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The Structures of High- and Low-Spin Nickel Chloride Complexes Containing the Macrocyclic Ligand [7*R*(*S*),14*S*(*R*)]-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

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Abstract

The crystal and molecular structures of the low-spin complex [Ni(*meso*-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O and the high-spin complex [NiCl$_2$(*meso*-Me$_6$[14]-aneN$_4$)].2CHCl$_3$, where *meso*-Me$_6$[14]aneN$_4$ is the title macrocyclic ligand, have been determined by single-crystal X-ray diffraction. [Low-spin form: P$\bar{1}$, $a = 8\cdot833$ (1), $b = 8\cdot721$ (1), $c = 8\cdot213$ (1) Å, $\alpha = 86\cdot79$ (1), $\beta = 100\cdot41$ (1), $\gamma = 118\cdot61$ (1)°; $R = 0\cdot031$, $R_w = 0\cdot040$ for 3018 observed reflexions. High-spin form: P$\bar{1}$, $a = 9\cdot656$ (2), $b = 11\cdot253$ (3), $c = 6\cdot787$ (1) Å, $\alpha = 93\cdot98$ (2), $\beta = 91\cdot29$ (2), $\gamma = 90\cdot32$ (2)°; $R = 0\cdot047$, $R_w = 0\cdot047$ for 2623 observed reflexions.] In the orange low-spin form, the Ni^{II} ion is surrounded by four N atoms of the macrocyclic ligand with an average Ni—N distance of 1·959 (2) Å, yielding a square-planar four-coordinate complex. The strong hydrogen-bond networks prevent the coordination of the Cl$^-$ ions and water molecules. In the violet high-spin complex, the Ni^{II} ion is surrounded pseudo-octahedrally by four N atoms of the ligand in a single plane with two independent Ni—N distances of 2·102 (3) and 2·060 (3) Å, and by two Cl$^-$ ions occupying the axial positions with a Ni—Cl separation of 2·562 (1) Å.

[14]aneN$_4$)]Cl$_2$.2H$_2$O, and a violet high-spin complex, [NiCl$_2$(*meso*-Me$_6$[14]aneN$_4$)] (Busch, 1967). The macrocyclic ligand *meso*-Me$_6$[14]aneN$_4$ is constrained by steric requirements to coordinate in a single plane. From their electronic spectra and magnetic properties, it has been shown that the orange dihydrate is a square-planar four-coordinate complex having a singlet ground state, whereas the violet anhydride is a pseudo-octahedral six-coordinate complex having a triplet ground state (Busch, 1967). Our recent study revealed that the solid, orange diamagnetic dihydrate is converted upon heating to a violet paramagnetic anhydride (Ito, Hiratsuka, Tsutsumi, Imamura & Fujimoto, 1978). Conversely, the solid, violet paramagnetic anhydrous complex readily reverts to [Ni(*meso*-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O when moisture is available (Busch, 1967). Of particular interest is the fact that two molecules of water are taken up to produce a diamagnetic Ni^{II} complex. Although water has considerable coordinating ability as compared with the Cl$^-$ ion, the incorporated water molecules are not involved in coordination in the dihydrate.

In an attempt to determine the role played by water in the high-spin–low-spin interconversion and for comparison of the structures with different spin states, the present study has been carried out.

Introduction

Nickel(II) chloride and the title macrocyclic ligand form an orange low-spin complex, [Ni(*meso*-Me$_6$-

Experimental

The orange dihydrate [Ni(*meso*-Me$_6$[14]aneN$_4$)]-Cl$_2$.2H$_2$O was prepared from the corresponding

perchlorate salt [Ni(*meso*-Me$_6$[14]aneN$_4$)](ClO$_4$)$_2$ (Warner & Busch, 1969) by ion exchange (Dowex 1X8) in the Cl$^-$ form. Slow evaporation of the eluate from the column yielded large orange prismatic crystals of [Ni(*meso*-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O.

