This complex ion has approximate C_2 symmetry. The coordination geometry about the Cu^{II} ion is intermediate between the two limiting structures for five-coordinate complexes: a trigonal bipyramid and a square-based pyramid. This geometry may be referred to as a buckled square-based pyramid or a squashed trigonal bipyramid. The four donor N atoms of the macrocyclic ligand form a buckled plane, and the Cu^{II} ion is 0·220 (3) Å out of this buckled plane towards the aqua group. The perchlorate ions are not within bonding distance of the cation. The four methyl groups are on the same side of the metal–nitrogen buckled plane. The two six-membered chelate rings exhibit a chair form, and the two five-membered rings take distorted eclipsed forms. All bond angles and distances are normal.

The configuration of the four chiral N centers is 1*SR*,4*RS*,8*SR*,11*RS*, which is also found in the divalent Ni complex which is prepared by combining the metal salt with this ligand in aqueous solution (D'Aniello, Mocella, Wagner, Barefield & Paul, 1975). It is interesting to note that the four donor N atoms of this Ni^{II} complex, $[Ni(tmc)N_3]^+$, form a perfect plane, while the four donor N atoms of $[Cu(tmc)H_2O]^{2+}$ form a buckled plane. The reason for this difference is readily seen on viewing the angular overlap model for these complexes (Purcell & Kotz, 1979). This model indicates that the square-based pyramid is significantly more favored over the trigonal bipyramid for a d^8 complex than for a d^9 complex.

A water molecule is situated between the perchlorate ion and the coordinated aqua group. The hydrogen-bonding network listed in Table 3 stabilizes the crystal lattice. Hence the crystal state collapses as soon as it is dehydrated following exposure to air for a few hours.

The temperature factors of some perchlorate O atoms are larger than usual. These unusually large temperature factors may be due to the disordered orientation of the perchlorate ion and is manifested in the residual peaks around the perchlorate ions in the difference Fourier map.

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Structure of [(1*RS*,4*RS*,7*RS*,8*SR*,11*SR*,14*SR*)-1,4,5,5,7,8,11,12,12,14-Decamethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Perchlorate

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Abstract. $[Ni(C_{20}H_{44}N_4)](ClO_4)_2$, $M_r = 598·21$, triclinic, $P\bar{1}$, $a = 8·562\ (2)$, $b = 8·898\ (3)$, $c = 10·812\ (3)$ Å, $\alpha = 68·72\ (3)$, $\beta = 59·09\ (3)$, $\gamma = 79·91\ (3)°$, $U = 658·47\ (3)$ Å^3, $Z = 1$, $D_x = 1·508$, $D_m = 1·48$ Mg m^{-3} (by flotation in CCl_4/hexane mixture), Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·9907$ mm^{-1}, $F(000) = 318·6$, $T = 296\ (4)$ K, $R(F) = 0·053$ for 1659 observed reflections $[I > 3\sigma(I)]$. The complex ion is centrosymmetric with respect to the Ni^{II} atom. The Ni^{II} and the four N donor atoms are coplanar. This complex has the (1*RS*,4*RS*,8*SR*,11*SR*) configuration at the chiral nitrogen centers. The ligand is in its most stable planar conformation with both six-membered chelate rings in a chair form and both five-membered rings in a *gauche* form.

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Introduction. The macrocyclic ligand 1,4,5,5,7,8,11,12,12,14-decamethyl-1,4,8,11-tetraazacyclotetradecane (represented by *L*) exists as two isomers, (7*RS*,14*RS*)-*L* and (7*RS*,14*SR*)-*L*. The present paper concerns the crystal structure of the most stable Ni^{II} complex of (7*RS*,14*SR*)-*L*.

