Table 2. *Bond lengths* (Å) *and bond angles* (°)

Ni(1)—O(1)	2.019 (5)	Ni(1)—O(2)	2.014 (4)
Ni(1)—O(3)	2.015 (5)	Ni(1)—O(4)	2.013 (4)
Ni(1)—O(5)	2.032 (4)	Ni(1)—O(6)	2.136 (4)
O(1)—C(3)	1.263 (7)	O(2)—C(1)	1.251 (8)
O(3)—C(6)	1.256 (6)	O(4)—C(8)	1.264 (7)
O(5)—C(13)	1.407 (10)	O(6)—C(11)	1.445 (9)
O(6)—C(12)	1.441 (7)	C(1)—C(2)	1.380 (11)
C(1)—C(4)	1.513 (12)	C(2)—C(3)	1.372 (10)
C(3)—C(5)	1.523 (12)	C(6)—C(7)	1.361 (9)
C(6)—C(9)	1.539 (13)	C(7)—C(8)	1.394 (11)
C(8)—C(10)	1.510 (11)	C(11)—C(12*A*)	1.509 (10)
C(12)—C(11*A*)	1.509 (10)	C(13)—C(14)	1.451 (13)

O(1)—Ni(1)—O(2)	91.2 (2)	O(1)—Ni(1)—O(3)	175.4 (2)
O(2)—Ni(1)—O(3)	88.5 (2)	O(1)—Ni(1)—O(4)	88.2 (2)
O(2)—Ni(1)—O(4)	174.8 (2)	O(3)—Ni(1)—O(4)	91.7 (2)
O(1)—Ni(1)—O(5)	90.7 (2)	O(2)—Ni(1)—O(5)	93.0 (2)
O(3)—Ni(1)—O(5)	93.9 (2)	O(4)—Ni(1)—O(5)	92.2 (2)
O(1)—Ni(1)—O(6)	87.8 (2)	O(2)—Ni(1)—O(6)	87.0 (2)
O(3)—Ni(1)—O(6)	87.6 (2)	O(4)—Ni(1)—O(6)	87.8 (1)
O(5)—Ni(1)—O(6)	178.5 (2)	Ni(1)—O(1)—C(3)	123.6 (5)
Ni(1)—O(2)—C(1)	124.1 (4)	Ni(1)—O(3)—C(6)	122.8 (4)
Ni(1)—O(4)—C(8)	123.3 (4)	Ni(1)—O(5)—C(13)	123.7 (5)
Ni(1)—O(6)—C(11)	124.1 (3)	Ni(1)—O(6)—C(12)	124.4 (4)
C(11)—O(6)—C(12)	111.2 (4)	O(2)—C(1)—C(2)	127.6 (6)
O(2)—C(1)—C(4)	113.9 (7)	C(2)—C(1)—C(4)	118.5 (6)
C(1)—C(2)—C(3)	124.8 (6)	O(1)—C(3)—C(2)	127.8 (7)
O(1)—C(3)—C(5)	113.2 (6)	C(2)—C(3)—C(6)	119.0 (6)
O(3)—C(6)—C(7)	129.2 (7)	O(3)—C(6)—C(9)	111.4 (6)
C(7)—C(6)—C(9)	119.4 (5)	C(6)—C(7)—C(8)	124.0 (5)
O(4)—C(8)—C(7)	127.7 (5)	O(4)—C(8)—C(10)	113.8 (6)
C(7)—C(8)—C(10)	118.5 (6)	O(6)—C(11)—C(12*A*)	108.9 (6)
O(6)—C(12)—C(11*A*)	109.8 (5)	O(5)—C(13)—C(14)	117.1 (9)

date, only chair conformations have been observed in complexes containing dioxane.

Unlike other systems containing dioxane ligands, the molecule of dioxane in the structure described here resulted from the condensation of two molecules of ethanol. We do not know if this represents a general class of reactions that can be carried out using bis(acac) adducts of the divalent transition metals, or if it is unique to the system described. As far as we know, it constitutes the first example of this type of reaction and additional experiments are underway in order to address this question as well as others that the isolation of this product raises.

