

**(5,16-Dimethyl-2,6,13,17-tetraazatricyclo-[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane- $\kappa^4$ N)dinitrato-copper(II) trihydrate****Jong-Ha Choi,<sup>a\*</sup> Takayoshi Suzuki<sup>b</sup> and Sumio Kaizaki<sup>b</sup>**<sup>a</sup>Department of Chemistry, Andong National University, Andong 760-749, Republic of Korea, and <sup>b</sup>Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan

Correspondence e-mail: jhchoi@andong.ac.kr

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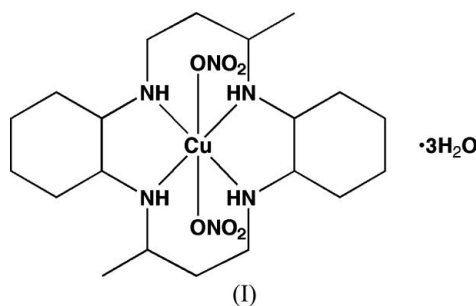
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**Key indicators**Single-crystal X-ray study  
T = 200 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
H-atom completeness 96%  
Disorder in solvent or counterion  
R factor = 0.030  
wR factor = 0.117  
Data-to-parameter ratio = 16.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $[\text{Cu}(\text{NO}_3)_2(\text{C}_{20}\text{H}_{40}\text{N}_4)] \cdot 3\text{H}_2\text{O}$ , the Cu atom lies on a crystallographic inversion centre and has a distorted octahedral geometry, with four N atoms of the macrocyclic ligand in the equatorial positions and two O atoms of the axial nitrate ligands. The long axial Cu—O bond of 2.746 (2) Å may result from the Jahn–Teller effect. The macrocyclic ligand adopts the most stable *trans*-III configuration with the two six-membered rings in chair form and two five-membered rings in a gauche form.

**Comment**

Tetraazamacrocyclic ligands are moderately flexible and can adopt both planar (*trans*) and folded (*cis*) configurations. For 14-membered tetraazamacrocycles such as cyclam, there are five configurational isomers, which differ in the set of chiralities of the sec-NH centres (Bakaj & Zimmer, 1999). It is also found that the physical, chemical and spectroscopic properties of copper(II) tetraazamacrocyclic complexes are largely influenced by structural characteristics such as stereochemistry, chelate-ring size and substituents of the macrocycles (Bakaj & Zimmer, 1999). For a modified cyclam ligand with two 1,2-diaminocyclohexane subunits and two methyl groups attached to the backbone C atoms, 5,16-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane (*L*), only a limited number of Cu<sup>II</sup>, Ni<sup>II</sup> and Zn<sup>II</sup> complexes have been described previously (Kang *et al.*, 1991; Kang & Kim, 2003; Choi *et al.*, 1996, 1997, 1998; Choi, 2004). Here, we report the structure of a Cu<sup>II</sup> nitrate complex with the cyclam-based macrocycle *L*,  $[\text{Cu}(\text{NO}_3)_2(\text{L})] \cdot 3\text{H}_2\text{O}$ , (I).



As shown in Fig. 1, the Cu1 atom lies on a crystallographic inversion centre and has a tetragonally distorted octahedral coordination environment, comprising four N atoms of the macrocycle in the equatorial positions and two O atoms, each from one nitrate ligand, in the elongated axial positions. The axial Cu—O bond length is relatively long (Table 1), which

may be due to the Jahn–Teller effect. The equatorial Cu–N bond lengths are approximately equal and can be compared to those in the related complexes, [Cu(L)(bip)<sub>2</sub>] (bip = 2-benzimidazolepropionate) and [Cu(L)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> (Choi *et al.*, 1996; Choi, 2004). Two methyl groups on the six-membered chelate rings are in the anti-positions with respect to the macrocycle plane. In the 14-membered macrocycle, the five- and six-membered chelate rings adopt a gauche and a chair conformation, respectively. The chelate bite angles of the five- and six-membered rings are 85.04 (7) and 94.96 (7)°, respectively. The dimensions of the L ligand are normal, compared to the uncoordinated tetraazamacrocycle itself (Choi *et al.*, 2006).

The complex is stabilized by the formation of intramolecular hydrogen bonds between the uncoordinated O atoms of the nitrate ligands and the secondary NH groups of the L ligand (Fig. 1 and Table 2). There are also intermolecular hydrogen bonds in the crystal structure. Atom N2 donates a H atom to O3 of the neighbouring molecule at (x, y + 1, z). The water molecule (O4) forms hydrogen bonds with the nitrate groups of two neighbouring molecules.

