

1010 measured reflections
526 independent reflections
400 observed reflections
[$I > 2\sigma(I)$]

3 standard reflections
frequency: 90 min

Refinement

Refinement on F^2

Final $R_1 = 0.0227$ for

$F > 4\sigma(F)$

$wR_2 = 0.0716$ for all F^2 data

$S = 1.084$

524 reflections

20 parameters

Calculated weights

$$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.5296P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.186 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.194 \text{ e } \text{\AA}^{-3}$$

Atomic scattering factors

from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Absolute structure determined according to Flack (1983)

Refinement was on F^2 for all reflections except for two flagged for possible systematic errors; the observed threshold $F > 4\sigma(F)$ is used only for calculating R_1 and wR_1 . The goodness-of-fit value is calculated using F^2 . The unweighted R factor is based on F and is intended for comparison with other refinements based on F . The methyl H atoms were located by difference Fourier synthesis, but in the refinement an idealized methyl group was allowed to rotate freely around the local threefold axis to optimize the torsion angle.

Data collection: *DIF4* 7.08 (Siemens diffractometer control software). Cell refinement: *DIF4* 7.08 (Siemens diffractometer control software). Data reduction: *REDU4* (Siemens diffractometer control software). Program(s) used to solve structure: *SHELXS92* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL92*.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z	U_{eq}
K1	0.82521 (2)	0.82521 (2)	0.82521 (2)	0.0284 (2)
Si1	0.62369 (3)	0.62369 (3)	0.62369 (3)	0.0225 (2)
O1	0.67561 (6)	0.67561 (6)	0.67561 (6)	0.0309 (4)
C1	0.61473 (14)	0.66142 (13)	0.52405 (10)	0.0370 (5)

Table 2. Geometric parameters (\AA , $^\circ$)

K1—O1 ⁱ	2.6290 (11)	Si1—C1	1.879 (2)
Si1—O1	1.580 (2)		
O1 ⁱ —K1—O1 ⁱⁱ	89.37 (5)	Si1—O1—K1 ⁱ	124.82 (4)
O1—Si1—C1	112.50 (7)	K1 ⁱ —O1—K1 ^{iv}	90.63 (5)
C1—Si1—C1 ⁱⁱⁱ	106.28 (8)		

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{3}{2} - z$; (ii) $\frac{3}{2} - x, y, \frac{3}{2} - z$; (iii) y, z, x ; (iv) $\frac{3}{2} - x, \frac{3}{2} - y, z$.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71100 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1040]

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Structure of a Phenyl Dioxocyclam Nickel Complex

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Abstract

The molecule, (3-phenyl-1,5,8,12-tetraazacyclotetradecane-2,4-dionato-*N,N',N'',N'''*)nickel(II), has near-mirror symmetry with its two amine N—H bonds directed to the same side of the coordination plane. The Ni—N(amide) bonds are shorter than the Ni—N(amine) bonds [mean values 1.880 (2) and 1.937 (2) \AA , respectively]. The crystal contains an extensive network of hydrogen bonds.

Comment

The compound was prepared as part of a programme investigating the influence of substitution on the properties of macrocyclic ligands. Spectroscopic data and assignments are given by Chinn (1987). The X-ray structure was determined because no dioxocyclam complexes had hitherto been reported.

The overall structure of the neutral complex is as expected, with square-planar coordination about Ni;

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it has near-mirror symmetry. Although the protons were not directly located, it can be assumed that the two amide protons are lost on formation of the Ni complex, these two N atoms showing almost planar geometry. The six-membered oxo-ring is essentially planar while the other six-membered ring is in the chair conformation; the two five-membered rings have *gauche* C—C bonds. The Ni—N(amide) distances are substantially shorter than those of Ni—N(amine) [mean values 1.880 (2) and 1.937 (2) Å, respectively]; such differences between amide and amine donors are normal. The orientation of the phenyl ring results in a comparatively short Ni—H approach (*ca* 1.96 Å). The amine N—H bonds are oriented towards the same side of the molecule.

The unit cell contains discrete molecules linked by hydrogen bonding from the O atoms to sheets of hydrogen-bonded water molecules (oriented in the 101 direction) (Fig. 2).