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Structures of *racemic* and *meso* (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) Perchlorate

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Abstract. The crystal structures of *racemic* and *meso* (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate, [Ni($C_{16}H_{32}N_4$)]$(ClO_4)_2$, $M_r = 538.06$, are reported at 295 K with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The *d* and *l* isomers cocrystallize to form the racemic structure in the orthorhombic space group *Pbca* with $a = 19.759$ (3), $b = 17.016$ (3), $c = 13.661$ (3) Å, $V = 4593$ (2) Å^3, $Z = 8$, $D_x = 1.556$ g cm^{-3}, $\mu = 11.2$ cm^{-1}, $F(000) = 2256$ and refined to $R = 0.051$ for 2245 reflections with $F_o > 3\sigma(F_o)$. The *meso* isomer crystallized in the monoclinic space group $P2_1/c$ with $a = 10.257$ (3), $b = 10.742$ (2), $c = 10.885$ (2) Å, $\beta = 111.46$ (2)°, $V = 1116.2$ (9) Å^3, $Z = 2$, $D_x = 1.601$ g cm^{-3}, $\mu = 11.6$ cm^{-1}, $F(000) = 564$ and refined to $R = 0.042$ for 2155 reflections with $F_o > 3\sigma(F_o)$. The values of the Ni—$N_{\rm amine}$ and Ni—

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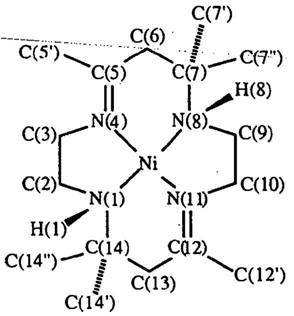
N_{imine} bond lengths are 1.915 (4) and 1.884 (5) Å for the *racemic* structure and 1.938 (2) and 1.907 (2) Å for the *meso* isomer.

Introduction. The structure of *rac*-[(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II)] perchlorate has been reported (Bailey & Maxwell, 1972) based on photographic data. The values reported for the Ni—N_{amine} and Ni—N_{imine} bond distances of 1.902 (9) and 1.856 (10) Å, respectively, have large standard deviations and are shorter than those found in similar compounds. Our analysis of the EXAFS (extended X-ray absorption fine structure) data for the complex in CH_3CN yielded an average Ni—N distance of 1.93 (2) Å (Furenlid, Renner, Szalda & Fujita, 1991). Since the difference between EXAFS and averaged X-ray results of 0.05 Å is outside the estimated uncertainty of ± 0.02 Å of the EXAFS measurements, we decided to redetermine the structure using counter data. Out of the crystallization which gave the *racemic* form, crystals of the *meso* isomer were also obtained. Its structure was also determined since only cell constants for the *meso* isomer have been reported (Bailey & Maxwell, 1966).

Experimental. The compound was prepared as previously reported (Tait & Busch, 1978) and recrystallized from hot water. The ^1H NMR of our sample in CD_3CN indicated that *d* and *l* isomers (over 90%) are the predominant species at room temperature. Both yellow crystals of *rac*-$[NiL](ClO_4)_2$ and yellow–orange crystals of *meso*-$[NiL](ClO_4)_2$, where L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, were obtained from the same recrystallization. In each case a crystal was mounted on the end of a glass fiber. The crystal of the *racemic* form was a hexagonal block 0.32 × 0.44 × 0.60 mm. The crystal of the *meso* isomer was a prism, 0.25 × 0.27 × 0.32 mm. Data were collected with graphite-monochromated Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer. For each structure, cell constants were determined by using 25 reflections with $2\theta > 25°$. The intensities of three standard reflections showed no systematic variations. The starting positions for the non-H atoms for the *racemic* form were those previously reported (Bailey & Maxwell, 1972). For the *meso* isomer the Ni atom was placed on a special position $(0,\frac{1}{2},\frac{1}{2})$ having inversion symmetry, and the other non-H atoms were located using a series of difference Fourier maps. All non-H atoms were refined with anisotropic thermal parameters. H atoms were placed at calculated positions and allowed to ride on the atom to which they were attached during the full-matrix least-squares refinement (Sheldrick, 1976). A common isotropic thermal parameter for all of the H atoms in each structure was refined. During the last cycle of full-matrix least-squares refinement on F the maximum shift was less than 0.01σ. The final difference map was featureless (less than 0.5 to -0.4 e Å^{-3}).

