

S = 0.994

2098 reflections

166 parameters

H-atom coordinates refined;

U(H) = 1.2U<sub>eq</sub>(C) $(\Delta/\sigma)_{\max} = -0.067$  $\Delta\rho_{\max} = 0.405 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.351 \text{ e } \text{\AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)*Acta Cryst.* (1997). **C53**, 204–206**Copper(II) and Nickel(II) Complexes of  
4-Methyl-4,7-diazadecane-1,10-diamine**TIAN-HUEY LU,<sup>a</sup> TAHIR H. TAHIROV,<sup>a</sup> KELUN SHU<sup>b</sup> AND  
CHUNG-SUN CHUNG<sup>b</sup><sup>a</sup>Department of Physics, National Tsing University, Hsinchu,  
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(Received 14 February 1994; accepted 13 May 1996)

Table 1. Selected geometric parameters (Å, °)

V—N1	1.653 (4)	V—C9	2.236 (6)
V—Cl1	2.258 (2)	V—Cl10	2.246 (6)
V—Cl2	2.259 (2)	V—Cl11	2.354 (5)
V—C7	2.351 (5)	V—Cp†	1.968 (6)
V—C8	2.263 (6)		
N1—V—Cl1	99.72 (14)	Cl1—V—Cp	114.1 (8)
N1—V—Cl2	102.30 (14)	Cl2—V—Cp	113.5 (8)
Cl1—V—Cl2	103.65 (6)	N1—V—Cp	121.2 (7)
Cl1—N1—V	169.1 (4)		

† Cp is the centroid of the Cp ring.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

The authors would like to thank the EPSRC (MCWC and JMC) and BP Chemicals Ltd (MCWC) for financial support.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: CF1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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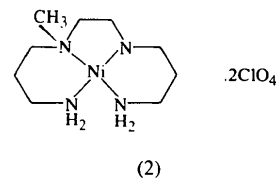
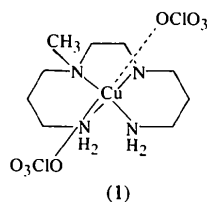
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**Abstract**

The X-ray crystal structures of (4-methyl-4,7-diazadecane-1,10-diamine-*N,N',N'',N'''*)(perchlorato-*O*)-copper(II) perchlorate, [Cu(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)(ClO<sub>4</sub>)]ClO<sub>4</sub>, and (4-methyl-4,7-diazadecane-1,10-diamine-*N,N',N'',N'''*)-nickel(II) diperchlorate, [Ni(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>, are isomorphous with minor dissimilarities. The copper(II) complex is six-coordinate in a distorted octahedral geometry, with the four N atoms of the tetradentate ligand equatorial and the two O atoms of the perchlorate groups axial. The nickel(II) complex is four-coordinate in a square-planar geometry. In both complexes, the conformations of the three consecutive six-, five- and six-membered rings are chair, *gauche* and chair, respectively. In both crystals, hydrogen bonds involving the amino groups and perchlorate O atoms help stabilize the crystal structure.

**Comment**

The crystal structures of the copper(II) complex of *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine and its associates have been reported previously (Lee *et al.*, 1986; Tahirov, Lu, Shu & Chung, 1994*a,b*, 1995). In order to investigate the steric effects of *N*-alkyl groups on the structures of the copper(II) and nickel(II) complexes, we have studied the crystal structures of the title complexes (4-methyl-4,7-diazadecane-1,10-diamine)(perchlorato-*O*)copper(II) perchlorate, (1), and (4-methyl-4,7-diazadecane-1,10-diamine)nickel(II) diperchlorate, (2).



