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**[7-Methyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene- $\kappa^4N$ ](nitrate- $\kappa O$ )copper(II) Nitrate Hydrate**

TIAN-HUEY LU,<sup>a</sup> SHU-FANG TUNG,<sup>b</sup> TA-YUNG CHI<sup>c</sup> AND CHUNG-SUN CHUNG<sup>c</sup>

<sup>a</sup>Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, <sup>b</sup>Southern Instrument Center, National Cheng Kung University, Tainan, Taiwan 700, and <sup>c</sup>Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300. E-mail: thlu@phys.nthu.edu.tw

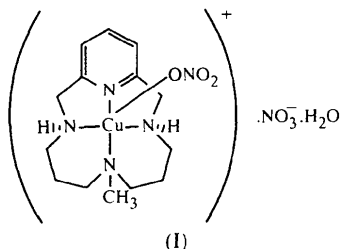
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**Abstract**

The Cu<sup>II</sup> ion of the title complex, [Cu(NO<sub>3</sub>)(C<sub>14</sub>H<sub>24</sub>N<sub>4</sub>)]·NO<sub>3</sub>·H<sub>2</sub>O, is five-coordinate and the geometry is distorted square pyramidal, with the four N atoms of the macrocyclic ligand equatorial and an O atom of the nitrate group axial. The tetradentate ligand adopts its most stable conformation, with two six-membered rings in chair forms and two five-membered rings in skew forms. The complex has the 3*RS*,11*SR* configuration for the two chiral N centers.

**Comment**

The metal-template method has been used in a versatile manner in the syntheses of macrocyclic ligands (Hippes & Busch, 1978; Alcock *et al.*, 1986, 1987; Foster *et al.*, 1986; Alexander, 1995). Previously, Moore and co-workers (Alcock *et al.*, 1986; Balakrishnan *et al.*, 1990) had reported the synthesis of the macrocyclic ligand, 7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, using copper(II) or nickel(II) ions as template reagents, but no crystallographic characterization of the complexes has been reported. We present herein the crystal structure of the title complex, (I), in order to confirm the synthesis results.



The Cu<sup>II</sup> ion is five-coordinate and the geometry is distorted square pyramidal, with the four N atoms of the macrocyclic ligand equatorial and an O atom of the nitrate group axial. The structure of the macrocyclic

ligand was the same as that predicted by Moore and co-workers (Balakrishnan *et al.*, 1990; Blake *et al.*, 1988). The Cu—N(pyridine) distance is 0.1 Å shorter than the other Cu—N distances, which are similar to the usual Cu—N distance found in Cu<sup>II</sup> macrocyclic complexes (Lu *et al.*, 1991). A similar shorter Cu—N bond has been observed for related pyridine-containing complexes (Alcock *et al.*, 1985; Restivo & Ferguson, 1976). The Cu—O(nitrate) distance [2.299 (2) Å] is slightly longer than that found in the structure of dinitrato{2,6-bis-[1-(phenylimino)ethyl]pyridine}copper(II) [2.213 (4) Å; Restivo & Ferguson, 1976], but shorter than that of the Cu<sup>2+</sup>–azacyclam complex unit [2.543 (9) (De Blas *et al.*, 1993), and 2.437 (3) and 2.673 (2) Å (Sardone & Licchelli, 1996)]. The *N*-methyl group and two of the amine H atoms are on the same side of the equatorial N<sub>4</sub> plane and opposite the coordinated nitrate group. The tetradentate ligand adopts its most stable conformation, with two six-membered rings in chair forms and two five-membered rings in *gauche* forms. The complex has the 3*RS*,11*SR* (or 3*SR*,11*RS*) configuration for the two chiral N centers. Hydrogen bonds help stabilize the crystal structure.

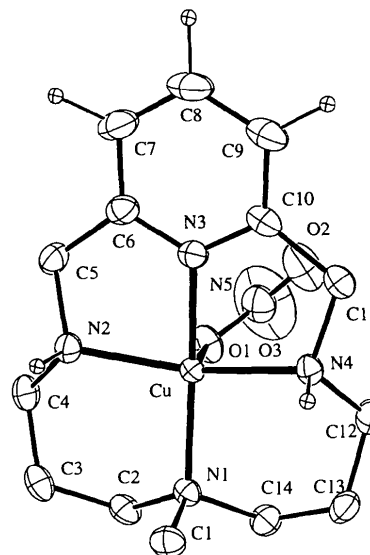


Fig. 1. A perspective view of the title complex with the atom-numbering scheme, excluding the non-coordinated nitrate ion, the water molecule and some H atoms attached to C atoms. Displacement ellipsoids are drawn at the 30% probability level (ORTEPII; Johnson, 1976)

**Experimental**

The title complex was prepared according to the literature method of Moore and co-workers (Balakrishnan *et al.*, 1990). The blue crystals obtained were recrystallized from ethanol.