Data reduction and analytical absorption correction were performed using the *CRYSNET* system (Berman, Bernstein, Bernstein, Koetzle & Williams, 1976) at Brookhaven National Laboratory. Neutral-atom scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Crystal data and information on data collection are given in Table 1. The atom-numbering system is shown below. Atom positional parameters for the *racemic* and *meso* structures are listed in Table 2. Selected bond lengths and angles for the two forms are given in Table 3.[*] Fig. 1 shows a view and the atom-numbering scheme for the *racemic* structure. Fig. 2 shows a view of the *meso* isomer and its atom-numbering scheme. Figs. 3 and 4 are views of the unit cells for the *racemic* and *meso* structures, respectively.



Atom-numbering scheme

Discussion. In the *racemic* structure of NiL^{2+} the two axial methyl groups on C(7) and C(14) are on one side of the macrocycle while the two H atoms attached to the amine N atoms are on the opposite side of the macrocycle (Fig. 1). The two amine H atoms are involved in weak hydrogen bonds [N(1)···O(13) = 3.079 and N(8)···O(22) = 3.029 Å] with the two perchlorate anions. There is also a close contact between one of the O atoms O(24) of one of the perchlorates and the Ni center, Ni···O(24) = 3.272 (6) Å. The two axial methyl groups essentially block the sixth coordination site of the Ni (Ni—HCH_2 = 2.74 and 2.65 Å). The bond lengths and

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles, and proposed hydrogen bonding, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55222 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0408]

Table 1. *Crystallographic data from the X-ray diffraction study of rac- and meso*-$[Ni(C_{16}H_{32}N_4)](ClO_4)_2$

	rac	*meso*
Scan	θ(crystal)–2θ(counter)	θ(crystal)–2θ(counter)
Transmission coefficient	0.7148, 0.6850	0.7819, 0.7029
Maximum, minimum 2θ limits (°)	4–50	4–60
Range of *hkl*	$-25 < h < 25$, $0 < k < 22$, $0 < l < 17$	$-14 < h < 14$, $0 < k < 15$, $-15 < l < 15$
Reflections collected	8719	6816
Unique reflections ($F_o > 0$)	3518	2962
$R_{\text{averaging}}$ ($F_o > 0$)	0.035	0.025
Reflections used [$F_o > 3\sigma(F_o)$]	2245	2155
Number of variables	281	143
k, g {$w = k/[\sigma^2(F_o) + g(F_o)^2]$}	1.6061, 0.000236	1.4782, 0.000354

Table 2. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms in rac- and meso*-$[Ni(C_{16}H_{32}N_4)](ClO_4)_2$