The structure of the Ni<sup>II</sup> complex is isomorphous with that of the Cu<sup>II</sup> complex with minor dissimilarities. Appreciable electron-density residues were observed in the penultimate difference Fourier map. The occupan-

cies of the disordered perchlorate O atoms in the Cu<sup>II</sup> complex, not found in the Ni<sup>II</sup> complex, were assigned in accordance with their relative peak heights and thus reduced the *R* factor in the structure refinement. The coordination geometry about the Cu<sup>II</sup> ion is octahedral, with the four N atoms equatorial and two perchlorate O atoms axial. Contrary to the copper(II) complex, the nickel(II) complex is four-coordinate (inferred from the *M*—O distances in Table 2) and the geometry about the Ni<sup>II</sup> ion is square planar. The Cu—N and Ni—N distances span very narrow ranges and are comparable to the average Cu—N and Ni—N distances of 2.03 (3) and 1.95 (4) Å found for Cu<sup>II</sup>–tetramine and Ni<sup>II</sup>–tetramine complexes, respectively (Lu, Chung & Ashida, 1991). Both of these complexes have either the *RS* or *SR* configuration for the two chiral amine-N centers. In the copper(II) complex, a perchlorate ion [Cl(1)O<sub>4</sub>] functions as a bridge ligand (Fig. 1) and is bonded to two Cu atoms, while another perchlorate anion [Cl(2)O<sub>4</sub>] is unbonded. In the nickel(II) complex, both perchlorate groups are unbonded. The planarity of the N<sub>4</sub> plane in the Ni<sup>II</sup> complex is better than that in the Cu<sup>II</sup> complex. The Ni<sup>II</sup> ion is 0.025 (3) Å from the best N<sub>4</sub> plane, which is coplanar within 0.012 (8) Å, and the corresponding values for the Cu<sup>II</sup> ion are 0.06 (1) and 0.021 (4) Å. In both the Cu<sup>II</sup> and Ni<sup>II</sup> complexes, the two lateral six-membered rings are in stable chair forms, while the central five-membered ring is in a stable *gauche* form. The hydro-

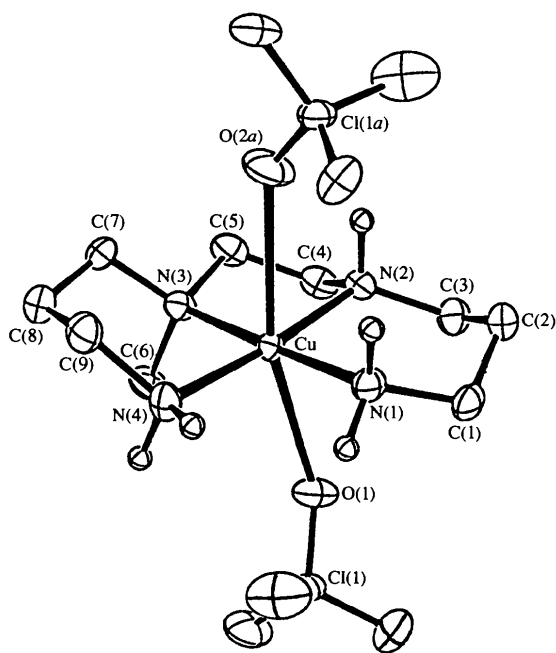


Fig. 1. A perspective view of the molecule of the Cu<sup>II</sup> complex with the atom-numbering scheme, excluding the perchlorate Cl(2)O<sub>4</sub> group and H atoms attached to C atoms. Displacement ellipsoids are drawn at the 30% probability level (ORTEP; Johnson, 1976). The molecule of the Ni<sup>II</sup> complex is isomorphous with that of the Cu<sup>II</sup> complex, but without the Cl(1)O<sub>4</sub> anion bonded to the metal.

gen bonds among the amino groups and the perchlorate O atoms are not linear in donor and acceptor arrangements and constitute weak bonding. They help stabilize the crystal structures of both title complexes.

## Experimental

The ligand was synthesized according to the method reported by Lu, Shan, Chao & Chung (1987). A solution of [Cu(ClO<sub>4</sub>)<sub>2</sub>].6H<sub>2</sub>O (7.3 g, 0.02 mol) in methanol (80 ml) was added dropwise to a solution of the ligand (3.76 g, 0.02 mol) in ethanol (80 ml). The color of the solution changed rapidly to violet. The resulting solution was stirred for 3 h on a steam bath and then evaporated to dryness. The solid obtained was dissolved in water and Cu(OH)<sub>2</sub> filtered off. Single crystals of the copper(II) complex were obtained from this aqueous solution by slow evaporation. The same procedure was used for the preparation of the nickel(II) complex.

