

Structural Studies on Metal Complexes of Chiral Cyclen. V.
Chloro[(2*RS*,5*RS*,8*RS*,11*SR*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraaza-
cyclododecane]copper(II) Dichlorocuprate(I) Ethanol Solvate, [CuCl(C₄₄H₆₀N₄)]-
[CuCl₂].3C₂H₆O

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(Received 16 November 1983; accepted 9 March 1984)

Abstract. $M_r = 1016.61$, triclinic, $P\bar{1}$, $a = 14.912$ (10), $b = 15.054$ (9), $c = 13.809$ (12) Å, $\alpha = 110.5$ (6), $\beta = 103.7$ (7), $\gamma = 67.68$ (5)°, $U = 2667$ (4) Å³, $Z = 2$, $D_m = 1.27$, $D_x = 1.266$ (2) Mg m⁻³, $T = 298$ K, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.991$ mm⁻¹, $F(000) = 1078$, $R = 0.112$ for 3016 observed reflections. The structure consists of complex cations, disordered anions and solvent molecules. The Cu^{II} ion is coordinated to four N atoms and a Cl⁻ ion in a distorted square pyramid which is displaced approximately 41% towards the trigonal-bipyramidal form; the 12-membered ring takes the [2334] conformation. The [CuCl₂]⁻ anion moiety is nearly linear.

Introduction. This paper is part of the series of investigations on the metal complexes of chiral cyclens* having four chiral centers which can be divided into four geometrical isomers, viz C_4 , S_4 , C_i and C_1 . The cyclens react with Cu^{II}Cl₂ to give complexes of the corresponding isomers; the structures of the C_4 , S_4 and C_i isomers have been determined by X-ray analyses (Sakurai, Kobayashi, Hasegawa, Tsuboyama & Tsuboyama, 1982; Kobayashi, Sakurai, Hasegawa, Tsuboyama & Tsuboyama, 1982; Sakurai, Kobayashi, Masuda, Tsuboyama & Tsuboyama, 1983). This paper reports the structure of the Cu^{II} complex with the remaining C_1 isomer (Sakurai, Hiramatsu, Tsuboyama & Tsuboyama, 1980).

Previous results showed that the geometries about the metal ion in the Cu^{II} complexes of the C_4 and C_i isomers are the typical and slightly distorted square-pyramidal coordinations, but that the geometry of the S_4 isomer is an approximate trigonal-bipyramidal coordination. It was also found that the 12-membered rings of the C_4 , C_i and S_4 isomers in the complexes take [3333], [2343] and [2424] conformations, respectively. The conformation type is expressed by a series of

* Abbreviations: cyclen: 1,4,7,10-tetraazacyclododecane; tbte-cyclen: 1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane; C_4 isomer: tbte-(*RRRR*)- or tbte-(*SSSS*)-cyclen; C_i isomer: tbte-(*RRRS*)- or tbte-(*SSSR*)-cyclen; C_1 isomer: tbte-(*RRSS*)-cyclen; S_4 isomer: tbte-(*RSRS*)-cyclen.

numbers, each giving the number of bonds in one side (Dale, 1973). From these results, one can assume that the conformation of the complex with the C_1 isomer is the most distorted in this series and the ring is the [2334] type. This assumption, which will be discussed later, is confirmed by the present analysis.

Experimental. The Cu complex was prepared by heating a mixture of CuCl₂·2H₂O (1 mmol) in absolute EtOH with the C_1 racemic isomer of the cyclen (1 mmol) in benzene. The light-green products were purified by recrystallization from EtOH. Thin plate crystal sealed in glass capillary with mother liquor, dimensions 0.30 × 0.30 × 0.07 mm. Rigaku automated diffractometer. Three standard reflections: 400, 060, 408: variation <9%. Within range $2\theta < 45^\circ$ 3782 reflections with $|F_o| > 3\sigma(F_o)$ obtained. Lorentz-polarization correction, no absorption correction. 3016 unique, 4277 unobserved reflections. Structure solved by heavy-atom method, and refined by block-diagonal least-squares method based on $|F_o|$. Weights $a_1 + b_1 \times |F_o|$ for $|F_o| < 20$, c_2 for $20 \leq |F_o| \leq 50$, $d_3/(a_3 + b_3 \times |F_o| + c_3|F_o|^2)$ for $|F_o| > 50$ where each coefficient was determined during the refinement cycle. Anisotropic temperature factors for all non-hydrogen atoms. H-atom coordinates generated assuming the standard bond lengths and angles, and included in the structure factor calculation with isotropic temperature factors. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