Table 1. *Experimental data and structure-refinement parameters*

Crystal size (mm)	0·3 × 0·3 × 0·35
Diffractometer and data-collection technique used	$\omega/2\theta$ scan; four-circle diffractometer (Syntex $P\bar{1}$) with graphite monochromator
Scan width (2θ)	($2{\cdot}0 + 0{\cdot}7\tan\theta$)°; starting 1° below $K\alpha_1$ and 1° above $K\alpha_2$
Number and range used for measuring lattice parameters	15 reflections with $12 < 2\theta < 25°$
Absorption correction applied	Experimental absorption correction based on ψ-scan (North, Phillips & Mathews, 1968)
Transmission factor	0·707
Maximum value of $(\sin\theta)/\lambda$ in intensity measurement	0·5947 $Å^{-1}$
Range of *h,k,l*	0, −10, −10 to 10, 10, 12
Standard reflections and intensity variation	3 (<3%)
Number of reflections measured	3108
Number of unique reflections	1659[$I > 3\sigma(I)$]
Method used to solve structure	Patterson and Fourier methods
Maximum height in final difference Fourier synthesis	0·55 e $Å^{-3}$
Parameters refined, nonhydrogen atoms	Coordinates, occupancies and anisotropic temperature factors (165 parameters)
hydrogen atoms	Coordinates and isotropic temperature factor (256 parameters)
Atomic scattering factors, f' and f''	*International Tables for X-ray Crystallography* (1974)
Number of reflections per parameter	4
R and wR, $w = 1/\sigma^2(F)$	0·053 and 0·047
S	0·646
R_{int}	0·032
$(\Delta/\sigma)_{max}$	0·67
Programs used	Tsing Hua University *XTAL* Package and *ORTEP*II (Johnson, 1976)
Computer	CDC Cyber-840

Table 2. *Atomic positional and thermal parameters of non-hydrogen atoms*

The equivalent isotropic thermal parameters ($Å^2$) $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j B_{ij}$, where the $\mathbf{a}_i$'s are the lattice vectors in direct space.

		x	y	z	B_{eq}
Ni	0·50*	0·0000	0·0000	0·0000	1·8 (1)
N(1)		−0·1174 (6)	−0·2216 (5)	0·1201 (5)	2·2 (5)
N(2)		0·0382 (6)	0·0067 (5)	0·1662 (5)	2·3 (5)
Cl		−0·5510 (2)	0·3318 (2)	0·2707 (2)	4·1 (2)
O(1)		−0·3775 (7)	0·3745 (7)	0·1433 (5)	6·3 (6)
O(2)	0·88*	−0·6880 (11)	0·3518 (13)	0·2386 (12)	13·2 (13)
O(3)	0·78*	−0·6031 (12)	0·4571 (12)	0·3325 (10)	9·5 (10)
O(4)	0·64*	−0·5712 (18)	0·1711 (13)	0·3054 (20)	13·1 (17)
O(5)	0·70*	−0·5363 (13)	0·2465 (19)	0·4005 (10)	12·6 (12)
C(1)		−0·1052 (12)	−0·2831 (8)	0·0039 (8)	3·0 (7)
C(2)		−0·0284 (8)	−0·3480 (7)	0·2036 (7)	2·5 (6)
C(3)		−0·0008 (9)	−0·2910 (8)	0·3077 (7)	2·8 (7)
C(4)		0·1255 (8)	−0·1443 (7)	0·2310 (7)	2·6 (6)
C(5)		0·1586 (10)	0·1513 (7)	0·1002 (8)	2·9 (7)
C(6)		−0·3167 (9)	−0·2048 (10)	0·2288 (9)	2·3 (7)
C(7)		−0·1370 (12)	−0·5078 (8)	0·2991 (9)	3·6 (8)
C(8)		0·1559 (14)	−0·1253 (11)	0·3538 (10)	4·4 (10)
C(9)		0·3069 (10)	−0·1729 (10)	0·1001 (10)	3·8 (8)
C(10)		−0·1425 (10)	0·0435 (11)	0·2887 (9)	3·4 (7)

* Population factor.

