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The effects of substitution on tetrakis(substituted imidazole)-copper(II) trifluoromethanesulfonates

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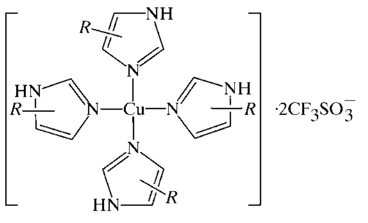
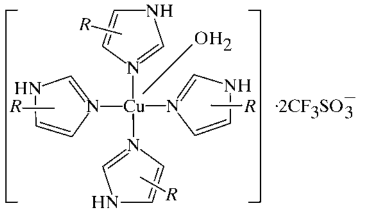
The organic ligands 4-methyl-1*H*-imidazole and 2-ethyl-4-methyl-1*H*-imidazole react with $Cu(CF_3SO_3)_2·6H_2O$ to give tetrakis(5-methyl-1*H*-imidazole-κN^3)copper(II) bis(trifluoromethanesulfonate), $[Cu(C_4H_6N_2)_4](CF_3SO_3)_2$, and aquatetrakis(2-ethyl-5-methyl-1*H*-imidazole-κN^3)copper(II) bis(trimethanesulfonate), $[Cu(C_6H_{10}N_2)_4(H_2O)](CF_3SO_3)_2$. In the former, the Cu atom has an elongated octahedral coordination environment, with four imidazole rings in equatorial positions and two trifluoromethanesulfonate ions in axial positions. This conformation is similar to those in the analogous complexes tetrakis(imidazole)copper(II) trifluoromethanesulfonate and tetrakis(2-methyl-1*H*-imidazole)copper(II) trifluoromethanesulfonate. In the second of the title compounds, the ethyl groups block the central Cu atom, and a square-pyramidal coordination environment is formed around the Cu atom, with the substituted imidazole rings in the basal positions and a water molecule in the axial position.

Comment

It is important to synthesize simple Cu^{II}–imidazole complexes and study their structures in order to help us understand the interactions of histidyl residues with copper ions in metalloproteins (Jian *et al.*, 1999; Wang *et al.*, 1999; Ohtsu *et al.*, 2001). For example, the counter-ion effects on the structures of copper complexes have been revealed by structural studies and comparisons of nitrate (McFadden *et al.*, 1976), sulfate (Fransson & Lundberg, 1972), perchlorate (Ivarsson, 1973) and trifluoromethanesulfonate (Liu & Su, 1995) complexes of tetrakis(imidazole)copper(II). Similarly, the effect of substituents of imidazoles on the structures of their complexes can be investigated *via* structural studies of the corresponding complexes. The crystal structures of tetrakis(imidazole)copper(II) trifluoromethanesulfonate, (I) (Liu & Su, 1995), and tetrakis(2-methylimidazole)copper(II) trifluoromethanesulfonate, (II) (Liu *et al.*, 2002), have been reported previously. We report here the preparation and X-ray crystal structure determination of another two analogous complexes, *viz.* tetrakis(5-methyl-1*H*-imidazole-κN^3)copper(II) bis(trifluoromethanesulfonate), (III), and aquatetrakis(2-ethyl-5-methyl-1*H*-imidazole-κN^3)copper(II) bis(trifluoromethanesulfonate), (IV).



(I) R=H
(II) R=2-CH_3
(III) R=5-Me



(IV) R=2-Et/5-Me

The crystal structure of (III) (Fig. 1), which consists of discrete molecules, is similar to the structures of (I) and (II). The coordination environment of the central Cu atom can be described as an elongated octahedron with four N atoms of the substituted imidazole rings in equatorial positions and two O atoms from the trifluoromethanesulfonate groups in axial positions. The lengths of the Cu—N bonds [1.992 (4)–2.001 (4) Å; Table 1] are normal, while the lengths of the axial

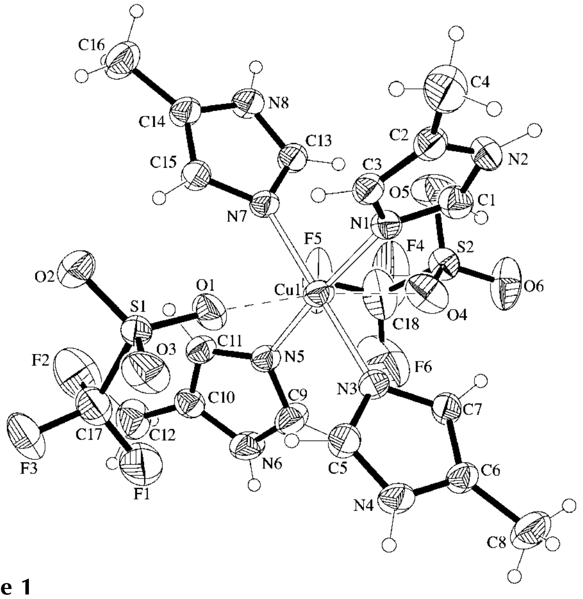


Figure 1
The molecular structure of (III), showing displacement ellipsoids at the 35% probability level and the atomic numbering scheme.

