Br1—C2	1.884 (7)	Br7—C17	1.885 (8)
Br2—C3	1.887 (8)	Br8—C18	1.870 (8)
N1—Cu—N2	90.1 (2)	N2—Cu—N3	89.9 (2)
N1—Cu—N3	171.0 (2)	N2—Cu—N4	171.5 (2)
N1—Cu—N4	91.2 (2)	N3—Cu—N4	90.2 (2)

Table 3. *Average distance* (Å) *of selected atoms from the plane of the* N *atoms*

	Cu	Ni
meso C	0.163	0.187
pyrrole C	1.12 (9)	1.18 (10)
Br	1.99 (22)	2.05 (24)
Br(1,3,5,7)	2.16 (10)	2.25 (11)
Br(2,4,6,8)	1.82 (15)	1.86 (13)

The structure of the nickel(II) compound was solved by *MULTAN*88 (Debaerdemaeker, Germain, Main, Refaat, Tate & Woolfson, 1988). The structure of the copper(II) compound was solved by using coordinates from the Ni compound. For each compound, F^2 magnitudes were used in full-matrix least-squares refinement of 570 parameters: coordinates and anisotropic displacement parameters of the Ni/Cu, Br, F atoms, five C atoms of each phenyl ring, and the C and Cl atoms of the solvent, coordinates and isotropic displacement parameters of the remaining atoms of the complex, and a scale factor. The H atom of the solvent was positioned by calculation and not refined. Weights were calculated as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\bar{I})^2$. Atomic scattering factors and values for f' were taken from Cromer & Waber (1974) and Cromer (1974). For the nickel(II) compound, the largest peaks and valleys in the final difference map were mostly near the C_6F_5 groups, with five (>1 e Å^{-3}) near Br atoms and one (1.3 e Å^{-3}) 1.2 Å from Ni. For the copper(II) compound, the largest peaks and valleys in the difference map were near Br atoms and F atoms. Programs used were those of the *CRYM Crystallographic Computing System* (Duchamp, 1964) and *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71204 (80 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1023]

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Structure of (2,5,8,11,14-Pentaazapentadecane)copper(II) Diperchlorate Monohydrate

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Abstract

The coordination geometry about the Cu^{II} ion is a distorted trigonal bipyramid. There is variation in the five Cu—N bond distances. The four chiral nitrogen centers are in the (2*SR*,5*RS*,11*RS*,14*RS*) configuration. The ligand is in its most stable conformation with all four five-membered chelate rings in a stable *gauche* form.

Comment

The crystal structures of open-chain tetraamine complexes have been studied extensively (Lee *et al.*, 1986;

Fawcett *et al.*, 1980; Marongiu, Lingafelter & Paoletti, 1969). However, the crystal structures of open-chain pentaamine complexes have received little attention (Gatehouse, Martin, McLachlan, Platts & Spiccia, 1992). In order to expand knowledge in this area, we have synthesized the title compound for X-ray structure determination.

The 2,5,8,11,14-pentaazapentadecane ligand was prepared according to the modified procedure of Richman & Atkins (1974). It was isolated as the pentahydrochloride salt. The product (4 g) was dissolved in distilled water (40 ml) and passed through an anion-exchange column (Amberlite IR400, OH^- form) directly into an aqueous solution of stoichiometric quantities of copper perchlorate. The resulting deep-blue solution was slowly evaporated to produce blue powders of the title complex which were filtered and recrystallized from aqueous solution.

The Cu^{II} ion is five-coordinated in a distorted trigonal bipyramid with the N(1), N(3) and N(5) atoms in equatorial positions and the N(2) and N(4) atoms in axial positions. The deviation of the Cu atom from the equatorial plane is 0.12 Å towards the N(4) atom. Both Cu—N(1) and Cu—N(5) distances are significantly longer than the average Cu—N distance of 2.03 (3) Å for Cu^{II}–tetraamine macrocyclic complexes (Lu, Chung & Ashida, 1991). The four chiral nitrogen centers are in the (2*SR*,5*RS*,11*RS*,14*RS*) configuration. The ligand is in its most stable conformation with all four five-membered chelate rings in a stable *gauche* form. Hydrogen bonds help stabilize the crystal structure.

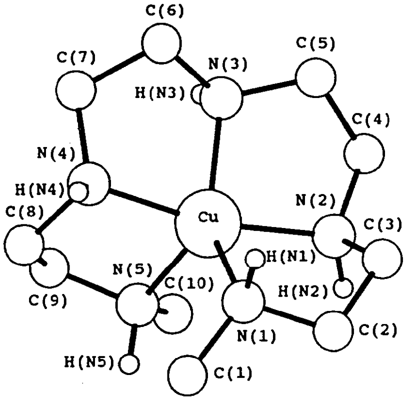

Fig. 1. Perspective view of the Cu^{II}–pentaamine complex with the atom-numbering scheme. The H atoms attached to C atoms are not shown.

