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# (1-Methylimidazole-$\kappa N^3$)[tris(2-aminoethyl)-amine-$\kappa^4 N$]copper(II) bis(perchlorate)

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**Key indicators**

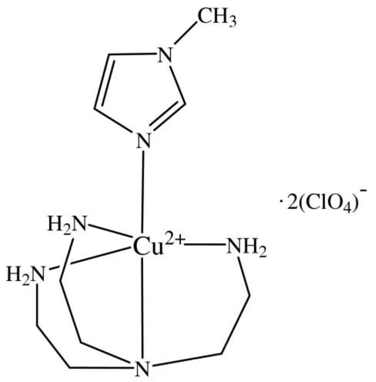
Single-crystal X-ray study
$T$ = 100 K
Mean $\sigma$(C–C) = 0.008 Å
$R$ factor = 0.049
$wR$ factor = 0.137
Data-to-parameter ratio = 19.1

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

The title complex, $[Cu(C_4H_6N_2)(C_6H_{18}N_4)](ClO_4)_2$ or $[Cu(Melm)(tren)](ClO_4)_2$ [Melm = *N*-methylimidazole and tren = tris(2-aminoethyl)amine], contains two $[Cu(MeIm)(tren)]^{2+}$ cations in the asymmetric unit with slightly different bond distances and angles. The coordination geometry of the $Cu^{II}$ ion is distorted trigonal–bipyramidal, with three primary amine groups of the tren ligand forming the equatorial plane. The tertiary amine group and the 1-methylimidazole are in the axial positions. Intra- and intermolecular N—H···O hydrogen bonds are observed in the crystal structure, which is stabilized by these N—H···O hydrogen bonds and also weak intra- and intermolecular C—H···O interactions. Crystals of the title complex are twinned.

## Comment

Complexes of tripodal ligands have attracted much attention because of their importance in coordination chemistry (Blackman, 2005), biochemistry (Ruf & Pierpont, 1998), and catalysis (Goodwin *et al.*, 2004). For example, copper(II) complexes with 2-{[bis(pyridylmethyl)amino]methyl}-4-methyl-6-formylphenol are able to cleave unactivated peptide bonds from bovine serum albumin (BSA) and the thermostable enzyme Taq DNA polymerase (de Oliveira *et al.*, 2005). Dinuclear copper complexes of aliphatic tripodal amino alcohols can catalyse catechol oxidation (Jocher *et al.*, 2005). In the present paper, we report the structure of the title compound, $[Cu(MeIm)(tren)][ClO_4]_2$, (I).



(I)

The asymmetric unit consists of two $[Cu(MeIm)(tren)]^{2+}$ cations and four $ClO_4^-$ anions (Fig. 1). The two cations have slightly different bond distances and angles (Table 1). The $Cu^{II}$ ions in both cations are in a distorted trigonal–bipyramidal geometry with the three primary amine groups of the tren ligand forming the equatorial plane and the tertiary amine and the imidazole molecule occupying the axial positions. The

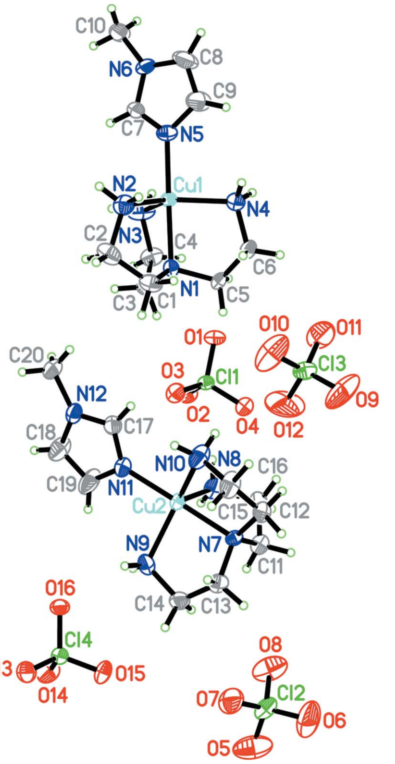


**Figure 1**
The asymmetric unit of (I), with the atom-labelling scheme; displacement ellipsoids are drawn at the 60% probability level.