$$U_{eq} = [U_{22} + (U_{11} + U_{33} + 2U_{13}\cos\beta)/\sin^2\beta]/3.$$

	x	y	z	U_{eq}
rac-$[Ni(C_{16}H_{32}N_4)](ClO_4)_2$				
Ni	0.12406 (3)	0.10700 (4)	0.19428 (5)	0.0373
N(1)	0.1828 (2)	0.1939 (3)	0.2201 (4)	0.049
C(2)	0.1676 (3)	0.2244 (3)	0.3188 (5)	0.064
C(3)	0.0933 (3)	0.2178 (3)	0.3340 (5)	0.060
N(4)	0.0745 (2)	0.1375 (2)	0.3055 (3)	0.042
C(5)	0.0253 (3)	0.1033 (4)	0.3486 (4)	0.045
C(5′)	−0.0154 (4)	0.1418 (4)	0.4274 (5)	0.083
C(6)	0.0023 (3)	0.0227 (3)	0.3215 (4)	0.053
C(7)	0.0463 (3)	−0.0276 (3)	0.2573 (4)	0.047
C(7′)	0.1094 (3)	−0.0538 (3)	0.3117 (5)	0.067
C(7″)	0.0043 (3)	−0.0997 (3)	0.2270 (5)	0.070
N(8)	0.0655 (2)	0.0193 (3)	0.1701 (3)	0.044
C(9)	0.0955 (3)	−0.0283 (4)	0.0904 (5)	0.063
C(10)	0.1250 (3)	0.0273 (4)	0.0190 (4)	0.065
N(11)	0.1671 (2)	0.0836 (3)	0.0745 (3)	0.047
C(12)	0.2205 (3)	0.1105 (4)	0.0358 (5)	0.060
C(12′)	0.2445 (4)	0.0900 (4)	−0.0644 (5)	0.087
C(13)	0.2645 (3)	0.1666 (4)	0.0911 (6)	0.080
C(14)	0.2567 (3)	0.1757 (4)	0.2009 (6)	0.065
C(14′)	0.2761 (3)	0.1012 (4)	0.2562 (5)	0.085
C(14″)	0.3013 (3)	0.2448 (4)	0.2351 (6)	0.102
Cl(1)	0.17411 (9)	0.39931 (11)	0.08855 (14)	0.067
O(11)	0.1326 (3)	0.4551 (3)	0.0462 (5)	0.131
O(12)	0.1740 (4)	0.4060 (4)	0.1870 (5)	0.178
O(13)	0.1504 (4)	0.3248 (3)	0.0716 (5)	0.143
O(14)	0.2375 (3)	0.4060 (4)	0.0524 (7)	0.201
Cl(2)	−0.04630 (9)	0.18444 (9)	0.09089 (13)	0.058
O(21)	−0.0985 (3)	0.2099 (3)	0.0306 (4)	0.110
O(22)	−0.0635 (2)	0.1103 (3)	0.1309 (3)	0.079
O(23)	−0.0364 (3)	0.2371 (4)	0.1654 (5)	0.141
O(24)	0.0133 (3)	0.1748 (3)	0.0374 (4)	0.116
meso-$[Ni(C_{16}H_{32}N_4)](ClO_4)_2$				
Ni	0.0000	0.5000	0.5000	0.0243
N(1)	−0.1342 (2)	0.4535 (2)	0.5791 (2)	0.028
C(2)	−0.0567 (3)	0.3928 (3)	0.7068 (3)	0.044
C(3)	0.0719 (3)	0.4680 (4)	0.7736 (3)	0.047
N(4)	0.1362 (2)	0.4928 (2)	0.6750 (2)	0.031
C(5)	0.2704 (3)	0.4994 (3)	0.7140 (2)	0.033
C(5′)	0.3670 (3)	0.4783 (3)	0.8527 (3)	0.049
C(6)	0.3402 (3)	0.5283 (3)	0.6190 (3)	0.038
C(7)	0.2631 (3)	0.6151 (3)	0.5052 (3)	0.030
C(7′)	0.2248 (4)	0.7369 (3)	0.5542 (3)	0.049
C(7″)	0.3587 (3)	0.6403 (3)	0.4282 (3)	0.049
Cl(1)	0.24907 (9)	0.15877 (7)	0.65649 (8)	0.0463
O(11)	0.2600 (4)	0.0316 (2)	0.6268 (3)	0.080
O(12)	0.1443 (4)	0.2192 (3)	0.5520 (3)	0.101
O(13)	0.2183 (4)	0.1711 (3)	0.7733 (3)	0.094
O(14)	0.3780 (3)	0.2181 (3)	0.6762 (4)	0.099

