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[2-(Imidazol-4-yl)ethylamine]-{[2-(imidazol-4-yl)ethyl][(1-methylimidazol-2-yl)methyl]amine}copper(II) diperchlorate

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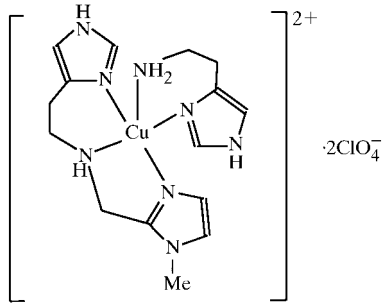
In the title mononuclear complex, $[Cu(C_5H_9N_3)(C_{10}H_{15}N_5)](ClO_4)_2$, the Cu^{II} centre is surrounded by two N-donor ligands, which impose a square-pyramidal environment on the metal. The new tridentate ligand [2-(imidazol-4-yl)ethyl][(1-methylimidazol-2-yl)methyl]amine (HISMIMA) lies in the basal plane, while the histamine ligand occupies the apical and one of the basal positions around the Cu^{II} ion.

Comment

Modelling the metal binding site of copper metalloenzymes is a target that has been pursued by bioinorganic chemists over the last few decades (Sorrel, 1989). In order to attain this objective, low molecular weight compounds that are susceptible to exhaustive investigation have been used (Doman *et al.*, 1989; Place *et al.*, 1998; Oberhausen *et al.*, 1990). However, one of the difficulties of the model approach is the synthesis of complexes with biologically relevant ligands. Thus, synthetic strategies employing imidazole groups to design new ligands have focused on mimicking the histidine amino acid, which is present in a large number of metalloenzymes (Chen *et al.*, 1994; Vencato *et al.*, 1998; Colacio *et al.*, 1998; Oberhausen *et al.*, 1989). Model complexes which mimic the main features of the active sites of these enzymes have been studied in relation to structure–function correlation, and the employment of such a strategy on mononuclear Cu^{II} complexes reinforces the development of new compounds, which will be helpful in the elucidation of the role of the Cu^{II} ion in these copper metalloenzymes. On the other hand, mononuclear Cu^{II} complexes have been used in the development of artificial nucleases for use in molecular genetics and genetic engineering (Sigman, 1990; Hegg & Burstyn, 1998; Liu *et al.*, 1999). Here, we present the synthesis of the new polyimidazole ligand [2-(imidazol-4-yl)ethyl][(1-methylimidazol-2-yl)methyl]amine (HISMIMA) and the crystal structure of its first Cu^{II} mononuclear complex, the title diperchlorate, (I).

Compound (I) consists of a mononuclear Cu^{II} complex in which the geometry around the Cu^{II} ion is best described as a distorted square pyramid, as can be seen in Fig. 1. Five N atoms from the imidazole and amine residues comprise the coordination environment around the metal, of which three from the HISMIMA ligand and one from the histamine imidazole ring define the basal plane (N8/N11/N21/N18). The mean displacement of these four N atoms from the least-squares plane defined by their positions is 0.049 Å and the Cu^{II} ion is out of this plane, towards N1, by 0.177 (2) Å.



(I)

The imidazole rings from the tridentate ligand are planar and the dihedral angle between them is 6.9 (3)°. The tridentate ligand is coordinated in the basal plane, where the amine N18 is *trans* to the histamine N8 and *cis* to the N11 and N21 imidazole atoms of the tridentate ligand. Completing the coordination environment, the N1 histamine is apical at 2.277 (3) Å, which is the longest coordination bond length.

The coordination mode of the bidentate ligand results in a six-membered ring with a bite angle of 92.21 (13)°, which is close to the ideal value of 90°, due to the flexibility of the ligand. This feature can also be observed in the tridentate ligand, where the histamine moiety coordinates with a bite angle of 91.51 (14)°. The remaining five-membered ring formed by the (1-methylimidazol-2-yl)methyl group shows a bite angle of 81.85 (14)°. This deviates significantly from 90° as a consequence of the rigidity of this ring.