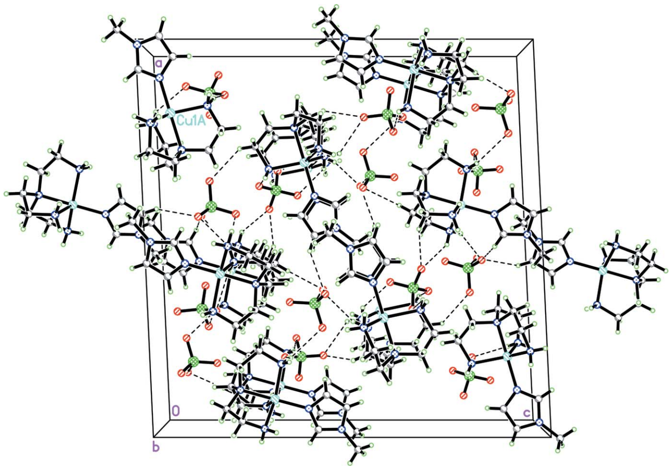


**Figure 2**
The crystal packing of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

geometry parameter $\tau$ values are 0.81 for Cu1 and 0.77 for Cu2, which indicate that the coordination geometry for two $Cu^{II}$ ions is close to a trigonal bipyridmidal configuration (Addison *et al.*, 1984). The $Cu^{II}$ ion is displaced from the equatorial plane towards the *N*-methylimidazole ligand, as indicated by the tren chelate angles which are less than 90° (Table 1). Bond distances to the axial Cu—N distances of the tertiary amine N atoms [*ca* 2.079 (5) Å on average] are longer than that of the Cu—N bond distances in an *N*-methylimidazole complex [*ca* 1.985 (4) Å on average], but shorter than those of the equatorial Cu—N bonds, as in most trigonal five-coordinate $Cu^{II}$ complexes with tren as one of the chelate ligands (Fun *et al.*, 1996; Lu *et al.*, 1997).

There are intramolecular and intermolecular N—H···O hydrogen bonds and C—H···O weak interactions between the amino groups and perchlorate anions (Fig. 2 and Table 2). These interactions stabilize the crystal structure and link the ions into a three-dimensional network.

Crystals of the title complex are twinned. Initial refinement, without recognition of the twinning problem, led to large *R* values. The final *R* values were obtained with refinement using the twin law [001/010/100] and a twin fraction of 0.471:0.529. Because of the recognition of the nature of this type of twinning from the twin law, the *a* and *c* axes were set equal in length.

## Experimental

To a solution of $[Cu(tren)](ClO_4)_2$ (1 mmol, 0.408 g) in boiling EtOH–MeCN (5:1), 30 ml of *N*-methylimidazole (1.1 mmol, 0.090 g) was added. The mixture was refluxed for 3 h. After cooling to room temperature, the precipitate was filtered off by suction and dried *in vacuo* over silica. Yield 85%. Blue needle-like single crystals of (I), of X-ray diffraction quality, were obtained by slow evaporation of an EtOH–MeCN (10:1) solution of (I).

### *Crystal data*

$[Cu(C_4H_6N_2)(C_6H_{18}N_4)](ClO_4)_2$
$M_r = 490.80$
Monoclinic, $P2_1/n$
$a = 21.9941$ (7) Å
$b = 7.8942$ (3) Å
$c = 21.9941$ (7) Å
$\beta = 92.607$ (2)°
$V = 3814.8$ (2) Å$^3$
$Z = 8$
$D_x = 1.709$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 1.48$ mm$^{-1}$
$T = 100.0$ (1) K
Needle, blue
0.43 × 0.13 × 0.10 mm

