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Copper(II) and Nickel(II) Complexes with 3,14-Dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane, [M(C₂₀H₄₀N₄)]Cl₂·2H₂O (M = Cu^{II} and Ni^{II})

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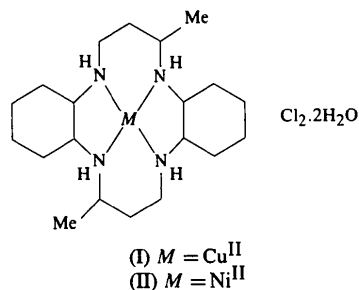
(Received 10 October 1995; accepted 21 February 1996)

Abstract

The structures of (3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane-*N,N',N'',N'''*)copper(II) dichloride dihydrate, [Cu(C₂₀H₄₀N₄)]Cl₂·2H₂O, and (3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane-*N,N',N'',N'''*)nickel(II) dichloride dihydrate, [Ni(C₂₀H₄₀N₄)]Cl₂·2H₂O, are presented. Both complexes have an MN₄ square plane involving the four N atoms of the docosane ligand. In the copper complex, water molecules occupy the two axial positions, though the Cu···O distances are longer than the normal coordination ranges. In the nickel complex, the water molecules are displaced too far from the metal coordination sphere to be considered bonded to the Ni atom.

Comment

To our knowledge, this is the first report of the structures of the Cu complex, (I), and the Ni complex, (II), with the 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0^{7,12}]docosane ligand. The ligand was synthesized by previously reported methods (Hay & Lawrence, 1975; Kang, Kweon & Jung, 1991) (see *Experimental*).



In both structures, the metal atom is located on an inversion center. The ligand contains two cyclohexane rings, which have chair conformations in both complexes, and a central ring of 14 atoms. The complexes contain MN₄ square-planar units. Because of the presence of the inversion center, the MN₄ atoms are exactly coplanar in each structure. The Cl⁻ ions in both structures participate in hydrogen bonding (Table 4). A major

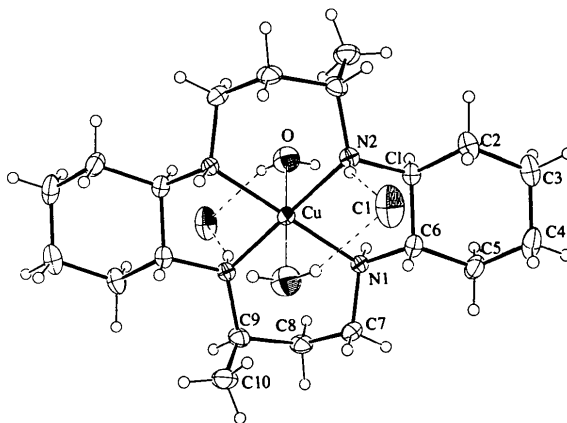


Fig. 1. ORTEP (Johnson, 1976) drawing of complex (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at 40% probability. Dashed lines indicate hydrogen bonds.

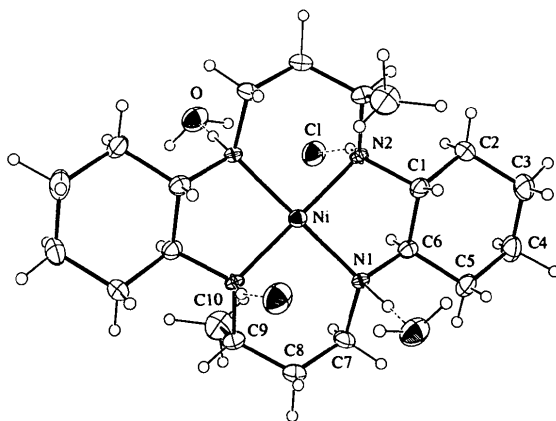


Fig. 2. ORTEP (Johnson, 1976) drawing of complex (II) with the atom-labelling scheme. Displacement ellipsoids are drawn at 40% probability. Dashed lines indicate hydrogen bonds.

difference between the two structures are the locations of the two water molecules with respect to the MN_4 group. In the Cu complex, (I), the two water molecules occupy the axial positions, but the $Cu \cdots O$ distance of 2.649 (2) Å is considerably longer than a normal C—O bond (Huheey, Keiter & Keiter, 1993). This long contact may be stabilized by hydrogen bonding. In complex (II), the O atom of the water molecule is located 2.711 (7) Å from the NiN_4 plane, but significantly displaced from the axial position of the NiN_4 equatorial plane.