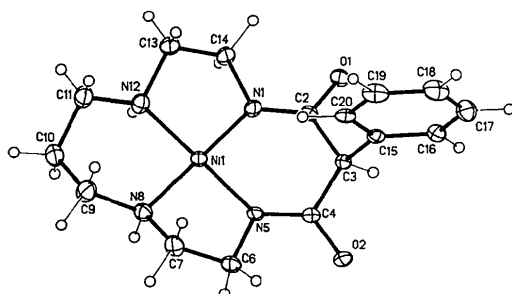


Fig. 1. View of the molecule showing the atomic numbering.

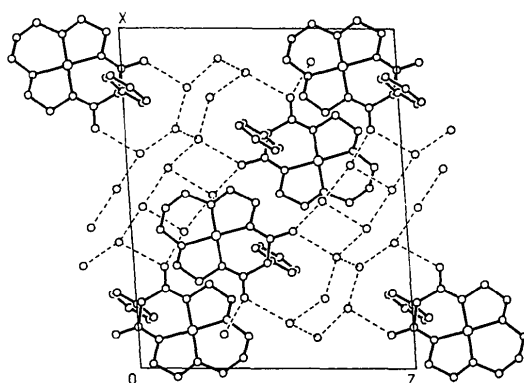


Fig. 2. Packing diagram viewed down *b*, showing the network of hydrogen bonds.

Structures have not been determined for either the parent dioxocyclam molecule, or for any metal-free derivatives. However, since this work was carried out, structures for two metal complexes have been reported: the Pt^{II} complex of methyl-dioxocyclam (Kimura, Korenari, Shionoya & Shino, 1988) and a Tc^V complex of dioxocyclam itself (Marchi, Rossi,

Magon, Duatti, Casellato, Graziani, Vidal & Riche, 1990). Both structures are very similar to that reported here, allowing for the larger *M*—*N* distances in them.

Experimental

Crystal data

[Ni(C₁₆H₂₂N₄O₂)]·7H₂O

M_r = 487.2

Monoclinic

*P*2₁/*n*

a = 19.798 (2) Å

b = 8.009 (1) Å

c = 14.524 (2) Å

β = 94.02 (1)°

V = 2298 Å³

Z = 4

D_x = 1.41 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 28 reflections

θ = 10–15°

μ = 0.90 mm⁻¹

T = 162 K

Blocks

0.45 × 0.43 × 0.27 mm

Dark orange

Data collection

Syntex *P*1 diffractometer

ω–2θ scans

Absorption correction:

none

6566 measured reflections

5316 independent reflections

4639 observed reflections

[*I*/σ(*I*) ≥ 2.0]

*R*_{int} = 0.015

θ_{max} = 27.5°

h = 0 → 25

k = 0 → 10

l = –18 → 18

3 standard reflections

monitored every 50

reflections

intensity variation: slight

increase

Refinement

Refinement on *F*

Final *R* = 0.052

wR = 0.079

S = 1.83

4639 reflections

271 parameters

w = 1/[σ²(*F*) + 0.0011*F*²]

(Δ/σ)_{max} = 0.21

Δρ_{max} = 2.2 e Å⁻³

Δρ_{min} = –0.7 e Å⁻³

Atomic scattering factors

stored in program

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)

Atoms O(07a) and O(07b) were refined isotropically with occupancies of 0.5 each. For other atoms, equivalent isotropic *U* is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

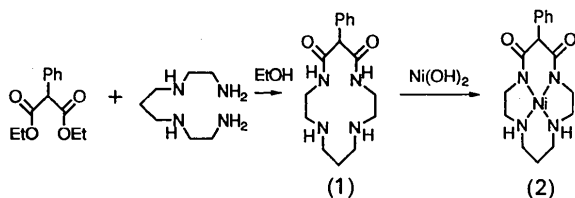
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} / <i>U</i> _{eq}
Ni(1)	0.11142 (2)	0.21794 (5)	0.19524 (2)	0.015 (1)
O(1)	0.29620 (9)	0.08726 (25)	0.10840 (13)	0.019 (1)
O(2)	0.09855 (10)	0.15814 (25)	–0.08371 (12)	0.018 (1)
N(1)	0.20149 (11)	0.15461 (30)	0.18208 (15)	0.016 (1)
C(2)	0.23201 (13)	0.11053 (33)	0.10816 (18)	0.014 (1)
C(3)	0.19175 (13)	0.07868 (33)	0.01717 (17)	0.013 (1)
C(4)	0.12038 (13)	0.14837 (33)	0.00045 (17)	0.014 (1)
N(5)	0.08407 (11)	0.18572 (29)	0.06962 (15)	0.014 (1)
C(6)	0.01343 (14)	0.23121 (39)	0.04516 (20)	0.020 (1)
C(7)	–0.0235 (2)	0.2130 (4)	0.1320 (2)	0.023 (1)
N(8)	0.01959 (12)	0.29322 (31)	0.20684 (16)	0.019 (1)
C(9)	–0.0127 (2)	0.2767 (5)	0.2961 (2)	0.027 (1)
C(10)	0.0313 (2)	0.3570 (4)	0.3737 (2)	0.028 (1)
C(11)	0.0938 (2)	0.2549 (4)	0.3971 (2)	0.023 (1)
N(12)	0.14119 (12)	0.26238 (31)	0.32299 (16)	0.019 (1)
C(13)	0.19954 (14)	0.15026 (40)	0.34485 (19)	0.021 (1)
C(14)	0.24571 (14)	0.16807 (41)	0.26776 (18)	0.020 (1)
C(15)	0.18653 (13)	–0.10950 (33)	0.00137 (17)	0.014 (1)