The possible space groups were $P1$ and $P\bar{1}$. Since the cyclen used is racemic, $P\bar{1}$ is most probable. However, the statistical distribution of intensities is not clear enough to distinguish between them. Therefore, the structure analyses were carried out for both space groups. However, for space group $P1$, two complex molecules are related to each other by centrosymmetry. Therefore, the space group was assumed to be $P\bar{1}$. Final R and wR 11.2 and 14.4%, respectively. Because of the disorder, the anion and solvent molecules are not well defined, and further improvements were not possible. $(\Delta/\sigma)_{\max} = 0.34$ in the final

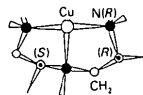
cycle. Max. height in final difference Fourier map $1.4 \text{ e } \text{Å}^{-3}$ near the Cu(2) ion. Crystallographic calculations performed on a FACOM M-380 computer of this Institute using the UNICSIII program system (Sakurai & Kobayashi, 1979).

Discussion. The atomic parameters are shown in Table 1.* Besides the complex moiety, a few atoms, C(S)'s, represent disordered solvents. Fig. 1* is a stereoscopic drawing of the molecule. The 12-membered ring has the [2334] conformation as predicted. The prediction was derived as follows. Starting with the molecule of the C_4 -(RRRR) complex already determined, whose four coordinated asymmetric N atoms all have *R* configurations, we considered steric interaction between the adjacent N and C substituents. The chiral ethyl groups must be situated so that they are not eclipsed with respect to the *R* benzyl groups and they are favorably located in equatorial positions.* As a result, in the chelate ring containing the *R* ethyl group the asymmetric C is situated at the corner, whereas the CH_2 group occupies the corner in the ring containing the *S* group.† Thus, the number of bonds in one side changes depending on the configurations of the two adjacent chiral centers in the ligand and the overall ring conformation depends on the stereochemistry.

The geometry about the Cu^{II} ion is shown in Fig. 2. The four N atoms are not coplanar; the dihedral angle between the N(1),N(4),N(7), and N(1),N(7),N(10) planes is 18.7° . Angles N(1)—Cu(1)—N(7) and N(4)—Cu(1)—N(10) are $157.7(5)$ and $138.0(6)^\circ$ respectively. The distorted conformation is basically a square pyramid (s.p.), but it is displaced about 41% along the Berry coordinate from the s.p. towards the trigonal bipyramid (t.b.) (Holmes & Deiters, 1977). The per cent displacement (s.p.%)‡ in this series decreases in the order $C_4(90)$, $C_1(85)$, $C_1(59)$ and $S_4(24)$. The Cu(1)—Cl(1) distance, $2.371(6) \text{ Å}$, and the mean bond

* Lists of structure factors, H-atom parameters, anisotropic thermal parameters and a stereodrawing of the molecule (Fig. 1) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39327 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The converse is also true for the ring of the C_4 -(SSSS) complex having four *S* N atoms, and there are two molecules in the unit cell of the present C_1 complex: RRRS—RRRR and SSSR—SSSS.



‡ The per cent displacement (s.p.%) was calculated from

$$\text{s.p.}\% = \left\{ \frac{1}{2} + \frac{[\sum_i |\delta_i - \delta_i(\text{s.p.})| - \sum_i |\delta_i - \delta_i(\text{t.b.})|]}{2[\sum_i |\delta_i(\text{t.b.}) - \delta_i(\text{s.p.})|]} \right\} \times 100,$$

where summation is for the nine dihedral angles, δ_i , between triangular faces, and $\delta_i(\text{s.p.})$, $\delta_i(\text{t.b.})$ are those for ideal s.p. and t.b. conformations respectively.

Table 1. Atomic parameters

Positional parameters are fractional coordinates multiplied by 10^4 . The equivalent isotropic temperature factor is defined by $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$.

