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# Structure of [(3*RS*,7*SR*)-3,7-Dimethyl-3,7-diazanonane-1,9-diamine]-perchloratocopper(II) Perchlorate, $[Cu(ClO_4)(C_9H_{24}N_4)](ClO_4)$

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## Abstract

The $Cu^{II}$ is coordinated in a slightly distorted square pyramid with the four N atoms equatorial and the O atom of the perchlorate group axial. The four donor N atoms are coplanar; $Cu^{II}$ is 0.0165 Å out of this plane towards the perchlorate group. This complex has the (3*RS*,7*SR*) configuration at the chiral N centers, with the two *N*-methyl groups on the same side of the plane of the four N atoms. The tetraamine binds to the $Cu^{II}$ atom in a relatively strain-free planar fashion; the central six-membered ring exhibits a stable chair form and the two terminal five-membered rings take stable skew forms.

## Comment

The crystal structures of open-chain tetraamine complexes containing primary and secondary amine groups have been extensively studied. However, analogous complexes containing tertiary amine groups have received very little attention. In order to study the steric effects of *N*-methyl groups on the structure of the copper(II) complex, we have prepared and studied the structure of the title complex.

1,9-Diamino-3,7-dimethyl-3,7-diazanonane was synthesized according to the method of Yoshikawa & Sekihara (1967). To its solution (3.76 g, 0.02 mol in 2-propanol, 80 ml), a solution of $Cu(ClO_4)_2.6H_2O$ (7.4 g, 0.02 mol in methanol, 80 ml) was added dropwise. The color of the solution changed rapidly to deep blue and blue precipitates formed. Single crystals were obtained from aqueous solution by slow evaporation.

As a result of the two bulky axial *N*-methyl groups lying above the metal ion and hindering the axial position, this complex is five coordinate; the geometry about the $Cu^{II}$ ion is slightly distorted square pyramidal with a tetraamine N atom equatorial and an O atom of the perchlorate group axial. The four N atoms of tetraamine are coplanar within 0.011 (3) Å. The deviation of $Cu^{II}$ ion from the best

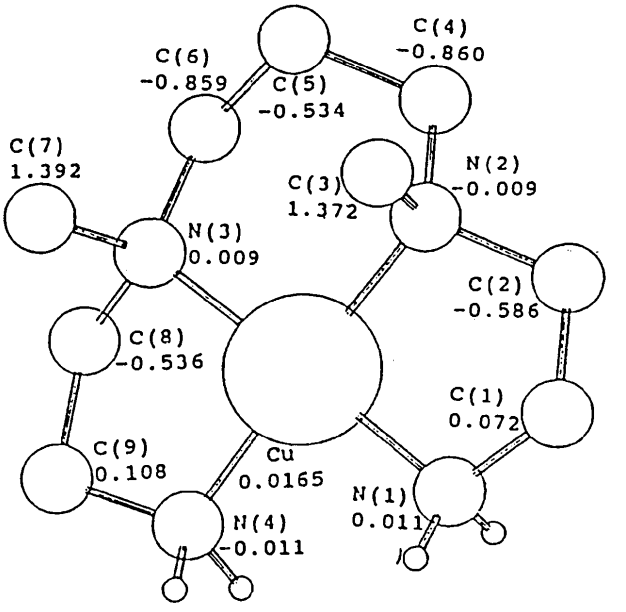


Fig. 1. A perspective view of the molecule with the numbering scheme excluding the H atoms attached to the C atoms and the perchlorate ions. The displacements (Å) of the atoms from the best plane formed by the four N atoms coordinated to the $Cu^{II}$ ion are indicated.

plane formed by these N atoms is 0.0165 Å towards the perchlorate O atom. The other unbonded perchlorate group in the crystal is disordered. In this complex the alternative five-, six- and five-membered chelate rings have the stable skew, chair and skew conformations, respectively, the configuration of the chiral N centers is (*3RS,7SR*).

## Experimental

*Crystal data*

$[Cu(ClO_4)(C_9H_{24}N_4)](ClO_4)$
$M_r$ = 450.76
Monoclinic
$P2_1/c$
$a$ = 8.4229 (5) Å
$b$ = 12.850 (3) Å
$c$ = 16.4655 (8) Å
$\beta$ = 94.959 (5)°
$V$ = 1775.5 (4) Å$^3$
$Z$ = 4
$D_x$ = 1.667 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 5.65–17.3°
$\mu$ = 1.58 mm$^{-1}$
$T$ = 298 (3) K
0.41 × 0.28 × 0.28 mm
Purple

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{min}$ = 0.905, $T_{max}$ = 0.999
3332 measured reflections
3106 independent reflections
2498 observed reflections [$I > 2.5\sigma(I)$]
$R_{int}$ = 0.019
$\theta_{max}$ = 24.9°
$h = -10 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: ±2.0%

