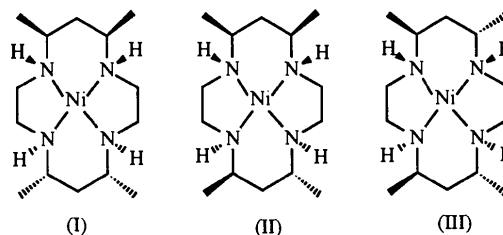


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complex, (I), with perchlorate has been reported (Hay *et al.*, 1982). This paper reports the crystallization and structure of complex (II).



Two molecules, *A* with coordinates (x_A, y_A, z_A) and *B* with coordinates near ($\frac{1}{2} - x_A, y_A, -\frac{1}{2} + z_A$), of the title complex cation are located in the asymmetric unit. The Ni²⁺ ion has square-planar coordination with the four N atoms of the macrocyclic ligand. These N atoms are coplanar within ± 0.054 (5) Å. The quadridentate ligand has the configuration 1*RS*,4*RS*,8*SR*,11*SR* for the four chiral N-atom centres. The two five-membered chelate rings are in skew forms and the two six-membered chelate rings are in chair forms. The Ni—N distances are close to the average Ni—N distance of 1.95 (4) Å for four-coordinate Ni^{II} macrocyclic complexes (Lu, Chung & Ashida, 1991). In both molecules *A* and *B* of the diastereoisomer (II) and in all three molecules of the diastereoisomer (I) (Hay *et al.*, 1982), the conformations of the 14-membered rings are similar.

All four perchlorate groups are disordered. The amino groups form hydrogen bonds with perchlorate O atoms.

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[(5*SR*,7*RS*,12*RS*,14*RS*)-5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradecane]-nickel(II) Diperchlorate

TAHIR H. TAHIROV AND TIAN-HUEY LU*

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300

GUEY-SUNG LIU, TA-YUNG CHI AND CHUNG-SUN CHUNG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

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Abstract

Two pseudosymmetrically related Ni^{II} complexes are located in the asymmetric unit of solid [Ni(C₁₄H₃₂N₄)]-(ClO₄)₂. The Ni²⁺ ion displays square-planar coordination with the four N atoms of the macrocyclic ligand. The quadridentate ligand adopts its stable conformation with two six-membered chelate rings in chair forms and two five-membered chelate rings in skew forms. The complex has a 1*RS*,4*RS*,8*SR*,11*SR* configuration for the four chiral N-atom centres and a 5*SR*,7*RS*,12*RS*,14*RS* configuration for the four chiral C-atom centres.

Comment

According to a previous report (Hay, Jeragh, Ferguson, Kaitner & Ruhe, 1982), the reduction of *C-meso*-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene can give three diastereoisomeric tetraamines and their Ni^{II} complexes, in which the 1*RS*,4*RS*,8*SR*,11*SR* arrangement of the chiral N-atom centres should be as indicated by (I), (II) and (III). The crystal structure of the two isomers of the nickel(II)

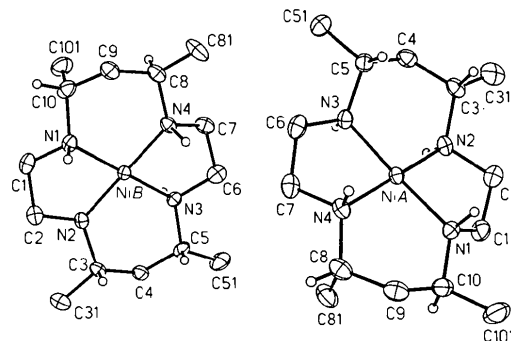


Fig. 1. A perspective view of the two crystallographically independent complex cations, *A* and *B*. The displacement ellipsoids are shown at the 50% probability level (Sheldrick, 1987). Perchlorate anions and selected H atoms are excluded for clarity.

Experimental

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared according to the reported method (Hay & Jeragh, 1977). The ligand contains two chiral C-atom centres. The preparation and separation of nickel(II) complexes of the two diastereoisomers, *C-meso*- and *C-rac*-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-

4,11-diene, were carried out as described by Kolinski & Korybut-Daszkiwicz (1975). (*C-meso*-5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) diperchlorate (13 g) was dissolved in hot water (333 K) and NaBH₄ (2 g) and Na₂B₂O₇ (0.5 g) were added in small portions to the solution with vigorous stirring. On completion, the solution was heated under reflux for *ca* 4 h, acetone added (165 ml) and then filtered. The volume of the filtrate was reduced to *ca* 200 ml by rotatory evaporation and then allowed to stand at room temperature. A crop of red crystals was obtained and filtered off. The filtrate was adjusted to pH 8–9 with an aqueous solution of NaOH; on addition of Na₂C₂O₄, a purple precipitate was obtained. 0.6 g of the precipitate was dissolved in HClO₄ solution (15 ml 60% HClO₄ + 7.5 ml H₂O). Orange crystals formed on slow evaporation.