The Cu1—N21 bond length [1.980 (3) Å] is the shortest in the coordination sphere and is very close to the distances observed in similar complexes, such as $[Cu(B\text{-}MIMA)(CH_3COO)]^+$ {Cu—N3 1.974 (2) Å; Oberhausen *et al.*, 1989; B-MIMA is bis[2-(1-methylimidazolyl)methyl]amine} and $[Cu(2\text{-}MeIm_2PrO)(H_2O)]^{2+}$ [Cu—N1 1.993 (2) Å; Doman *et al.*, 1989; 2-$MeIm_2$PrO is 1,3-bis(*N*-methylimidazolimine)-propan-2-ol], in which the Cu^{II} ion is attached to the 1-methylimidazole group. However, all these values are shorter than those observed in other similar complexes with this same ligand type, such as $[Cu(bipa)Cl]^+$ {Cu—N2 2.009 (3) Å; Oberhausen *et al.*, 1990; bipa is bis[2-(1-methylimidazolyl)methyl][2-(pyridyl)methyl]amine}, $[Cu(tmima)Cl]^+$ {Cu—N2 2.062 (3) Å; Oberhausen *et al.*, 1990; tmima is tris[2-(1-methylimidazolyl)methyl]amine}, $[Cu(L^1)Cl]^+$ {Cu—N4 2.078 Å; Chen *et al.*, 1994; L^1 is bis[(1-methylimidazol-2-yl)-methyl][(1-methylimidazol-4-yl)methyl]amine} and $[Cu(L^2)Cl]^+$ {Cu—N2 2.042 Å; Chen *et al.*, 1994; L^2 is bis[(1-methylimidazol-4-yl)methyl][(1-methylimidazol-2-yl)methyl]amine}.

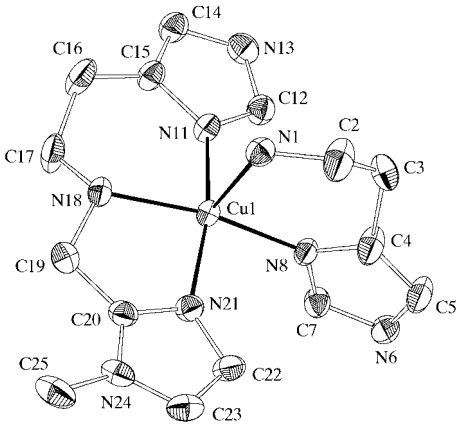


Figure 1
The molecular view of the cation of (I) with the atom-numbering scheme and 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

In complex (I), the Cu—$N_{imidazole}$ bond lengths are slightly larger than those described by Colacio *et al.* (1998) in [Cu(hfac)(*L*)Zn(hfac)$_2$(*L*)(hfac)Cu] {hfac is hexafluoroacetylacetonate; *L* is [2-(imidazol-2-yl)ethyl][2-(methylimidazolyl)methyl]imine}, and by Place *et al.* (1998) in $[Cu(BIK)_2]^{2+}$ [BIK is bis(imidazol-2-yl) ketone], where the Cu—$N_{imidazole}$ distances are 1.946 (4) and 1.961 (7) Å, respectively.

Finally, the Cu—N_{amine} distance in the tridentate ligand is longer than either of the Cu—$N_{imidazole}$ distances, which is probably due to the greater π-bonding ability of the imidazole groups compared with the alkylamines, which are exclusively σ donors, and also to the constraining nature of the tripodal ligand (Chen *et al.*, 1994).

The N—H sites in both the histamine and HISMIMA ligands take part in several intermolecular hydrogen bonds with neighbouring perchlorate groups. The donor–acceptor distances in these interactions are in the range 3.018 (9)–3.665 (15) Å. Since the H atoms were not found from a $\Delta\rho$ map, the connectivity for the hydrogen bonds was deduced from the distances and favourable geometry between donors and acceptors.

Experimental

The HISMIMA ligand was prepared in high yield by a condensation reaction between a methanolic solution of histamine dihydrochloride (3.1 g, 17 mmol), previously neutralized with KOH (1.9 g, 34 mmol), and 1-methyl-2-imidazolecarboxaldehyde (1.4 g, 17 mmol), according to the procedure of Oberhausen *et al.* (1989). The reaction mixture was stirred for 3 h at 273 K and then reduced by catalytic hydrogenation (Pd/C 5%) for 18 h. The catalyst was filtered off and the resulting solution was evaporated under reduced pressure, yielding a clear oil that was used without further purification (yield 2.2 g, 85%). Spectroscopic analysis: ^{1}H NMR (d_6-DMSO + D_2O, δ, p.p.m.): 2.74–2.86 (*m*, 4H, CH_2), 3.75 (*s*, 3H, CH_3 1-mim), 3.92 (*m*, 2H, CH_2), 6.99–7.06 (*m*, 2H, CH_{arom}), 7.18 (*s*, 1H, CH_{arom}), 7.78 (*s*, 1H, CH_{arom}). Complex (I) was obtained by the addition of one equivalent of $Cu(ClO_4)_2{\cdot}6H_2O$ to a methanolic solution containing equimolar amounts of histamine and HISMIMA, affording a blue precipitate, which was filtered off and washed with cold propan-2-ol and ether. Single crystals of (I) suitable for X-ray analysis were obtained by recrystallization from a methanol–propan-2-ol (2:1) solution.

