simulating superposition of two orientations of the molecule as discussed above for $[SnBr_2Cl_2(Me_2SO)_2]$. Refinements in $P2_1$ and $P\overline{1}$, starting with the model in $P2_1/n$, show bad convergence and give no significant (Hamilton, 1965) changes. In both subgroups, tests were also made for several alternatives with respect to the molecular orientation, but they show considerably higher residual errors ($R \approx 0{\cdot}10$–$0{\cdot}12$).

In view of these results, essential deviations from the model in $P2_1/n$ towards one of its subgroups are improbable, and the observed incongruencies (small deviation from $-n-$, small difference Fourier map maxima corresponding to the alternative molecular orientation, *e.g.* B_t in Fig. 2) are more likely due to a domain structure involving the pseudosymmetry $C2/c$. One possibility would be the accidental replacement of the 2_1 screw by the centring operation $(\frac{1}{2}+,\frac{1}{2}+,0)$ for packing of adjacent molecules, *e.g.* A and B in Fig. 2. It seems plausible that the tendency for this mistake is greater for the title compound than for its Cl analogue, where the organic ligands play a more important role in determining the packing. A similar model might also apply to the packing of $[SnBr_2Cl_2(Me_2SO)_2]$, where the symmetry indetermination is greatest due to the Cl–Br substitutional disorder.

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Structure of $[Ni(Me_8[14]ane\mathit{C\alpha})](ClO_4)_2$ ($Me_8[14]ane$ = 2,5,5,7,9,12,12,14-Octamethyl-1,4,8,11-tetraazacyclotetradecane)

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Abstract. $[Ni(C_{18}H_{40}N_4)](ClO_4)_2$, $M_r = 570{\cdot}2$, monoclinic, $P2_1/n$, $a = 10{\cdot}222\,(2)$, $b = 8{\cdot}741\,(1)$, $c = 14{\cdot}495\,(3)$ Å, $\beta = 99{\cdot}60\,(2)°$, $V = 1277{\cdot}1\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}48$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 10{\cdot}2$ cm^{-1}, room temperature, $R = 0{\cdot}042$ for 1916 observed reflections. The nickel(II) complex contains a centrosymmetric cation with square planar nickel and Ni—N distances 1·961 (2) and 1·948 (3) Å; the configuration at the chiral nitrogen centres is *RSSR* or *SRRS*. The perchlorate anion is disordered over two sites and is hydrogen bonded to the N—H groups of the cation, with N···O distances 2·99 to 3·20 Å.

Introduction. 1,2-Propanediamine reacts (Curtis, Swann, Waters & Maxwell, 1969) with acetone to

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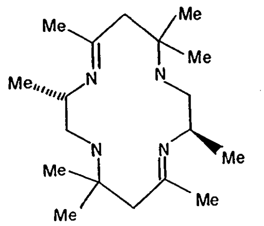
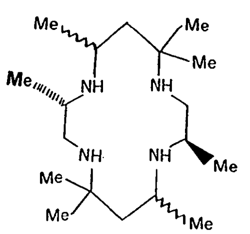
yield 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me[14]diene) (I). The reaction is completely stereospecific and yields only the *C-meso*-3,10-dimethyl substituted macrocycle. Reduction of (I) with $NaBH_4$ yields a mixture of isomeric saturated macrocycles, Me[14]anes (II), which can be resolved into three distinct isomers. Each isomer yields two diastereoisomeric nickel(II) complexes due to nitrogen chirality. Our analysis establishes the structure (III) of the α-isomer $[Ni(Me_8[14]aneC\alpha)](ClO_4)_2$ proposed on the basis of ^1H NMR studies (Bembi, Jhanji & Roy, 1989).



(I)



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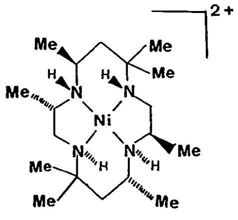
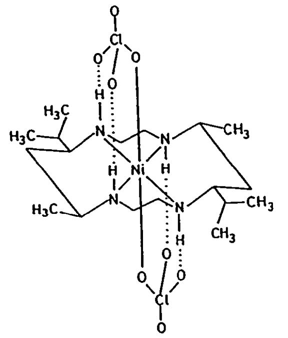


(III)



(IV)