Experimental

A solution of the docosane ligand (0.10 mmol) in water (10 ml) was added dropwise to a stirred solution of $CuCl_2 \cdot 2H_2O$ (0.1 mmol) in water (10 ml). The pH of the reaction was adjusted to 5.0 with 0.10 M KOH and the resulting solution was allowed to reflux for 3 h. The volume of the pink solution was reduced to 10 ml and violet crystals formed when the solution was allowed to stand at room temperature for a period of several days. This procedure was also used to produce the nickel complex using hydrated nickel(II) chloride instead of copper(II) chloride.

Complex (I)

Crystal data

$[Cu(C_{20}H_{40}N_4)]Cl_2 \cdot 2H_2O$

$M_r = 507.04$

Monoclinic

$P2_1/c$

$a = 8.999$ (1) Å

$b = 18.174$ (2) Å

$c = 7.857$ (1) Å

$\beta = 109.86$ (1)°

$V = 1208.6$ (3) Å³

$Z = 2$

$D_x = 1.39$ Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

Absorption correction:
none

2134 measured reflections

1591 independent reflections

1424 observed reflections

$[F > 3\sigma(F)]$

Refinement

Refinement on F

$R = 0.026$

$wR = 0.021$

$S = 2.67$

1424 reflections

221 parameters

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = <0.001$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25
reflections

$\theta = 12.36$ – 14.65 °

$\mu = 1.32$ mm⁻¹

$T = 290$ K

Cube

$0.33 \times 0.33 \times 0.30$ mm

Violet

$\theta_{\max} = 24$ °

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 8$

3 standard reflections

frequency: 180 min

intensity decay: 3%

$\Delta\rho_{\max} = 0.36$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

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

$$B_{eq} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Cu	0	1/2	1/2	2.16 (2)
Cl	0.2071 (1)	0.58653 (4)	0.0623 (1)	5.11 (4)
O	0.1112 (4)	0.4508 (2)	0.2495 (3)	4.71 (14)
N1	0.2214 (2)	0.5079 (1)	0.6791 (3)	2.14 (10)
N2	0.0460 (3)	0.6005 (1)	0.4140 (3)	2.20 (10)
C1	0.1921 (3)	0.6300 (1)	0.5515 (3)	2.18 (12)
C2	0.2653 (4)	0.6942 (2)	0.4845 (4)	3.31 (16)
C3	0.4223 (4)	0.7170 (2)	0.6232 (4)	3.79 (17)
C4	0.5333 (4)	0.6524 (2)	0.6784 (5)	4.15 (18)
C5	0.4613 (3)	0.5904 (2)	0.7532 (4)	3.37 (15)
C6	0.3050 (3)	0.5659 (1)	0.6132 (3)	2.32 (12)
C7	0.3100 (3)	0.4379 (2)	0.7263 (4)	3.11 (15)
C8	0.2236 (4)	0.3822 (2)	0.7999 (4)	3.20 (15)
C9	0.0831 (3)	0.3450 (2)	0.6624 (4)	2.86 (14)
C10	0.1242 (5)	0.3057 (2)	0.5157 (5)	4.20 (19)

Complex (II)

Crystal data

$[Ni(C_{20}H_{40}N_4)]Cl_2 \cdot 2H_2O$

$M_r = 502.20$

Monoclinic

$P2_1/c$

$a = 9.376$ (1) Å

$b = 16.042$ (1) Å

$c = 8.177$ (2) Å

$\beta = 102.51$ (1)°

$V = 1200.7$ (3) Å³

$Z = 2$

$D_x = 1.39$ Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

Absorption correction:
none

2103 measured reflections

1569 independent reflections

1141 observed reflections

$[F > 3\sigma(F)]$

Refinement

Refinement on F

$R = 0.039$

$wR = 0.024$

$S = 1.45$

1141 reflections

221 parameters

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = <0.001$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25
reflections

$\theta = 10.58$ – 14.05 °

$\mu = 1.03$ mm⁻¹

$T = 293$ K

Rectangular

$0.30 \times 0.17 \times 0.10$ mm

Orange

$\theta_{\max} = 24$ °

$h = -10 \rightarrow 10$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 9$

3 standard reflections

frequency: 180 min

intensity decay: 2%

$\Delta\rho_{\max} = 0.61$ e Å⁻³

$\Delta\rho_{\min} = -0.49$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)

$$B_{eq} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Ni	0	0	0	2.06 (4)
Cl	0.2377 (2)	0.04765 (9)	-0.3145 (2)	4.5 (1)
O	-0.0362 (6)	0.1108 (3)	0.4185 (6)	4.6 (3)