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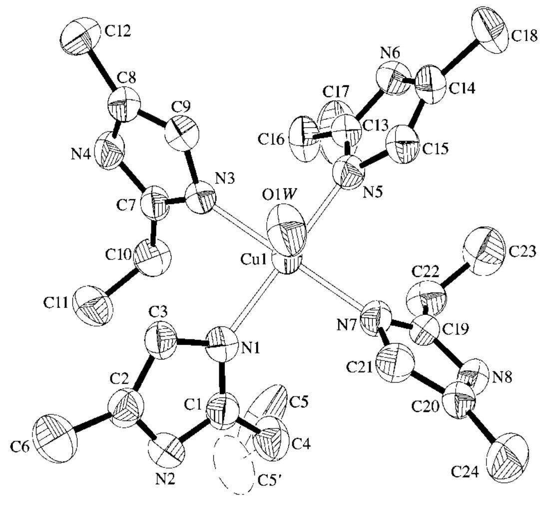

Figure 2
The molecular structure of (IV), showing displacement ellipsoids at the 35% probability level and the atomic numbering scheme.

Cu—O bonds [2.639 (3) and 2.867 (4) Å] are significantly longer than those found in (I) (2.593 Å; Liu & Su, 1995) and shorter than those found in (II) (2.651 and 3.069 Å; Liu *et al.*, 2002). However, in (IV), the larger substituents, *i.e.* the ethyl groups, at the 2-positions of the imidazole rings block the central Cu atom, thus allowing the coordination environment around the Cu atom to become square pyramidal, with four N atoms of the substituted imidazole rings in the basal positions and a water molecule in the axial position, as shown in Fig. 2. The Cu—N bonds [1.999 (5)–2.026 (5) Å; Table 3] have typical lengths and the axial Cu—O bond is 2.372 (5) Å, which is significantly shorter than those found in the hexacoordinated copper complexes (I), (II) and (III). The closest-contact distance between the Cu atom and an O atom of a trifluoromethanesulfonate group is longer than 4 Å, which suggests that the anion groups are free counter-ions in the crystal structure of (IV). Figs. 3 and 4 show the crystal packing of (III) and (IV), respectively. The complex cations and trifluoromethanesulfonate ions are connected by possible hydrogen-bonding interactions (Tables 2 and 4), which are denoted by dashed lines in Figs. 3 and 4.

It was found that the conformations of the organic ligands in (I)–(IV) are affected by the substituents on the imidazole ring and the substituted positions. The dihedral angles between the imidazole planes and the CuN_4 plane of the coordination polyhedron are listed in Table 5.

In (I), which contains unsubstituted imidazole rings, two imidazole rings are almost perpendicular to the equatorial plane and the other two are tilted by 59.4°. All imidazole rings with a substituent at the 2-position in (II) and (IV) are tilted [by 47.2 (2)–61.3 (3)°] with respect to the CuN_4 plane of the coordination polyhedron. However, in (III), one of the imidazole rings with a substituent at the 5-position is almost parallel to the equatorial plane, and the other three lie nearly perpendicular to it.

We conclude that the substituents and their positions on the imidazole ring can affect the structure of copper–imidazole complexes, specifically the coordination number of the Cu atom, the bond lengths of axial Cu—O bonds and the dihedral angles between the planes of the imidazole rings and the CuN_4