## Crystal data

[Cu(NO<sub>3</sub>)(C<sub>14</sub>H<sub>24</sub>N<sub>4</sub>)]NO<sub>3</sub>·  
H<sub>2</sub>O  
M<sub>r</sub> = 453.94  
Triclinic  
P1̄  
a = 7.2603 (12) Å  
b = 9.4959 (7) Å  
c = 14.0498 (10) Å  
α = 90.273 (6)°  
β = 99.462 (11)°  
γ = 89.944 (9)°  
V = 955.45 (19) Å<sup>3</sup>  
Z = 2  
D<sub>x</sub> = 1.578 Mg m<sup>-3</sup>  
D<sub>m</sub> not measured

## Data collection

Nonius CAD-4 diffractometer  
θ/2θ scans  
Absorption correction:  
empirical (North *et al.*,  
1968)  
T<sub>min</sub> = 0.671, T<sub>max</sub> = 0.726  
3584 measured reflections  
3362 independent reflections

## Refinement

Refinement on F  
R = 0.033  
wR = 0.061  
S = 1.05  
3032 reflections  
254 parameters  
H atoms not refined  
w = 1/[σ<sup>2</sup>(F) + 0.003F<sup>2</sup>]  
(Δ/σ)<sub>max</sub> < 0.001

Mo Kα radiation  
λ = 0.7107 Å  
Cell parameters from 25  
reflections  
θ = 6.46–15.48°  
μ = 1.19 mm<sup>-1</sup>  
T = 293 K  
Pillar  
0.44 × 0.34 × 0.31 mm  
Blue

3032 reflections with  
I<sub>net</sub> > 2.5σ(I<sub>net</sub>)  
R<sub>int</sub> = 0.007  
θ<sub>max</sub> = 24.93°  
h = -8 → 8  
k = 0 → 11  
l = -16 → 16  
3 standard reflections  
frequency: 60 min  
intensity decay: 1.0%

Δρ<sub>max</sub> = 0.36 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.49 e Å<sup>-3</sup>  
Extinction correction:  
Larson (1970)  
Extinction coefficient:  
6 (6) × 10<sup>3</sup>  
Scattering factors from *Inter-  
national Tables for X-ray  
Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Cu—N1	2.009 (2)	N3—C6	1.331 (4)
Cu—N2	2.040 (2)	N3—C10	1.329 (4)
Cu—N3	1.934 (2)	N4—C11	1.480 (4)
Cu—N4	2.030 (2)	N4—C12	1.491 (4)
Cu—O1	2.299 (2)	N5—O1	1.235 (4)
N1—C1	1.499 (4)	N5—O2	1.175 (5)
N1—C2	1.502 (4)	N5—O3	1.173 (6)
N1—C14	1.502 (4)	N6—O4	1.205 (4)
N2—C4	1.494 (4)	N6—O5	1.230 (3)
N2—C5	1.477 (4)	N6—O6	1.243 (4)
N1—Cu—N2	97.40 (9)	Cu—N1—C1	108.86 (16)
N1—Cu—N3	171.90 (9)	Cu—N1—C2	111.74 (17)
N1—Cu—N4	96.23 (9)	Cu—N1—C14	110.70 (17)
N1—Cu—O1	92.04 (9)	Cu—N2—C4	116.21 (17)
N2—Cu—N3	81.47 (9)	Cu—N2—C5	109.44 (16)
N2—Cu—N4	155.50 (9)	Cu—N3—C6	118.7 (2)
N2—Cu—O1	92.50 (8)	Cu—N3—C10	118.8 (2)
N3—Cu—N4	82.17 (10)	Cu—N4—C11	110.93 (18)
N3—Cu—O1	96.02 (9)	Cu—N4—C12	112.67 (16)
N4—Cu—O1	107.27 (8)	Cu—O1—N5	123.9 (2)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
OW—HW1...O1	1.042	1.884	2.899 (3)	163.6
OW—HW1...O3	1.042	2.220	3.060 (6)	136.3
OW—HW2...O5 <sup>i</sup>	0.873	1.991	2.847 (3)	166.7
N2—HN2...OW <sup>ii</sup>	1.040	1.882	2.902 (3)	166.1
N4—HN4...O6 <sup>ii</sup>	1.032	2.448	3.140 (4)	123.7

Symmetry codes: (i) x, 1 + y, z; (ii) 1 + x, y, z.

The structure was solved by direct methods, difference Fourier and least-squares fit. The H atoms were located from a difference Fourier map and refined with isotropic displacement parameters.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES* (version of January 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1033). Services for accessing these data are described at the back of the journal.

## References

- Alcock, N. W., Balakrishnan, K. P., Moore, P. & Pike, G. A. (1987). *J. Chem. Soc. Dalton Trans.* pp. 889–894.
- Alcock, N. W., Moore, P. & Omar, H. A. A. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1058–1059.
- Alcock, N. W., Moore, P. & Omar, H. A. A. (1986). *J. Chem. Soc. Dalton Trans.* pp. 985–989.
- Alexander, V. (1995). *Chem. Rev.* **95**, 273–342.
- Balakrishnan, K. P., Omar, H. A. A., Moore, P., Alcock, N. W. & Pike, G. A. (1990). *J. Chem. Soc. Dalton Trans.* pp. 2965–2969.
- Blake, A. J., Hyde, T. I. & Schroder, M. (1988). *J. Chem. Soc. Dalton Trans.* pp. 1165–1168.
- De Blas, A., De Santis, G., Fabbri, L., Licchelli, M., Manotti Lanfredi, A. M., Morosini, P., Pallavicini, P. & Uguzzoli, F. (1993). *J. Chem. Soc. Dalton Trans.* pp. 1411–1416.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Foster, K. A., Barefield, E. K. & van Derveer, D. G. (1986). *J. Chem. Soc. Chem. Commun.* pp. 680–681.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lec, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Hipps, C. J. & Busch, D. H. (1978). *Coordination Chemistry*. Vol. 2. pp. 221–475. ACS Monograph 174.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Lu, T. H., Chung, C. S. & Ashida, T. (1991). *J. Chin. Chem. Soc.* **38**, 147–153.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Restivo, R. J. & Ferguson, G. (1976). *J. Chem. Soc. Dalton Trans.* pp. 518–521.
- Sardone, N. & Licchelli, M. (1996). *Acta Cryst.* **C52**, 2713–2716.