N1	0.0236 (4)	0.1138 (3)	0.0871 (5)	2.4 (2)
N2	0.2115 (4)	-0.0071 (3)	0.0631 (4)	2.1 (2)
C1	0.2692 (6)	0.0668 (3)	0.1704 (6)	2.5 (3)
C2	0.4304 (6)	0.0836 (4)	0.1847 (8)	3.5 (3)
C3	0.4764 (6)	0.1600 (6)	0.2977 (8)	4.3 (3)
C4	0.3836 (6)	0.2350 (4)	0.2296 (8)	4.0 (3)
C5	0.2221 (6)	0.2166 (3)	0.2117 (7)	3.3 (3)
C6	0.1773 (5)	0.1400 (3)	0.1019 (6)	2.3 (2)
C7	-0.0805 (6)	0.1800 (3)	0.0150 (8)	3.5 (3)
C8	-0.2356 (6)	0.1546 (4)	-0.0013 (7)	3.3 (3)
C9	-0.2863 (6)	0.0858 (3)	-0.1270 (7)	2.9 (3)
C10	-0.2603 (9)	0.1068 (4)	-0.3009 (8)	4.9 (4)

parameters were used for all non-H atoms and H atoms were refined isotropically.

For both compounds, data collection: *SDP* (Enraf-Nonius, 1985); cell refinement: *SDP*; data reduction: *SDP*; program(s) used to solve structures: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to refine structures: *NRCVAX*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *NRCVAX*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1220). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected bond distances (Å) and angles (°) for complexes (I) and (II)

	(I)	(II)
M—N1	2.017 (2)	1.954 (4)
M—N2	2.038 (2)	1.941 (3)
M—O	2.649 (2)	
N1—C6	1.486 (3)	1.481 (6)
N1—C7	1.480 (4)	1.477 (6)
N2—C1	1.489 (3)	1.504 (7)
N2—C9 ⁱ	1.490 (3)	1.483 (7)
C1—C6	1.513 (4)	1.493 (7)
N1—M—N1 ⁱ	180.0	180.0
N1—M—N2	84.5 (1)	86.0 (2)
N1—M—N2 ⁱ	96.5 (1)	94.1 (2)
N1—M—O	90.6 (1)	
N1—M—O ⁱ	89.5 (1)	
N2—M—N2 ⁱ	180.0	180.0
N2—M—O	83.4 (1)	
N2—M—O ⁱ	96.6 (1)	
O—M—O ⁱ	180.0	
Cu—N1—C6	107.7 (1)	109.1 (3)
Cu—N1—C7	115.7 (2)	120.9 (3)
C6—N1—C7	113.8 (2)	112.0 (4)
Cu—N2—C1	108.1 (1)	109.1 (3)
Cu—N2—C9 ⁱ	120.8 (2)	121.4 (3)
C1—N2—C9 ⁱ	115.4 (2)	112.5 (4)
N2—C1—C2	113.9 (2)	114.4 (4)
N2—C1—C6	106.6 (2)	107.2 (4)
C2—C1—C6	112.4 (2)	112.0 (4)
N1—C6—C1	107.1 (2)	106.2 (4)
N1—C6—C5	114.0 (2)	114.6 (4)
C1—C6—C5	111.1 (2)	110.5 (4)

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Diiodobis(η⁵-trimethylsilylcyclopentadienyl)titanium(IV)

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Abstract

The title compound, [TiI₂(η⁵-C₅H₄SiMe₃)₂], has crystallographic C₂ symmetry with the metal atom in a distorted tetrahedral environment bonded to two I atoms [Ti—I 2.771 (3) Å] and to two cyclopentadienyl rings [Ti—C 2.308 (14)–2.387 (17) Å].

Symmetry codes: (i) $-x, 1-y, 1-z$, for complex (I); (ii) $-x, -y, -z$, for complex (II).

Table 4. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
(I)				
N1—HN1...Cl ⁱ	0.84 (2)	2.54 (2)	3.374 (2)	173 (2)
N2—HN2...Cl	0.76 (2)	2.81 (2)	3.539 (2)	162 (2)
O—HO1...Cl	0.84 (3)	2.32 (3)	3.139 (3)	164 (2)
O—HO2...Cl ⁱⁱ	0.74 (3)	2.44 (3)	3.147 (3)	164 (2)
(II)				
N1—HN1...O	0.75 (3)	2.13 (3)	2.883 (6)	173 (4)
N2—HN2...Cl	0.84 (3)	2.46 (3)	3.270 (4)	165 (3)
O—HO1...Cl ⁱ	0.88 (4)	2.31 (4)	3.171 (5)	164 (4)
O—HO2...Cl ⁱⁱ	0.82 (4)	2.34 (5)	3.156 (6)	178 (5)

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

All non-H atoms were placed by a combination of difference Fourier and least-squares calculations. Methyl H atoms were located from difference Fourier maps, while other H atoms were placed in calculated positions. Anisotropic displacement