

(11,13-Dimethyl-1,4,7,10-tetraazacyclo-trideca-10,13-dienato)copper(II) perchlorate

Xiao-qiang He

 Chemical Technology & Medicine College, Jingchu University of Technology, Jingmen, Hubei 448000, People's Republic of China
 Correspondence e-mail: jclghxq@126.com

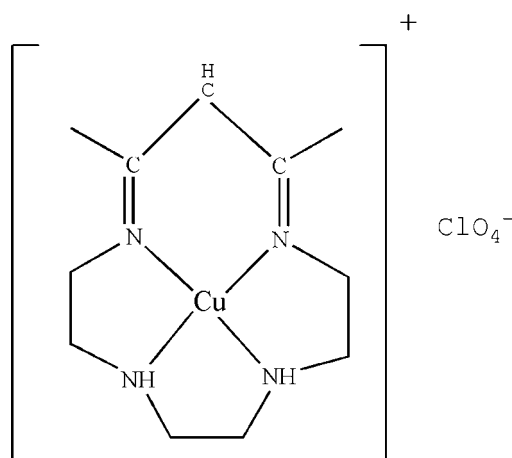
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.067; wR factor = 0.216; data-to-parameter ratio = 13.8.

The title complex, $[\text{Cu}(\text{C}_{11}\text{H}_{21}\text{N}_4)]\text{ClO}_4$, comprises $[\text{Cu}^{\text{II}}(\text{L})]^+$ ($\text{L} = 11,13$ -dimethyl-1,4,7,10-tetraazacyclo-trideca-10,12-dienate) cations and a perchlorate anion. The Cu atom is located on a twofold crystallographic symmetry axis and is coordinated by four N atoms in a slightly distorted square-planar geometry. Intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds are present.

Related literature

For macrocyclic ligands containing four N atoms in a square-planar coordination geometry, see: Andrews *et al.* (1999); Kim *et al.* (2004); Richardson & Sievers (1972).



Experimental

Crystal data

$[\text{Cu}(\text{C}_{11}\text{H}_{21}\text{N}_4)]\text{ClO}_4$	$V = 1541.2 (11) \text{ \AA}^3$
$M_r = 372.31$	$Z = 4$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 12.530 (5) \text{ \AA}$	$\mu = 1.61 \text{ mm}^{-1}$
$b = 14.469 (6) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 8.501 (4) \text{ \AA}$	$0.15 \times 0.13 \times 0.11 \text{ mm}$

Data collection

Bruker APEXII CCD area-detector diffractometer	6834 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	1349 independent reflections
$T_{\text{min}} = 0.794$, $T_{\text{max}} = 0.843$	950 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$	98 parameters
$wR(F^2) = 0.216$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$
1349 reflections	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}^{\text{ii}}$	0.91	2.02	2.917 (8)	168

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2468).

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supporting information

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(11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-dienato)copper(II) perchlorate

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S1. Comment

Macrocyclic ligands containing four N atoms located in a square planar coordination geometry have been intensely studied during the past several decades (Richardson, *et al.*, 1972; Andrews, *et al.*, 1999; Kim, *et al.*, 2004). Here, we report a macrocycle tetraaza copper(II) complex based on the condensation of triethylenetetraamine (trien) with acetylacetone in the presence of copper(II) perchlorate.