The violet high-spin complex [NiCl$_2$(*meso*-Me$_6$[14]-aneN$_4$)] was prepared by heating the dihydrate [Ni(*meso*-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O in an oven at 363 K for 10 h. The crystals used for X-ray work were obtained from a chloroform solution of the anhydrous complex by slow evaporation. The X-ray analysis revealed that the recrystallized complexes are a chloroform solvate, [NiCl$_2$(*meso*-Me$_6$[14]aneN$_4$)].-2CHCl$_3$. Elemental analyses for both of the compounds gave satisfactory results.

Intensities of reflexions were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.7107 Å), the θ–2θ scan technique being employed. Unit-cell dimensions were determined on the diffractometer. The intensity data were corrected for Lorentz–polarization factors, but no absorption correction was applied.

For the orange low-spin form, [Ni(*meso*-Me$_6$[14]-aneN$_4$)]Cl$_2$.2H$_2$O, a specimen shaped approximately into a sphere with a diameter of 0.33 mm was used for the intensity measurements. A total of 3021 intensities were measured up to 2θ = 60°. Of these, 3018 reflexions with $|F_o| > 3\sigma(|F_o|)$ were used in the calculations. Crystal data are: [Ni(C$_{16}$H$_{36}$N$_4$)]-Cl$_2$.2H$_2$O, M_r = 450.12, triclinic, $P\bar{1}$, Z = 1, a = 8.833(1), b = 8.721(1), c = 8.213(1) Å, α = 86.79(1), β = 100.41(1), γ = 118.61(1)°, U = 545.88(4) Å^3, D_x = 1.36$_9$, D_m = 1.37$_1$ Mg m^{-3}, μ(Mo $K\alpha$) = 1.147 mm^{-1}.

Crystals of the violet high-spin form, [NiCl$_2$(*meso*-Me$_6$[14]aneN$_4$)].2CHCl$_3$, easily lose chloroform and take up moisture to give the orange dihydrate when exposed to air at room temperature. To avoid this disintegration, a crystal with dimensions 0.45 × 0.45 × 0.30 mm was sealed in a Lindemann-glass capillary under saturated chloroform vapor and used for intensity measurements. The maximum decrease in the $|F_o|$ values during the data collection was less than 3% for the three standard reflexions measured every 50 reflexions. Of 3724 measured intensities, 2623 with $|F_o| > 3\sigma(|F_o|)$ were used in the calculations. Crystal data are: [Ni(C$_{16}$H$_{36}$N$_4$)Cl$_2$].2CHCl$_3$, M_r = 652.82, triclinic, $P\bar{1}$, Z = 1, a = 9.656 (2), b = 11.253 (3), c = 6.787 (1) Å, α = 93.98 (2), β = 91.29 (2), γ = 90.32 (2)°, U = 735.5 (3) Å^3, D_x = 1.47 Mg m^{-3}, μ(Mo $K\alpha$) = 1.393 mm^{-1}.

Determination of the structure

Both structures were solved by the conventional heavy-atom method. The positions of all the H atoms

Table 1. *Fractional positional parameters* [×10^5 *for* (*a*); ×10^4 *for* (*b*)] *and equivalent isotropic temperature factors for non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)*
(*a*) [Ni(*meso*-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O				
Ni	50000	50000	50000	1.7
Cl	10473 (8)	35222 (7)	69444 (6)	4.9
N(1)	28152 (14)	29704 (14)	40221 (14)	2.2
N(2)	45169 (14)	66636 (14)	35957 (14)	2.2
C(1)	38127 (21)	16842 (19)	63485 (21)	3.3
C(2)	28905 (23)	13595 (19)	45824 (22)	3.6
C(3)	20409 (17)	28421 (18)	22086 (17)	2.4
C(4)	18809 (18)	44822 (19)	17779 (18)	2.7
C(5)	35785 (18)	61772 (19)	18449 (18)	2.6
C(6)	1851 (21)	12978 (21)	18856 (23)	3.5
C(7)	31983 (25)	26275 (25)	11758 (22)	3.7
C(8)	31940 (26)	76024 (25)	10326 (25)	4.4
O	24372 (20)	73322 (19)	56131 (21)	5.1
(*b*) [NiCl$_2$(*meso*-Me$_6$[14]aneN$_4$)].2CHCl$_3$				
Ni	5000	5000	5000	2.4
Cl(1)	6460 (1)	5692 (1)	8070 (1)	3.2
N(1)	4654 (3)	6835 (3)	4867 (4)	2.9
N(2)	3395 (3)	4744 (3)	6877 (4)	2.9
C(1)	6853 (4)	6561 (4)	3209 (6)	3.8
C(2)	5482 (5)	7200 (4)	3195 (6)	3.9
C(3)	3269 (5)	7405 (4)	5148 (6)	3.8
C(4)	2550 (4)	6794 (4)	6812 (6)	4.1
C(5)	2155 (4)	5475 (4)	6501 (5)	3.5
C(6)	3480 (6)	8738 (4)	5825 (9)	5.9
C(7)	2401 (5)	7293 (5)	3240 (7)	4.9
C(8)	950 (4)	5192 (6)	7837 (7)	5.5
Cl(2)	3068 (2)	625 (2)	655 (3)	8.9
Cl(3)	1059 (2)	1152 (1)	3622 (2)	6.6
Cl(4)	449 (2)	1615 (2)	−401 (2)	7.5
C(9)	1748 (5)	1579 (4)	1393 (7)	4.7