### *Data collection*

Bruker SMART APEX2 CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.794$, $T_{max} = 0.863$
41516 measured reflections
9198 independent reflections
7032 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 28.0°$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.137$
$S = 1.04$
9198 reflections
482 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.89$ e Å$^{-3}$
$\Delta\rho_{min} = -1.04$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—N5 | 1.986 (4) | Cu2—N11 | 1.985 (4) |
| Cu1—N1 | 2.051 (4) | Cu2—N7 | 2.039 (4) |
| Cu1—N4 | 2.053 (5) | Cu2—N9 | 2.071 (4) |
| Cu1—N3 | 2.061 (5) | Cu2—N10 | 2.090 (4) |
| Cu1—N2 | 2.138 (4) | Cu2—N8 | 2.127 (4) |
| | | | |
| N5—Cu1—N1 | 177.58 (17) | N11—Cu2—N7 | 178.76 (17) |
| N1—Cu1—N4 | 85.04 (17) | N7—Cu2—N9 | 83.68 (17) |
| N1—Cu1—N3 | 83.47 (16) | N7—Cu2—N10 | 83.81 (16) |
| N1—Cu1—N2 | 84.00 (16) | N7—Cu2—N8 | 84.20 (16) |

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**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*C*···O11$^{i}$ | 0.90 | 2.28 | 3.086 (6) | 150 |
| N2—H2*D*···O13$^{ii}$ | 0.90 | 2.26 | 3.110 (6) | 157 |
| N3—H3*C*···O6$^{iii}$ | 0.90 | 2.56 | 3.260 (7) | 136 |
| N3—H3*D*···O9$^{iv}$ | 0.90 | 2.40 | 3.151 (7) | 141 |
| N4—H4*C*···O10$^{iv}$ | 0.90 | 2.22 | 3.072 (6) | 157 |
| N4—H4*D*···O11$^{i}$ | 0.90 | 2.56 | 3.193 (7) | 128 |
| N8—H8*B*···O7$^{v}$ | 0.90 | 2.33 | 3.094 (6) | 143 |
| N8—H8*C*···O3 | 0.90 | 2.44 | 3.267 (5) | 154 |
| N8—H8*C*···O4 | 0.90 | 2.47 | 3.218 (6) | 141 |
| N9—H9*B*···O8$^{vi}$ | 0.90 | 2.23 | 3.050 (6) | 152 |
| N9—H9*C*···O16 | 0.90 | 2.50 | 3.100 (6) | 125 |
| N9—H9*C*···O7$^{v}$ | 0.90 | 2.43 | 3.086 (7) | 130 |
| N10—H10*D*···O12 | 0.90 | 2.53 | 3.340 (8) | 150 |
| N10—H10*E*···O2$^{vii}$ | 0.90 | 2.28 | 3.070 (6) | 146 |
| C3—H3*A*···O6$^{iii}$ | 0.97 | 2.35 | 3.173 (6) | 142 |
| C3—H3*B*···O3 | 0.97 | 2.58 | 3.547 (6) | 172 |
| C6—H6*B*···O1$^{i}$ | 0.97 | 2.50 | 3.237 (6) | 132 |
| C8—H8*A*···O13$^{viii}$ | 0.96 | 2.56 | 3.360 (8) | 143 |
| C12—H12*A*···O12 | 0.97 | 2.53 | 3.426 (8) | 153 |
| C15—H15*B*···O14$^{vi}$ | 0.97 | 2.54 | 3.511 (6) | 177 |
| C17—H17*A*···O2$^{vii}$ | 0.93 | 2.56 | 3.318 (7) | 139 |
| C18—H18*A*···O3$^{ix}$ | 0.93 | 2.52 | 3.377 (7) | 153 |
| C20—H20*B*···O2$^{ix}$ | 0.96 | 2.60 | 3.385 (7) | 140 |

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vii) $x, y+1, z$; (viii) $x+1, y, z$; (ix) $-x+1, -y, -z$.

H atoms attached to N atoms were initially located in a difference map to check the correctness of their positions. For the final refinement, all H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.90 Å. The $U_{\rm iso}$ values were constrained to be $1.5U_{\rm eq}$ of the carrier atoms for the methyl H atoms and $1.2U_{\rm eq}$ of the carrier atoms for the others. The deepest residual density hole is 0.91 Å from atom Cu2.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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