃SO₃)₂], was prepared by the following procedure: Cu(CF₃SO₃)₂·6H₂O (1 mmol) and 2-methylimidazole (4 mmol) were dissolved in acetonitrile containing 5% of 2,2-dimethoxypropane. After stirring the mixture at room temperature for 2 h, diethyl ether was added dropwise until a precipitate began to appear. The solution was stored in a refrigerator for 2 d, yielding dark blue crystals (83%).

Crystal data

[Cu(CH₃C₃H₃N₂)₄(CF₃SO₃)₂]
M_r = 690.11
 Monoclinic, *P*2₁/*c*
a = 18.763 (4) Å
b = 10.674 (2) Å
c = 16.064 (3) Å
 β = 115.02 (3)°
V = 2915.3 (12) Å³
Z = 4

D_x = 1.572 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 10.0–13.5°
 μ = 0.98 mm⁻¹
T = 293 (2) K
 Prism, dark blue
 0.32 × 0.22 × 0.16 mm

Data collection

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.035$ $\theta_{\text{max}} = 25.0^\circ$
ω scans	$h = -22 \rightarrow 20$
Absorption correction: ψ scan (North <i>et al.</i> 1968)	$k = -12 \rightarrow 0$ $l = 0 \rightarrow 19$
$T_{\text{min}} = 0.742$, $T_{\text{max}} = 0.855$	3 standard reflections
5291 measured reflections	frequency: 120 min
5092 independent reflections	intensity decay: 15%
2600 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 10P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.65 \text{ e } \text{\AA}^{-3}$
5092 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{\AA}^{-3}$
370 parameters	
H-atom parameters constrained	

Table 1

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

Cu1—N1	2.002 (5)	Cu1—N7	2.026 (5)
Cu1—N3	1.994 (5)	Cu1—O2	2.651 (4)
Cu1—N5	2.004 (4)	Cu1—O6	3.069 (6)
N3—Cu1—N1	94.0 (2)	N5—Cu1—O2	87.97 (18)
N3—Cu1—N5	87.19 (18)	N7—Cu1—O2	82.96 (18)
N1—Cu1—N5	175.0 (2)	N1—Cu1—O6	91.0 (2)
N3—Cu1—N7	175.4 (2)	N3—Cu1—O6	84.99 (18)
N1—Cu1—N7	90.3 (2)	N5—Cu1—O6	93.97 (17)
N5—Cu1—N7	88.8 (2)	N7—Cu1—O6	93.13 (19)
N1—Cu1—O2	87.0 (2)	O2—Cu1—O6	175.61 (14)
N3—Cu1—O2	99.05 (17)		

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2A \cdots O5 ⁱ	0.90	2.02	2.812 (7)	146
N4—H4D \cdots O4 ⁱⁱ	0.90	1.92	2.822 (6)	177
N6—H6A \cdots O3 ⁱⁱⁱ	0.90	1.95	2.826 (6)	164
N8—H8D \cdots O1 ^{iv}	0.90	1.95	2.823 (7)	162

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The H atoms were positioned geometrically with C—H bonds of 0.96 \AA and N—H bonds of 0.90 \AA . They were included in the final refinement in the riding motion approximation with fixed isotropic temperature factors of 0.12 \AA^2 for the methyl H atoms and 0.08 \AA^2 for all other H atoms.

Data collection: *CAD-4/PC Software* (Enraf-Nonius, 1992); cell refinement: *CAD-4/PC Software*; data reduction: *XCAD4* (Harms, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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