* The equivalent isotropic temperature factor is calculated from $B_{eq} = \frac{4}{3}\sum_i \sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$, where the $\mathbf{a}_i$'s are the unit-cell edges in direct space.

were identified in subsequent difference-Fourier maps. The structures were refined by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974). For H, the values given by Stewart, Davidson & Simpson (1965) were used. The weighting scheme $w = [\sigma^2_{count} + (0.015|F_o|)^2]^{-1}$ was employed. The final R indices were R = 0.031 and R_w = 0.040 for the low-spin form, and R = 0.047 and R_w = 0.047 for the high-spin form. Atomic parameters of each crystal are given in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, and positional and thermal parameters for hydrogen atoms for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35604 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Description of the structures and discussion

Perspective drawings of the orange low-spin and the violet high-spin complex are presented in Fig. 1. In each complex, the central Ni^{II} ion is required to be at a center of symmetry. Bond lengths and bond angles are listed in Table 2. In the low-spin complex, [Ni(meso-Me₆[14]aneN₄)]Cl₂.2H₂O, the Ni^{II} ion is surrounded by four secondary N atoms of the macrocyclic ligand, yielding a square-planar diamagnetic Ni^{II} complex. On the other hand, the Ni^{II} ion in the high-spin complex, [NiCl₂(meso-Me₆[14]aneN₄)].2CHCl₃, is surrounded pseudo-octahedrally. Four N atoms of the macrocyclic ligand are coordinated to the Ni^{II} ion in a single plane.
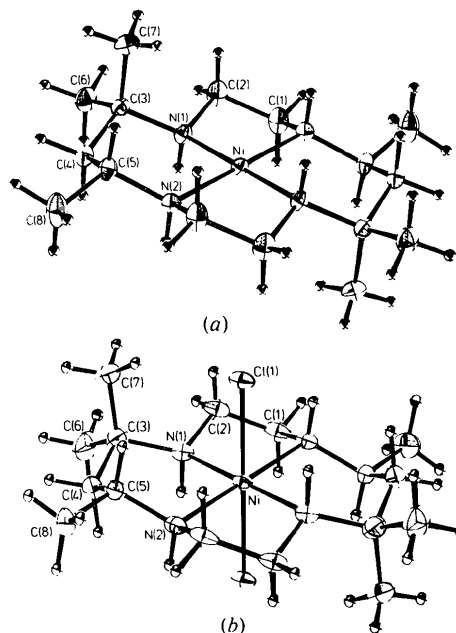

(a)

(b)

Fig. 1. Perspective views of (a) |Ni(meso-Me₆[14]aneN₄)|²⁺ (low-spin) and (b) |NiCl₂(meso-Me₆[14]aneN₄)| (high-spin).