Experimental

Crystal data

$[Cu(C_{10}H_{27}N_5)](ClO_4)_2.$-
H_2O
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
$M_r = 497.82$
Orthorhombic
Pcab
$a = 14.506$ (2) Å
$b = 14.823$ (2) Å
$c = 19.243$ (2) Å
$V = 4137.8$ (9) Å^3
$Z = 8$
$D_x = 1.602$ Mg m^{-3}
Cell parameters from 25 reflections
$\theta = 9.76$–$13.09°$
$\mu = 4.37$ mm^{-1}
$T = 298$ (3) K
Cubic
0.32 × 0.30 × 0.25 mm
Blue

Data collection

AFC-5*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (ψ scan); North, Phillips & Mathews (1968)
$T_{min} = 0.845$, $T_{max} = 1.0$
2622 measured reflections
2622 independent reflections
2285 observed reflections $[I \geq 2.5\sigma(I)]$
$\theta_{max} = 59°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 60 min
intensity variation: ±2%

Refinement

Refinement on *F*
Final $R = 0.048$
$wR = 0.049$
$S = 10.44$
2285 reflections
332 parameters
Only H-atom *U*'s refined
Unit weights applied
$(\Delta/\sigma)_{max} = 2.621$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}
Extinction coefficient: 0.051 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0.79752 (6)	0.42343 (5)	0.14013 (4)	4.18 (4)
Cl(1)	0.34695 (14)	0.37818 (12)	0.13877 (10)	4.95 (9)
Cl(2)	0.02194 (13)	0.71319 (12)	0.08738 (10)	4.41 (8)
O(1)†	0.4021 (12)	0.3697 (12)	0.1949 (7)	12.9 (10)
O(2)†	0.3611 (8)	0.4554 (6)	0.1033 (7)	11.1 (7)
O(3)†	0.2561 (5)	0.3886 (8)	0.1599 (5)	10.6 (6)
O(4)†	0.3507 (10)	0.3006 (7)	0.0977 (7)	12.4 (8)
O(5)†	0.1163 (5)	0.7252 (7)	0.0809 (6)	9.5 (5)
O(6)†	−0.0068 (6)	0.6610 (7)	0.0314 (5)	11.2 (6)
O(7)†	−0.0321 (7)	0.7863 (6)	0.0842 (5)	11.6 (6)
O(8)	−0.0003 (6)	0.6675 (8)	0.1466 (5)	11.7 (7)
O(*W*)	0.5437 (4)	0.5304 (4)	0.0872 (5)	10.9 (5)
O(1′)‡	0.429 (5)	0.337 (5)	0.120 (5)	14 (2)
O(2′)‡	0.312 (5)	0.308 (4)	0.163 (4)	14 (4)
O(3′)‡	0.388 (4)	0.388 (5)	0.077 (2)	11 (4)
O(4′)‡	0.405 (5)	0.418 (5)	0.189 (5)	7 (5)
O(5′)‡	0.022 (2)	0.6217 (18)	0.091 (2)	4.4 (15)
O(6′)‡	0.057 (4)	0.744 (3)	0.035 (3)	10 (2)
O(7′)‡	0.063 (3)	0.752 (3)	0.143 (2)	8 (2)
N(1)	0.9279 (4)	0.3739 (4)	0.1667 (3)	4.5 (3)
N(2)	0.7768 (4)	0.4272 (4)	0.2436 (3)	4.6 (3)
N(3)	0.6640 (4)	0.3829 (4)	0.1360 (3)	4.7 (3)
N(4)	0.7987 (4)	0.3979 (3)	0.0368 (3)	4.1 (2)
N(5)	0.8129 (3)	0.5627 (3)	0.1097 (3)	4.2 (2)
C(1)	1.0104 (5)	0.4088 (6)	0.1317 (5)	6.5 (5)
C(2)	0.9358 (5)	0.3815 (6)	0.2428 (4)	6.2 (4)
C(3)	0.8428 (6)	0.3642 (6)	0.2746 (4)	6.4 (4)
C(4)	0.6791 (5)	0.4070 (6)	0.2592 (6)	6.2 (4)
C(5)	0.6430 (5)	0.3433 (6)	0.2052 (4)	6.3 (4)
C(6)	0.6557 (5)	0.3231 (5)	0.0744 (4)	5.5 (3)

C(7)	0.7037 (5)	0.3696 (5)	0.0152 (4)	5.3 (3)
C(8)	0.8285 (5)	0.4823 (5)	0.0011 (4)	5.3 (4)
C(9)	0.7884 (5)	0.5628 (5)	0.0355 (4)	5.0 (3)
C(10)	0.7615 (6)	0.6310 (5)	0.1491 (4)	6.4 (4)

† Occupancy of 0.85.
‡ Occupancy of 0.15.