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for rac- and meso*-$[Ni(C_{16}H_{32}N_4)](ClO_4)_2$

For the *meso* structure N(8) is related to N(1) by a crystallographic center of inversion.

	rac	*meso*		*rac*	*meso*
Metal coordination sphere					
Ni—N(1)	1.914 (4)	1.938 (2)	Ni—N(8)	1.916 (4)	–
Ni—N(4)	1.881 (4)	1.907 (2)	Ni—N(11)	1.887 (5)	–
N(1)—Ni—N(4)	87.4 (2)	85.7 (1)	N(4)—Ni—N(8)	92.3 (2)	–
N(1)—Ni—N(8)	179.2 (2)	–	N(4)—Ni—N(11)	173.6 (2)	–
N(1)—Ni—N(11)	92.9 (2)	–	N(8)—Ni—N(11)	87.6 (2)	–
Ligand					
N(1)—C(2)	1.475 (7)	1.477 (3)	N(8)—C(9)	1.481 (6)	–
C(2)—C(3)	1.486 (8)	1.490 (4)	C(9)—C(10)	1.479 (8)	–
C(3)—N(4)	1.470 (6)	1.476 (3)	C(10)—N(11)	1.478 (7)	–
N(4)—C(5)	1.277 (6)	1.286 (3)	N(11)—C(12)	1.266 (7)	–
C(5)—C(5′)	1.494 (7)	1.489 (3)	C(12)—C(12′)	1.491 (8)	–
C(5)—C(6)	1.492 (7)	1.490 (4)	C(12)—C(13)	1.496 (9)	–
C(6)—C(7)	1.502 (7)	1.521 (4)	C(13)—C(14)	1.515 (9)	–
C(7)—C(7′)	1.518 (7)	1.517 (4)	C(14)—C(14′)	1.524 (8)	–
C(7)—C(7″)	1.539 (7)	1.529 (4)	C(14)—C(14″)	1.543 (8)	–
C(7)—N(8)	1.483 (6)	1.499 (3)	C(14)—N(1)	1.515 (7)	–
C(14)—N(1)—Ni	113.2 (3)	117.7 (2)	N(4)—C(5)—C(6)	122.4 (5)	120.7 (2)
Ni—N(1)—C(2)	108.4 (3)	107.9 (2)	C(5)—C(6)—C(7)	119.5 (5)	117.0 (2)
C(14)—N(1)—C(2)	115.3 (5)	114.2 (2)	C(6)—C(7)—C(7′)	110.9 (5)	111.5 (2)
N(1)—C(2)—C(3)	107.7 (5)	107.2 (2)	C(6)—C(7)—C(7″)	107.3 (5)	108.0 (2)
C(2)—C(3)—N(4)	106.4 (5)	107.1 (2)	C(7′)—C(7)—C(7″)	109.9 (5)	110.0 (2)
C(3)—N(4)—Ni	109.8 (4)	112.0 (2)	C(6)—C(7)—N(8)	108.1 (4)	106.0 (2)
Ni—N(4)—C(5)	130.1 (4)	129.2 (2)	C(7′)—C(7)—N(8)	110.0 (5)	110.8 (2)
C(3)—N(4)—C(5)	119.6 (5)	118.6 (2)	C(7″)—C(7)—N(8)	110.6 (4)	110.5 (2)
N(4)—C(5)—C(5′)	122.8 (6)	124.2 (2)	C(7)—N(8)—Ni	115.8 (3)	–
C(5′)—C(5)—C(6)	114.7 (5)	115.2 (2)	Ni—N(8)—C(9)	108.2 (3)	–
C(7)—N(8)—C(9)	113.4 (4)	–	N(11)—C(12)—C(13)	120.3 (6)	–
N(8)—C(9)—C(10)	107.0 (5)	–	C(12)—C(13)—C(14)	120.4 (5)	–
C(9)—C(10)—N(11)	107.3 (5)	–	C(13)—C(14)—C(14′)	112.4 (6)	–
C(10)—N(11)—Ni	109.1 (4)	–	C(13)—C(14)—C(14″)	108.6 (6)	–
Ni—N(11)—C(12)	131.4 (5)	–	C(14′)—C(14)—C(14″)	109.9 (5)	–
C(10)—N(11)—C(12)	119.3 (5)	–	C(14′)—C(14)—N(1)	109.1 (5)	–
N(11)—C(12)—C(12′)	124.4 (7)	–	C(14″)—C(14)—N(1)	110.0 (5)	–
C(12′)—C(12)—C(13)	115.3 (6)	–			