Crystal data[Ni(C₁₄H₃₂N₄)](ClO₄)₂*M_r* = 514.049

Monoclinic

*P*2₁/*a**a* = 15.665 (1) Å*b* = 16.352 (3) Å*c* = 17.252 (1) Å

β = 95.725 (7)°

V = 4397.1 (9) Å³*Z* = 8*D_x* = 1.553 Mg m⁻³Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 7.40–17.51°

μ = 1.18 mm⁻¹*T* = 298 (3) K

Rectangular pillar

0.43 × 0.31 × 0.28 mm

Orange

Data collection

Enraf–Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

ψ scan (North, Phillips

& Mathews, 1968)

T_{min} = 0.883, *T_{max}* =

0.999

8038 measured reflections

7725 independent reflections

5267 observed reflections

[*I* ≥ 2σ(*I*)]*R_{int}* = 0.012θ_{max} = 25°*h* = -18 → 18*k* = 0 → 19*l* = 0 → 20

3 standard reflections

frequency: 60 min

intensity decay: 2%

*Refinement*Refinement on *F**R* = 0.048*wR* = 0.058*S* = 1.38

5267 reflections

668 parameters

Only H-atom *U*'s refined*w* = 1/[σ²(*F*) + 0.0008*F*²](Δ/σ)_{max} = 0.115Δρ_{max} = 0.53 (8) e Å⁻³Δρ_{min} = -0.39 (8) e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

C1	1.0	0.3171 (4)	0.5113 (3)	0.9712 (3)	5.2 (3)
C2	1.0	0.2252 (4)	0.5321 (3)	0.9695 (3)	4.9 (3)
C3	1.0	0.0863 (3)	0.4913 (3)	0.9013 (3)	4.4 (2)
C31	1.0	0.0498 (4)	0.5720 (4)	0.9264 (3)	6.8 (3)
C4	1.0	0.0413 (3)	0.4660 (3)	0.8233 (3)	4.8 (2)
C5	1.0	0.0638 (3)	0.3816 (3)	0.7935 (3)	4.4 (2)
C51	1.0	0.0053 (4)	0.3614 (4)	0.7201 (3)	6.5 (3)
C6	1.0	0.1797 (4)	0.3007 (3)	0.7414 (3)	5.0 (3)
C7	1.0	0.2742 (4)	0.2967 (3)	0.7479 (3)	5.0 (3)
C8	1.0	0.3982 (3)	0.3030 (3)	0.8485 (3)	5.1 (3)
C81	1.0	0.4438 (4)	0.3666 (4)	0.8034 (4)	7.0 (3)
C9	1.0	0.4225 (3)	0.3079 (4)	0.9357 (3)	5.6 (3)
C10	1.0	0.4125 (3)	0.3917 (3)	0.9708 (3)	5.0 (3)
C101	1.0	0.4430 (4)	0.3901 (4)	1.0576 (4)	7.4 (4)

Molecule *B*

Ni	1.0	0.26142 (3)	0.41155 (3)	0.36598 (3)	2.94 (2)
N1	1.0	0.2211 (2)	0.3095 (2)	0.3203 (2)	3.55 (16)
N2	1.0	0.3558 (2)	0.4031 (2)	0.3005 (2)	3.43 (16)
N3	1.0	0.3002 (2)	0.5179 (2)	0.4068 (2)	3.45 (16)
N4	1.0	0.1710 (2)	0.4184 (2)	0.4352 (2)	3.71 (16)
C1	1.0	0.2615 (4)	0.2989 (3)	0.2471 (3)	4.5 (3)
C2	1.0	0.3536 (3)	0.3195 (3)	0.2651 (3)	4.3 (2)
C3	1.0	0.4440 (3)	0.4266 (3)	0.3348 (3)	4.1 (2)
C31	1.0	0.5099 (3)	0.4171 (4)	0.2746 (4)	5.9 (3)
C4	1.0	0.4451 (3)	0.5139 (3)	0.3641 (3)	4.8 (2)
C5	1.0	0.3933 (3)	0.5311 (3)	0.4310 (3)	4.5 (2)
C51	1.0	0.4110 (4)	0.6182 (4)	0.4606 (4)	7.0 (3)
C6	1.0	0.2468 (4)	0.5423 (3)	0.4696 (3)	5.1 (3)
C7	1.0	0.1601 (3)	0.5082 (3)	0.4505 (3)	4.8 (2)
C8	1.0	0.0852 (3)	0.3770 (3)	0.4231 (3)	5.0 (2)
C81	1.0	0.0440 (4)	0.3707 (4)	0.4992 (4)	7.5 (4)
C9	1.0	0.0941 (3)	0.2922 (3)	0.3898 (3)	5.3 (3)
C10	1.0	0.1283 (3)	0.2901 (3)	0.3105 (3)	5.0 (2)
C101	1.0	0.0793 (4)	0.3426 (4)	0.2508 (4)	6.8 (3)

