

- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Williard, P. G. & Salvino, J. M. (1986). *J. Chem. Soc. Chem. Commun.* pp. 153–154.

Acta Cryst. (1998). **C54**, 1240–1242

Two Conformational (Configurational) Isomers of Diperchlorato[(5*RS*,6*RS*,12*SR*,13*SR*)-5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradecane- κ^4 N]copper(II)

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(Received 2 October 1997; accepted 4 March 1998)

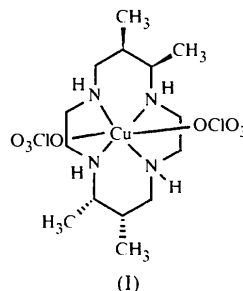
Abstract

The crystal structure of the title compound, [Cu(ClO₄)₂·(C₁₄H₃₂N₄)], has been determined by X-ray diffraction. X-ray structure analysis reveals that, owing to disorder, the compound exists in two forms, *A* and *B*. The coordination polyhedron about the Cu^{II} ion is centrosymmetric. The Cu^{II} ion is six-coordinated in a distorted octahedral geometry, with the four N atoms of the macrocyclic ligand in equatorial positions and the two perchlorate O atoms in axial positions. The four chiral N-atom centres have a 1*RS*,4*RS*,8*SR*,11*SR* configuration and a 1*SR*,4*RS*,8*RS*,11*SR* configuration, respectively, for the two forms, *A* and *B*. However, both have a 5*RS*,6*RS*,12*SR*,13*SR* configuration for the four chiral C-atom centres. Hydrogen bonds help stabilize the crystal structure.

Comment

Transition metal complexes of 14-membered tetraaza macrocyclic ligands attract extensive study because of their particular stereochemical and biological significance (Boeyens & Dobson, 1987; Bosnich *et al.*, 1965; Cabiness & Margerum, 1969). Similarly, the extreme kinetic inertness and very high thermodynamic stability of tetraaza macrocyclic ligand complexes are of particular coordination interest, since they greatly

enhance the number of potentially isolable isomers (Liang & Chung, 1980; Lee *et al.*, 1984). To the best of our knowledge, only one structure of the *C*-configuration isomer, *i.e.* the [(5*SR*,6*RS*,12*RS*,13*SR*)-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) complex, has been reported (Krajewski *et al.*, 1978). To continue our interest in establishing the coordination geometry around the metal ion and the conformation of the chelate rings, two isomeric structures of diperchlorato[(5*RS*,6*RS*,12*SR*,13*SR*)-5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradecane]copper(II), (*I*), are reported herein.



Owing to disorder, two different conformations (denoted *A* and *B*) of the title compound, (*I*), exist. The complex cation reveals a six-coordinate nature in a distorted octahedral geometry around the Cu^{II} ion, with the four N atoms of the macrocyclic ligand being equatorial and the two O atoms of the perchlorate ions being axial. The Cu^{II} ion is located at the inversion centre. Both forms are similar to that of (1,4,8,11-tetraazacyclotetradecane)copper(II) (Tasker & Sklar, 1975). Form *A* has a 1*RS*,4*RS*,8*SR*,11*SR* configuration (*trans*-III) (Bosnich *et al.*, 1965) with 75% occupancy, and its tetradentate ligand adopts a stable conformation, with the two six-membered rings in a chair form and the two five-membered rings in a *gauche* form. The *B* form has a 1*SR*,4*RS*,8*RS*,11*SR* configuration (*cis*-IV) with 25% occupancy for the four chiral N-atom centres, and its tetradentate ligand adopts a less stable conformation, with the two six-membered rings in a twisted form and the two five-membered rings in an eclipsed form (Warner & Busch, 1969).