angles for the *racemic* structure are similar to those previously reported (Bailey & Maxwell, 1972), but have much smaller standard deviations. This can be attributed to the use of counter data in this study. The most significant differences are in the Ni—N$_{\text{amine}}$ and Ni—N$_{\text{imine}}$ bond lengths which are 0.013 and 0.030 Å longer in this determination. As can be seen in Figs. 1 and 3, the metal complex and the perchlorate anions are connected by hydrogen bonding and weak Ni···O interactions into discrete neutral units of $[NiL](ClO_4)_2$. These units interact with other units by polar and nonpolar forces which hold the unit cell together.

In the *meso* isomer the Ni is situated on a crystallographic inversion center. This requires the complex to have inversion symmetry and the Ni to lie in the plane of the four N atoms (Fig. 2). In this isomer the two axial methyl groups are on opposite sides of the macrocycle, as are the two amine H atoms. The Ni ion is involved in a weak interaction with the two O atoms of inversion-related perchlorate ions [Ni···O(12) = 3.316 (3) Å]. The two H atoms on the amine N atoms are involved in weak hydrogen bonds [N(1)···O(13) = 3.131 Å] with O atoms of two other symmetry-related perchlorate anions. These interactions allow the complexes to stack along the *b* axis in the unit cell (Fig. 4).

The most significant differences in the bond lengths and angles within the complexes in the two structures are in Ni—N bond lengths. The Ni—N$_{\text{amine}}$ and Ni—N$_{\text{imine}}$ bond lengths are significantly different in the two structures (Table 3). Both the Ni—N$_{\text{amine}}$ and Ni—N$_{\text{imine}}$ bond lengths in the *meso* form are each 0.023 (4) Å longer than those found for the *racemic* form. The differences in bond length between the two diastereomers must result from the folding of the macrocycle in the *racemic* structure. The dihedral angle formed by the planes containing N(1), N(4) and N(11), and N(4), N(8) and N(11) is 7.0° for the *racemic* form *vs* 0.0° as required by symmetry for the *meso* form. The folding of the macrocycle results in a decrease in the size of the hole of the macrocycle by a shortening of the N(1)—N(8) and N(4)—N(11) distances by 0.046 and 0.053 Å, respectively, thus allowing for the decrease in the Ni—N bond lengths. In the *racemic* form the Ni lies 0.05 Å out of the plane of the four N atoms towards the two axial methyl groups, while in the *meso* form it is situated in the plane of the four N atoms.

Tait & Busch (1978) prepared the pure *meso* isomer by keeping a suspension of the finely powdered *racemic* solid at 298 K under a saturated aqueous solution for two weeks with occasional agitation. Although our Ni*L*(ClO_4)$_2$ sample (Furenlid, Renner, Szalda & Fujita, 1991) was originally