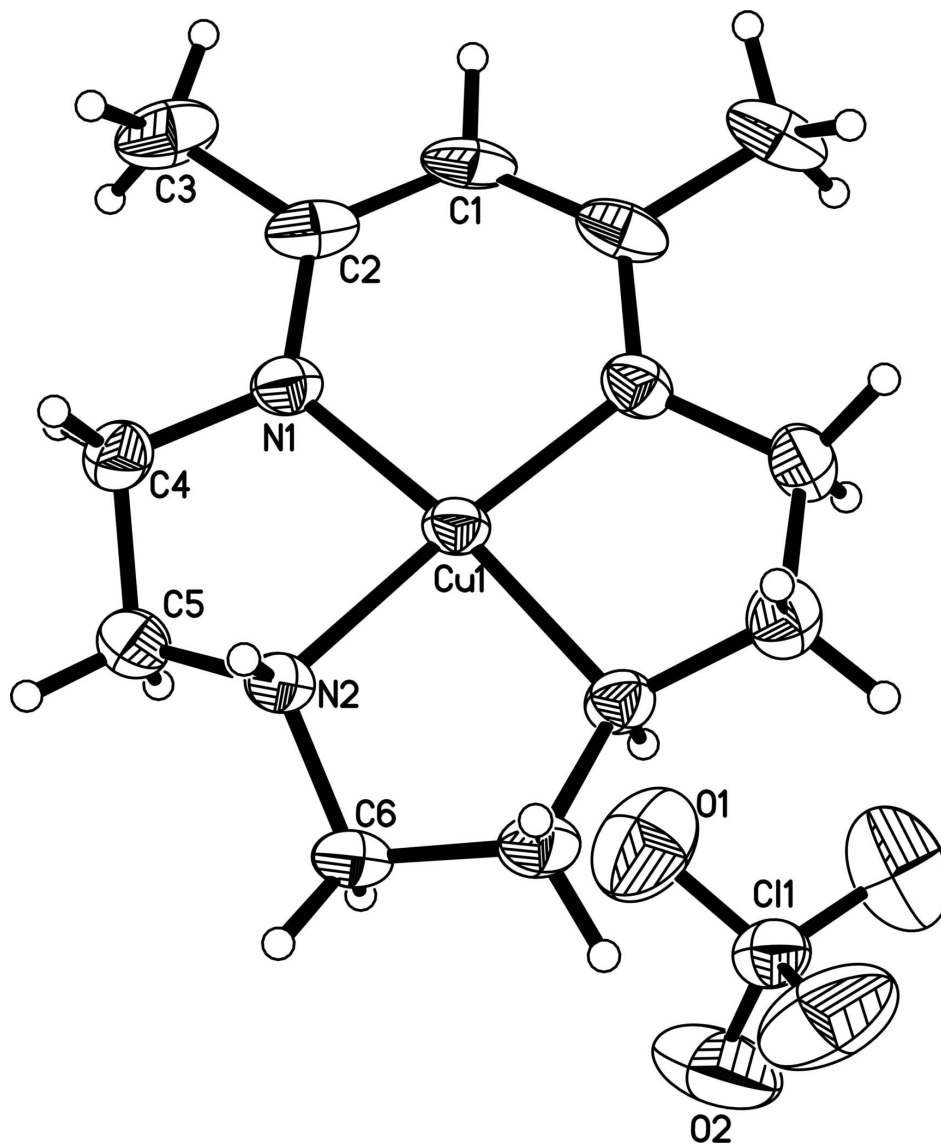
The geometry and labelling scheme for the crystal structure of the title complex are depicted in Figure 1. The coordination sphere for the Cu^{II} ion in the title complex, which coordinates to four N atoms from triethylenetetraamine, is square planar with a mean deviation from the plane formed by the Cu atom and four N atoms of 0.0929 Å. The bond lengths of Cu1—N1 and Cu1—N2 are 1.809 (4) and 1.876 (4) Å, respectively, which are slightly shorter than the corresponding distances found in another macrocycle copper complex 13,14-benzo-2,4,9,11-tetramethyl-1,5,8,12-tetraazacyclotetradeca-1,3,9,11-tetraenato(2-)copper(II) (Kim, *et al.*, 2004).

S2. Experimental

The title complex has been synthesized by the template method used commonly for synthesize metal complexes of macrocycle ligand. After the mixture, which is formed by acetylacetone, trien and Cu(ClO₄)₂·6H₂O with a molar ratio 1:1:1 in methanol/water(v:v, 1:1), has been stirred for 6 h at 323 K, it was filtered and the filtrate was allowed to partial evaporate in air for one week to produce crystals suitable for X-ray diffraction with a yield of about 45%.

S3. Refinement

All the H atoms were constrained with C—H distances of 0.93, 0.96, 0.97 Å and N—H distances of 0.91 Å, respectively, and were allowed for as riding atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$ and $1.5U_{\text{eq}}(\text{C})$.