The average Cu—N bond length in form *A* is 2.012(4) Å and that in form *B* is 2.019(7) Å; the Cu—O bond lengths in forms *A* and *B* are 2.535(4) and 2.679(15) Å, respectively (Lu *et al.*, 1991). The axial bond length is longer due to the Jahn–Teller effect (Hitchman & Deeth, 1986). The structure of the perchlorate group is also disordered, with occupancies of 75 and 25%. The geometry of the perchlorate group is slightly distorted tetrahedral, with the Cl—O distances in the range 1.32(1)–1.49(1) Å and O—Cl—O angles in the range 104.7(7)–114.9(14)°. The two methyl groups of C4 and its inversion-related atom (C4') occupy axial

positions, while the two methyl groups of atoms C3 and C3' are equatorial. The N—H bonds of atoms N2 and N2' are *cis* to the adjacent axial methyl groups. Hydrogen bonds (lengths ranging from 2.76 to 3.28 Å) between the N atoms of the amino groups and the O atoms of the perchlorate ions help stabilize the disordered structures.

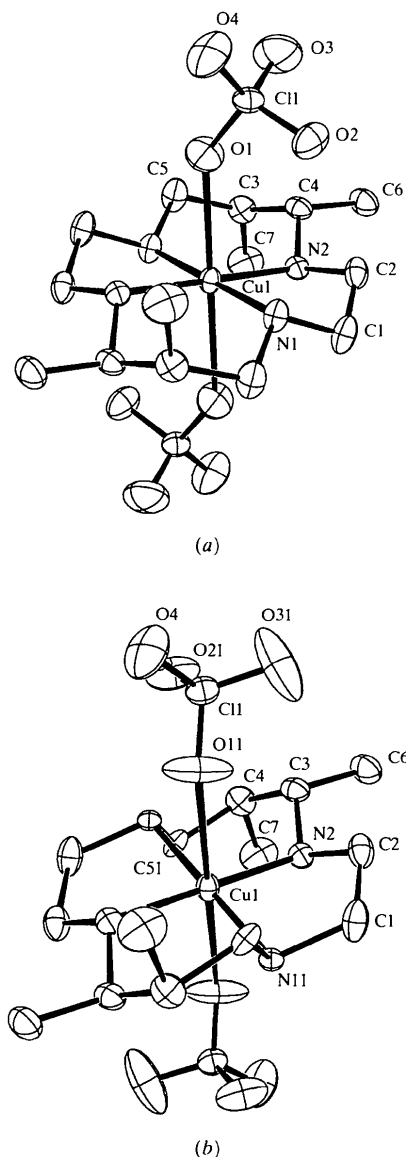


Fig. 1. Plot showing the structures of the two conformers of the title compound, (a) with 75% occupancy and (b) with 25% occupancy. Displacement ellipsoids are shown at 30% probability and H atoms have been excluded for clarity. Only half of the centrosymmetric atoms are labelled.

Experimental

5, 6, 12, 13-Tetramethyl-1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene dihydroperchlorate was prepared according to literature

methods (Hay *et al.*, 1977; Ferguson *et al.*, 1979; Murray-Rust & Murray-Rust, 1979). To a suspension of *C-meso*-5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate (10 g) in methanol (200 ml), NaBH₄ (5 g) was added in small portions at 273 K. After complete addition, the solution was refluxed for 2 h and cooled to room temperature. The solvent was removed on a rotary evaporator and sodium hydroxide solution (1.5 M) was added. The aqueous solution was then continuously extracted with chloroform. The extract was dried and dissolved in hot xylene. Colourless transparent crystals were obtained after several days. White crystals were filtered off, washed with diethyl ether and dried *in vacuo* (yield: 5 g free ligand). This ligand (1 g) and copper(II) perchlorate hexahydrate (1 g) were dissolved in water (100 ml) and stirred for 4 h in an ice bath (273 K). Purple crystals were recrystallized by slow evaporation from a 1:1 (v/v) methanol/acetone solution.