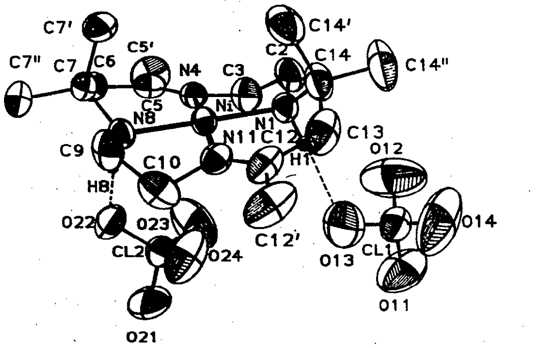

Fig. 1. An *ORTEP* (Johnson, 1976) view of *rac*-[Ni*L*](ClO_4)$_2$. The thermal ellipsoids are at the 50% probability level and the H atoms (except for the two amine H atoms) are omitted for clarity. The O atom O(24) of the perchlorate anion forms a weak interaction with the Ni center while O(22) and O(13) of the percholate anions shown form hydrogen bonds with the amines of the macrocycle.

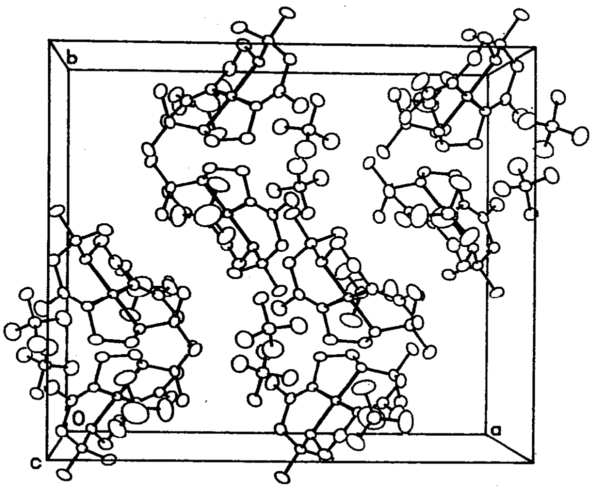

Fig. 3. A perspective view of the unit cell of *rac*-[Ni*L*](ClO_4)$_2$ down the *c* axis.

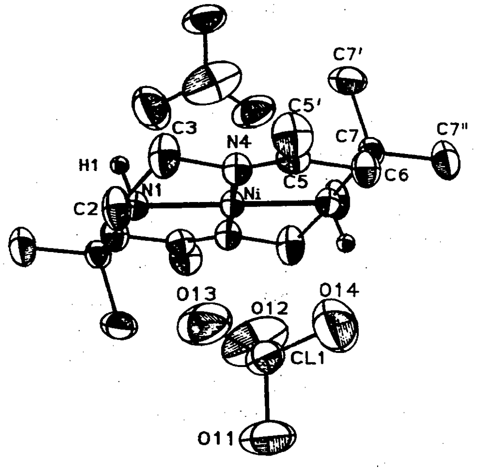

Fig. 2. An *ORTEP* (Johnson, 1976) view of *meso*-[Ni*L*](ClO_4)$_2$. The thermal ellipsoids are at the 50% probability level and the H atoms (except for the amine H atoms) are omitted for clarity. A crystallographic inversion center relates the labeled atoms to the unlabeled ones. O(12) of the perchlorate ions shown forms a weak interaction with the Ni center. H(1) forms a hydrogen bond with symmetry-related perchlorate O atom O(13) ($-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$).

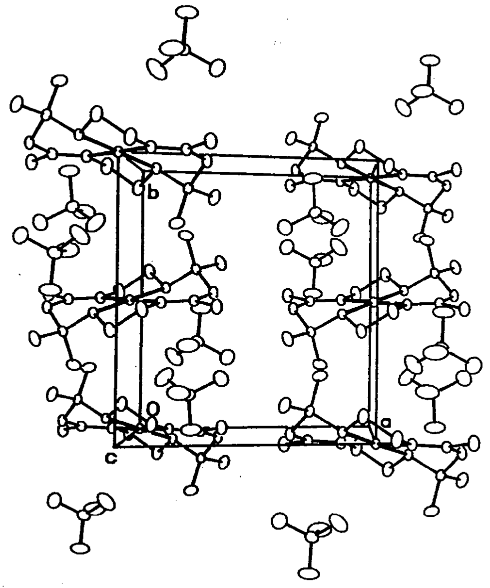

Fig. 4. A perspective view of the unit cell of *meso*-[Ni*L*](ClO_4)$_2$ down the *c* axis.