**Figure 1**

A view of the cation of the title complex with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

(11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-dienato)copper(II) perchlorate

Crystal data

[Cu(C₁₁H₂₁N₄)]ClO₄
M_r = 372.31
 Orthorhombic, *Pbcn*
 Hall symbol: -P 2n 2ab
a = 12.530 (5) Å
b = 14.469 (6) Å
c = 8.501 (4) Å
V = 1541.2 (11) Å³
Z = 4
F(000) = 772

D_x = 1.605 Mg m⁻³
D_m = 1.605 Mg m⁻³
D_m measured by not measured
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 1838 reflections
 θ = 3.2–24.7°
 μ = 1.61 mm⁻¹
T = 293 K
 Block, blue
 0.15 × 0.13 × 0.11 mm

Data collection

Bruker APEXII CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 φ and ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 2003)
 $T_{\min} = 0.794$, $T_{\max} = 0.843$

6834 measured reflections
1349 independent reflections
950 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -14 \rightarrow 12$
 $k = -15 \rightarrow 17$
 $l = -9 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.216$
 $S = 1.05$
1349 reflections
98 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.144P)^2 + 0.9336P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.10 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.0000	0.32069 (5)	0.2500	0.0431 (4)
Cl1	0.0000	0.14239 (18)	0.7500	0.0660 (7)
O1	0.0525 (6)	0.2000 (6)	0.6429 (9)	0.139 (3)
O2	0.0806 (8)	0.0904 (4)	0.8238 (11)	0.160 (3)
N1	0.0904 (3)	0.4014 (3)	0.1568 (5)	0.0481 (11)
N2	0.0740 (3)	0.2278 (3)	0.1414 (5)	0.0476 (11)
H2	0.0427	0.2219	0.0453	0.057*
C1	0.0000	0.5334 (6)	0.2500	0.060 (2)
H1	0.0000	0.5976	0.2500	0.072*
C2	0.0803 (4)	0.4932 (3)	0.1651 (7)	0.0579 (15)
C3	0.1590 (5)	0.5506 (4)	0.0804 (9)	0.078 (2)
H3A	0.2298	0.5334	0.1122	0.117*
H3B	0.1471	0.6146	0.1047	0.117*
H3C	0.1513	0.5412	-0.0308	0.117*
C4	0.1727 (4)	0.3589 (4)	0.0637 (7)	0.0576 (14)
H4A	0.2396	0.3916	0.0780	0.069*

H4B	0.1537	0.3613	-0.0469	0.069*
C5	0.1840 (4)	0.2618 (4)	0.1151 (8)	0.0597 (14)
H5A	0.2253	0.2581	0.2114	0.072*
H5B	0.2193	0.2254	0.0347	0.072*
C6	0.0587 (5)	0.1407 (4)	0.2241 (7)	0.0574 (15)
H6A	0.1056	0.1369	0.3147	0.069*
H6B	0.0732	0.0888	0.1552	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0446 (7)	0.0320 (6)	0.0526 (7)	0.000	-0.0004 (3)	0.000
Cl1	0.0883 (17)	0.0572 (14)	0.0526 (13)	0.000	0.0019 (10)	0.000
O1	0.113 (5)	0.182 (6)	0.122 (6)	-0.012 (5)	-0.020 (4)	0.056 (5)
O2	0.244 (10)	0.106 (4)	0.130 (6)	0.077 (6)	-0.015 (7)	0.003 (5)
N1	0.045 (2)	0.039 (2)	0.060 (3)	-0.0019 (17)	-0.004 (2)	0.0077 (19)
N2	0.055 (3)	0.038 (2)	0.049 (2)	0.0060 (18)	0.0024 (19)	0.0023 (17)
C1	0.069 (5)	0.022 (3)	0.090 (7)	0.000	-0.026 (5)	0.000
C2	0.058 (3)	0.041 (3)	0.075 (4)	-0.011 (3)	-0.031 (3)	0.012 (3)
C3	0.078 (4)	0.051 (3)	0.104 (5)	-0.027 (3)	-0.026 (4)	0.020 (3)
C4	0.048 (3)	0.057 (3)	0.068 (4)	-0.002 (2)	0.006 (3)	0.011 (3)
C5	0.053 (3)	0.059 (3)	0.068 (4)	0.010 (2)	0.002 (3)	0.008 (3)
C6	0.070 (4)	0.034 (3)	0.068 (4)	0.007 (3)	0.002 (3)	0.004 (2)

