

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Occupancy	x	y	z	B _{eq}	
Cu	1.0	0.74126 (4)	0.37845 (6)	0.24688 (7)	2.542 (23)
Cl(1)	1.0	0.64326 (11)	0.62300 (12)	0.26226 (15)	4.10 (6)
Cl(2)	1.0	0.11192 (10)	0.38133 (14)	0.32904 (15)	4.16 (7)
O(1)	1.0	0.7221 (4)	0.5553 (4)	0.2490 (7)	7.7 (3)
O(2)	1.0	0.6726 (6)	0.6980 (5)	0.3424 (9)	12.4 (5)
O(3)	0.8	0.5557 (7)	0.5791 (9)	0.2984 (16)	11.9 (10)
O(3')	0.2	0.599 (3)	0.580 (3)	0.367 (3)	6.0 (16)
O(4)	0.8	0.6130 (10)	0.6513 (11)	0.1383 (10)	15.2 (9)
O(4')	0.2	0.6721 (21)	0.6972 (18)	0.1770 (22)	5.0 (11)
O(5)	1.0	0.0487 (5)	0.4639 (5)	0.3228 (8)	9.7 (4)
O(6)	0.8	0.1514 (11)	0.3626 (9)	0.2073 (10)	11.6 (7)
O(6')	0.2	0.0847 (22)	0.351 (4)	0.218 (4)	11.2 (28)
O(7)	0.8	0.0494 (8)	0.3116 (8)	0.3732 (15)	15.4 (9)
O(7')	0.2	0.142 (3)	0.2874 (19)	0.370 (3)	8.7 (20)
O(8)	0.8	0.1857 (9)	0.3950 (12)	0.4221 (12)	15.0 (9)
O(8')	0.2	0.2003 (16)	0.4346 (23)	0.334 (3)	5.9 (15)
N(1)	1.0	0.8661 (4)	0.4025 (4)	0.1423 (5)	4.2 (3)
N(2)	1.0	0.6578 (3)	0.3516 (3)	0.0825 (4)	2.96 (20)
N(3)	1.0	0.6102 (3)	0.3562 (3)	0.3429 (4)	3.02 (19)
N(4)	1.0	0.8198 (4)	0.4010 (5)	0.4151 (5)	4.5 (3)
C(1)	1.0	0.8589 (5)	0.4519 (6)	0.0124 (7)	4.8 (3)
C(2)	1.0	0.7849 (5)	0.4038 (5)	-0.0788 (6)	4.9 (3)
C(3)	1.0	0.6767 (5)	0.4121 (5)	-0.0363 (6)	4.5 (3)
C(4)	1.0	0.5503 (4)	0.3605 (5)	0.1182 (5)	3.56 (24)
C(5)	1.0	0.5324 (4)	0.3122 (4)	0.2500 (6)	3.52 (25)
C(6)	1.0	0.4264 (5)	0.3398 (6)	0.2959 (8)	5.3 (4)
C(7)	1.0	0.5456 (5)	0.2039 (5)	0.2411 (8)	4.8 (3)
C(8)	1.0	0.6138 (6)	0.3092 (6)	0.4742 (7)	5.1 (3)
C(9)	1.0	0.6847 (5)	0.3631 (6)	0.5685 (6)	5.1 (4)
C(10)	1.0	0.7925 (5)	0.3509 (6)	0.5377 (6)	5.2 (3)

Table 2. Selected geometric parameters (Å, °)