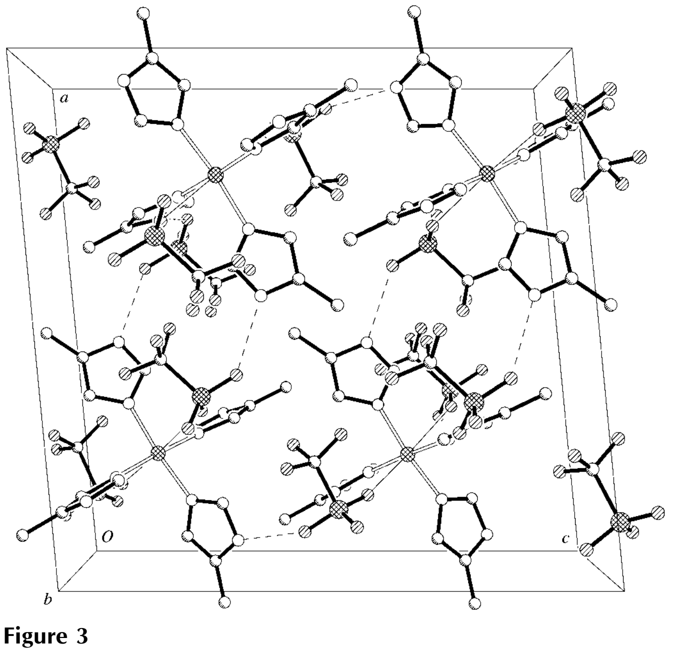

Figure 3
The crystal packing of (III), viewed along the *b* direction. Crosshatched circles denote Cu and S atoms, circles shaded by slanting lines denote F and O atoms, open circles denote N atoms, and partially shaded circles denote C atoms. Hydrogen bonds are denoted by dashed lines.

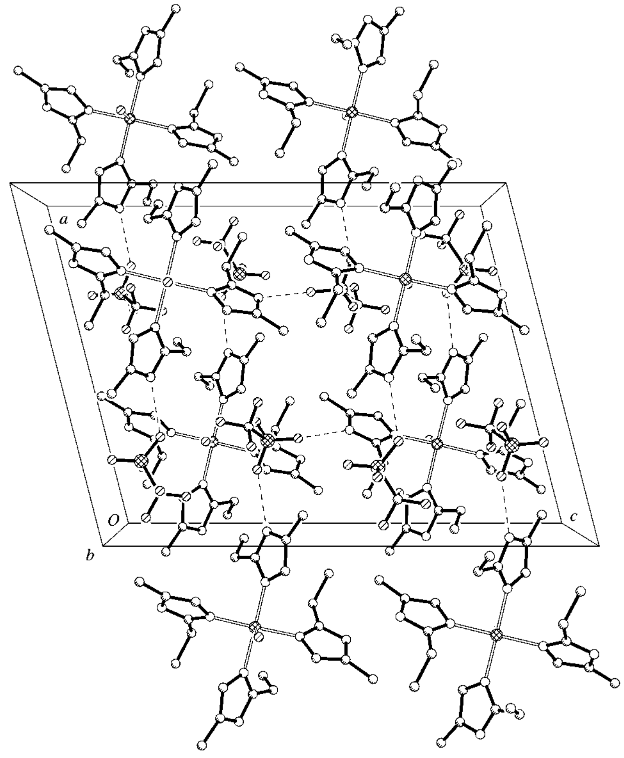

Figure 4
The crystal packing of (IV), viewed along the *b* direction; atoms are represented as described in Fig. 3. Hydrogen bonds are denoted by dashed lines.

plane of the coordination polyhedron. However, there is almost no influence on the Cu—N bond lengths.

Experimental

The organic ligands 4-methyl-1*H*-imidazole and 2-ethyl-4-methyl-1*H*-imidazole (Merck) and 2,2′-dimethoxypropane (Aldrich), cupric oxide (Merck), trifluoromethanesulfonic acid (Aldrich), and organic solvents of reagent grade were used as received. $Cu(CF_3SO_3)_2{\cdot}6H_2O$ was prepared from CuO and CF_3SO_3H. The title compounds were prepared by the following procedure: $Cu(CF_3SO_3)_2{\cdot}6H_2O$ (1 mmol) and the corresponding ligand (4 mmol) were dissolved in acetonitrile containing 5% 2,2-dimethoxypropane. The mixture was stirred at room temperature for 2 h and then diethyl ether was added dropwise until a precipitate began to appear. The solution was stored in a refrigerator for 2 d and yielded dark-blue crystals [yield 92 and 65% for (III) and (IV), respectively].

Compound (III)

Crystal data

$[Cu(C_4H_6N_2)_4](CF_3SO_3)_2$
$M_r = 690.11$
Monoclinic, $P2_1/c$
$a = 16.400$ (3) Å
$b = 10.174$ (2) Å
$c = 17.016$ (3) Å
$\beta = 95.50$ (3)°
$V = 2826.1$ (9) Å^3
$Z = 4$
$D_x = 1.622$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.3$–15.0°
$\mu = 1.01$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.4 × 0.3 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.706$, $T_{max} = 0.817$
5140 measured reflections
4954 independent reflections
2890 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25.0°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 7200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.103$
$S = 1.03$
4954 reflections
370 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 7P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (III).