Table 2. *Bond distances* (Å) *and angles* (°) *with their standard deviations in parentheses*

	[Ni(meso-Me₆[14]-aneN₄)]Cl₂.2H₂O (low-spin form)	[NiCl₂(meso-Me₆[14]-aneN₄)].2CHCl₃ (high-spin form)
Ni—N(1)	1·957 (1)	2·102 (3)
Ni—N(2)	1·961 (1)	2·060 (3)
Ni—Cl(1)		2·562 (1)
N(2)—C(1')	1·484 (2)	1·483 (5)
N(1)—C(2)	1·482 (2)	1·483 (5)
N(1)—C(3)	1·508 (2)	1·497 (5)
N(2)—C(5)	1·495 (2)	1·484 (5)
C(1)—C(2)	1·498 (2)	1·510 (6)
C(3)—C(4)	1·520 (3)	1·539 (6)
C(4)—C(5)	1·514 (2)	1·528 (6)
C(3)—C(6)	1·530 (2)	1·548 (7)
C(3)—C(7)	1·521 (3)	1·524 (6)
C(5)—C(8)	1·528 (3)	1·537 (6)
C(9)—Cl(2)		1·732 (5)
C(9)—Cl(3)		1·762 (5)
C(9)—Cl(4)		1·731 (5)
N(1)—Ni—N(2)	93·80 (5)	94·69 (12)
N(1)—Ni—Cl(1)		82·97 (8)
N(2)—Ni—Cl(1)		87·18 (8)
Ni—N(1)—C(2)	108·80 (10)	105·50 (23)
Ni—N(2)—C(1')	108·00 (8)	105·97 (22)
Ni—N(1)—C(3)	122·01 (8)	123·72 (24)
Ni—N(2)—C(5)	121·06 (9)	114·04 (23)
C(2)—N(1)—C(3)	112·10 (12)	117·21 (31)
C(1')—N(2)—C(5)	109·91 (10)	115·33 (30)
N(2')—C(1)—C(2)	106·69 (12)	109·51 (33)
N(1)—C(2)—C(1)	107·58 (13)	109·00 (33)
N(1)—C(3)—C(4)	108·45 (12)	107·59 (33)
N(2)—C(5)—C(4)	110·16 (11)	109·11 (30)
N(1)—C(3)—C(6)	109·71 (10)	109·18 (36)
N(1)—C(3)—C(7)	109·59 (14)	111·04 (34)
N(2)—C(5)—C(8)	112·26 (14)	112·22 (36)
C(3)—C(4)—C(5)	116·54 (14)	119·35 (34)
C(4)—C(3)—C(6)	106·89 (13)	108·14 (37)
C(4)—C(3)—C(7)	111·46 (14)	111·16 (36)
C(4)—C(5)—C(8)	109·49 (14)	110·08 (36)
C(6)—C(3)—C(7)	110·68 (14)	109·64 (39)
Cl(2)—C(9)—Cl(3)		110·04 (28)
Cl(2)—C(9)—Cl(4)		111·70 (28)
Cl(3)—C(9)—Cl(4)		110·18 (28)

Symmetry code: (') 1 − x, 1 − y, 1 − z.

The two axial coordination sites are occupied by two Cl^- ions with a Ni—Cl bond distance of 2·562 (1) Å.

A point of particular interest is the correspondence of the Ni—N bond lengths with the spin states of the Ni^{II} ion. In the orange diamagnetic complex, [Ni(meso-Me₆[14]aneN₄)]Cl₂.2H₂O, the average Ni—N bond length is 1·959 (2) Å, while in the violet high-spin complex, [NiCl₂(meso-Me₆[14]aneN₄)].2CHCl₃, the Ni—N bond lengths are 2·102 (3) and 2·060 (3) Å. These distances are typical of those found in low- and high-spin Ni^{II} complexes with four planar N donors (Madaule-Aubry & Brown, 1968; Madaule-Aubry, Busing & Brown, 1968; Hawkinson & Fleischer, 1969). The difference in the Ni—N bond distances causes the change in the in-plane ligand field strength and produces the spin-state variation in the Ni^{II} complexes with the same ligand. In each compound, the macrocyclic ligand adopts the most stable conformation: the six-membered rings take the chair form with the C(5)—CH₃ bonds in equatorial positions; the five-membered rings are in the *gauche* conformation.