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Cu(1)	1954 (2)	3089 (2)	4051 (2)	2.6 (0.1)
Cl(1)	290 (4)	3633 (4)	3361 (4)	4.0 (0.2)
Cl(2)	5287 (5)	1618 (6)	5574 (7)	8.2 (0.4)
N(1)	2625 (11)	3025 (11)	2817 (12)	2.8 (0.6)
N(4)	2437 (11)	4300 (11)	4938 (13)	3.2 (0.7)
N(7)	1865 (10)	2964 (10)	5468 (11)	2.3 (0.6)
N(10)	2520 (12)	1538 (11)	3589 (12)	3.4 (0.6)
C(2)	3268 (14)	3659 (14)	3302 (15)	3.3 (0.8)
C(3)	3401 (15)	3924 (15)	4489 (18)	4.0 (0.9)
C(5)	2560 (14)	4388 (14)	6072 (13)	3.0 (0.8)
C(6)	2644 (13)	3358 (14)	6177 (15)	2.9 (0.8)
C(8)	2058 (13)	1888 (14)	5353 (13)	2.5 (0.7)
C(9)	2810 (14)	1223 (15)	4555 (15)	3.2 (0.8)
C(11)	3405 (15)	1384 (17)	3145 (16)	4.0 (0.9)
C(12)	3094 (15)	1955 (14)	2347 (17)	3.9 (0.9)
C(11)	1868 (14)	3453 (17)	1994 (15)	3.8 (0.9)
C(12)	2340 (15)	3408 (19)	1098 (17)	5.2 (1.1)
C(13)	2530 (21)	2527 (22)	222 (18)	6.8 (1.3)
C(14)	2959 (24)	2504 (25)	-536 (22)	9.1 (1.6)
C(15)	3252 (24)	3264 (26)	-533 (25)	9.1 (1.7)
C(16)	3034 (20)	4126 (23)	259 (23)	7.2 (1.4)
C(17)	2573 (19)	4230 (21)	1104 (18)	6.0 (1.2)
C(21)	4272 (15)	3257 (16)	2944 (17)	4.2 (0.9)
C(22)	4779 (16)	4020 (19)	3234 (21)	6.0 (1.2)
C(41)	1767 (13)	5298 (15)	4750 (15)	3.1 (0.8)
C(42)	2112 (14)	6168 (13)	5242 (17)	3.6 (0.8)
C(43)	2624 (17)	6407 (16)	4714 (19)	4.9 (1.0)
C(44)	2968 (22)	7180 (22)	5163 (23)	7.3 (1.5)
C(45)	2783 (19)	7787 (18)	6156 (27)	7.8 (1.4)
C(46)	2222 (18)	7602 (17)	6680 (21)	6.2 (1.1)
C(47)	1897 (17)	6779 (15)	6205 (20)	5.0 (1.0)
C(51)	3460 (16)	4652 (16)	6720 (13)	3.6 (0.9)
C(52)	3350 (21)	5083 (22)	7869 (21)	7.0 (1.4)
C(71)	847 (13)	3595 (14)	5772 (14)	2.8 (0.8)
C(72)	633 (14)	3644 (14)	6787 (17)	3.8 (0.9)
C(73)	883 (15)	4252 (16)	7704 (15)	4.1 (0.9)
C(74)	623 (18)	4297 (18)	8631 (17)	5.9 (1.0)
C(75)	99 (23)	3713 (22)	8634 (20)	7.4 (1.5)
C(76)	-172 (20)	3135 (20)	7714 (23)	6.9 (1.3)
C(77)	91 (18)	3051 (18)	6760 (20)	5.6 (1.1)
C(81)	2442 (15)	1566 (16)	6333 (15)	3.8 (0.8)
C(82)	2301 (18)	556 (18)	6238 (19)	5.2 (1.1)
C(101)	1807 (15)	1066 (16)	2766 (15)	4.0 (0.9)
C(102)	1370 (14)	510 (15)	3141 (14)	3.3 (0.8)
C(103)	447 (16)	961 (17)	3421 (20)	5.1 (1.0)
C(104)	41 (19)	455 (23)	3746 (23)	7.4 (1.4)
C(105)	494 (21)	-539 (21)	3721 (25)	7.6 (1.5)
C(106)	1392 (19)	-986 (19)	3415 (22)	6.3 (1.3)
C(107)	1831 (16)	-511 (15)	3064 (19)	4.8 (1.0)
C(111)	4004 (17)	266 (16)	2712 (20)	5.3 (1.0)
C(112)	5036 (21)	127 (22)	2567 (27)	8.4 (1.5)
Cu(2)	5850 (3)	2565 (3)	6815 (4)	10.7 (0.2)
Cl(3)	6535 (14)	3567 (11)	7880 (14)	22.0 (1.1)
C(S)1	1862 (55)	437 (33)	9 (41)	21.9 (4.3)
C(S)2	8716 (63)	2702 (43)	287 (68)	28.0 (6.2)
C(S)3	6050 (55)	1679 (56)	416 (53)	31.4 (4.9)

length Cu(1)—N, 2.09 Å , correlate with the square pyramidal. In this series of the complexes, the axial bond length decreases, and the equatorial one increases in the same order.