Perchlorate groups

C11	1.0	0.17460 (9)	0.26542 (8)	0.02627 (7)	4.91 (6)
C12	1.0	0.79522 (10)	0.42225 (8)	0.31711 (8)	5.48 (7)
C13	1.0	0.23840 (9)	0.56785 (8)	0.18901 (7)	4.85 (6)
C14	1.0	0.65851 (8)	0.70703 (8)	0.45650 (7)	4.51 (5)
O1	0.8	0.1567 (5)	0.2593 (5)	-0.0540 (3)	12.2 (5)
O1'	0.2	0.186 (3)	0.2169 (17)	-0.0304 (11)	15 (3)
O2	1.0	0.1339 (4)	0.2130 (3)	0.0714 (3)	11.1 (3)
O3	0.2	0.1011 (15)	0.3116 (15)	0.020 (2)	15 (2)
O3'	0.8	0.1681 (5)	0.3469 (3)	0.0475 (4)	11.2 (5)
O4	0.8	0.2609 (4)	0.2496 (5)	0.0425 (5)	11.9 (5)
O4'	0.2	0.2455 (14)	0.3060 (15)	0.0604 (8)	9.4 (12)
O5	1.0	0.8223 (5)	0.4944 (3)	0.3512 (3)	12.4 (4)
O6	1.0	0.7472 (3)	0.3728 (3)	0.3631 (2)	8.5 (3)
O7	0.4	0.8789 (8)	0.3840 (10)	0.3354 (10)	13.3 (10)
O7'	0.6	0.8418 (7)	0.3859 (5)	0.2617 (6)	11.6 (6)
O8	0.6	0.7540 (7)	0.4275 (6)	0.2447 (4)	11.1 (6)
O8'	0.4	0.7320 (9)	0.4758 (10)	0.2805 (12)	14.2 (12)
O9	0.7	0.1915 (6)	0.5471 (7)	0.2518 (4)	14.3 (6)
O9'	0.3	0.1862 (10)	0.5021 (9)	0.1923 (14)	12.3 (14)
O10	0.4	0.3148 (9)	0.6064 (9)	0.2038 (12)	14.5 (12)
O10'	0.6	0.2699 (8)	0.6107 (5)	0.2565 (5)	12.4 (7)
O11	1.0	0.1913 (3)	0.6175 (3)	0.1357 (2)	8.2 (3)
O12	0.6	0.2646 (6)	0.4941 (4)	0.1596 (4)	9.3 (5)
O12'	0.4	0.3146 (8)	0.5379 (9)	0.1681 (7)	10.9 (8)
O13	1.0	0.6360 (3)	0.7051 (4)	0.5332 (2)	9.4 (3)
O14	1.0	0.7464 (3)	0.7165 (4)	0.4535 (3)	11.3 (4)
O15	0.7	0.6222 (5)	0.7735 (4)	0.4152 (4)	10.2 (4)
O15'	0.3	0.5944 (9)	0.7216 (12)	0.4042 (7)	8.9 (9)
O16	1.0	0.6437 (5)	0.6298 (4)	0.4274 (4)	14.6 (5)

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

Occupancy	$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>	
Molecule <i>A</i>					
Ni	1.0	0.24159 (3)	0.40039 (3)	0.86728 (3)	3.04 (2)
N1	1.0	0.3222 (2)	0.4215 (2)	0.9582 (2)	3.86 (16)
N2	1.0	0.1810 (2)	0.4980 (2)	0.8964 (2)	3.45 (16)
N3	1.0	0.1565 (2)	0.3792 (2)	0.7792 (2)	3.64 (17)
N4	1.0	0.3042 (2)	0.3085 (2)	0.8318 (2)	3.81 (17)

Table 2. Selected geometric parameters (Å, °)