C(16)	0.2197 (2)	-0.1848 (4)	-0.0693 (2)	0.019 (1)
C(17)	0.2142 (2)	-0.3553 (4)	-0.0844 (2)	0.026 (1)
C(18)	0.1752 (2)	-0.4521 (4)	-0.0289 (2)	0.027 (1)
C(19)	0.1419 (2)	-0.3786 (4)	0.0416 (2)	0.024 (1)
C(20)	0.14769 (14)	-0.20789 (35)	0.05690 (19)	0.017 (1)
O(001)	0.82579 (12)	0.88181 (31)	0.23602 (15)	0.032 (1)
O(002)	-0.00916 (12)	0.65810 (31)	0.19841 (15)	0.030 (1)
O(003)	0.59024 (13)	0.17736 (33)	0.14658 (17)	0.036 (1)
O(004)	0.7030 (2)	0.6985 (3)	0.1847 (2)	0.045 (1)
O(005)	0.40115 (13)	0.29689 (34)	0.19072 (21)	0.045 (1)
O(006)	0.63206 (12)	0.89429 (37)	0.04974 (17)	0.041 (1)
O(07a)	0.4731 (3)	0.3344 (7)	0.0450 (3)	0.031 (1)
O(07b)	0.5036 (3)	0.4018 (8)	0.0673 (4)	0.043 (1)

Table 2. Selected bond lengths (Å) and angles (°)

Ni(1)—N(1)	1.877 (2)	Ni(1)—N(8)	1.934 (2)
Ni(1)—N(12)	1.940 (2)	O(1)—C(2)	1.284 (3)
O(2)—C(4)	1.270 (3)	N(1)—C(2)	1.317 (4)
N(1)—C(14)	1.475 (3)	C(2)—C(3)	1.516 (4)
C(3)—C(4)	1.523 (4)	C(3)—C(15)	1.527 (4)
C(4)—N(5)	1.310 (3)	N(5)—C(6)	1.465 (4)
C(6)—C(7)	1.508 (4)	C(7)—N(8)	1.481 (4)
N(8)—C(9)	1.491 (4)	C(9)—C(10)	1.518 (4)
C(10)—C(11)	1.503 (5)	C(11)—N(12)	1.477 (4)
N(12)—C(13)	1.480 (4)	C(13)—C(14)	1.501 (4)
C(15)—C(16)	1.395 (4)	C(15)—C(20)	1.396 (4)
C(16)—C(17)	1.386 (4)	C(17)—C(18)	1.391 (5)
C(18)—C(19)	1.386 (5)	C(19)—C(20)	1.388 (4)
Ni(1)—N(5)	1.884 (2)		
N(1)—Ni(1)—N(5)	94.3 (1)	C(3)—C(15)—C(16)	120.5 (2)
N(5)—Ni(1)—N(8)	85.4 (1)	N(1)—Ni(1)—N(8)	177.4 (1)
N(5)—Ni(1)—N(12)	177.1 (1)	N(8)—Ni(1)—N(12)	94.8 (1)
N(1)—Ni(1)—N(12)	87.9 (1)	Ni(1)—N(1)—C(14)	114.0 (2)
Ni(1)—N(1)—C(2)	130.5 (2)	O(1)—C(2)—N(1)	123.2 (2)
C(2)—N(1)—C(14)	115.4 (2)	N(1)—C(2)—C(3)	120.8 (2)
O(1)—C(2)—C(3)	116.0 (2)	C(2)—C(3)—C(15)	108.8 (2)
C(2)—C(3)—C(4)	120.2 (2)	O(2)—C(4)—C(3)	115.3 (2)
C(4)—C(3)—C(15)	106.6 (2)	C(3)—C(4)—N(5)	120.9 (2)
O(2)—C(4)—N(5)	123.7 (2)	Ni(1)—N(5)—C(6)	113.9 (2)
Ni(1)—N(5)—C(4)	129.6 (2)	N(5)—C(6)—C(7)	106.5 (2)
C(4)—N(5)—C(6)	115.9 (2)	Ni(1)—N(8)—C(7)	107.3 (2)
O(1)—C(7)—N(8)	106.5 (2)	C(7)—N(8)—C(9)	109.9 (2)
Ni(1)—N(8)—C(9)	120.7 (2)	C(9)—C(10)—C(11)	110.9 (3)
N(8)—C(9)—C(10)	110.5 (3)	Ni(1)—N(12)—C(11)	121.6 (2)
C(10)—C(11)—N(12)	111.6 (2)	C(11)—N(12)—C(13)	110.2 (2)
Ni(1)—N(12)—C(13)	105.9 (2)	N(1)—C(14)—C(13)	105.4 (2)
N(12)—C(13)—C(14)	106.8 (2)		