The Cu^{II} ion shifts $0.745(5) \text{ Å}$ from the midpoint of the line connecting N(4) and N(10) towards the Cl(1) side. This value is smaller than that observed in the S_4 complex. Each five-membered chelate ring has a different form as shown in Table 2. The bond parameters of the tbte-cyclen part are shown in Fig. 3. The conformations of the benzyl groups are similar to that observed in the Cu^{II} complex of the S_4 isomer. The disposition of the anion part containing the diamagnetic

Cu^I ion is shown in Fig. 2. The disordered anion group is almost linear [169.5 (8)°], and is similar in shape to that observed in the complex of the C_i isomer. The line connecting Cl(1), Cu(1) and Cl(2) is nearly straight, deviating 7.7 (3)° from linearity. The Cu(1)—Cu(2) separation is 6.09 (8) Å. The complex cations are well separated with no intermolecular close contacts less than 3.5 Å.

Further discussion will be given elsewhere.

Table 2. Conformations of the five-membered rings

Conformation*	Pseudorotation angle P [in units of (2π/20)radian],* present complex
	3T(δ) 12
	3E(ε) 11
	3T(λ) 10
	3E(ε) 19

* These notations are those given by Altona & Sundaralingam (1972).

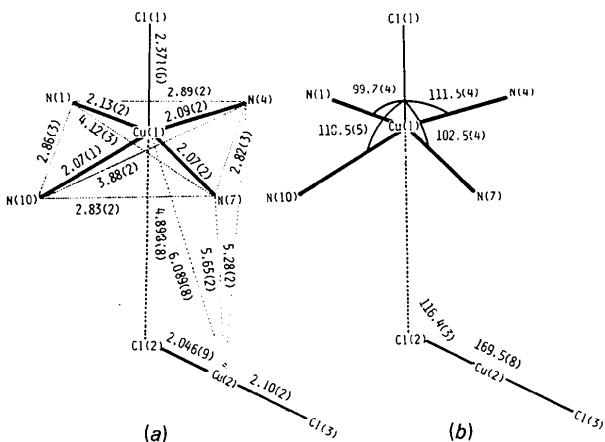


Fig. 2. The bond parameters about the Cu atoms. (a) Bond lengths (Å). (b) Bond angles (°).