Geometric parameters (Å, °)

Cu1—N1 ⁱ	1.809 (4)	C1—C2 ⁱ	1.367 (7)
Cu1—N1	1.809 (4)	C1—H1	0.9300
Cu1—N2 ⁱ	1.876 (4)	C2—C3	1.477 (8)
Cu1—N2	1.876 (4)	C3—H3A	0.9600
Cl1—O1 ⁱⁱ	1.399 (8)	C3—H3B	0.9600
Cl1—O1	1.399 (8)	C3—H3C	0.9600
Cl1—O2	1.407 (8)	C4—C5	1.479 (8)
Cl1—O2 ⁱⁱ	1.407 (8)	C4—H4A	0.9700
N1—C2	1.337 (6)	C4—H4B	0.9700
N1—C4	1.438 (7)	C5—H5A	0.9700
N2—C6	1.455 (7)	C5—H5B	0.9700
N2—C5	1.481 (7)	C6—C6 ⁱ	1.535 (13)
N2—H2	0.9100	C6—H6A	0.9700
C1—C2	1.367 (7)	C6—H6B	0.9700
N1 ⁱ —Cu1—N1	99.6 (3)	C1—C2—C3	120.7 (5)
N1 ⁱ —Cu1—N2 ⁱ	86.43 (19)	C2—C3—H3A	109.5
N1—Cu1—N2 ⁱ	170.85 (17)	C2—C3—H3B	109.5
N1 ⁱ —Cu1—N2	170.85 (17)	H3A—C3—H3B	109.5
N1—Cu1—N2	86.43 (19)	C2—C3—H3C	109.5
N2 ⁱ —Cu1—N2	88.4 (2)	H3A—C3—H3C	109.5
O1 ⁱⁱ —Cl1—O1	106.9 (7)	H3B—C3—H3C	109.5

O1 ⁱⁱ —C11—O2	111.4 (5)	N1—C4—C5	108.2 (4)
O1—C11—O2	105.8 (5)	N1—C4—H4A	110.1
O1 ⁱⁱ —C11—O2 ⁱⁱ	105.8 (5)	C5—C4—H4A	110.1
O1—C11—O2 ⁱⁱ	111.4 (5)	N1—C4—H4B	110.1
O2—C11—O2 ⁱⁱ	115.3 (7)	C5—C4—H4B	110.1
C2—N1—C4	121.5 (4)	H4A—C4—H4B	108.4
C2—N1—Cu1	124.0 (4)	C4—C5—N2	105.8 (4)
C4—N1—Cu1	114.5 (3)	C4—C5—H5A	110.6
C6—N2—C5	118.9 (4)	N2—C5—H5A	110.6
C6—N2—Cu1	108.5 (3)	C4—C5—H5B	110.6
C5—N2—Cu1	107.2 (3)	N2—C5—H5B	110.6
C6—N2—H2	107.2	H5A—C5—H5B	108.7
C5—N2—H2	107.2	N2—C6—C6 ⁱ	105.3 (4)
Cu1—N2—H2	107.2	N2—C6—H6A	110.7
C2—C1—C2 ⁱ	129.7 (7)	C6 ⁱ —C6—H6A	110.7
C2—C1—H1	115.1	N2—C6—H6B	110.7
C2 ⁱ —C1—H1	115.1	C6 ⁱ —C6—H6B	110.7
N1—C2—C1	121.3 (6)	H6A—C6—H6B	108.8
N1—C2—C3	118.0 (6)		

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $-x, y, -z+3/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots C11 ⁱⁱⁱ	0.91	2.81	3.668 (5)	157
N2—H2 \cdots O1 ⁱ	0.91	2.02	2.917 (8)	168

Symmetry codes: (i) $-x, y, -z+1/2$; (iii) $x, y, z-1$.