Experimental. Orange crystals grown from acetonitrile. Accurate cell dimensions and crystal orientation matrix determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 15°$. Crystal dimensions $0·25 \times 0·50 \times 0·36$ mm; intensities of reflections with indices h 0 to 13, k 0 to 11, l −18 to 18, and with $2 < 2\theta < 54°$ were measured; ω–2θ scans, ω scan width $(0·6 + 0·35\tan\theta)°$; graphite-monochromatized Mo $K\alpha$ radiation; intensities of three reflections measured every 2h showed no evidence of crystal decay. 3112 reflections measured, 2781 unique, 1916 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement; $R_{\rm int}$ = 0·014. Data corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0·784, 0·633), Gaussian integration, grid $8 \times 12 \times 12$. Space group $P2_1/n$ uniquely from systematic absences $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$. With $Z = 2$, the Ni atom lies on an inversion centre and the coordinates of the remaining non-H atoms were found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps revealed peaks in the vicinity of the ClO_4^- anion consistent with disordered O atom sites. These were allowed for by appropriate occupancy factors based on integrated peak heights; in the final stages of refinement these minor contributions were included and refined with isotropic thermal parameters. Difference maps also showed maxima in positions consistent with the expected locations of the H atoms; in the final rounds of calculations the H atoms were positioned on geometrical grounds (C—H, N—H 0·95 Å) and included (as riding atoms) in the structure factor calculations with an overall $B_{\rm iso}$ of 5·0 $Å^2$. The final cycle of refinement included 163 variable parameters, $R = 0·042$, $wR = 0·060$, goodness-of-fit 1·53, $w = 1/[\sigma^2(F_o) + 0·06 \times (F_o)^2]$. Max. shift/e.s.d. $< 0·005$; density in final difference map $\pm 0·37$ e $Å^{-3}$; no chemically significant features. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (Frenz, 1983). Atomic coordinates and details of molecular geometry are given in Tables 1 and 2 respectively.* Fig. 1 is a view of the molecule prepared using *ORTEP*II (Johnson, 1976).

Discussion. The metal complex lies across a crystallographic centre of symmetry and has the *trans* (III) arrangement (configuration *RSSR* or *SRRS*) of the chiral nitrogen centres [as shown in Fig. 1 and (III)] with four methyl groups equatorial and four axial. In the perchlorate ion, three of the O atoms are disordered over two sites (0·86/0·14 occupancies). The anion is hydrogen bonded to pairs of adjacent N—H groups (Fig. 1), with normal N···O distances in the range 2·992 (18) to 3·204 (5) Å (Table 2). In contrast to what was found in (IV) (Hay, Jeragh, Ferguson, Kaitner & Ruhl, 1982), no perchlorate oxygen is directly bonded to nickel. Apart from these distances, there are no untoward inter-ion contacts.

The centrosymmetric cation has (necessarily) *trans*-square-planar coordination with Ni—N distances 1·961 (2) and 1·948 (3) Å in accord with values reported previously (Curtis, Swann & Waters, 1973; Hay, Jeragh, Ferguson, Kaitner & Ruhl, 1982);

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* Lists of structure factors, thermal parameters, calculated hydrogen coordinates, mean planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52204 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}]$.

	x	y	z	B(Å^2)
Ni	0·0	0·0	0·0	2·588 (9)
Cl	0·3045 (1)	0·3269 (1)	0·05453 (7)	4·14 (2)
O1	0·2847 (5)	0·2871 (5)	−0·0410 (2)	8·4 (1)
O2	0·3231 (6)	0·4780 (4)	0·0768 (4)	9·9 (2)
O2*	0·1984 (24)	0·4232 (30)	0·0578 (15)	6·6 (5)
O3	0·1980 (5)	0·2694 (6)	0·0949 (4)	10·8 (1)
O3*	0·3163 (18)	0·2151 (20)	0·1165 (12)	4·0 (3)
O4	0·4140 (5)	0·2432 (6)	0·0979 (3)	10·5 (1)
O4*	0·4280 (23)	0·4032 (26)	0·0781 (15)	5·8 (5)
N1	0·1551 (3)	−0·0719 (3)	0·0875 (2)	2·75 (5)
N4	−0·0952 (3)	−0·0014 (3)	0·1057 (2)	2·92 (5)
C2	0·1053 (4)	−0·1355 (4)	0·1710 (2)	4·01 (8)
C3	0·0039 (4)	−0·0223 (5)	0·1912 (2)	4·36 (8)
C5	−0·1960 (3)	0·1224 (4)	0·1157 (2)	3·54 (7)
C6	−0·3021 (3)	0·1159 (4)	0·0303 (3)	3·64 (7)
C7	−0·2636 (3)	0·1685 (4)	−0·0601 (2)	3·20 (7)
C21	0·0530 (4)	−0·2956 (5)	0·1558 (3)	5·47 (9)
C51	−0·2623 (4)	0·0874 (7)	0·2003 (3)	6·1 (1)
C52	−0·1281 (4)	0·2778 (5)	0·1254 (3)	4·78 (9)
C71	−0·3847 (4)	0·1678 (5)	−0·1372 (3)	4·83 (9)

* O2*, O3* and O4* are disordered O atom sites and were refined with isotropic thermal parameters. The O2/O2*, O3/O3* and O4/O4* site occupancies are 0·86/0·14.