	Molecule <i>A</i>	Molecule <i>B</i>
Ni—N1	1.945 (4)	1.925 (4)
Ni—N2	1.949 (3)	1.953 (4)
Ni—N3	1.950 (4)	1.950 (4)
Ni—N4	1.928 (4)	1.947 (4)
N1—C1	1.489 (6)	1.477 (6)
N1—C10	1.491 (6)	1.482 (6)
N2—C2	1.485 (6)	1.495 (6)
N2—C3	1.498 (6)	1.499 (6)

N3—C5	1.497 (6)	1.493 (6)
N3—C6	1.500 (6)	1.487 (6)
N4—C7	1.489 (6)	1.503 (6)
N4—C8	1.474 (7)	1.501 (6)
C1—C2	1.476 (8)	1.484 (8)
C3—C31	1.519 (7)	1.543 (7)
C3—C4	1.514 (7)	1.513 (7)
C4—C5	1.525 (8)	1.502 (7)
C5—C51	1.524 (7)	1.529 (7)
C6—C7	1.474 (8)	1.475 (8)
C8—C81	1.520 (8)	1.523 (8)
C8—C9	1.518 (8)	1.512 (8)
C9—C10	1.513 (8)	1.519 (8)
C10—C101	1.526 (8)	1.493 (8)
N1—Ni—N2	86.6 (2)	86.4 (2)
N1—Ni—N3	177.4 (2)	176.9 (2)
N1—Ni—N4	94.9 (2)	94.2 (2)
N2—Ni—N3	91.9 (2)	92.7 (2)
N2—Ni—N4	175.6 (1)	177.4 (2)
N3—Ni—N4	86.8 (2)	86.9 (2)
C10—N1—C1—C2	-171.4 (6)	-179.6 (5)
C3—N2—C2—C1	161.2 (5)	169.9 (5)
C6—N3—C5—C4	-173.6 (5)	-174.4 (5)
C8—N4—C7—C6	177.9 (6)	174.5 (5)
N1—C1—C2—N2	-52.3 (3)	-54.1 (3)
C3—C4—C5—N3	-63.9 (4)	-64.5 (4)
N4—C8—C9—C10	-72.3 (4)	-61.8 (4)
C1—N1—C10—C9	-163.3 (6)	173.1 (5)
C2—N2—C3—C4	173.3 (5)	175.4 (5)
C5—N3—C6—C7	-166.4 (5)	-165.5 (5)
C7—N4—C8—C9	-174.9 (6)	166.9 (5)
N2—C3—C4—C5	63.9 (4)	65.0 (4)
N3—C6—C7—N4	53.2 (3)	52.0 (3)
C8—C9—C10—N1	59.9 (4)	73.2 (4)

The structure was solved by direct and Fourier methods. Refinement was by full-matrix least-squares methods. H atoms were located by difference Fourier methods. *NRCVAX* (Gabe, Le Page, White & Lee, 1987) was used for all crystallographic computations.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: AB1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(μ -benzoato-*O*:*O'*)bis(*N,N*-diethylnicotinamide-*N'*)dicopper(II)

TUNCER HÖKELEK*

Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey

HACALI NECEFOĞLU AND METİN BALCI

Atatürk University, Department of Chemistry, 25240 Erzurum, Turkey

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Abstract

The title molecule, [Cu₂(C₆H₅COO)₄(C₁₀H₁₄N₂O)₂], is a crystallographically centrosymmetric binuclear complex, with Cu atoms [Cu...Cu' = 2.613 (1) Å] bridged by four benzoate ligands. The four nearest O atoms around each Cu atom form a square-planar arrangement with the square-pyramidal coordination completed by the pyridine N atom of the *N,N*-diethylnicotinamide ligand at a distance of 2.162 (6) Å. Each Cu atom is displaced by 0.190 (1) Å from the plane of the four O atoms, with an average Cu—O distance of 1.974 (6) Å.

Comment

N,N-Diethylnicotinamide (DENA) is known as an important respiration stimulant. The structures of some complexes obtained from the reactions of transition metal(II) ions with DENA have been determined previously: Cd(DENA)(SCN)₂ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1972), Mn(DENA)₂(NCS)₂ (Bigoli, Braibanti, Pellinghelli & Tiripicchio, 1973*a*), Zn(DENA)₂(NCS)₂(H₂O)₂ (Bigoli, Braibanti, Pellinghelli, 1973*b*). In Mn(DENA)₂(NCS)₂, DENA is a bidentate ligand, bonded to the metal atom through the pyridine N and amide O atoms. Alternatively, in Cd(DENA)(SCN)₂ and Zn(DENA)₂(NCS)₂(H₂O)₂, DENA is a monodentate ligand coordinated through only the pyridine N atom, which is more basic than the O atom. The title compound, (I), is a binuclear com-