Crystal data

[Cu(ClO₄)₂(C₁₄H₃₂N₄)]

M_r = 518.88

Monoclinic

*P*2₁/*n*

a = 9.147 (2) Å

b = 13.360 (2) Å

c = 9.379 (2) Å

β = 113.83 (2)°

V = 1048.4 (4) Å³

Z = 2

D_x = 1.644 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 14.74–23.06°

μ = 1.346 mm⁻¹

T = 293 (2) K

Pillar

0.30 × 0.19 × 0.15 mm

Purple

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction: ψ scan (North *et al.*, 1968)

T_{min} = 0.722, *T_{max}* = 0.815

3044 measured reflections

3044 independent reflections

1902 reflections with

I > 2σ(*I*)

θ_{max} = 29.97°

h = -12 → 11

k = 0 → 18

l = 0 → 13

3 standard reflections

frequency: 60 min

intensity decay: 2%

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.051

wR(*F*²) = 0.130

S = 0.990

3044 reflections

230 parameters

All H atoms refined

w = 1/[σ²(*F_o*²) + (0.0712*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.005

Δρ_{max} = 0.593 e Å⁻³

Δρ_{min} = -0.322 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—N1	2.006 (4)	C3—C4	1.529 (5)
Cu1—N2	2.018 (3)	C3—C6	1.526 (5)
Cu1—N11	2.019 (10)	C4—C5	1.550 (7)
Cu1—O1	2.535 (4)	C4—C51	1.54 (2)
Cu1—O11	2.679 (15)	C4—C7	1.504 (6)
N1—C1	1.486 (5)	C11—O1	1.416 (4)
N1—C5'	1.467 (6)	C11—O2	1.459 (4)
N11—C1	1.60 (1)	C11—O3	1.402 (5)

N11—C51 ¹	1.52 (2)	C11—O4	1.401 (3)
N2—C2	1.481 (4)	C11—O11	1.32 (1)
N2—C3	1.488 (4)	C11—O21	1.49 (1)
C1—C2	1.484 (6)	C11—O31	1.36 (2)
N1 ¹ —Cu1—N1	180.0	N2—C2—C1	108.0 (3)
N11 ¹ —Cu1—N11	180.0	N2—C3—C6	111.7 (3)
N1 ¹ —Cu1—N2	94.7 (1)	N2—C3—C4	111.0 (3)
N1—Cu1—N2	85.3 (1)	C6—C3—C4	111.8 (3)
N2 ¹ —Cu1—N11	91.7 (3)	C7—C4—C3	114.9 (4)
N2—Cu1—N11	88.3 (3)	C7—C4—C51	88.6 (6)
N2 ¹ —Cu1—N2	180.0	C3—C4—C51	117.7 (5)
N1—Cu1—O1	88.0 (2)	C7—C4—C5	117.7 (5)
N11—Cu1—O11	85.5 (5)	C3—C4—C5	112.4 (3)
N2—Cu1—O1	82.9 (2)	N1 ¹ —C5—C4	112.8 (4)
N2—Cu1—O11	81.8 (5)	N11 ¹ —C51—C4	106.3 (10)
O1 ¹ —Cu1—O1	180.0	O1—C11—O2	106.1 (3)
O11 ¹ —Cu1—O11	180.0	O1—C11—O3	109.0 (5)
C5 ¹ —N1—C1	110.0 (4)	O1—C11—O4	114.3 (3)
C5 ¹ —N1—Cu1	118.1 (3)	O2—C11—O3	107.9 (4)
C1—N1—Cu1	106.4 (3)	O2—C11—O4	110.4 (3)
C5 ¹ —N11—C1	103.8 (8)	O3—C11—O4	108.9 (3)
C5 ¹ —N11—Cu1	102.5 (7)	O11—C11—O21	106.2 (10)
C1—N11—Cu1	101.3 (5)	O11—C11—O31	111 (2)
C2—N2—C3	113.9 (3)	O11—C11—O4	108.7 (10)
C2—N2—Cu1	105.4 (2)	O21—C11—O31	114.9 (14)
C3—N2—Cu1	116.3 (2)	O21—C11—O4	104.7 (7)
C2—C1—N1	104.6 (3)	O31—C11—O4	111.4 (11)
C2—C1—N11	119.0 (4)		

Symmetry code: (i) $-x, -y, -z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL93*.

