

C(24)	-0.1781 (6)	1.1636 (5)	0.2799 (5)	0.061 (3)
C(25)	-0.1528 (5)	1.0499 (5)	0.2534 (5)	0.047 (3)
C(30)	0.1513 (5)	0.8852 (5)	0.3330 (4)	0.039 (2)
C(31)	0.2561 (5)	0.8587 (6)	0.3100 (5)	0.061 (3)
C(32)	0.3679 (6)	0.8608 (8)	0.3884 (7)	0.086 (4)
C(33)	0.3773 (7)	0.8852 (7)	0.4854 (6)	0.087 (4)
C(34)	0.2731 (8)	0.9127 (6)	0.5126 (5)	0.083 (4)
C(35)	0.1606 (6)	0.9114 (6)	0.4346 (4)	0.060 (3)
C(40)	-0.2321 (5)	0.5554 (4)	0.0955 (4)	0.038 (2)
C(41)	-0.2184 (6)	0.4372 (5)	0.0659 (4)	0.051 (3)
C(42)	-0.2942 (7)	0.3603 (6)	-0.0324 (5)	0.066 (3)
C(43)	-0.3806 (7)	0.4032 (6)	-0.0988 (5)	0.071 (3)
C(44)	-0.3969 (6)	0.5206 (6)	-0.0706 (5)	0.067 (3)
C(45)	-0.3217 (5)	0.5954 (5)	0.0280 (4)	0.050 (3)
C(50)	-0.2390 (4)	0.6491 (5)	0.2971 (4)	0.037 (2)
C(51)	-0.2552 (5)	0.7514 (5)	0.3580 (4)	0.049 (3)
C(52)	-0.3292 (6)	0.7440 (7)	0.4154 (5)	0.066 (3)
C(53)	-0.3884 (6)	0.6341 (7)	0.4101 (5)	0.071 (3)
C(54)	-0.3722 (6)	0.5314 (7)	0.3476 (5)	0.069 (3)
C(55)	-0.2986 (5)	0.5358 (6)	0.2903 (4)	0.052 (3)
C(60)	-0.0022 (5)	0.6014 (4)	0.2798 (4)	0.045 (2)
C(61)	0.0762 (6)	0.5680 (6)	0.2264 (6)	0.065 (3)
C(62)	0.1914 (6)	0.5375 (6)	0.2769 (7)	0.076 (4)
C(63)	0.2273 (6)	0.5432 (6)	0.3784 (7)	0.076 (4)
C(64)	0.1528 (7)	0.5768 (6)	0.4314 (6)	0.079 (4)
C(65)	0.0385 (5)	0.6064 (5)	0.3830 (5)	0.055 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Au(1)—S(1)	2.288 (2)	S(2)—C(1 ⁱⁱ)	1.733 (7)
Au(1 ⁱ)—S(2)	2.285 (2)	C(1)—N(1)	1.326 (8)
Au(1)···Au(1 ⁱ)	2.813 (1)	N(1)—C(2)	1.314 (8)
S(1)—C(1)	1.727 (6)	C(2)—N(2)	1.138 (10)
S(1)—Au(1)—S(2 ⁱ)	172.3 (1)	S(1)—C(1)—N(1)	113.0 (5)
S(1)—Au(1)···Au(1 ⁱ)	94.7 (1)	S(2 ⁱ)—C(1)—N(1)	118.5 (4)
S(2 ⁱ)—Au(1)···Au(1 ⁱ)	92.9 (1)	N(1)—C(2)—N(2)	171.3 (9)
Au(1)—S(1)—C(1)	111.0 (2)	C(1)—N(1)—C(2)	120.3 (6)
S(1)—C(1)—S(2 ⁱ)	128.5 (4)		

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

The *SHELXTL-Plus* program package (Sheldrick, 1991) was used for crystallographic computations.