Fig. 2(a) shows the arrangement of Cl^- ions and water molecules around the low-spin complex, [Ni(meso-Me₆[14]aneN₄)]Cl₂.2H₂O, as viewed perpendicularly to the coordination plane. As shown in Fig. 2(a), the Cl^- ions and the O atoms of waters of crystallization are not located near the fifth or sixth coordination site but are situated just above the H atoms of the N—H bonds with respect to the coordination plane. From the positions of the H atoms, which were clearly found in the difference map, there appear to be four hydrogen bonds of importance in the structure.
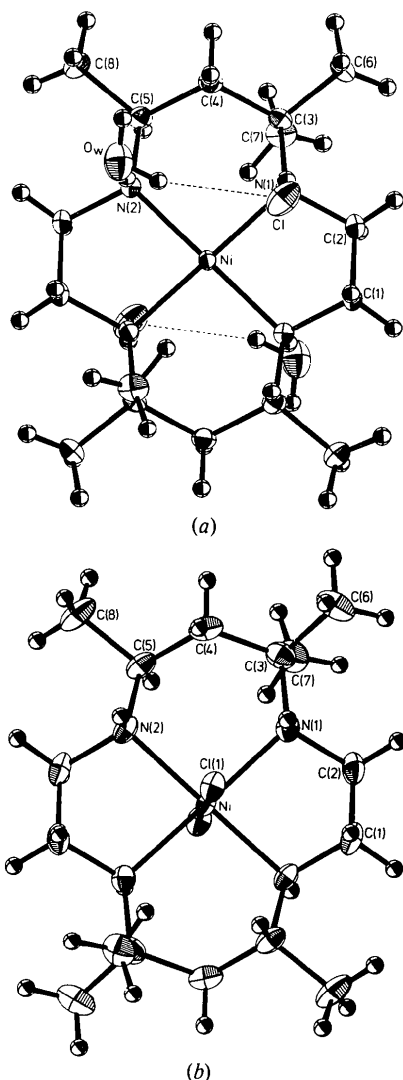
(a)

(b)

Fig. 2. Perspective view along the normal to the NiN$_4$ plane. (a) [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O, showing the disposition of the water molecule and the Cl$^-$ ion. (b) [NiCl$_2$(meso-Me$_6$-[14]aneN$_4$)], showing the tilt of the Ni—Cl bond from the normal to the NiN$_4$ plane.

These are N(1)—H$\cdots$Cl [3·261 (2) Å], N(2)—H$\cdots$O [2·948 (3) Å], O—H(1)$\cdots$Cl [3·149 (2) Å], and O—H(2)$\cdots$Cl' [3·175 (2) Å] (see Fig. 3). The parameters for the hydrogen bonds are listed in Table 3. All H atoms involved in these hydrogen bonds lie close to the respective lines joining the donor and acceptor atoms. The enthalpy of the thermal dehydration of [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O is reported to be 100·4 kJ mol^{-1} for the loss of two moles of water (Ito et al., 1978). The average value of $\Delta H = 50$·2 kJ mol^{-1} for the loss of one mole of water is close to the enthalpy of sublimation of ice [ΔH(sublimation) = 51·9 kJ mol^{-1} at 298 K] and those for dehydration reactions of many simple inorganic hydrates (Grindstaff & Fogel,
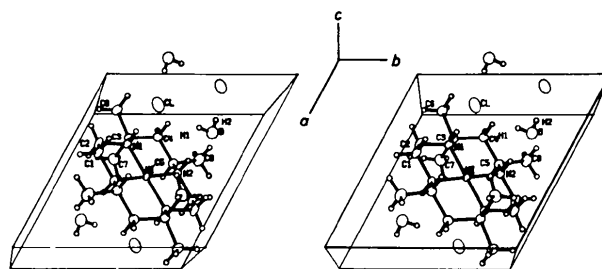

Fig. 3. Stereoscopic drawing of the crystal structure of [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O.

