group $P2_1$ with an Rh—Rh distance of 4·32 Å (Schurig, 1983).

While racemic dicarbonyl(3-trifluoroacetylcamphorato)rhodium(I) and dicarbonyl(3-trifluoroacetylcamphorato)iridium(I) form dichroic solids containing one-dimensional metal chains with a $(-1R-1R-1S-1S)_\infty$ alternating arrangement of the ligands, in the unit cell of (1) only homochiral molecules are present. Thus, upon crystallization of racemic carbonylchloro(3-trifluoroacetylcamphorato)platinum(II), not the racemate but pure enantiomers are formed as a conglomerate. Of the two possible geometric isomers, only that with a *trans* relationship between Cl(1) and O(2) is present in the crystal.

The formation of a racemic columnar structure, stabilized by a short Pt—Pt contact, as in the case with Rh^I or Ir^I, is not observed.

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Structure of a Five-Coordinate Copper(II) Hexaaza Macrotricyclic Complex: Chloro(1,3,6,9,11,14-hexaazatricyclo[12.2.1.1⁶,⁹]octadecane)copper(II) Perchlorate

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Abstract. [CuCl(C₁₂H₂₆N₆)]ClO₄, $M_r = 452·7$, orthorhombic, $P2_12_12$, $a = 14·124$ (11), $b = 9·837$ (4), $c = 6·570$ (4) Å, $V = 912·8$ (2) Å³, $Z = 2$, $D_x = 1·647$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 14·9$ cm⁻¹, $F(000) = 470$, $T = 291$ K, $R = 0·059$ for 649 reflections with $I \geq 3\sigma(I)$. The Cu ion is coordinated to four N atoms of the macrocycle and a Cl⁻ ion to form a distorted square-pyramidal geometry. The cation possesses crystallographic twofold symmetry through the Cu—Cl bond. The Cu ion lies 0·316 (1) Å above the basal coordination plane. The Cu—N [2·043 (8) and 2·022 (8) Å] and Cu—Cl [2·483 (4) Å] coordination bond distances are normal. Two 1,3-diazacyclopentane ring moieties of the ligand are in the same direction as the Cl⁻ ligand and are almost perpendicular to the ruffled 14-membered macrocycle. The perchlorate anion which is on the twofold symmetry axis is statistically disordered in two positions.

Introduction. Macrocyclic complexes show enhanced thermodynamic and kinetic stabilities and the characteristic properties inaccessible to complexes with non-cyclic chelate ligands. They are often prepared by metal template reactions because they provide selective and high yielding routes to the complexes of new ligands. Recently, the structure of a four-coordinate Ni^{II} complex {[Ni(L)]Cl₂.2H₂O} of a hexaaza macrotricyclic ligand 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1⁶,⁹]octadecane (L) has been reported (Suh, Shin, Kang, Lah & Chung, 1989). L is unique in that the hexaaza macrocycle acts as a tetradentate ligand. Here we report the crystal structure of a five-coordinate Cu^{II} complex {[Cu(L)Cl]ClO₄} (Suh, Kang & Chung, 1990).

Experimental. Title complex synthesized by the template condensation reaction of diethylenetriamine and formaldehyde in the presence of CuCl₂.2H₂O (Suh *et al.*, 1990). Blue crystals recrystallized from hot aqueous solution. Crystal *ca* 0·3 × 0·3 × 0·6 mm, Rigaku AFC diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $2\theta \leq 52°$, ω-2θ scan, scan speed 2° min⁻¹ in 2θ, ω-scan width $(2·3 + 0·3\tan\theta)°$ which is rather large due to split peaks, background measured for 10 s on either side of the peak; cell parameters by least-squares fit to observed 2θ values for 20 centered reflections with $14 \leq 2\theta \leq$

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$[CuCl(C_{12}H_{26}N_6)]ClO_4$

Table 1. Atomic coordinates ($\times 10^4$) and thermal parameters ($\mathring{A}^2 \times 10^3$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}	S.o.f
Cu	0	0	2324 (2)	22	0·5
Cl	0	0	−1455 (5)	51	0·5
N(1)	1740 (8)	1839 (11)	4216 (15)	48	1·0
C(2)	836 (10)	2487 (13)	4489 (16)	46	1·0
N(3)	63 (9)	2003 (8)	3002 (12)	37	1·0
C(4)	−918 (10)	2402 (11)	3708 (18)	43	1·0
C(5)	−1617 (8)	1681 (13)	2424 (20)	53	1·0
N(6)	−1434 (6)	191 (11)	2608 (13)	42	1·0
C(7)	−2009 (11)	−600 (14)	1093 (18)	58	1·0
C(8)	−2125 (9)	−2023 (15)	2115 (18)	57	1·0
C(9)	−1725 (9)	−412 (13)	4571 (16)	52	1·0
Cl(p)	0	5000	−935 (6)	44	0·5
O(1)	−586 (16)	4647 (21)	−2713 (22)	105	0·502
O(2)	599 (16)	3936 (20)	−517 (22)	77	0·502
O(1′)	620 (16)	4972 (24)	816 (22)	104	0·498
O(2′)	−401 (15)	3790 (20)	−1208 (21)	72	0·498