Ligand preparation followed the scheme below, based on the procedures of Kimura, Machida & Kodama (1984).



Phenyl-dioxocyclam (1). *N,N'*-Bis(2-aminoethyl)-1,3-propanediamine (5.0 g, 31 mmol) (Eastman-Kodak) and diethyl phenylmalonate (7.4 g, 31 mmol) (Fluka), both purified by vacuum distillation, were added to absolute ethanol (630 cm³) and refluxed under a N₂ blanket for 4 weeks. Removal of solvent under vacuum at 313 K gave a cream-coloured solid. This was dissolved in hot dried acetone (50 cm³), cooled to 273 K, and the solid collected by filtration; repetition of this procedure gave an overall yield of 1.4 g (15%). Analysis calculated for C₁₆H₂₄N₄O₂: C 63.10, H 7.95, N 18.40%; found: C 63.15, H 8.20, N 18.55%; m.p. 480–481 K (decomp.).

Phenyl-dioxocyclamato-nickel(II) (2). Freshly prepared nickel(II) hydroxide (0.30 g, 3.3 mmol) was added to a solution of (1) (0.50 g, 1.6 mmol) in methanol (40 cm³). The solution was refluxed for 3 d under N₂, during which time a yellow precipitate formed. After addition of H₂O (10 cm³), the solution was filtered through celite. Solvent was removed *in vacuo* at 313 K, and the yellow precipitate recrystallized from hot water to give dark orange crystals which quickly lost solvent under vacuum or on exposure to air. The analysed sample was dried at 373 K (1.33 kPa) for 8 h. Yield 0.24 g (32%). Analysis calculated for C₁₆H₂₂N₄O₂Ni·2H₂O: C 48.40, H 6.60, N 14.10, Ni 14.80%; found: C 48.70, H 6.45, N 14.05, Ni 14.20%.

Structure determination. The crystal was held at 162 K with a Nicolet LT-1 low temperature device. Scan speed was 1–12° (ω) min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The data were rescaled to correct for the slight change in standards (presumably owing to increasing mosaicity). Reflections were processed using profile analysis. Systematic reflection conditions indicated the space group unambiguously. The Ni atom was located by Patterson methods and the light atoms then found by successive Fourier syntheses. Of the seven water molecules, six were ordered, but the seventh was represented by two half-occupancy positions close to one of the crystallographic centres of inversion. Anisotropic temperature factors were used for non-H atoms except for the half-occupancy water O atoms. H atoms were given fixed isotropic temperature factors, *U* = 0.08 Å². Those in the ligand molecule were inserted at calculated positions and not refined; those of water molecules were omitted. Although nine of the top ten peaks on the final difference synthesis were in plausible positions for water H atoms, some appeared to be disordered. The single largest peak was in the vicinity of the Ni atom, possibly the result of the neglect of absorption. Final computing was performed with *SHELXTL-Plus* (Sheldrick, 1986) on a DEC MicroVAX II; a variety of programs were used at earlier stages.

Data collection was carried out by Dr J. Gallucci, whose assistance is gratefully acknowledged. Support has been received from NATO for the Warwick/Ohio/Kansas collaboration.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71060 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1017]

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