The authors thank the National Science Council of Taiwan for support under grants NSC86-2112-M007-028, NSC86-2811-M007-0041, NSC87-2112-M007-009 and NSC87-2113-M007-041.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1262). Services for accessing these data are described at the back of the journal.

References

- Boeyens, J. C. A. & Dobson, S. M. (1987). *Stereochemical and Stereophysical Behavior of Macrocycles*, Vol. 2, pp. 48–70. New York: Elsevier.
- Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.
- Cabbiness, D. K. & Margerum, D. W. (1969). *J. Am. Chem. Soc.* **91**, 6540–6541.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Ferguson, G., Restivo, R. R. & Hay, R. W. (1979). *Acta Cryst.* **B35**, 159–162.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Hay, R. W., Piplani, D. P. & Jeragh, B. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1951–1956.
- Hitchman, M. A. & Deeth, R. J. (1986). *Inorg. Chem.* **25**, 1225–1233.
- Krajewski, J. W., Urbanczyk-Lipkowska, Z. & Gluzinski, P. (1978). *Pol. J. Chem.* **52**, 1513–1523.
- Lee, T.-J., Lu, T.-H., Chung, C.-S. & Lee, T.-Y. (1984). *Acta Cryst.* **C40**, 70–72.

- Liang, B.-F. & Chung, C.-S. (1980). *Inorg. Chem.* **19**, 1867–1871.
- Lu, T.-H., Chung, C.-S. & Ashida, T. (1991). *J. Chin. Chem. Soc. (Taipei)*, **38**, 147–153.
- Murray-Rust, P. & Murray-Rust, J. (1979). *Acta Cryst.* **B35**, 1704–1706.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL 93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Tasker, P. A. & Sklar, L. (1975). *J. Cryst. Mol. Struct.* **5**, 329–344.
- Warner, L. G. & Busch, D. H. (1969). *J. Am. Chem. Soc.* **91**, 4092–4101.

Acta Cryst. (1998). **C54**, 1242–1244

trans-Diaquabis(nicotinamide-*N*¹)bis(4-nitrobenzoato-*O*)cobalt(II)

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(Received 15 December 1997; accepted 24 March 1998)

Abstract

The title cobalt complex, [Co(C₇H₄NO₄)₂(C₆H₆N₂O)₂·(H₂O)₂], is monomeric and centrosymmetric, and contains two water molecules, two 4-nitrobenzoate and two nicotinamide (NA) ligands, all acting as monodentate ligands. The four nearest O atoms around the Co atom form a slightly distorted square-planar arrangement, with a distorted octahedral coordination completed by the pyridine N atoms of the NA ligand, at a distance of 2.134 (2) Å. The water molecules are hydrogen bonded to the carboxyl O atoms [O...O 2.634 (5) Å].

Comment

There are only a few examples of structure determinations of Co^{II} complexes with nicotinic and/or benzoic acid derivatives as ligands, *e.g.* [Co(C₇H₅O₃)₂(DENA)₂(H₂O)₂] (where DENA is diethylnicotinamide, C₁₀H₁₄N₂O; Hökelek & Necefoğlu, 1997), [Co(CH₃CO₂)₂(DENA)₂(H₂O)₂] (Mikelashvili, 1982), [Co(H₂O)₄(*p*-O₂NC₆H₄COO)₂] (Nadzhafov *et al.*, 1981) and [Co(H₂O)₄(*p*-H₂NC₆H₄COO)₂] (Amiraslanov *et al.*, 1979). The structure–function–coordination relationships of the arylcarboxylate ion in Co^{II} complexes of benzoic acid derivatives change depending on the