Cu1—N1	1.992 (4)	Cu1—N3	2.001 (4)
Cu1—N5	1.994 (4)	Cu1—O1	2.639 (3)
Cu1—N7	2.000 (4)	Cu1—O4	2.867 (4)
N1—Cu1—N5	172.42 (16)	N7—Cu1—O1	88.63 (14)
N1—Cu1—N7	88.55 (16)	N3—Cu1—O1	89.00 (14)
N5—Cu1—N7	92.67 (16)	N1—Cu1—O4	88.29 (14)
N1—Cu1—N3	89.41 (16)	N5—Cu1—O4	84.14 (14)
N5—Cu1—N3	89.70 (15)	N7—Cu1—O4	97.01 (14)
N7—Cu1—N3	176.70 (16)	N3—Cu1—O4	85.50 (14)
N1—Cu1—O1	95.62 (14)	O1—Cu1—O4	173.23 (12)
N5—Cu1—O1	91.89 (14)		

Table 2
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O2^{i}	0.90	2.16	2.910 (6)	141
N4—H4A···O5^{ii}	0.90	2.04	2.839 (6)	147
N6—H6A···O6^{iii}	0.90	1.96	2.840 (6)	167
N8—H8A···O3^{iv}	0.90	1.99	2.872 (5)	165

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

Table 3
Selected geometric parameters (Å, °) for (IV).

Cu1—N3	1.999 (5)	Cu1—N1	2.026 (5)
Cu1—N7	2.000 (5)	Cu1—O1W	2.372 (5)
Cu1—N5	2.010 (6)		
N3—Cu1—N7	173.9 (3)	N5—Cu1—N1	178.5 (3)
N3—Cu1—N5	89.4 (2)	N3—Cu1—O1W	94.0 (2)
N7—Cu1—N5	89.4 (2)	N7—Cu1—O1W	92.0 (2)
N3—Cu1—N1	89.8 (2)	N5—Cu1—O1W	92.3 (2)
N7—Cu1—N1	91.3 (2)	N1—Cu1—O1W	89.0 (2)

Compound (IV)

Crystal data

$[Cu(C_6H_{10}N_2)_4(H_2O)](CF_3SO_3)_2$
$M_r = 820.34$
Monoclinic, $P2_1/c$
$a = 15.408$ (3) Å
$b = 12.627$ (3) Å
$c = 20.380$ (4) Å
$\beta = 104.37$ (3)°
$V = 3841.0$ (14) Å^3
$Z = 4$
$D_x = 1.419$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.8$–12.5°
$\mu = 0.76$ mm^{-1}
$T = 293$ (2) K
Prism, blue
0.25 × 0.15 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.807$, $T_{max} = 0.913$
6948 measured reflections
6740 independent reflections
2847 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.0°$
$h = -18 \rightarrow 17$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 7200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.155$
$S = 1.02$
6740 reflections
460 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 14P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 4
Hydrogen-bonding geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O5	0.90	1.95	2.849 (9)	178
N4—H4A···O6^{v}	0.90	2.37	3.211 (12)	155
N6—H6A···O1^{vi}	0.90	2.00	2.897 (10)	177
N8—H8A···O2	0.90	1.94	2.841 (9)	179
O1W—H1A···O3^{i}	0.85	2.12	2.957 (10)	167

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

Table 5

The dihedral angles (°) between the imidazole planes and the CuN_4 plane in compounds (I)–(IV).

Complexes	Dihedral angles	References
(I)	59.4 (×2), 88.2 (×2)	Liu & Su (1995)
(II)	47.2 (2), 47.8 (3), 51.3 (2), 51.9 (3)	Liu *et al.* (2002)
(III)	26.7 (2), 71.6 (2), 77.6 (2), 79.9 (1)	This work
(IV)	48.1 (3), 55.4 (2), 57.9 (3), 61.3 (3)	This work

All H atoms were positioned geometrically and were treated as riding on their parent atoms in the final refinement. The C4/C5 ethyl group in (IV) is orientationally disordered, and the occupancies of atoms C5 and C5′ were fixed at 0.55 and 0.45, respectively, in the final refinement, according to the results of occupancy refinement.

For both compounds, data collection: *CAD*-4/*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4/*PC Software*; data reduction: *XCAD*4/*PC* (Harms, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1148). Services for accessing these data are described at the back of the journal.

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