Table 2. *Bond lengths* (Å) *and angles* (°), *and hydrogen-bond dimensions* (Å *and* °)

Ni—N1	1·961 (2)	C5—C52	1·522 (5)
Ni—N4	1·948 (3)	C6—C7	1·502 (5)
N1—C2	1·496 (5)	C7—C71	1·523 (5)
N1—C7^{i}	1·499 (4)	Cl—O1	1·409 (4)
N4—C3	1·475 (4)	Cl—O2	1·365 (4)
N4—C5	1·518 (4)	Cl—O2*	1·380 (3)
C2—C3	1·497 (6)	Cl—O3	1·412 (5)
C2—C21	1·501 (6)	Cl—O3*	1·319 (2)
C5—C6	1·505 (4)	Cl—O4	1·396 (5)
C5—C51	1·528 (6)	Cl—O4*	1·418 (2)

N1—Ni—N4	86·9 (1)	C6—C5—C52	111·4 (3)
Ni—N1—C2	107·2 (2)	C51—C5—C52	111·1 (3)
Ni—N1—C7^{i}	124·3 (2)	C5—C6—C7	116·6 (3)
C2—N1—C7^{i}	111·8 (3)	N1^{i}—C7—C6	111·8 (3)
Ni—N4—C3	107·4 (2)	N1^{i}—C7—C71	110·5 (3)
Ni—N4—C5	120·4 (2)	C6—C7—C71	109·8 (3)
C3—N4—C5	113·0 (3)	O1—Cl—O2	117·5 (3)
N1—C2—C3	104·7 (3)	O1—Cl—O3	109·0 (3)
N1—C2—C21	112·9 (3)	O1—Cl—O4	106·7 (3)
C3—C2—C21	113·8 (3)	O2—Cl—O3	109·5 (4)
N4—C3—C2	108·5 (3)	O2—Cl—O4	109·3 (3)
N4—C5—C6	107·6 (3)	O2*—Cl—O3*	114 (1)
N4—C5—C51	109·4 (3)	O2*—Cl—O4*	112 (1)
N4—C5—C52	109·8 (3)	O3—Cl—O4	104·0 (3)
C6—C5—C51	107·3 (3)	O3*—Cl—O4*	102 (1)

N1···O3	3·014 (6)	O3···HN1—N1	158
N1···O3*	2·992 (2)	O3*···HN1—N1	160
N4···O1^{i}	3·204 (5)	O1^{i}···HN4—N4	168
NH1···O3	2·11		
HN1···O3*	2·08		
HN4···O1^{i}	2·27		

Symmetry code: (i) $-x$, $-y$, $-z$.

* Indicates minor component of disordered atoms.

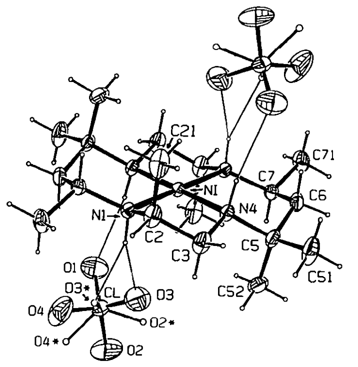

Fig. 1. A view of molecule (III) with our numbering scheme. Ellipsoids are at the 25% probability level.

the C—C and C—N distances are in the normal ranges for such molecules (Hay, Pujari, Korybut-Daszkiewicz, Ferguson & Ruhl, 1989, and references therein). The unique six-membered ring adopts a slightly flattened chair conformation, with the N—H moieties axial. The unique five-membered ring has the methyl group at C2 axial and the usual slightly flattened *gauche* conformation [N—C—C—N torsion angle 54·9 (3)°].

The structure of one of the isomers of the present complex has already been reported (Ito, Ito & Toriumi, 1981) but in that case the complex had twofold crystallographic symmetry, with all four N—H groups on the same side of the coordination plane, the 14-membered ring in a basket configuration and Ni—N distances 1·926 (2) and 1·931 (2) Å.

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