### Complex (1)

#### Crystal data

[Cu(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)(ClO<sub>4</sub>)]ClO<sub>4</sub>  
*M<sub>r</sub>* = 450.76  
 Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 8.781 (1) Å  
*b* = 15.021 (2) Å  
*c* = 13.452 (3) Å  
 $\beta$  = 102.18 (2)°  
*V* = 1734.4 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.726 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 8.65–19.01°  
 $\mu$  = 1.62 mm<sup>-1</sup>  
*T* = 298 (3) K  
 Rod  
 0.34 × 0.31 × 0.22 mm  
 Blue–violet

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: empirical *via*  $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min}$  = 0.59,  $T_{\max}$  = 0.70  
 3218 measured reflections  
 3048 independent reflections

2601 reflections with  $I \geq 1.5\sigma(I)$   
 $R_{\text{int}}$  = 0.028  
 $\theta_{\text{max}}$  = 25°  
 $h$  = -10 → 10  
 $k$  = 0 → 17  
 $l$  = 0 → 15  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: ±0.8%

#### Refinement

Refinement on *F*  
 $R$  = 0.036  
 $wR$  = 0.047  
 $S$  = 1.19  
 2601 reflections  
 278 parameters  
 Only H-atom *U*'s refined  
 $w = 1/[(F_o)^2 + 0.001|F_o|^2]$   
 $(\Delta/\sigma)_{\text{max}}$  = 0.740

$\Delta\rho_{\text{max}}$  = 0.65 (8) e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.56 (8) e Å<sup>-3</sup>  
 Extinction correction: Zachariasen (1968)  
 Extinction coefficient: 0.46 (6) (length in mm)  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

### Complex (2)

#### Crystal data

[Ni(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub>  
*M<sub>r</sub>* = 445.92

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å

Monoclinic  
*P*2<sub>1</sub>/*n*  
*a* = 8.732 (1) Å  
*b* = 14.800 (2) Å  
*c* = 13.655 (3) Å  
 $\beta$  = 100.14 (2)°  
*V* = 1737.1 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.705 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

#### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  
 empirical via  $\psi$  scans  
 (North, Phillips &  
 Mathews, 1968)  
*T*<sub>min</sub> = 0.63, *T*<sub>max</sub> = 0.66  
 5252 measured reflections  
 5066 independent reflections

#### Refinement

Refinement on *F*  
*R* = 0.078  
*wR* = 0.087  
*S* = 1.24  
 4056 reflections  
 218 parameters  
 H atoms not refined  
 Unit weights applied  
 $(\Delta/\sigma)_{\max}$  = 0.001

Cell parameters from 25  
 reflections  
 $\theta$  = 7.52–17.17°  
 $\mu$  = 1.47 mm<sup>-1</sup>  
*T* = 298 (3) K  
 Parallelepiped  
 0.44 × 0.38 × 0.28 mm  
 Orange

4056 reflections with  
 $I \geq 1.5\sigma(I)$   
 $\theta_{\max}$  = 29.9°  
 $h = -12 \rightarrow 12$   
 $k = 0 \rightarrow 20$   
 $l = 0 \rightarrow 19$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay:  $\pm 0.5\%$

$\Delta\rho_{\max}$  = 1.10 (8) e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -1.72 (8) e Å<sup>-3</sup>  
 Extinction correction:  
 Zachariasen (1968)  
 Extinction coefficient:  
 0.09(1) (length in mm)  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

