

3.50 Å contacts in  $\text{UO}_2\text{Cl}_2(\text{dibenzylideneacetone})_2$  (Alcock, de Meester & Kemp, 1979) immediately explains why the crotonate complex does not dimerize in the solid state.

The most striking feature of the structure is the interaction between the coordinated  $\text{H}_2\text{O}$  and the uranyl oxygen [O(1)]. The two O atoms are 3.06 Å apart, this distance being controlled by the geometry around the U atom. The protons on O(4) are not constrained by the rest of the structure, and H(7) is found to be close to the O(4)—O(1) line, with O(4)—H(7)···O(1) 161°. This is undoubtedly a hydrogen-bond interaction even though the unfavourable orientation at O(1) implies that the attraction is principally electrostatic. A normal hydrogen bond is formed by H(6), to O(3) of another molecule.

Comparisons can only usefully be made with the two uranyl nitrate complexes, as these are the only  $\text{H}_2\text{O}$ -containing uranyl complexes where the protons have been located. In the hexahydrate (Taylor & Mueller, 1965), there is a network of intermolecular hydrogen bonds, and the protons of the water molecules lie in the uranyl equatorial plane. In the dihydrate (Dalley *et al.*, 1971), one water molecule again forms intermolecular hydrogen bonds, but the other is twisted towards the orientation in the crotonate

complex; however, the bond angle O—H···O(uranyl) is 111°, indicating that the involvement with the uranyl oxygen must be weaker than in the crotonate. It seems likely that the bulk of the crotonate ligand, compared to nitrate, has the effect of holding the complex molecules too far apart for them to form a full intermolecular hydrogen-bonding network.

Fig. 2 shows the packing of the molecules.

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## Structural Studies on Metal Complexes of Chiral Cyclen. II. Chloro[(2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]copper(II) Chloride, and Related Complexes

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#### Abstract

Three related metal complexes,  $\text{C}_{16}\text{H}_{36}\text{Cl}_2\text{CuN}_4$  [tetragonal, space group  $P4_12_1$ ,  $a = b = 15.564$  (2),  $c = 9.843$  (1) Å,  $U = 2384.5$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_o = 1.30$ ,  $D_c = 1.298$  Mg m<sup>-3</sup>, final  $R = 5.5\%$  for 1246 observed reflections],  $\text{C}_{44}\text{H}_{60}\text{Cl}_2\text{CuN}_4$  [orthorhombic, space group  $C222_1$ ,  $a = 15.487$  (9),  $b = 20.013$  (9),  $c = 14.287$  (7) Å,  $U = 4429$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_o = 1.31$ ,  $D_c = 1.27$  Mg m<sup>-3</sup>, final  $R = 7.0\%$  for 1780 observed reflections], and  $\text{C}_{44}\text{H}_{60}\text{Cl}_2\text{CoN}_4$  [orthorhombic, space group  $C222_1$ ,  $a = 15.31$  (1),  $b = 19.84$  (1),  $c = 15.02$  (1) Å,  $U = 4566$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_o = 1.26$ ,  $D_c =$

1.24 Mg m<sup>-3</sup> (first crystal);  $a = 15.37$  (1),  $b = 20.07$  (1),  $c = 14.54$  (1) Å,  $U = 4489$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_o = 1.26$ ,  $D_c = 1.26$  Mg m<sup>-3</sup> (second crystal); final  $R = 12.4\%$  for 741 observed reflections], were studied. The 12-membered ligand ring forms a square conformation. The metal atoms form a square-pyramidal structure with five coordination. The deviations of metal atoms from the plane formed by the four N atoms are 0.544 (3) and 0.73 (1) Å for Cu and Co respectively. Markedly short apical metal–chlorine distances are observed; *viz.* 2.42 (2) Å for Cu and 2.26 (1) Å for Co.