Cu—O(1)	2.455 (5)	N(3)—C(8)	1.480 (8)
Cu—N(1)	2.013 (5)	N(4)—C(10)	1.474 (9)
Cu—N(2)	2.019 (4)	C(1)—C(2)	1.49 (1)
Cu—N(3)	2.035 (4)	C(2)—C(3)	1.51 (1)
Cu—N(4)	2.008 (5)	C(4)—C(5)	1.516 (8)
N(1)—C(1)	1.485 (9)	C(5)—C(6)	1.539 (8)
N(2)—C(3)	1.490 (8)	C(5)—C(7)	1.509 (9)
N(2)—C(4)	1.486 (7)	C(8)—C(9)	1.52 (1)
N(3)—C(5)	1.513 (7)	C(9)—C(10)	1.48 (1)
O(1)—Cu—N(1)	85.9 (2)	Cu—N(3)—C(8)	118.8 (4)
O(1)—Cu—N(2)	97.7 (2)	C(5)—N(3)—C(8)	113.2 (4)
O(1)—Cu—N(3)	93.2 (2)	Cu—N(4)—C(10)	120.7 (4)
O(1)—Cu—N(4)	83.7 (2)	N(1)—C(1)—C(2)	112.0 (6)
N(1)—Cu—N(2)	92.4 (2)	C(1)—C(2)—C(3)	114.2 (6)
N(1)—Cu—N(3)	176.6 (2)	N(2)—C(3)—C(2)	111.3 (5)
N(1)—Cu—N(4)	90.0 (2)	N(2)—C(4)—C(5)	110.2 (4)
N(2)—Cu—N(3)	84.5 (2)	N(3)—C(5)—C(4)	104.8 (4)
N(2)—Cu—N(4)	177.3 (2)	N(3)—C(5)—C(6)	109.4 (5)
N(3)—Cu—N(4)	93.1 (2)	N(3)—C(5)—C(7)	110.9 (5)
Cu—O(1)—Cl(1)	137.4 (3)	C(4)—C(5)—C(6)	108.5 (5)
Cu—N(1)—C(1)	120.2 (4)	C(4)—C(5)—C(7)	111.3 (5)
Cu—N(2)—C(3)	117.8 (4)	C(6)—C(5)—C(7)	111.8 (5)
Cu—N(2)—C(4)	107.5 (3)	N(3)—C(8)—C(9)	111.1 (5)
C(3)—N(2)—C(4)	109.2 (4)	C(8)—C(9)—C(10)	113.7 (6)
Cu—N(3)—C(5)	110.2 (3)	N(4)—C(10)—C(9)	112.3 (5)

The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least-squares techniques; H atoms were located from difference Fourier maps. All computing was performed using the NRCVAX system of programs (Gabe, Le Page, White & Lee, 1987).

The authors thank the National Science Council for support under grants NSC82-0208-M007-32. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and hydrogen-bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71619 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1066]

References

- Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* **A43**, C-294.
 Lee, T.-Y., Lee, T.-J., Hong, C.-Y., Hsieh, M.-Y., Wu, D.-T. & Chung, C.-S. (1986). *Acta Cryst.* **C42**, 1316–1319.
 Lu, T.-H., Chung, C.-S. & Ashida, T. (1991). *J. Chin. Chem. Soc. (Taipei)*, **38**, 147–153.
 Lu, T.-H., Shan, H.-C., Chao, M.-S. & Chung, C.-S. (1987). *Acta Cryst.* **C43**, 207–209.
 Tasker, P. A. & Sklar, L. J. (1975). *J. Cryst. Mol. Struct.* **5**, 329–344.
 Zachariassen, W. H. (1967). *Acta Cryst.* **A23**, 558–564.

Acta Cryst. (1994). **C50**, 514–516

[(2RS,5SR,8SR,12SR,15SR)-2,5,8,12,15-Pentaazahexadecane-κ⁵N^{2,5,8,12,15}]copper(II) Diperchlorate

TAHIR H. TAHIROV AND TIAN-HUEY LU*

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300

YUH-LIANG LIU AND CHUNG-SUN CHUNG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

(Received 4 March 1993; accepted 15 September 1993)

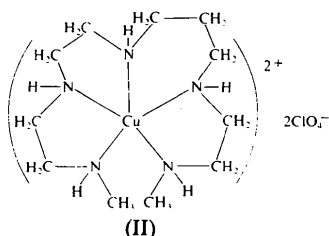
Abstract

The Cu^{II} atom in the title complex, [Cu(C₁₁H₂₉N₅)]-(ClO₄)₂, is five-coordinate and is in a distorted trigonal-bipyramidal conformation. The longer Cu(equatorial)—N bond distances compared to the Cu(axial)—N distances indicate the steric influence of the two N-methyl groups. The ligand is in its stable conformation with the three five-membered chelate rings in stable skew forms and the six-membered ring in a stable chair form.

Comment

The crystal structures of open-chain tetraamine complexes have been studied extensively (Lee *et al.*, 1986;

Fawcett *et al.*, 1980; Marongiu, Lingafelter & Paoletti, 1969). The crystal structures of open-chain pentaamine complexes, however, have received little attention (Gatehouse, Martin, McLachlan, Platts & Spiccia, 1992). The crystal structure of (2,5,8,11,14-pentaazapentadecane)copper(II) diperchlorate monohydrate (I) has been reported (Liu, Tahirov, Lu & Chung, 1992). In recent research we altered one of the four five-membered rings to a six-membered ring; the structure of this new Cu^{II} complex (II) is reported herein.