N(2)—M—N(3)	85.2 (1)	86.7 (2)
N(2)—M—N(4)	174.0 (1)	177.2 (2)
N(3)—M—N(4)	90.7 (1)	91.5 (2)
M—O(1)—C(1)	128.0 (2)	118.4 (4)
M—O(2)—C(1)	135.6 (2)	130.4 (5)
M—N(1)—C(1)	120.4 (2)	124.3 (5)
M—N(2)—C(3)	120.0 (2)	122.8 (5)
M—N(2)—C(4)	106.3 (2)	107.3 (4)
C(3)—N(2)—C(4)	112.2 (3)	111.9 (6)
M—N(3)—C(5)	106.1 (2)	107.5 (4)
M—N(3)—C(6)	110.6 (2)	110.3 (4)
M—N(3)—C(7)	112.2 (2)	112.9 (4)
C(5)—N(3)—C(6)	108.7 (3)	107.1 (6)
C(5)—N(3)—C(7)	108.9 (3)	108.0 (6)
C(6)—N(3)—C(7)	110.2 (3)	110.8 (6)
M—N(4)—C(9)	115.1 (2)	116.1 (5)
N(1)—C(1)—C(2)	112.5 (3)	113.4 (6)
C(1)—C(2)—C(3)	113.2 (3)	113.2 (6)
N(2)—C(3)—C(2)	112.1 (3)	112.3 (7)
N(2)—C(4)—C(5)	106.2 (3)	106.2 (6)
N(3)—C(5)—C(4)	109.9 (3)	109.7 (6)
N(3)—C(7)—C(8)	114.6 (3)	112.7 (6)
C(7)—C(8)—C(9)	114.5 (3)	114.4 (7)
N(4)—C(9)—C(8)	112.0 (3)	112.2 (6)

† Atoms O(1) and O(2) of the Ni complex and atom O(2) of the Cu complex are not considered to be bonded. ‡ The symmetry code ( $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ) applies to the O(2) atom of the Cu complex and ( $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ) to the O(2) atom of the Ni complex.

The structures were solved by direct and Fourier methods and full-matrix least-squares refinements were carried out. H atoms were located by difference Fourier methods. The program used for calculations was *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

The authors are indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data. We also thank the National Science Council, ROC, for support under grants NSC82-0208-M007-119 and NSC82-0208-M007-32.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: HR1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Selected geometric parameters (Å, °) for complexes (1) and (2)

	(1) <i>M</i> = Cu	(2) <i>M</i> = Ni†
M—O(1)	2.558 (3)	2.886 (7)
M—O(2)‡	2.713 (3)	2.901 (7)
M—N(1)	2.026 (3)	1.938 (5)
M—N(2)	2.017 (3)	1.943 (6)
M—N(3)	2.058 (3)	1.956 (5)
M—N(4)	2.011 (3)	1.930 (6)
N(1)—C(1)	1.483 (4)	1.468 (9)
N(2)—C(3)	1.473 (4)	1.46 (1)
N(2)—C(4)	1.491 (4)	1.48 (1)
N(3)—C(5)	1.489 (4)	1.486 (9)
N(3)—C(6)	1.490 (4)	1.471 (9)
N(3)—C(7)	1.497 (4)	1.51 (1)
N(4)—C(9)	1.486 (4)	1.48 (1)
C(1)—C(2)	1.499 (5)	1.50 (1)
C(2)—C(3)	1.519 (6)	1.52 (1)
C(4)—C(5)	1.489 (5)	1.46 (1)
C(7)—C(8)	1.510 (6)	1.52 (1)
C(8)—C(9)	1.512 (6)	1.48 (1)
O(1)—M—O(2)	164.1 (1)	159.2 (3)
O(1)—M—N(1)	86.9 (1)	84.0 (2)
O(1)—M—N(2)	86.4 (1)	84.0 (2)
O(1)—M—N(3)	95.3 (1)	96.9 (2)
O(1)—M—N(4)	98.4 (1)	98.4 (2)
O(2)—M—N(1)	87.5 (1)	88.1 (2)
O(2)—M—N(2)	79.1 (1)	77.3 (3)
O(2)—M—N(3)	89.9 (1)	91.1 (2)
O(2)—M—N(4)	96.5 (1)	100.6 (3)
N(1)—M—N(2)	93.5 (1)	93.5 (2)
N(1)—M—N(3)	177.3 (1)	179.1 (2)
N(1)—M—N(4)	90.5 (1)	88.2 (2)