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Table 1. Additional crystal data

Crystal Formula Solvent*	(a)		(b)		(c)	
	[Cu <sup>(II)</sup> Cl(C <sub>4</sub> H <sub>9</sub> N) <sub>4</sub> ]Cl-Solvent 2·6H <sub>2</sub> O		[Cu <sup>(II)</sup> Cl(C <sub>11</sub> H <sub>15</sub> N) <sub>4</sub> ]Cl-Solvent ½CHCl <sub>3</sub> ·¼CH <sub>3</sub> NO <sub>2</sub>		[Co <sup>(III)</sup> Cl(C <sub>11</sub> H <sub>15</sub> N) <sub>4</sub> ]Cl-Solvent ½CHCl <sub>3</sub> ·H <sub>2</sub> O	
<i>M<sub>r</sub></i>	465.77		842.53		852.52	
Analytical values (%)	Observed	Calculated	Observed	Calculated	Observed	Calculated
C	41.41	41.26	63.29	64.43	62.03	62.69
H	8.76	8.92	7.37	7.54	7.14	7.39
N	12.27	12.03	7.66	7.07	6.40	6.57
Cl		15.22	10.51	11.57	15.03	14.56
Metal		13.64	7.54	6.34	6.56	6.88
Colour	Violet		Blue		Violet	
Refinement	Full-matrix		Block-diagonal		Block-diagonal	
H atoms	Included		Included		Included	

\* The number of solvent molecules is estimated so as to give the best analytical value.

## Introduction

Systematic investigations on the structure of the chiral cyclens have been reported\* (Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978*a,b*; Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979; Sakurai, Hiramatsu, Tsuboyama & Tsuboyama, 1980; Sakurai, Watanabe, Tsuboyama & Tsuboyama, 1981). The chirality of the asymmetric carbon was found to have a significant effect on the conformation of the 12-membered ring. These molecules form metal complexes as the quadridentate ligand (Melson, 1979), and the

\* Abbreviations: cyclen: 1,4,7,10-tetraazacyclododecane; tbcyclen: 1,4,7,10-tetrabenzylcyclen; te-(*RRRR*)-cyclen: (2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethylcyclen; tbte-(*RRRR*)-cyclen: (2*R*,5*R*,8*R*,11*R*)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethylcyclen.

Table 2. Atomic parameters

Positional parameters are multiplied by 10<sup>4</sup>. Invariant parameters are presented without the standard deviations. The equivalent temperature factor is defined by

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (a_i^* a_j^*)$$

(a) [Cu<sup>(II)</sup>Cl]{te-(*RRRR*)-cyclen}Cl

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> )
Cu	851 (1)	851 (1)	0	4.3 (0.1)
Cl(1)	-254 (3)	-254 (3)	0	5.6 (0.1)
Cl(2)	3046 (5)	3046 (5)	0	19.9 (0.5)
N(1)	208 (4)	1985 (4)	-95 (8)	4.9 (0.2)
N(4)	1150 (6)	1053 (6)	-1978 (7)	4.8 (0.3)
C(2)	681 (7)	2487 (6)	-1177 (10)	4.6 (0.3)
C(3)	742 (7)	1887 (6)	-2407 (12)	5.4 (0.3)
C(5)	2099 (6)	1015 (7)	-2057 (8)	4.5 (0.3)
C(6)	2372 (9)	231 (8)	-1261 (13)	6.1 (0.4)
C(2)1	232 (9)	3321 (8)	-1569 (14)	6.9 (0.4)
C(2)2	826 (15)	3895 (11)	-2403 (21)	9.8 (0.6)
C(5)1	2444 (7)	1017 (10)	-3538 (11)	7.3 (0.4)
C(5)2	3419 (11)	1088 (15)	-3525 (16)	10.6 (0.7)
O(1)	3729 (8)	3333 (7)	2753 (19)	18.8 (0.7)
O(2)	-2904 (26)	-2904 (26)	0	23.6 (2.0)

Table 2 (cont.)