The 2,5,8,12,15-pentaazahexadecane ligand was synthesized according to the modified procedure of Richman & Atkins (1974). Its aqueous solution was added to an aqueous solution of a stoichiometric quantity of copper perchlorate. The solution changed from red to blue after adjustment to pH > 12 with 0.1 *N* NaOH; filtration removed the precipitate of Cu(OH)₂. The filtrate was readjusted to *ca* pH 7 with HClO₄. The resulting blue solution was evaporated slowly to produce a blue solid; recrystallization was from a 1:1 methanol–2-propanol solution.

The Cu^{II} ion is five-coordinate and has a distorted trigonal-bipyramidal conformation with the N(1), N(3) and N(5) atoms in equatorial positions and the N(2) and N(4) atoms axial. The deviation of the Cu atom from the equatorial plane is 0.11 Å towards the N(4) atom. The three Cu–N distances involving atoms N(2), N(3) and N(4) span a narrow range, 1.977 (8) to 2.037 (8) Å, and are close to the average Cu–N distance of 2.03 (3) Å for Cu^{II}–tetraamine macrocyclic complexes (Lu, Chung & Ashida, 1991); however, the other two Cu–N(terminal) distances to N(1) and N(5) of 2.121 (9) and 2.182 (7) Å, are significantly longer than this length. The five chiral N centres are in the 2*RS*, 5*SR*, 8*SR*, 12*SR*, 15*SR* configuration. The ligand is in its stable conformation within three five-membered chelate rings in stable skew forms and the six-membered ring in a stable chair form. The hydrogen bonds formed between perchlorate ions and amine groups help stabilize the crystal structure. The axial N–Cu–N bond angle is 179.1 (4)° and the equatorial N–Cu–N bond angles are 131.2 (4), 113.1 (3) and 114.8 (3)°. These results indicate that the coordination centre of the present structure is less distorted than that in complex (I).

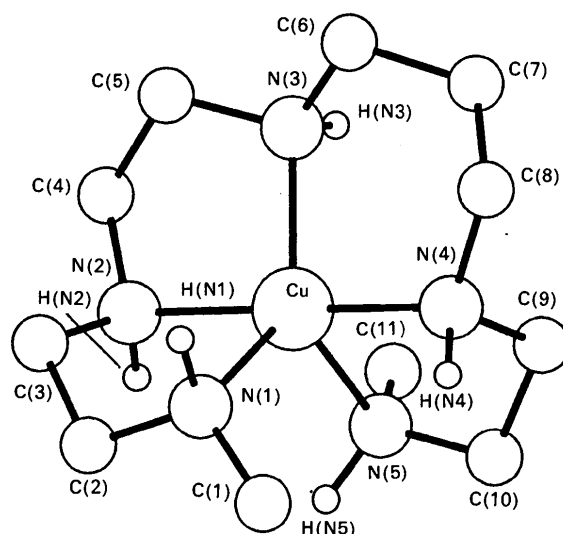


Fig. 1. A perspective view of the title molecule with the atom-numbering scheme, excluding the perchlorate ions and the H atoms attached to the C atoms.

Experimental

Crystal data

[Cu(C₁₁H₂₉N₅)](ClO₄)₂
M_r = 493.832
 Orthorhombic
Pcab
a = 14.599 (1) Å
b = 14.919 (4) Å
c = 18.756 (3) Å
V = 4085 (1) Å³
Z = 8
D_x = 1.606 Mg m⁻³

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 7.5–16.9°
 μ = 1.38 mm⁻¹
T = 298 (3) K
 Hexagonal plate
 0.47 × 0.25 × 0.19 mm
 Blue

Data collection

Nonius CAD-4 diffractometer
 θ/2θ scans
 Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.874, *T_{max}* = 0.991
 3582 measured reflections
 3582 independent reflections

2073 observed reflections
 [*I* ≥ 2.5σ(*I*)]
 θ_{max} = 25°
h = 0 → 17
k = 0 → 17
l = 0 → 22
 3 standard reflections
 frequency: 60 min
 intensity variation: ±3%

Refinement

Refinement on *F*
R = 0.062
wR = 0.058
S = 0.95
 2073 reflections
 295 parameters
 Only H-atom *U*'s refined
 Unit weights applied