Experimental. (*C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) perchlorate was prepared using earlier procedures (Curtis, Curtis & Powell, 1966; Warner & Busch, 1969; Curtis, 1972; Liang, 1979; Lee, 1983). 5 g of this compound was dissolved in 40 ml of Me_2SO. About 10 g of finely pulverized KOH was added and the mixture was stirred vigorously for 15 min. The flask was fitted with an efficient reflux condenser and 10 ml of methyl iodide was added slowly over 5–10 min. A vigorous reaction took place and the temperature of the reaction mixture rose abruptly. After 10–15 min, a brick-red precipitate began to form. The mixture was allowed to cool and an equal volume of ethanol was added. The red powder and the excess KOH were removed by filtration and the potassium hydroxide was removed by washing with absolute ethanol. The iodide salt was converted to the perchlorate by dissolving the red precipitate in 200 ml of hot water. The mixture was filtered and a slight excess of $AgClO_4$ was added to the filtrate, then filtered again to remove AgI precipitate. Crystallization of the brick-red product started immediately. The product was collected, washed with ethanol and then ether, and dried *in vacuo*. The crystals for X-ray diffraction analysis were recrystallized from hot water (Wagner & Barefield, 1976).

Experimental data and structure solution parameters together with the refinement procedure are listed in Table 1. Five peaks corresponding to the perchlorate O atoms were found around the Cl atom, in the Fourier map. Refining the population parameters and coordinates of these O atoms alternately in the least-squares calculation indicates that the four O atoms, O(2), O(3), O(4), O(5) are situated in the torus-shaped base of a tilt cone with Cl—O(1) as an axis. The population factors of these O atoms are listed in Table 2. With the perchlorate O atoms arranged in this way, the $R(F)$ factor was reduced from 0·093 to 0·066 abruptly. The temperature factors of H atoms were assigned according to $B_H = B_n + 1$ where n is the atom to which the H atom is bonded (Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar, 1980; Lee, Lee, Juang & Chung, 1985). With isotropic temperature factors of H atoms assigned in this way their coordinates were refined. In the last cycle of the least-squares calculation, $R(F)$ fell to 0·053.

Discussion. The atomic coordinates and temperature factors are listed in Table 2.* Bond lengths and angles are listed in Table 3. The structure of this brick-red complex and the deviations of atoms from the CuN_4

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42895 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane are shown in Fig. 1, where it can be seen that this complex has a center of symmetry and the $\mathrm{Ni^{II}}$ ion is in square-planar coordination. The $\mathrm{Ni^{II}}$ and the four donor N atoms are coplanar within 0·0004 Å (standard deviation). The Ni—N bond lengths are normal for the coordination of a tertiary amino-group to a diamagnetic $\mathrm{Ni^{II}}$ ion. Fig. 2 shows a stereoview of the molecule.

Table 3. *Bond lengths* (Å) *and angles* (°)

Ni—N(1)	2·020 (4)	N(1)—Ni—N(2)	92·9 (2)
Ni—N(2)	2·006 (7)	N(1)—Ni—N(2·2)	87·1 (2)
C(1)—N(1)	1·494 (12)	Ni—N(1)—C(2)	104·6 (3)
C(2)—N(1)	1·526 (14)	N(1)—C(1)—C(5·2)	108·7 (6)
C(2)—C(3)	1·519 (13)	C(1)—C(5·2)—N(2·2)	107·8 (8)
C(3)—C(4)	1·532 (9)	C(5)—N(2)—Ni	106·8 (4)
C(4)—N(2)	1·536 (8)	Ni—N(1)—C(2)	117·5 (4)
C(5)—N(2)	1·508 (9)	N(1)—C(2)—C(3)	112·9 (5)
C(1)—C(5·2)*	1·495 (12)	C(2)—C(3)—C(4)	116·5 (5)
C(2)—C(7)	1·538 (9)	C(3)—C(4)—N(2)	109·9 (6)
C(4)—C(8)	1·546 (16)	C(4)—N(2)—Ni	115·0 (4)
C(4)—C(9)	1·531 (9)	Ni—N(1)—C(6)	109·0 (4)
C(6)—N(1)	1·515 (7)	Ni—N(2)—C(10)	108·0 (6)
C(10)—N(2)	1·513 (8)	O(1)—Cl—O(2)	115·0 (5)
Cl—O(1)	1·402 (4)	O(1)—Cl—O(3)	105·9 (4)
Cl—O(2)	1·351 (13)	O(1)—Cl—O(4)	106·0 (6)
Cl—O(3)	1·397 (12)	O(2)—Cl—O(3)	95·3 (7)
Cl—O(4)	1·359 (13)	O(2)—Cl—O(4)	86·4 (10)
Cl—O(5)	1·392 (11)	O(3)—Cl—O(4)	143·7 (8)

* The number 2 after the decimal point in parentheses indicates the second equivalent atoms [symmetry code: $-x$, $-y$, $-z$; *International Tables for Crystallography* (1983), p. 20].