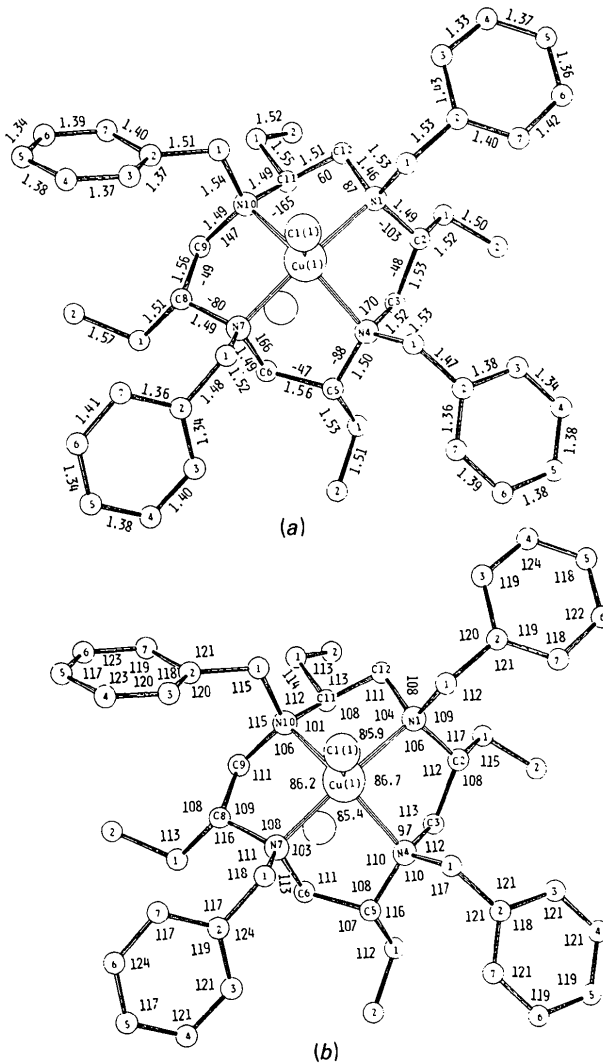


Fig. 3. The bond parameters in the tbt-cyclen complex. (a) Bond lengths (Å) and torsion angles (°). Torsion angles around the ring are given by the figures inside the ring. Other values are bond lengths. (b) Bond angles (°). The standard deviations are: bond lengths (Å): N—C 0.03, C—C(ring) 0.04, C—C(ring—ethyl) 0.03, C—C(ethyl) 0.04, N—C(benzyl) 0.03, C—C(benzyl methylene) 0.04, C—C(phenyl) 0.06; torsion angles (°): 2; bond angles (°): in the ring 2, in the ring—ethyl 2, in the ethyl 2, in the benzyl methylene 3, in the phenyl 4.

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Structure du Tricarbonyl(hydroxyméthyl-2 phényl-2 propanol)chrome(III), [Cr(CO)₃(C₁₀H₁₄O₂)]

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(Reçu le 25 avril 1983, accepté le 27 mars 1984)

Abstract. $M_r = 302.2$, monoclinic, $P2_1/c$, $a = 6.579$ (2), $b = 31.249$ (8), $c = 8.547$ (3) Å, $\beta = 133.04$ (5)°, $V = 1284.26$ Å³, $Z = 4$, $D_m = 1.53$ (4), $D_x = 1.56$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.942$ mm⁻¹, $F(000) = 624$, $T = 298$ K. Final $R = 0.035$ for 1884 unique observed diffractometer data. The molecular structure shows that the arene C atoms are nearly staggered with respect to the carbonyl ligands. The phenyl ring and one hydroxymethyl group are in eclipsed conformation. The Cr atom is pseudo-octahedrally coordinated by the carbonyl groups. Crystal packing is by hydrogen bonds and van der Waals forces.

Introduction. Les carbanions sont des intermédiaires réactionnels importants en synthèse organique et la coordination sur un groupement chrome tricarbonyle favorise la formation des anions benzyliques (Semmelhack, Seufert & Keller, 1980). La production de ces carbanions est effectuée par déprotonation directe du carbone benzylique par le *tert*-butylate de potassium. Cette propriété a été préconisée comme méthode synthétique pour l'alkylation du groupement benzylique d'hydrocarbures aromatiques (Simonneaux & Jaouen, 1979). Récemment, la fonctionnalisation d'arène chrome tricarbonyle (Brocard, Lebibi & Couturier, 1981) sur la position benzylique a été obtenue par cette méthode. Elle s'est avérée être une voie d'accès unique et efficace à toute une série de composés. Nous présentons dans la présente communication la première

détermination structurale d'un composé de cette série, le tricarbonyl(hydroxyméthyl-2 phényl-2 propanol)-chrome dans le but de donner un support structural à l'interprétation de la fonctionnalisation du tricarbonyl(éthylbenzène)chrome par des composés carbonylés.

Partie expérimentale. Réaction du tricarbonyl(éthylbenzène)chrome avec le formaldéhyde, en solution dans le diméthylsulfoxyde, en présence de *tert*-butylate de potassium; caractérisé par analyse élémentaire, spectre infrarouge et spectre RMN ¹H, paramètres de maille à partir des angles de 25 réflexions, cristal en aiguille, 0,06 × 0,08 × 0,26 mm, masse volumique mesurée par flottation, diffractomètre PW 1100, 3200 réflexions avec $2 \leq \theta \leq 28^\circ$, $0 \leq h \leq 7$, $0 \leq k \leq 35$, $-8 \leq l \leq 8$, dont 2028 avec $I > 3\sigma(I)$, 1884 réflexions indépendantes, trois réflexions de référence (202, 071, 251), correction de Lorentz-polarisation, pas de correction d'absorption, méthode de l'atome lourd, affinement par moindres carrés (matrice entière, basé sur F) et synthèses Fourier différence successifs, H localisés par synthèse Fourier différence, puis affinement de leur position, autres atomes: affinement position, B isotrope puis anisotrope, $R = 0.035$, $R_w = 0.037$, $w = 1$, $(\Delta/\sigma)_{\max} = 0,1$, valeurs maximale et minimale de la densité électronique dans la série de Fourier finale des ΔF : 0,15 et $-0,10$ e Å⁻³, facteurs de diffusion (Cromer & Waber, 1965), corrigés de la dispersion anormale (Cromer & Liberman, 1970).