(Δ/σ)_{max} = 2.79
 Δρ_{max} = 0.77 e Å⁻³
 Δρ_{min} = -0.45 e Å⁻³
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Occupancy	x	y	z	B _{eq}	
Cu	1.0	0.76043 (6)	0.57319 (6)	0.12616 (6)	3.47 (4)
Cl(1)	1.0	0.2207 (2)	0.6122 (2)	0.11995 (18)	7.28 (16)
Cl(2)	1.0	0.50818 (18)	0.33499 (18)	0.15953 (15)	5.26 (12)
O(11)	0.7	0.1733 (12)	0.5371 (18)	0.0924 (10)	11.5 (10)
O(12)	1.0	0.1812 (8)	0.6887 (6)	0.0923 (6)	12.2 (7)
O(13)	0.7	0.1895 (15)	0.6008 (18)	0.1894 (10)	16.7 (19)
O(14)	1.0	0.3087 (7)	0.6007 (9)	0.0975 (7)	15.3 (9)
O(21)	1.0	0.4724 (9)	0.2868 (7)	0.2133 (7)	15.9 (9)
O(22)	1.0	0.4619 (8)	0.4166 (6)	0.1594 (6)	12.8 (8)
O(23)	0.7	0.4830 (13)	0.2777 (11)	0.1073 (10)	14.5 (12)
O(24)	1.0	0.5956 (7)	0.3496 (9)	0.1710 (8)	16.2 (10)
O(11')	0.3	0.1321 (3)	0.573 (3)	0.093 (2)	11.3 (12)
O(13')	0.3	0.260 (4)	0.6491 (3)	0.1855 (19)	15 (4)
O(23')	0.3	0.539 (2)	0.346 (2)	0.0928 (15)	8.6 (18)
N(1)	1.0	0.6936 (6)	0.6488 (6)	0.2066 (5)	6.7 (5)
N(2)	1.0	0.6286 (5)	0.5475 (5)	0.0969 (5)	5.8 (5)
N(3)	1.0	0.7809 (6)	0.5988 (6)	0.0196 (4)	6.0 (5)
N(4)	1.0	0.8876 (5)	0.5987 (6)	0.1561 (5)	5.7 (4)
N(5)	1.0	0.7929 (5)	0.4367 (5)	0.1594 (4)	4.7 (3)
C(1)	1.0	0.7333 (11)	0.6499 (11)	0.2773 (7)	9.8 (9)
C(2)	1.0	0.5981 (8)	0.6210 (8)	0.2056 (8)	7.4 (7)
C(3)	1.0	0.5686 (7)	0.6114 (7)	0.1299 (9)	7.4 (7)
C(4)	1.0	0.6211 (8)	0.5477 (8)	0.0180 (6)	6.3 (6)
C(5)	1.0	0.6891 (8)	0.6158 (9)	-0.0114 (6)	7.2 (6)
C(6)	1.0	0.8455 (7)	0.6677 (8)	-0.0009 (7)	6.9 (6)
C(7)	1.0	0.9369 (9)	0.6536 (9)	0.0367 (7)	7.8 (7)
C(8)	1.0	0.9381 (7)	0.6698 (8)	0.1127 (7)	7.0 (6)
C(9)	1.0	0.9378 (7)	0.5119 (8)	0.1580 (7)	7.2 (6)
C(10)	1.0	0.8791 (7)	0.4444 (7)	0.1976 (6)	6.1 (5)
C(11)	1.0	0.7958 (8)	0.3724 (6)	0.1009 (6)	6.3 (6)

Table 2. Selected geometric parameters (Å, °)