(b) [Cu<sup>(II)</sup>Cl]{tbte-(*RRRR*)-cyclen}Cl

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> )
C(Sol)	0	5628 (14)	2500	11.8 (1.2)
C(Sol)2	0	4664 (14)	2500	9.2 (0.9)
Cu	0	1072 (1)	2500	4.0 (0.1)
Cl(1)	0	-128 (2)	2500	5.3 (0.1)
Cl(2)	0	3313 (2)	2500	5.4 (0.1)
N(1)	1062 (6)	1334 (5)	3272 (7)	4.4 (0.3)
N(4)	719 (6)	1350 (5)	1342 (7)	4.3 (0.3)
C(2)	1739 (7)	1618 (5)	2594 (14)	4.6 (0.3)
C(3)	1301 (8)	1865 (6)	1744 (9)	4.2 (0.3)
C(5)	121 (10)	1646 (5)	610 (8)	4.3 (0.3)
C(6)	706 (8)	1873 (6)	3904 (9)	4.4 (0.3)
C(1)-1	1422 (9)	746 (7)	3801 (11)	5.5 (0.4)
C(1)-2	2181 (9)	872 (6)	4478 (10)	5.3 (0.4)
C(1)-3	3033 (9)	749 (7)	4106 (12)	6.5 (0.5)
C(1)-4	3750 (11)	871 (8)	4684 (14)	8.3 (0.6)
C(1)-5	3660 (13)	1105 (8)	5574 (12)	8.6 (0.6)
C(1)-6	2822 (14)	1207 (9)	5937 (13)	9.3 (0.7)
C(1)-7	2082 (11)	1087 (8)	5366 (10)	7.1 (0.5)
C(2)-1	2320 (8)	2180 (6)	3020 (9)	4.9 (0.4)
C(2)-2	3128 (7)	2278 (6)	2473 (17)	6.4 (0.4)
C(4)-1	1217 (8)	744 (6)	963 (9)	4.3 (0.3)
C(4)-2	1856 (8)	882 (6)	187 (10)	5.2 (0.4)
C(4)-3	1612 (9)	865 (6)	-743 (10)	5.3 (0.4)
C(4)-4	2178 (11)	942 (8)	-1487 (12)	7.4 (0.5)
C(4)-5	3014 (12)	1078 (9)	-1299 (14)	8.6 (0.6)
C(4)-6	3329 (10)	1107 (8)	-365 (15)	8.7 (0.7)
C(4)-7	2726 (9)	988 (8)	422 (12)	7.2 (0.5)
C(5)-1	461 (8)	2220 (7)	10 (11)	5.3 (0.4)
C(5)-2	-73 (14)	2338 (8)	-862 (10)	7.3 (0.5)

(c) [Co<sup>(III)</sup>Cl]{tbte-(*RRRR*)-cyclen}Cl (part)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> )
Co	0	965 (3)	2500	6.1 (0.2)
Cl(1)	0	-173 (5)	2500	7.3 (0.5)
Cl(2)	0	3350 (5)	2500	7.4 (0.5)
N(1)	1124 (18)	1356 (16)	3265 (17)	7.5 (1.4)
N(4)	788 (15)	1321 (12)	1410 (15)	4.8 (1.0)
C(2)	1800 (23)	1576 (17)	2522 (50)	10.4 (1.9)
C(3)	1428 (26)	1915 (19)	1752 (26)	8.7 (1.5)
C(5)	102 (34)	1662 (14)	673 (20)	7.3 (1.2)
C(6)	677 (25)	1929 (18)	3906 (26)	8.3 (1.5)

structure of  $[\text{Co}^{(\text{III})}\text{BrH}_2\text{O}\{\text{te-}(\text{RRRR})\text{-cyclen}\}]\text{Br}_2$  has been determined (Sakurai, Tsuboyama & Tsuboyama, 1980: part I of this series). Several other complexes have been prepared (Tsuboyama, Tsuboyama, Sakurai & Uzawa, 1980), and electronic absorption, circular dichroism and ESR spectra reveal that the form of the complex is also affected by the chirality of the ligand (Tsuboyama, Tsuboyama, Sakurai, Kobayashi, Hasegawa, Kajikawa & Ishizu, 1981). A series of structural investigations is now in progress. In this paper we report the structures of three related complexes with the ligand chirality *RRRR*. These are: (a)  $[\text{Cu}^{(\text{II})}\text{Cl}\{\text{te-}(\text{RRRR})\text{-cyclen}\}]\text{Cl}$ , (b)  $[\text{Cu}^{(\text{II})}\text{Cl}\{\text{tbte-}(\text{RRRR})\text{-cyclen}\}]\text{Cl}$ , (c)  $[\text{Co}^{(\text{III})}\text{Cl}\{\text{tbte-}(\text{RRRR})\text{-cyclen}\}]\text{Cl}$ .