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Lists of structure factors, H-atom coordinates, complete geometry and structure of the $[(C_{18}H_{15}P)_2N]_2$ cation have been deposited with the IUCr (Reference: BK1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(1-methylcytosinium) Tetrachlorocuprate(II)

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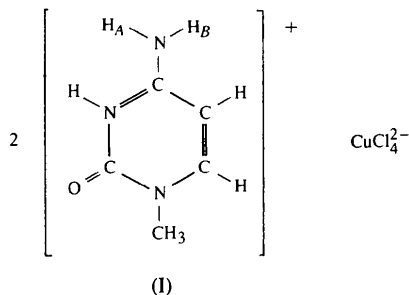
(Received 21 March 1995; accepted 23 May 1995)

Abstract

The structure consists of discrete $C_5H_8N_3O^+$ (4-amino-1-methyl-2-oxo-1,2-dihydropyrimidinium) and $CuCl_4^{2-}$ ions. The coordination about the Cu atom is distorted tetrahedral with an average *trans* Cl—Cu—Cl angle of $127.7(1)^\circ$.

Comment

The title compound, (I), has been found to exhibit a band maximum in the near IR spectrum at *ca* 9100 cm^{-1} . According to an established correlation (Halvorson, Paterson & Willet, 1990), this would correspond to an average *trans* Cl—Cu—Cl angle of about 130° , markedly different from the value of $139.2(1)^\circ$ observed in the closely related compound biscytosinium tetrachlorocuprate, (II) (Ogawa, Nishitani, Fujiwara, Shirotake & Tomita, 1979). To explain this difference, the present crystal structure analysis was undertaken.



The structure consists of discrete $C_5H_8N_3O^+$ and $CuCl_4^{2-}$ ions. There are no intermolecular $Cu \cdots Cl$ contacts less than 4 \AA . Each cation is hydrogen bonded to one anion through N(3)H and N(4)H(A) and to two $C_5H_8N_3O^+$ units related by translation through

† Deceased.

N(4)H(B) and O(2). The average *trans* Cl—Cu—Cl angle in (I) is $11.5(1)^\circ$ less than that in (II) and the average Cu—Cl bond length is $0.010(4) \text{ \AA}$ longer in (I) than in (II). Hydrogen bonding is postulated to remove charge from the Cl atoms, thus reducing interligand repulsions and allowing the $CuCl_4^{2-}$ anion to move toward a square-planar configuration (Halvorson, Patterson & Willet, 1990). However, it is questionable whether this effect can be larger in (II) than in (I). In (II), one Cl atom is not hydrogen bonded, while the others make one $[3.372(10) \text{ \AA}]$ or two $[3.352(9) \text{ and } 3.110(9) \text{ \AA}; 3.279(10) \text{ and } 3.257(10) \text{ \AA}]$ N—H...Cl contacts. Instead, the change in the geometry of the $CuCl_4^{2-}$ anion can be attributed to the difference between the hydrogen-bonding patterns of 1-methylcytosinium and cytosinium. There are two non-equivalent cations in (II); one set of $C_4H_6N_3O^+$ units are hydrogen bonded to one another through N(1)H and O(2), and to $CuCl_4^{2-}$ ions through N(3)H, N(4)H(A) and N(4)H(B), and the other $C_4H_6N_3O^+$ units are hydrogen bonded to one another through N(4)H(B) and O(2) contacts, and to $CuCl_4^{2-}$ ions through N(1)H and N(4)H(A).

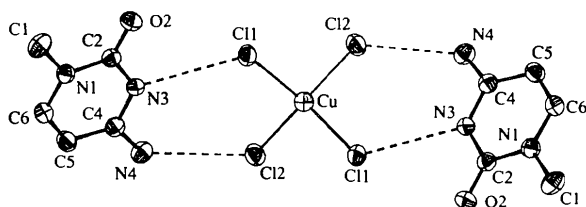


Fig. 1. ORTEP plot (Johnson, 1976) of the stoichiometric unit $2C_5H_8N_3O^+ \cdot CuCl_4^{2-}$. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystals were obtained by slow evaporation of a 1:1 mixture of $CuCl_2$ and 1-methylcytosine in concentrated hydrochloric acid.