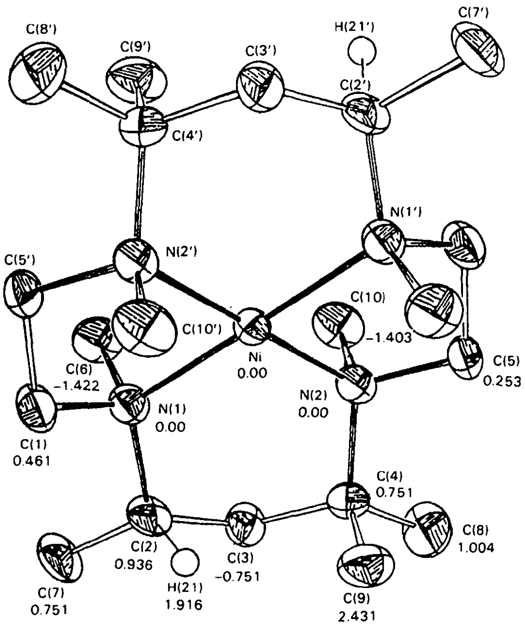

Fig. 1. Perspective view of the structure of $[\mathrm{Ni}(C_{20}H_{44}N_4)]^{2+}$, showing the atom numbering scheme and displacements of atoms from the $\mathrm{CuN_4}$ plane. Only the H atoms on the chiral centers are plotted; the e.s.d.'s are around 0·006 Å. Thermal ellipsoids are depicted at the 50% probability level (Johnson, 1976).

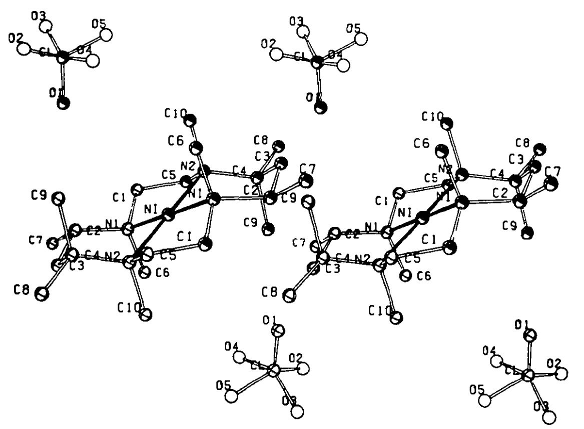

Fig. 2. Stereoview of the molecule. Center-related atoms are plotted as shaded spheres, perchlorate O atoms on the base are plotted as plain circles. Population factors are indicated in Table 2.

The four chiral nitrogen centers are in the (1*RS*,4*RS*,8*SR*,11*SR*) configuration. The two methyl groups attached to the asymmetric carbons C(2) and C(2′) are equatorial, while the four methyl groups attached to the asymmetric N chiral centers are axial. The ligand is in its most stable planar conformation with both six-membered chelate rings in a chair form and both five-membered rings in a *gauche* form. The chelate angles subtended at $\mathrm{Ni^{II}}$ are 87·1 (2)° for the five-membered and 92·9 (2)° for the six-membered rings. These angles are normal for planar tetraamine 14-membered macrocyclic ligand complexes of $\mathrm{Ni^{II}}$, with alternating five- and six-membered chelate rings. There appears to be no axial coordination for the complex ion as the closest contact distance is 4·334 (5) Å for perchlorate oxygen. Since the $\mathrm{Ni^{II}}$—O distance is dramatically longer than the normal axial $\mathrm{Ni^{II}}$ bonds, the $\mathrm{Ni^{II}}$—O interaction is not significant, and the $\mathrm{Ni^{II}}$ is four-coordinate. The perchlorate groups are distorted as would be expected.