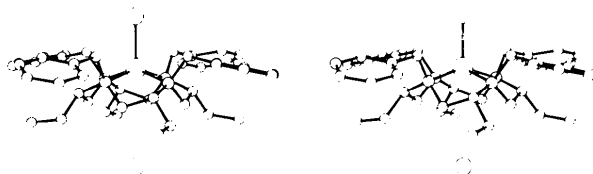


Fig. 1. A stereoscopic drawing of  $[\text{CuCl}(\text{tbtecyclen})]\text{Cl}$ .

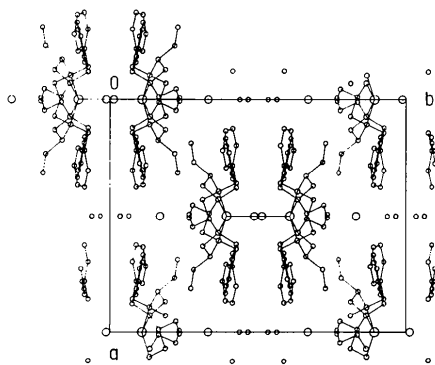


Fig. 2. Crystal structure of  $[\text{CuCl}(\text{tbtecyclen})]\text{Cl}$  projected along *c*.

## Experimental

The Cu complexes were prepared by heating mixtures of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with the corresponding cyclen in absolute EtOH. The Co complex was prepared similarly with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . The ttecyclen complex was recrystallized from  $\text{C}_3\text{H}_7\text{OH}-\text{CH}_3\text{COOC}_2\text{H}_5$ , and the tbte complexes were from  $\text{CHCl}_3-\text{CH}_3\text{NO}_2$ .

X-ray diffraction data were measured on a Rigaku automated four-circle AFC diffractometer, with graphite-monochromatized  $\text{Mo } K\alpha$  radiation. All these crystals contain solvent molecules in the crystal lattice, and decompose rapidly when they are exposed to air. Therefore, crystal (a) was coated with lacquer. Crystals (b) and (c) were sealed into glass capillaries with a trace of crystallization solvent. The structures were solved by

Table 4. Conformations of the five-membered rings

Ring	Conformation*	Pseudorotation angle <i>P</i> [in units of $(2\pi/20)$ radian]*	Present complex
$\text{Cu}[\text{tbte-}(\text{RRRR})\text{-cyclen}]$ N(4)-----Cu-----C(2)-N(1) C(3) -0.67 (2) Å	$^3E$		11
N(1)'-----Cu-----C(5)-N(4) C(6) -0.67 (2) Å	$^3E$		11
$\text{Cu}[\text{te-}(\text{RRRR})\text{-cyclen}]$ 0.70 (1) Å C(2) N(4)-C(3)---Cu-----N(1)	$^2E$		9
0.63 (1) Å C(5) N(1)'-C(6)---Cu-----N(4)	$^2E$		9

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

Table 3. Bond parameters around the metal (Å and deg)

	(a)	(b)	(c)
	Cu-ttecyclen	Cu-tbtecyclen	Cu-tbcyclen* Co-tbtecyclen
$M-\text{Cl}(1)$	2.430 (3)	2.400 (4)	2.367
$M-\text{N}(1)$	2.032 (7)	2.049 (10)	2.066†
$M-\text{N}(4)$	2.027 (7)	2.071 (10)	2.258 (11)
$\text{Cl}(1)-M-\text{N}(1)$	105.5 (2)	104.8 (3)	2.21 (3)
$\text{Cl}(1)-M-\text{N}(4)$	105.8 (2)	105.6 (3)	2.15 (3)
<i>M</i> from N plane	0.546 (2)	0.541 (5)	0.55
$\text{Cu}-\text{Cl}(2)$	4.831 (6)	4.486 (5)	0.73 (1)
			4.732 (12)

\* DeSimone, Blinn & Mucker (1980).

† Average value.

the heavy-atom method. Additional crystal data are summarized in Table 1. For the Co complex, two different crystals with slightly different lattice parameters were obtained from the same batch. This would be due to different solvent content, and the result of the structure analysis was poor. The Co structure is isomorphous with the Cu complex; therefore only the geometry around the Co atom is given.