Table 2. Bond distances ($\mathring{A}$) and angles (°)

Cu—Cl	2·483 (4)	Cu—N(3)	2·022 (8)
Cu—N(6)	2·043 (8)	N(1)—C(2)	1·439 (18)
N(1)—C(8′)	1·495 (16)	N(1)—C(9′)	1·423 (17)
C(2)—N(3)	1·541 (17)	N(3)—C(4)	1·513 (18)
C(4)—C(5)	1·479 (18)	C(5)—N(6)	1·493 (17)
N(6)—C(7)	1·502 (16)	N(6)—C(9)	1·478 (14)
C(7)—C(8)	1·561 (20)		
Cl(p)—O(1)	1·473 (18)	Cl(p)—O(1′)	1·446 (18)
Cl(p)—O(2)	1·373 (21)	Cl(p)—O(2′)	1·331 (20)

N(3)—Cu—Cl	102·7 (2)	N(6)—Cu—Cl	95·2 (2)
N(3)—Cu—N(3′)	154·6 (3)	N(3)—Cu—N(6′)	91·5 (5)
N(6)—Cu—N(3)	86·2 (5)	N(6)—Cu—N(6′)	169·5 (3)
C(2)—N(3)—Cu	118·1 (7)	C(4)—N(3)—Cu	106·3 (7)
C(5)—N(6)—Cu	104·7 (7)	C(7)—N(6)—Cu	115·3 (8)
C(9)—N(6)—Cu	108·6 (7)	N(3)—C(2)—N(1)	114·4 (9)
C(4)—N(3)—C(2)	112·0 (8)	C(5)—C(4)—N(3)	108·2 (9)
N(6)—C(5)—C(4)	108·0 (9)	C(7)—N(6)—C(5)	111·2 (9)
C(8)—C(7)—N(6)	103·7 (9)	C(9)—N(6)—C(5)	114·6 (9)
C(9)—N(6)—C(7)	102·7 (9)	C(8′)—N(1)—C(2)	112·6 (9)
C(9′)—N(1)—C(2)	113·8 (10)	C(9′)—N(1)—C(8′)	106·1 (10)
O(2)—Cl(p)—O(1)	108·9 (11)	O(2′)—Cl(p)—O(1′)	110·3 (12)
O(2)—Cl(p)—O(1′)	56·9 (11)	O(2′)—Cl(p)—O(1)	56·1 (10)
O(2′)—Cl(p)—O(2)	66·9 (12)	O(1′)—Cl(p)—O(1)	165·0 (12)

22°; intensity checks for three standard reflections showed little (± 1%) variation; 1068 independent reflections (h 0 to 18, k 0 to 12, l 0 to 8), 649 (60·9%) observed with $I \geq 3\sigma(I)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by Patterson heavy-atom methods and refined by full-matrix least squares on F with anisotropic thermal parameters using *SHELX*76 (Sheldrick, 1976). Two sets of disordered O-atom positions of the perchlorate anion indentified in the difference map and their site occupancy factors refined to 0·502 and 0·498, four O atoms refined anisotropically; positional parameters of H atom on N(3) refined isotropically; other H-atom positions calculated with ideal geometry and included in structure-factor calculation with isotropic thermal parameters of 1·3 times those of the bonded C atoms. $\Sigma w(|F_o| - |F_c|)^2$ minimized, $w = k/[\sigma^2(F_o) + gF_o^2]$, $\sigma(F)$ from counting statistics, k and g

optimized in the least-squares procedure ($k = 0.621$, $g = 0.0072$); $wR = 0.061$ for 649 observed reflections, 149 variables, $R = 0.153$ for all data, $S = 0.36$, $(\Delta/\sigma)_{max} = 0.288$ [x coordinate of H on C(8)] in final refinement cycle; max. and min. heights in final difference map 1·01 and −1·01 e $\mathring{A}^{-3}$, respectively. All calculations performed with *SHELX*76 on an IBM 3090. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are listed in Table 1.* An *ORTEP*II (Johnson, 1976) view of the complex with the atomic numbering scheme is presented in Fig. 1. Bond distances and angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters and coordinates of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53635 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
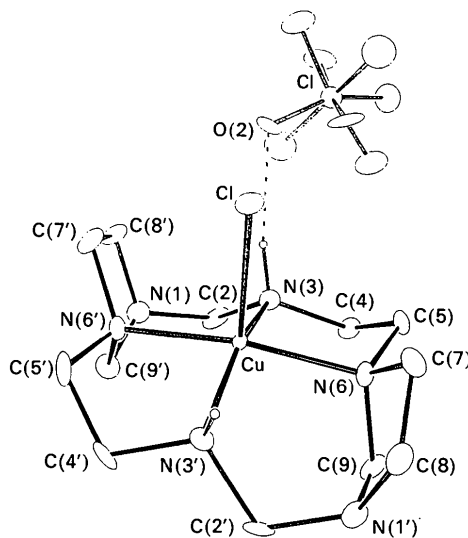