Crystal data

$[Cu(C_5H_9N_3)(C_{10}H_{15}N_5)](ClO_4)_2$
M_r = 578.86
Monoclinic, $P2_1/c$
a = 16.785 (3) Å
b = 10.211 (2) Å
c = 14.054 (3) Å
β = 102.54 (3)°
V = 2351.3 (8) Å^3
Z = 4
D_x = 1.635 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.46–15.44°
μ = 1.215 mm^{-1}
T = 293 (2) K
Irregular, blue
0.43 × 0.26 × 0.23 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*PLATON*; Spek, 1990)
T_{min} = 0.690, T_{max} = 0.793
4335 measured reflections
4146 independent reflections
2528 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25°
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 12$
$l = -16 \rightarrow 0$
3 standard reflections
every 200 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.114
S = 1.021
4146 reflections
389 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N21	1.980 (3)	Cu1—N18	2.082 (3)
Cu1—N11	1.980 (3)	Cu1—N1	2.277 (3)
Cu1—N8	2.003 (3)		
N21—Cu1—N11	165.65 (14)	N8—Cu1—N18	170.11 (14)
N21—Cu1—N8	90.59 (14)	N21—Cu1—N1	96.60 (14)
N11—Cu1—N8	94.41 (14)	N11—Cu1—N1	96.64 (14)
N21—Cu1—N18	81.85 (14)	N8—Cu1—N1	92.21 (13)
N11—Cu1—N18	91.51 (14)	N18—Cu1—N1	94.97 (14)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O5^{i}	0.90	2.79	3.665 (15)	164
N1—H1B···O5′^{i}	0.90	2.51	3.405 (19)	174
N6—H6···O8	0.86	2.28	3.055 (14)	149
N6—H6···O8′	0.86	2.16	2.99 (2)	162
N13—H13···O5^{ii}	0.86	2.33	2.982 (11)	133
N13—H13···O5′^{ii}	0.86	2.35	3.089 (18)	144
N13—H13···O4^{i}	0.86	2.34	3.025 (16)	136
N13—H13···O4′^{i}	0.86	2.54	3.126 (12)	126
N18—H18···O3^{iii}	0.91	2.42	3.31 (3)	167
N18—H18···O3′^{iii}	0.91	2.11	3.018 (9)	175

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x, \frac{3}{2}-y, z-\frac{1}{2}$.

H atoms attached to C atoms were placed in idealized positions and refined using a riding model, with C—H distances of 0.97, 0.96 and 0.93 Å, and with U_{eq} fixed at 1.2, 1.5 and 1.2 times U_{iso} of the parent atom for CH_2, CH_3 and CH_{arom}, respectively. The N—H

distances were also fixed and these are listed in Table 2. The isotropic displacement parameters for H atoms on N atoms were constrained to be 1.2 times U_{iso} of their respective parent atom. A torsional parameter for the conformation of the methyl group was refined. One C atom of the histamine ligand was found disordered over two positions. The site occupancies for C3 and C3′ were refined to 0.531 (12) and 0.469 (12), respectively. Some distances in the modelled disorder are out of the range of the expected values for a C—C single bond. This reflects that the resources are limited in the modelling process. Only one peak from a Fourier map was present at the C2 position, so it was not possible to resolve any disorder at this site. The two perchlorate counter-ions were also found disordered and the disorder in these groups could be modelled. For each O atom, two alternative positions were distinguished and their occupancy factors were refined. The site occupancies for the O atoms were found to be 0.40 (2) and 0.60 (2) for the first perchlorate group (Cl1), and 0.67 (3) and 0.33 (3) for the second perchlorate group (Cl2).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET*4 in *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai *et al.*, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1308). Services for accessing these data are described at the back of the journal.

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