### Experimental

L was prepared according to a literature method (Kang *et al.*, 1991). A methanol suspension (15 ml) of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.242 g, 1 mmol) and L (0.670 g, 2 mmol) was heated to reflux for 30 min. After it had been cooled to room temperature, the red–violet product was filtered off, washed with methanol, and air-dried. Recrystallization of the product from hot acetonitrile–water (1:2 v/v) solution gave reddish pink crystals of (I), suitable for X-ray analysis. Analysis calculated for C<sub>20</sub>H<sub>16</sub>CuN<sub>6</sub>O<sub>9</sub>: C 41.55, H 8.02, N 14.54%; found: C 41.91, H 8.25, N 14.72%.

#### Crystal data

[Cu(NO<sub>3</sub>)<sub>2</sub>(C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>)]·3H<sub>2</sub>O  
*M<sub>r</sub>* = 578.17  
 Triclinic, P1̄  
*a* = 7.813 (5) Å  
*b* = 8.746 (7) Å  
*c* = 10.715 (7) Å  
 α = 93.06 (3)°  
 β = 106.86 (2)°  
 γ = 108.43 (3)°  
*V* = 656.2 (8) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 1.463 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 μ = 0.89 mm<sup>-1</sup>  
*T* = 200 (2) K  
 Block, red–pink  
 0.20 × 0.18 × 0.10 mm

#### Data collection

Rigaku R-Axis RAPID diffractometer  
 ω scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
*T<sub>min</sub>* = 0.842, *T<sub>max</sub>* = 0.916  
 6435 measured reflections  
 2969 independent reflections  
 2809 reflections with *F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)  
*R<sub>int</sub>* = 0.016  
 θ<sub>max</sub> = 27.5°

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.030  
*wR*(*F*<sup>2</sup>) = 0.117  
*S* = 1.19  
 2969 reflections  
 178 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 0.2496P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.53 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.42 e Å<sup>-3</sup>

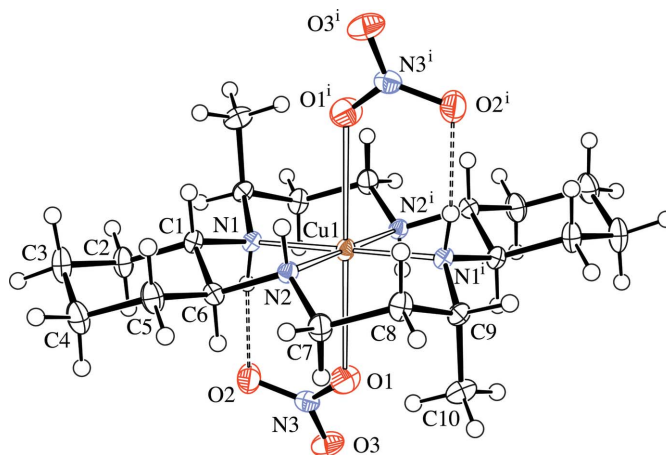


Figure 1

A perspective view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds. Water molecules have been omitted for clarity. [Symmetry code: (i) -x, -y, -z.]

Table 1

Selected geometric parameters (Å, °).

Cu1–N2	2.021 (2)	Cu1–O1	2.746 (2)
Cu1–N1	2.029 (2)		
N2–Cu1–N1	85.04 (7)	N1–Cu1–N2 <sup>i</sup>	94.96 (7)
N2–Cu1–O1	97.83 (9)	N1–Cu1–O1 <sup>i</sup>	95.92 (6)
N1–Cu1–O1	84.08 (6)	N2–Cu1–O1 <sup>i</sup>	82.17 (9)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1N...O2	0.93	2.05	2.975 (3)	171
N2–H2N...O3 <sup>ii</sup>	0.93	2.32	3.133 (3)	145
O4–H4P...O2	0.79 (4)	2.10 (3)	2.870 (3)	169 (4)
O4–H4O...O1 <sup>iii</sup>	0.84 (4)	2.25 (4)	3.036 (2)	158 (4)

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

H atoms bonded to C and N atoms were positioned geometrically and refined as riding atoms, with C–H = 1.00 (CH), 0.99 (CH<sub>2</sub>) and 0.98 Å (CH<sub>3</sub>), N–H = 0.93 Å, and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N). The H atoms bonded to O4 (water molecule) were located in a difference map and refined isotropically. The position of another water molecule (O5) can be located in the difference map, but the electron density of this peak was relatively low. Because the elemental analysis gave a satisfactory result for a trihydrate of (I), the occupancy of O5 was assumed to be 0.5. The H atoms bonded to O5 were not located.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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