*Refinement*

Refinement on $F$
$R$ = 0.032
$wR$ = 0.032
$S$ = 0.97
2498 reflections
265 parameters
Only H-atom $U$'s refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.108
$\Delta\rho_{max}$ = 0.39 (6) e Å$^{-3}$
$\Delta\rho_{min}$ = −0.30 (6) e Å$^{-3}$
Extinction correction: *NRCVAX*
Extinction coefficient: 0.114 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$B_{eq} = (32\pi^2/3)\Sigma_i\Sigma_j U_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Cu | 0.82172 (5) | 0.22141 (3) | 0.099151 (24) | 2.564 (15) |
| Cl(1) | 0.88029 (10) | 0.82662 (7) | 1.03938 (5) | 3.25 (3) |
| Cl(2) | 0.41540 (14) | 0.56737 (8) | 0.25770 (6) | 4.66 (5) |
| O(1) | 0.7915 (3) | 0.87182 (22) | 0.96994 (16) | 4.58 (12) |
| O(2) | 0.7753 (3) | 0.7862 (3) | 1.09406 (18) | 6.06 (16) |
| O(3) | 0.9771 (3) | 0.74417 (21) | 1.01066 (19) | 4.96 (13) |
| O(4) | 0.9836 (4) | 0.90423 (23) | 1.07715 (19) | 5.51 (14) |
| O(51) | 0.4074 (15) | 0.6642 (8) | 0.2936 (9) | 11.3 (7) |
| O(52) | 0.347 (3) | 0.6600 (13) | 0.2664 (16) | 11.9 (14) |
| O(61) | 0.5303 (10) | 0.5689 (13) | 0.2024 (7) | 10.9 (6) |
| O(62) | 0.4460 (24) | 0.5336 (21) | 0.1875 (9) | 10.5 (14) |
| O(71) | 0.6505 (11) | −0.0109 (4) | 0.1955 (4) | 11.8 (5) |
| O(72) | 0.471 (3) | 0.520 (3) | 0.3181 (16) | 14.0 (20) |
| O(81) | 0.2665 (7) | 0.5647 (7) | 0.2077 (4) | 10.0 (4) |
| O(82) | 0.5611 (15) | 0.5591 (11) | 0.3152 (9) | 9.7 (7) |
| N(1) | 0.7306 (3) | 0.09938 (21) | 0.03570 (19) | 3.30 (13) |
| N(2) | 0.6627 (3) | 0.30778 (20) | 0.02707 (17) | 2.95 (11) |
| N(3) | 0.9219 (3) | 0.34142 (22) | 0.16599 (17) | 3.26 (12) |
| N(4) | 0.9791 (4) | 0.13095 (23) | 0.16539 (19) | 3.60 (13) |
| C(1) | 0.5977 (4) | 0.1318 (3) | −0.02304 (24) | 3.94 (16) |
| C(2) | 0.6281 (4) | 0.2427 (3) | −0.04738 (22) | 3.73 (16) |
| C(3) | 0.5114 (4) | 0.3238 (3) | 0.0664 (3) | 4.24 (18) |
| C(4) | 0.7256 (4) | 0.4103 (3) | 0.00220 (23) | 3.56 (16) |
| C(5) | 0.7915 (5) | 0.4784 (3) | 0.07220 (25) | 4.04 (17) |
| C(6) | 0.9434 (5) | 0.4376 (3) | 0.11768 (24) | 3.92 (17) |
| C(7) | 0.8283 (6) | 0.3663 (3) | 0.2362 (3) | 4.69 (20) |
| C(8) | 1.0827 (5) | 0.3014 (3) | 0.19769 (25) | 4.41 (18) |
| C(9) | 1.0690 (5) | 0.1924 (3) | 0.22961 (25) | 4.52 (18) |

Table 2. *Selected bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Cu—O(3) | 2.620 (3) | N(3)—C(6) | 1.490 (5) |
| Cu—N(1) | 2.000 (3) | N(3)—C(7) | 1.489 (5) |
| Cu—N(2) | 2.040 (3) | N(3)—C(8) | 1.499 (5) |
| Cu—N(3) | 2.035 (3) | N(4)—C(9) | 1.476 (5) |
| Cu—N(4) | 2.012 (3) | C(1)—C(2) | 1.509 (5) |
| N(1)—C(1) | 1.475 (5) | C(4)—C(5) | 1.514 (6) |
| N(2)—C(2) | 1.491 (4) | C(5)—C(6) | 1.519 (6) |
| N(2)—C(3) | 1.493 (5) | C(8)—C(9) | 1.504 (6) |
| N(2)—C(4) | 1.490 (4) | | |
| N(1)—Cu—N(2) | 85.39 (11) | Cu—N(3)—C(7) | 111.09 (23) |
| N(1)—Cu—N(3) | 177.50 (12) | Cu—N(3)—C(8) | 104.37 (21) |
| N(1)—Cu—N(4) | 92.01 (12) | C(6)—N(3)—C(7) | 109.4 (3) |
| N(2)—Cu—N(3) | 97.08 (11) | C(6)—N(3)—C(8) | 108.8 (3) |
| N(2)—Cu—N(4) | 177.00 (12) | C(7)—N(3)—C(8) | 109.1 (3) |
| N(3)—Cu—N(4) | 85.51 (12) | Cu—N(4)—C(9) | 110.65 (23) |
| Cu—N(1)—C(1) | 110.87 (21) | N(1)—C(1)—C(2) | 107.7 (3) |
| Cu—N(2)—C(2) | 104.19 (19) | N(2)—C(2)—C(1) | 109.7 (3) |
| Cu—N(2)—C(3) | 111.39 (22) | N(2)—C(4)—C(5) | 114.7 (3) |
| Cu—N(2)—C(4) | 114.17 (21) | C(4)—C(5)—C(6) | 114.4 (3) |
| C(2)—N(2)—C(3) | 108.7 (3) | N(3)—C(6)—C(5) | 114.5 (3) |
| C(2)—N(2)—C(4) | 108.6 (3) | N(3)—C(8)—C(9) | 110.3 (3) |
| C(3)—N(2)—C(4) | 109.5 (3) | N(4)—C(9)—C(8) | 107.3 (3) |
| Cu—N(3)—C(6) | 113.83 (22) | | |

Occupancy factors of the disordered perchlorate group are: O(51) 0.65, O(52) 0.35, O(61) 0.65, O(62) 0.35, O(71) 0.77, O(72) 0.23, O(81) 0.6 and O(82) 0.4. The structure was solved using the *NRCVAX* program (Gabe, Le Page, White & Lee, 1987).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71379 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1041]

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