Cu—N(1)	2.121 (9)	N(3)—C(6)	1.45 (1)
Cu—N(2)	2.037 (8)	N(4)—C(8)	1.53 (1)
Cu—N(3)	2.056 (8)	N(4)—C(9)	1.49 (1)
Cu—N(4)	1.977 (8)	N(5)—C(10)	1.45 (1)
Cu—N(5)	2.182 (7)	N(5)—C(11)	1.46 (1)
N(1)—C(1)	1.45 (2)	C(2)—C(3)	1.49 (2)
N(1)—C(2)	1.45 (2)	C(4)—C(5)	1.52 (2)
N(2)—C(3)	1.44 (1)	C(6)—C(7)	1.52 (2)
N(2)—C(4)	1.48 (1)	C(7)—C(8)	1.45 (2)
N(3)—C(5)	1.48 (1)	C(9)—C(10)	1.52 (2)
N(1)—Cu—N(2)	81.8 (4)	Cu—N(3)—C(6)	119.0 (7)
N(1)—Cu—N(3)	131.2 (4)	C(5)—N(3)—C(6)	111.2 (9)
N(1)—Cu—N(4)	97.3 (4)	Cu—N(4)—C(8)	115.8 (6)
N(1)—Cu—N(5)	113.1 (3)	Cu—N(4)—C(9)	107.6 (6)
N(2)—Cu—N(3)	84.8 (4)	C(8)—N(4)—C(9)	112.3 (8)
N(2)—Cu—N(4)	179.1 (4)	Cu—N(5)—C(10)	104.8 (5)
N(2)—Cu—N(5)	96.1 (3)	Cu—N(5)—C(11)	113.8 (6)
N(3)—Cu—N(4)	96.0 (4)	C(10)—N(5)—C(11)	113.5 (8)
N(3)—Cu—N(5)	114.8 (3)	N(1)—C(2)—C(3)	108.4 (9)
N(4)—Cu—N(5)	83.9 (3)	N(2)—C(3)—C(2)	107 (1)
Cu—N(1)—C(1)	118.2 (8)	N(2)—C(4)—C(5)	108.3 (8)
Cu—N(1)—C(2)	106.3 (7)	N(3)—C(5)—C(4)	109.4 (9)
C(1)—N(1)—C(2)	114 (1)	N(3)—C(6)—C(7)	110.4 (9)
Cu—N(2)—C(3)	109.6 (7)	C(6)—C(7)—C(8)	116 (1)
Cu—N(2)—C(4)	109.8 (6)	N(4)—C(8)—C(7)	113.8 (9)
C(3)—N(2)—C(4)	113 (1)	N(4)—C(9)—C(10)	108.1 (9)
Cu—N(3)—C(5)	106.4 (7)	N(5)—C(10)—C(9)	107.5 (8)

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. H atoms were located by difference Fourier methods and theoretical calculation. The high value of ($\Delta\sigma$)_{max} is a result of the disordered perchlorate groups. *NRCVAX* (Gabe, Le Page, White & Lee, 1987) was used for all calculations.

The authors thank the National Science Council for support under grants NSC82-0208-M007-119 and NSC82-0208-M007-032. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and hydrogen-bonding geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71636 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1059]

References

- Fawcett, T. G., Rudich, S. M., Toby, B. H., Lalancette, R. A., Potenza, J. A. & Schugar, H. J. (1980). *Inorg. Chem.* **19**, 940–945.
- Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* **A43**, C-294.
- Gatehouse, B. M., Martin, R. L., McLachlan, G., Platts, S. N. & Spiccia, L. (1992). *Acta Cryst.* **C48**, 271–274.
- Lee, T.-Y., Lee, T.-J., Hong, C.-Y., Hsieh, M.-Y., Wu, D.-T. & Chung, C.-S. (1986). *Acta Cryst.* **C42**, 1316–1319.
- Liu, Y.-L., Tahirov, T. H., Lu, T.-H. & Chung, C.-S. (1992). *Int. Symp. Inorg. Org. Chem.* I-50.
- Lu, T.-H., Chung, C.-S. & Ashida, T. (1991). *J. Chin. Chem. Soc. (Taipei)*, **38**, 147–153.
- Marongiu, G., Lingafelter, E. C. & Paoletti, P. (1969). *Inorg. Chem.* **8**, 2763–2767.
- North, A. C. T., Phillips, D. C. & Mathews, F. W. (1968). *Acta Cryst.* **A24**, 351–359.
- Richman, J. E. & Atkins, T. J. (1974). *J. Am. Chem. Soc.* **96**, 2268–2270.

Acta Cryst. (1994). **C50**, 516–518

[(4*RS*,7*SR*,11*RS*)-4,12-Dimethyl-4,7,11-triazatridecylamine-*N,N',N'',N'''*]nickel(II) Diperchlorate

TAHIR H. TAHIROV AND TIAN-HUEY LU*

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300

KELUN SHU AND CHUNG-SUN CHUNG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

(Received 4 March 1993; accepted 15 September 1993)

Abstract

The Ni^{II} ion of the title complex, [Ni(C₁₂H₃₀N₄)](ClO₄)₂, is four-coordinate with the four N atoms in equatorial positions. The Ni^{II} coordination is planar