Table 3. Parameters for the hydrogen bonds in the crystal structure of [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O

X—H$\cdots$Y	$X\cdots Y$	H$\cdots Y$	$\angle XHY$
N(1)—H$\cdots$Cl	3·261 (2) Å	[2·44 (2) Å]	160 (2)°
N(2)—H$\cdots$O	2·948 (3)	[2·06 (2)]	177 (2)
O—H(1)$\cdots$Cl	3·149 (2)	[2·35 (2)]	161 (2)
O—H(2)$\cdots$Cl*	3·175 (2)	[2·35 (2)]	173 (2)

* Transformed by the symmetry operation $(-x, 1 - y, 1 - z)$.

1972, 1973; Nolan, Haralson, McAdams & Fogel, 1977). All of these facts indicate that the hydrogen-bond networks in [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O are strong.

When the anhydrous high-spin complex takes up two water molecules from atmospheric moisture to produce the low-spin dihydrate, the water molecules displace the Cl$^-$ ions from the coordination sites of the high-spin complex but do not substitute for the Cl$^-$ ions at the coordination sites. In view of the relative coordinating abilities, this is unexpected. The formation of the hydrogen bonds in the crystal is responsible for this unexpected result. The crystal structure of the corresponding complex of nickel(II) fluoride, which is a pentahydrate, [NiF$_2$(meso-Me$_6$[14]aneN$_4$)].5H$_2$O, has been studied (Toriumi & Ito, 1981). In the structure of [NiF$_2$(meso-Me$_6$[14]aneN$_4$)].5H$_2$O, four water molecules are located above the H atoms of the four N—H bonds and occupy nearly the same positions as the Cl$^-$ ions and the water molecules in [Ni(meso-Me$_6$[14]-aneN$_4$)]Cl$_2$.2H$_2$O. The feature of the hydrogen bonds in the vicinity of the [NiF$_2$(meso-Me$_6$[14]aneN$_4$)] molecule is very similar to that found in the structure of [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O. In addition, the F$^-$ ions in [NiF$_2$(meso-Me$_6$[14]aneN$_4$)].5H$_2$O are involved in the coordination bonds.

In the light of all of these facts, for the formation of the preferable hydrogen-bond networks in the crystal of [Ni(meso-Me$_6$[14]aneN$_4$)]Cl$_2$.2H$_2$O, the dispositions of the water molecules and the Cl$^-$ ions above the H atoms of N—H bonds would be essential and much more favorable over the hypothetical occupation by the

water molecules at the coordination sites. As a result, the water molecules in the dihydrate fail to coordinate, thereby yielding a four-coordinate low-spin Ni^{II} complex. The size of the Cl^- ion could also be responsible for this situation. As shown in Fig. 2, the thermal ellipsoid of the Cl^- ion is elongated towards the apical coordination site. This feature may reflect the ease with which, upon dehydration by heating, the Cl^- ions move to and occupy the coordination sites to produce the six-coordinate Ni^{II} complex.

In the high-spin complex, $|NiCl_2(meso-Me_6[14]-aneN_4)|.2CHCl_3$, the Cl^- ions are displaced slightly from the normal apical coordination sites towards the H atom bonded to N(1) so as to minimize the steric interaction with the axial methyl group of C(7) (Fig. 2b). As a result, the Ni–Cl bond is tilted 7·8° from the normal to the NiN_4 plane. A very similar distortion has been reported in the structure of the complex trans-dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II) (Bosnich, Mason, Pauling, Robertson & Tobe, 1965). The axial methyl C(7) is also displaced from the apical coordination site as compared with that in $|Ni(meso-Me_6[14]aneN_4)]Cl_2.2H_2O$ (see Fig. 2). C(7) is 3·599 (1) Å from Cl(1). All intermolecular contacts in the structure of $[NiCl_2(meso-Me_6[14]aneN_4)].2CHCl_3$ appear to be normal. The closest approach is between the chloroform C(9) and the chloride Cl(1) [3·510 (5) Å].

The calculations were carried out on the HITAC M-180 computer at the Computer Center of the Institute for Molecular Science, with the *Universal* *Crystallographic Computation Program System UNICS* III (Sakurai & Kobayashi, 1979).

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