Table 2. *Geometric parameters* (Å, °)

Cu—N(1)	2.092 (5)	N(3)—C(6)	1.484 (9)
Cu—N(2)	2.015 (5)	N(4)—C(7)	1.499 (9)
Cu—N(3)	2.030 (5)	N(4)—C(8)	1.491 (9)
Cu—N(4)	2.025 (5)	N(5)—C(9)	1.471 (8)
Cu—N(5)	2.157 (5)	N(5)—C(10)	1.47 (1)
N(1)—C(1)	1.467 (9)	C(2)—C(3)	1.50 (1)
N(1)—C(2)	1.474 (9)	C(4)—C(5)	1.50 (1)
N(2)—C(3)	1.46 (1)	C(6)—C(7)	1.50 (1)
N(2)—C(4)	1.480 (9)	C(8)—C(9)	1.48 (1)
N(3)—C(5)	1.49 (1)		
N(1)—Cu—N(2)	84.4 (2)	Cu—N(3)—C(6)	106.6 (4)
N(1)—Cu—N(3)	140.2 (2)	C(5)—N(3)—C(6)	117.5 (6)
N(1)—Cu—N(4)	99.6 (2)	Cu—N(4)—C(7)	108.5 (4)
N(1)—Cu—N(5)	108.0 (2)	Cu—N(4)—C(8)	107.3 (4)
N(2)—Cu—N(3)	84.6 (2)	C(7)—N(4)—C(8)	111.9 (5)
N(2)—Cu—N(4)	167.8 (2)	Cu—N(5)—C(9)	103.8 (4)
N(2)—Cu—N(5)	104.9 (2)	Cu—N(5)—C(10)	117.9 (4)
N(3)—Cu—N(4)	85.1 (2)	C(9)—N(5)—C(10)	112.1 (5)
N(3)—Cu—N(5)	111.8 (2)	N(1)—C(2)—C(3)	108.7 (6)
N(4)—Cu—N(5)	84.9 (2)	N(2)—C(3)—C(2)	108.2 (6)
Cu—N(1)—C(1)	120.1 (5)	N(2)—C(4)—C(5)	108.8 (6)
Cu—N(1)—C(2)	106.7 (4)	N(3)—C(5)—C(4)	107.4 (6)
C(1)—N(1)—C(2)	111.4 (6)	N(3)—C(6)—C(7)	107.1 (6)
Cu—N(2)—C(3)	106.7 (4)	N(4)—C(7)—C(6)	110.2 (5)
Cu—N(2)—C(4)	109.7 (4)	N(4)—C(8)—C(9)	110.9 (5)
C(3)—N(2)—C(4)	114.5 (6)	N(5)—C(9)—C(8)	109.7 (5)
Cu—N(3)—C(5)	106.1 (4)		

The structure was solved for non-H atoms by direct and Fourier methods, and refinement was by full-matrix least squares [O(1′) refined isotropically]. H atoms were found by a difference Fourier method and theoretical calculation. The high value of $(\Delta/\sigma)_{\max}$ results from the disordered perchlorate groups. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen bonds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71180 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1026]

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Preparation of Chiral Tricarbonyl-(η^6-arene)chromium(0) Complexes Derived from (*S*)-2-Indolinecarboxylic Acid

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Abstract

The title diastereomeric mixture of (*S*,*S*)- and (*R*,*S*)-tricarbonyl[methyl *N*-*tert*-butyldimethylsilyl-(*S*)-η^6-indolene-2-carboxylate]chromium(0) was prepared by first converting (*S*)-2-indolinecarboxylic acid to *N*-*tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester. The enantiomerically pure ester was subjected to complexation conditions using triammine(tricarbonyl)chromium and hexacarbonylchromium to yield a 1:1 diastereomeric mixture of the corresponding tricarbonyl(η^6-arene)chromium(0) complexes. Chromatographic separation of the two diastereomers which result from addition of the tricarbonyl fragment to either face of the arene portion of the ester was effected. The bonding distances for the two diastereomers are very similar, but they have significantly different molecular conformations. These differences appear to result primarily from differences in the steric interaction between the acid ester group and the tricarbonylchromium fragment.

Comment

(*S*)-α,α-Diphenyl(indolin-2-yl)methanol, when converted to the corresponding oxazaborolidine using borane, has been shown to be effective as a catalyst for the enantioselective reduction of prochiral ketones using boranes (Martens, Dauelsberg, Behnen & Wallbaum, 1992). This observation was in accordance with pioneering work (Corey, Bakshi & Shibata, 1987) which established the general utility of chiral (*S*)-proline derived oxazaborolidines as extremely versatile enantioselective catalysts for the reduction of a variety of prochiral ketones using hydrides. The preparation and separation of both diastereomers (1-*S*,*S* and 1-*R*,*S*) of the tricarbonyl(η^6-arene)chromium(0) complexes of *N*-*tert*-butyldimethylsilyl-(*S*)-2-indolinecarboxylic acid methyl ester has been achieved. The structures represent synthetic precursors to both diastereomers of the tricarbonyl(η^6-arene)chromium(0) complexes of