The atomic coordinates are given in Table 2.\*

\* Lists of structure factors, H-atom coordinates, and anisotropic temperature factors for the Cu complexes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36208 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

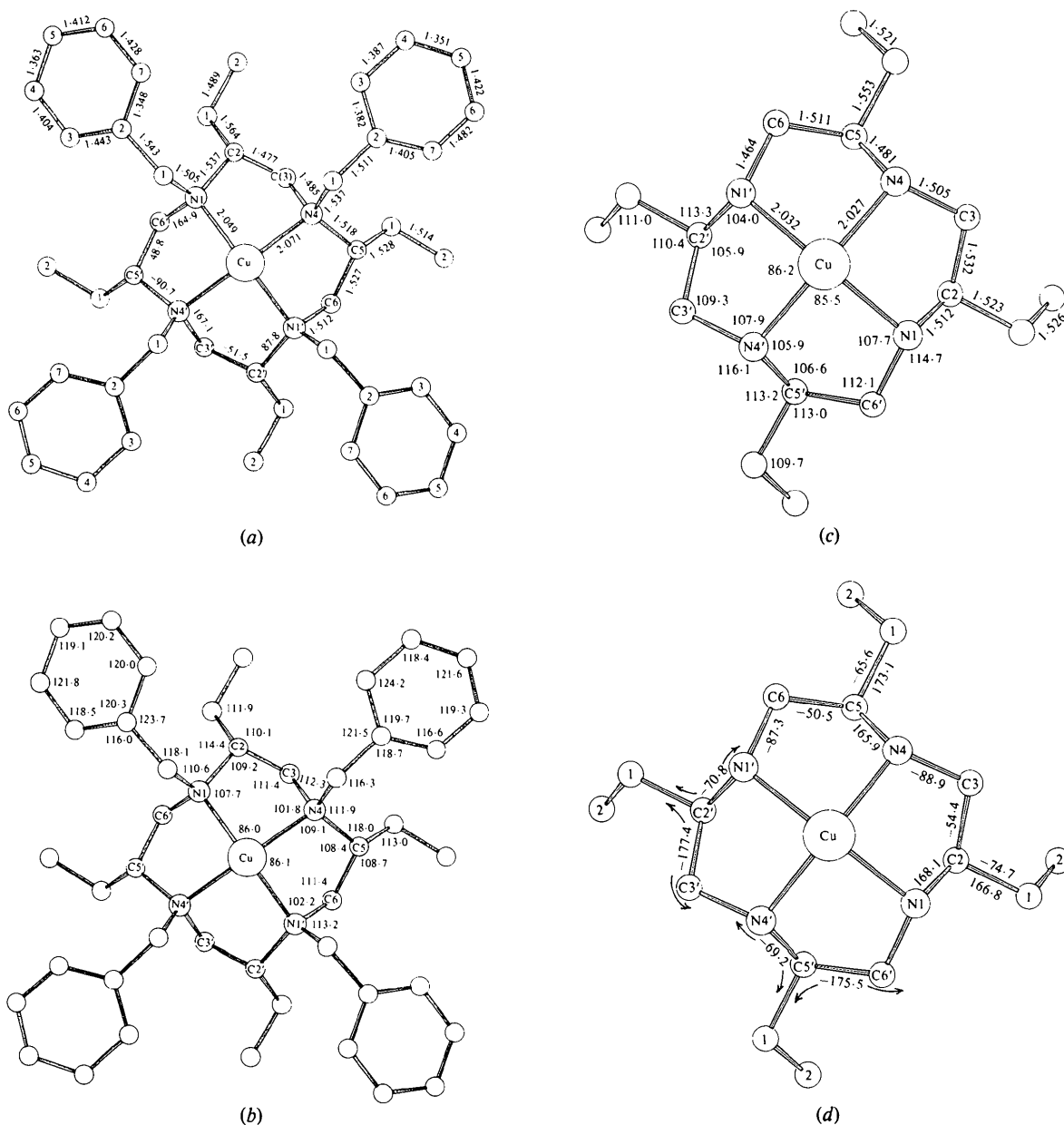


Fig. 3. The bond parameters. (a) Bond lengths (Å) and bond angles (°) in [CuCl(tbtccyclen)]Cl. (b) Torsion angles (°) in [CuCl(tbtccyclen)]Cl. (c) Bond lengths (Å) and torsion angles (°) of [CuCl(teccyclen)]Cl. Torsion angles are expressed by the figures inside the 12-membered ring. (d) Bond angles (°) of [CuCl(teccyclen)]Cl. The standard deviations are: tccyclen(tbtccyclen): N—C 0.013 (0.017), C—C(ring) 0.015 (0.02), C—C(substituent) 0.02 (0.03) Å, C—N—C(ring) and N—C—N(ring) 0.8 (1.0), C—C—C(substituent) 1 (1.6), torsion angles 1 (1.2)°.

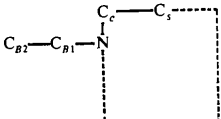
### Discussion of the structure

The shape of the complex is shown in Fig. 1, and the crystal structure is shown in Fig. 2. In all cases, both metal and Cl atoms are situated on the crystallographic twofold axes [parallel to [110] in (a) and to **b** in (b) and (c)]. Therefore, the molecules also have exact twofold symmetry. A few residual peaks between the molecules are assigned as the solvent atoms, but the exact form of the solvent molecules was not obtained. For Cu tetryclen, one of the residual peaks, located 2.95 (2) Å from the Cl atoms, may be assigned as the hydrogen-bonded water molecule. There are no particularly short intermolecular distances.

The coordination about the metal is square pyramidal with the Cl atom at the apex. A similar form was reported for the Cu<sup>(II)</sup> complex of tbcyclen (DeSimone, Blinn & Mucker, 1980). The counter anion Cl<sup>-</sup> is at the opposite side of the apical chlorine, and on the twofold axis of the molecule. The bond parameters around the metal atom are shown in Table 3. For a number of Cu complexes with square-pyramidal coordination, the apical Cu—Cl distance ranges from 2.73 to 3.19 Å (Hathaway, 1973). In the present case, it is 2.42 (2) Å for Cu and 2.26 (1) Å for Co. In spite of the bulky benzyl