Fig. 1. *ORTEP*II view of the complex with the atomic numbering scheme. H atoms on the C atoms are omitted for clarity. The dotted line denotes the possible hydrogen bond. Thermal ellipsoids are depicted at the 20% probability level.
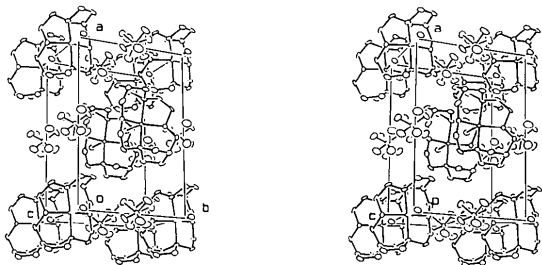

Fig. 2. Crystal packing drawing of $[CuCl(C_{12}H_{26}N_6)]ClO_4$.

The Cu ion is coordinated to the four N atoms of the macrocycle and a Cl⁻ ion to form a distorted square-pyramidal geometry. The cation possesses crystallographic twofold symmetry through the Cu—Cl bond. Both 1,3-diazacyclopentane ring moieties in [Cu(L)Cl]ClO$_4$ are situated in the same direction with respect to the coordination plane toward the apical Cl⁻ ligand while they are situated oppositely in square-planar [Ni(L)]Cl$_2$. The Cu and Ni complexes correspond to the *trans*-I and *trans*-III conformers, respectively (Thöm, Fox, Boeyens & Hancock, 1984).

Two pairs of the twofold-related N donors are disposed [± 0·129 (8) Å] on the opposite sides of their least-squares plane, showing a slight tetrahedral distortion. The Cu ion lies 0·316 (1) Å above this plane toward the Cl⁻ ion. The five-membered chelate ring assumes a half-chair form [N—C—C—N 58 (1)°]. The six-membered chelate ring assumes a conformation intermediate between the normal and half-chair forms. The 1,3-diazacyclopentane ring moiety assumes an envelope form [N—C—C—N 8·4 (9)°] and is situated perpendicular to the basal coordination plane with a dihedral angle of 102 (1)°.

Cu—N(6)(tertiary) [2·043 (8) Å] is slightly longer than Cu—N(3)(secondary) [2·022 (8) Å]. These coordination bond distances are consistent with those of Cu complexes of the 14-membered macrocycle (Lee, Lee, Juang & Chung, 1985) and longer than those of [Ni(L)]Cl$_2$. The Cu—Cl bond distance, 2·483 (4) Å, is the typical value for Cu^{II} complexes. The average C—N distance involving coordinated tertiary N(6) (1·49 ± 0·02 Å) is slightly shorter than

that involving coordinated secondary N(3) (1·53 ± 0·02 Å). The Cl⁻ ligand makes a close contact with C(7) [3·348 (15) Å] which is shorter than the van der Waals contact of 3·5 Å (Bondi, 1964).

Crystal packing is shown in Fig. 2. The perchlorate anion is located on the twofold symmetry axis and statistically disordered in two positions with almost equal site occupancy. One O atom of the perchlorate ion may be involved in a hydrogen bond [N(3)···O(2), 3·09 (2), N(3)—H, 0·90 (2), H···O(2), 2·24 (3) Å, N(3)—H···O(2), 159 (3)°] although disordering phenomena may diminish this effect. The Cl⁻ ligand is 4·087 (2) Å above the Cu ion of the cation related by one unit-cell translation along the *c* axis.

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Structure of *trans*-Dichlorotetrakis(dimethyl sulfoxide)rhodium(III) Tetrafluoroborate

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Abstract. (*OC*-6-13)-Dichlorobis(dimethyl sulfoxide-*O*)bis(dimethyl sulfoxide-*S*)rhodium(III) tetrafluoroborate, [RhCl$_2$(C$_2$H$_6$OS)$_4$]BF$_4$, M_r = 573·15, triclinic, $P\bar{1}$, a = 9·178 (4), b = 10·459 (3), c = 11·194 (5) Å, α = 92·71 (2), β = 96·77 (2), γ = 91·43 (2)°, V = 1065·4 (7) Å^3, Z = 2, D_x = 1·787 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 14·6 cm^{-1}, $F(000)$ = 576, T = 294 K, R = 0·032, wR = 0·042 for 4017 unique observed reflections. The structure of the cation is characterized by a *trans*-Cl octahedral coordination around the metal atom. Two of the four dimethyl sulfoxide (dmso) ligands are O-bonded to the Rh atom, the others are S-bonded, with O—dmso *trans* to S—dmso. Average bond distances are: Rh—Cl, 2·327 (4); Rh—S, 2·259 (7); Rh—O, 2·0798 (8) Å.