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Structures of Copper(II)–Imidazole Complexes: Diethylenetriamine(imidazole)copper(II) Perchlorate (1) and Diethylenetriamine(1-ethylimidazole)copper(II) Perchlorate (2)

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Abstract. (1): $[Cu(C_3H_4N_2)(C_4H_{13}N_3)](ClO_4)_2$, $M_r = 433{\cdot}69$, orthorhombic, $Pnma$, $a = 14{\cdot}043\,(2)$, $b = 9{\cdot}322\,(2)$, $c = 12{\cdot}347\,(2)$ Å, $U = 1616{\cdot}3\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}782$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}78$ mm^{-1}, $F(000) = 884$, $T = 293$ K, final $R = 0{\cdot}061$ for 1596 observed reflections. (2): $[Cu(C_4H_{13}N_3)(C_5H_8N_2)](ClO_4)_2$, $M_r = 461{\cdot}75$, monoclinic, $P2_1/c$, $a = 8{\cdot}326\,(2)$, $b = 14{\cdot}600\,(3)$, $c = 15{\cdot}055\,(3)$ Å, $\beta = 94{\cdot}88\,(2)°$, $U = 1823{\cdot}4\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}682$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}58$ mm^{-1}, $F(000) = 948$, $T = 293$ K, final $R = 0{\cdot}074$ for 2859 observed reflections. The structures of both complexes are similar to each other. The coordination geometry around the Cu atom in each complex is octahedral, with the four N atoms from the diethylenetriamine and imidazole ligands occupying the equatorial sites and two O atoms of the perchlorate anions semicoordinated at the apical sites. Bond lengths and angles in the diethylenetriamine ligand and between the Cu atom and the ligand are normal.

Introduction. It is well known that the imidazole of the histidine residue plays an important role in metalloproteins. In this connection, the chemistry of imidazolate-bridged bimetallic complexes has been widely investigated. Recently, it has been found that a copper(II)–imidazolate complex of the type [Cu(dien)(Im)]ClO_4* (3) is afforded from the treatment of a corresponding copper(II)–imidazole complex, [Cu(dien)(ImH)$(ClO_4)_2$] (1), with a strong base, and X-ray crystallography has revealed that the structure of (3) is of a polynuclear type with trigonal-bipyramidal Cu^{II} atoms (Sato, Nagae, Ohmae, Nakaya, Miki & Kasai, 1986). We describe here the structures of the starting material of the above-mentioned reaction, (1), and of its 1-ethylimidazole analogue, [Cu(dien)(ImEt)$(ClO_4)_2$] (2), where the pyrrole H atom of the imidazole in (1) is replaced by an ethyl group.

Experimental. Both complexes were prepared by the addition of equimolar amounts of cupric perchlorate, dien and imidazole ligand in methanol–acetonitrile solutions. Crystals used were obtained from methanol solutions containing about 10% water (by volume). Systematic absences of (1), $0kl$ $k+l$ odd and $hk0$ h odd, indicated space group $Pn2_1a$ or $Pnma$, while that of (2) was uniquely determined as $P2_1/c$.

Purple, prismatic crystals with approximate dimensions of 0·25 × 0·25 × 0·40 mm for (1) and 0·15 × 0·25 × 0·35 mm for (2). Rigaku automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters by least-squares refinement, θ–2θ scan technique, scan range $\Delta(2\theta) = (1{\cdot}8 + 0{\cdot}70\tan\theta)°$, scan speed 4° min^{-1} in 2θ, background intensity measured 7·5 s at both ends of a scan, $2\theta_{\max} = 54°$, index range $h = 0$ to 17, $k = 0$ to 11, $l = 0$ to 15 for (1) and $h = -10$ to 10, $k = 0$ to 18, $l = 0$ to 19 for (2). Three standard reflections [600, 060, and 0,10,0 for (1), 400, 006, and 080 for (2)] measured

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* Abbreviations used: dien = diethylenetriamine, ImH = imidazole, ImEt = 1-ethylimidazole and Im = imidazolate.

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