Crystal data

$(C_5H_8N_3O)_2[CuCl_4]$

$M_r = 457.6$

Monoclinic

$C2/c$

$a = 12.811(2) \text{ \AA}$

$b = 7.771(1) \text{ \AA}$

$c = 18.098(2) \text{ \AA}$

$\beta = 109.6(1)^\circ$

$V = 1697(1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.79 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7-12^\circ$

$\mu = 1.94 \text{ mm}^{-1}$

Room temperature

Prism

$0.4 \times 0.3 \times 0.2 \text{ mm}$

Orange-yellow

Data collection

Philips PW1100 diffractometer

$\theta/2\theta$ scans

Absorption correction: none

$R_{int} = 0.02$

$\theta_{max} = 28^\circ$

$h = -16 \rightarrow 15$

$k = 0 \rightarrow 10$

$l = 0 \rightarrow 23$

2118 measured reflections
2045 independent reflections
1537 observed reflections
 $[F > 3\sigma(F)]$

Refinement

Refinement on F

$R = 0.05$

$wR = 0.055$

$S = 1.13$

1537 reflections

135 parameters

Only H-atom U 's refined

$w = 1/[\sigma^2(F) + 0.002386F^2]$

$(\Delta/\sigma)_{max} = 0.511$

3 standard reflections
monitored every 50 reflections
intensity decay: none

$\Delta\rho_{max} = 1.78 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -2.21 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from SHELX76 (Sheldrick, 1976); *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cu	1/2	0.18730 (9)	1/4	0.0291 (2)
Cl(1)	0.64355 (8)	0.3225 (1)	0.33918 (5)	0.0339 (3)
Cl(2)	0.41740 (8)	0.0684 (1)	0.32841 (6)	0.0362 (3)
N(1)	0.7619 (3)	-0.0766 (4)	0.3784 (2)	0.028 (1)
C(2)	0.7610 (3)	-0.0148 (5)	0.4496 (2)	0.028 (1)
N(3)	0.8452 (3)	0.1017 (4)	0.4861 (2)	0.028 (1)
C(4)	0.9187 (3)	0.1648 (5)	0.4543 (2)	0.028 (1)
C(5)	0.9119 (3)	0.1049 (5)	0.3793 (2)	0.032 (1)
C(6)	0.8338 (3)	-0.0137 (5)	0.3442 (2)	0.031 (1)
Cl(1)	0.6796 (4)	-0.2081 (5)	0.3397 (3)	0.039 (1)
O(2)	0.6941 (2)	-0.0587 (4)	0.4805 (2)	0.040 (1)
N(4)	0.9941 (3)	0.2756 (5)	0.4950 (2)	0.035 (1)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Cu—Cl(1)	2.258 (2)	Cu—Cl(2)	2.235 (2)
N(1)—C(2)	1.379 (5)	N(1)—C(6)	1.360 (6)
N(1)—C(1)	1.466 (5)	C(2)—N(3)	1.393 (5)
C(2)—O(2)	1.219 (6)	N(3)—C(4)	1.351 (6)
C(4)—C(5)	1.410 (6)	C(4)—N(4)	1.318 (5)
C(5)—Cl(6)	1.352 (5)		
Cl(1)—Cu—Cl(2)	101.6 (1)	Cl(1)—Cu—Cl(1')	124.4 (1)
Cl(2)—Cu—Cl(2')	131.0 (1)	C(2)—N(1)—C(1)	117.3 (4)
C(2)—N(1)—C(6)	121.2 (3)	N(1)—C(2)—O(2)	124.0 (4)
N(1)—C(2)—N(3)	115.0 (4)	N(3)—C(2)—O(2)	121.0 (4)
C(2)—N(3)—C(4)	125.0 (3)	N(3)—C(4)—N(4)	118.9 (4)
N(3)—C(4)—C(5)	117.6 (4)	C(5)—C(4)—N(4)	123.4 (4)
C(4)—C(5)—C(6)	118.3 (4)	N(1)—C(6)—C(5)	122.6 (4)
C(6)—N(1)—C(1)	121.4 (4)		