90% *d* and *l* isomers it is possible that some of the isomers converted to the *meso* isomer between the preparation of the solution and the EXAFS measurement. Since these isomers exist in equilibrium in solution and both *racemic* and *meso* forms crystallize from the same solution, care must be taken in analyzing and interpreting results using techniques such as EXAFS where bulk samples are used.

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Structure of a Permethylcyclopentadienyl-μ-tetramethylcyclopentadienylmethylene Scandium Dimer

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Abstract. Bis(η^5-pentamethylcyclopentadienyl)-bis[μ-2,3,4,5-tetramethyl-1-methylene-ScC^1:Sc$'$(η^5)-cyclopentadienyl]-discandium(III), $[Sc_2(C_{10}H_{15})_2(C_{10}H_{14})_2]$, $M_r = 628.90$, triclinic, $P\bar{1}$, $a = 8.641$ (5), $b = 9.478$ (2), $c = 12.338$ (5) Å, $\alpha = 75.58$ (3), $\beta = 80.39$ (4), $\gamma = 63.75$ (3)°, $V = 875.8$ (7) Å^3, $Z = 1$, $D_x = 1.19$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 4.11$ cm^{-1}, $F(000) = 340$, room temperature, R (on F) = 0.046 for 2241 reflections with $F_o^2 > 3\sigma(F_o^2)$. Two bis(pentamethylcyclopentadienyl)scandium molecules are joined across a center of symmetry. One of the Cp* methyl groups has lost an H atom and that methylene group bonds to the symmetry-related Sc atom: Sc—C6$'$ = 2.282 (5) Å. Other aspects of the bis-Cp*Sc geometry are normal.

Introduction. Alkyl and hydride derivatives of permethylscandocene are of interest both for their C—H bond-activation chemistry (Thompson, Baxter, Bulls, Burger, Nolan, Santarsiero, Schaefer & Bercaw, 1987) and as model systems for Ziegler–Natta catalysis (Burger, Thompson, Cotter & Bercaw, 1990). A notable feature of these complexes is their ability to activate the primary C—H bonds of molecules such as CH_4, $CH_3CH_2CH_3$, $Si(CH_3)_4$ and $P(CH_3)_3$ (Thompson *et al.*, 1987). During the course of some recent mechanistic studies, we have observed that the cyclopentylmethyl derivative, $Cp^*_2ScCH_2$-(*cyclo*-C_5H_8) [$Cp^* = \eta^5$-$C_5(CH_3)_5$], slowly and cleanly decomposes in cyclohexane to give methylcyclopentane and a yellow crystalline precipitate. The ^{1}H NMR spectrum of the yellow product is consistent with a compound containing one Cp* and one (η^5,η^1)-$C_5(CH_3)_4CH_2$, the latter arising *via* metallation of a Cp* ligand (*i.e.* a 'tuck-in' complex). This same tuck-in complex has been previously obtained from thermolysis of $Cp^*_2ScCH_3$ (Thompson *et al.*, 1987); however, the solid product obtained previously was not crystalline and was postulated to be oligomeric based on its solubility properties. We report herein the structure of the complex which crystallizes as the dimer, $[Cp^*Sc\{\mu$-(η^5,η^1)-$C_5(CH_3)_4CH_2\}]_2$, when allowed to form slowly at room temperature.

Experimental. A parallelepiped, 0.4 × 0.2 × 0.05 mm, crystal was used for data collection on a CAD-4 diffractometer with ω scans. 25 reflections with $24 < 2\theta < 28°$ were used for determination of the unit cell. No absorption correction was applied to the data

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† Contribution No. 8551.