group, the coordination about the metal atom is similar in tetryclen, tbcyclen and tbtetryclen. However, small but significant differences exist in the metal to Cl distance. This distance is also affected by the chirality of the ligand, which will be discussed later with other structures. The chirality of all the N atoms is *R*. The five-membered chelate ring has the <sub>3</sub>*E* envelope conformation for tbtetryclen and <sup>2</sup>*E* for tetryclen according to the notation of Altona & Sundaralingam (1972) (Table 4).

Table 5. Comparison of the directions of the benzyl groups

Torsion angles are in deg.



	Free molecule			Cu[tbte-( <i>RRRR</i> )-cyclen]Cl <sub>2</sub>
	<i>RRSS</i>	<i>RRRS</i>	<i>RSRS</i>	
C <sub>5</sub> —C <sub>c</sub> —N—C <sub>B1</sub>	153 (7)	159 (5)	150 (1)	144 (2)
C <sub>c</sub> —N—C <sub>B1</sub> —C <sub>B2</sub>	-75 (5)	-80 (4)	-72 (3)	66 (1)

The 12-membered ring has a square conformation, and the bond parameters are given in Fig. 3. The conformation of the tbte ligand is different from the free molecule in two respects. One is the direction of the benzyl group, and the other is the kind of corner group. In the free molecule, the corner groups are either the methylene or the benzyl groups. In the present case, the ethyl groups are at the corners. The benzyl groups in the free molecule have axial directions when they are situated at the side of the ring. In the present case, they are directed away from the center of the ring as shown in Fig. 1. If two torsion angles C<sub>5</sub>—(side carbon)—C<sub>c</sub>(corner carbon)—N—C<sub>B1</sub> and C<sub>c</sub>—N—C<sub>B1</sub>—C<sub>B2</sub> are considered (Table 5), they are +*ap* and -*sc* for the free molecules, and +*ap* and +*sc* in the complex.

The chirality of the asymmetric carbon must have a significant effect on the shape of the ring, and large deformations are expected with the variation of the chirality. The succeeding reports will clarify these points.

Calculations were performed on a FACOM 230-75 computer of this Institute using the *UNICS* III program system (Sakurai & Kobayashi, 1979).

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