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

Table 3. Contact distances (\AA)

N(3)...Cl(1')	3.171 (3)	N(4)...O(2 ⁱⁱ)	2.957 (5)
N(4)...Cl(2')	3.247 (4)		

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

The Cu atoms was first located from a Patterson map and then a difference Fourier map revealed the other atoms.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: SHELX76 (Sheldrick, 1976); SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELX76. Molecular graphics: ORTEP II (Johnson, 1976). Geometric calculations: PARST (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diperchlorato[(2*RS*,5*SR*,9*RS*,12*RS*)-2,5,9,12-tetraazatridecane]copper(II)

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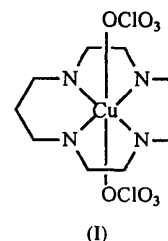
Abstract

The Cu^{II} ion in the title compound, [Cu(C₉H₂₄N₄)(ClO₄)₂], is six-coordinate in a distorted square-bipyramidal environment; four tetraamine N atoms are equatorial and two O atoms, one from each perchlorate ion, are axial. The quadridentate ligand is in its stable planar conformation with the central six-membered chelate ring in a chair form and both terminal five-membered rings in *gauche* forms. The four chiral N-atom centres have configurations 2*RS*, 5*SR*, 9*RS* and 12*RS*.

Comment

The Cu^{II} complexes of aliphatic tetraamines have been studied extensively because of their diverse stereochemistry. We describe here the crystal structure of

the title compound, diperchlorato(2,5,9,12-tetraazatri-decane)copper(II), [Cu(α,ω -*N*-Me₂-2,3,2-tet)(ClO₄)₂], (I) (where tet = tetraazatridecane).



The coordination geometry around the Cu^{II} ion is slightly distorted square bipyramidal with the four tetraamine N atoms equatorial and the two O atoms, one from each perchlorate ion, axial. The quadridentate ligand is in its stable planar conformation with the central six-membered chelate ring in a chair form and both five-membered rings in *gauche* forms. The arrangement of the tetraamine ligand in the title complex appears to be relatively free of strain. The configurations of the four chiral N-atom centres are 2*RS*, 5*SR*, 9*RS* and 12*RS*. The hydrogen bonds between the tetraamine and the perchlorate ions, O(4)··H(N1)—N(1) [3.05 (1) Å], O(4)··H(N2)—N(2) [3.12 (1) Å] and O(8)··H(N4)—N(4) [3.17 (1) Å], stabilize the crystal structure.

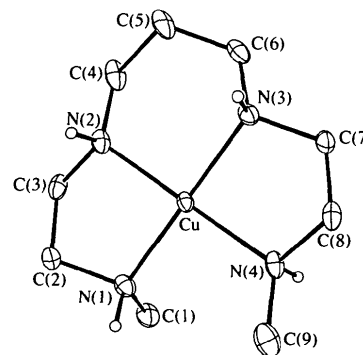


Fig. 1. A perspective view of the molecule with the atom-numbering scheme, excluding the perchlorate ions and the H atoms attached to C atoms. The displacement ellipsoids are drawn at the 50% probability level (Sheldrick, 1987).

The crystal structure of the title complex is almost the same as that of [Cu(2,3,2-tet)(ClO₄)₂] (Fawcett *et al.*, 1980). The stability constant of (I) is smaller than that of Cu(2,3,2-tet)²⁺. In addition, [Cu(α,ω -*N*-Me₂-2,2,2-tet)]²⁺ is more stable than [(Cu(2,2,2-tet)]²⁺, but [Cu(α,ω -*N*-Me₂-2,3,2-tet)]²⁺ is less stable than [Cu(2,3,2-tet)]²⁺ (Clay, Corr, Micheloni & Paoletti, 1985). The effects of the two terminal *N*-Me groups in [Cu(α,ω -*N*-Me₂-2,3,2-tet)]²⁺ and [Cu(α,ω -*N*-Me₂-2,2,2-tet)]²⁺ are completely different from each other.