Fig. 4. The stacking of the cytosine molecules. The symmetry operations for Cyt(I), Cyt(II) and Cyt(III) are (x,y,z), $(-x, 1-y, 1-z)$ and $(1-x, 1-y, 1-z)$, respectively.

chain parallel to the c axis. The apical Cl(2) and water oxygen $O(W)$ form $O(W)-H\cdots Cl(2)$ hydrogen bonds which mutually link the polymeric chains lying along the c axis, and the base moieties of the polymerized sheets are mutually sandwiched (Fig. 2). There are two kinds of base-stacking arrangements with interplanar spacings of 3·459 and 3·571 Å (Fig. 4).

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The Structure of cis-(SSSR)-{Bromo[dibromoaqua(2–)][(2R,5R,8R,11R)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]}cobalt(III)

By Tosio Sakurai, Sei Tsuboyama and Kaoru Tsuboyama

The Institute of Physical and Chemical Research (Rikagaku Kenkyusho), Wako-shi, Saitama 351, Japan

Abstract

[CoBr(Br$_2$H$_2$O)(C$_{16}$H$_{36}$N$_4$)], monoclinic, $P2_1$, a = 12·089 (10), b = 12·384 (14), c = 7·698 (5) Å, β = 95·59 (7)°, U = 1147 (2) Å^3, Z = 2, D_m = 1·72, D_c = 1·740 (3) Mg m^{-3}. The structure was refined to a final R of 4·2%. The 12-membered tetramine ring is coordinated to Co^{III} atoms as a quadridentate ligand, and the two ligands Br and O are cis to each other; the two other Br atoms are hydrogen bonded to the O atom. The chiralities of the N atoms are assigned as 1S, 4S, 7S and 10R. The complex formed can be written as cis-$\Delta\Delta(-)_{589}$-(SSSR)-[CoBr(OH$_2\cdots$Br$_2$)-(2R,5R,8R,11R-Et$_4$-[12]-ane-1,4,7,10-N$_4$)$\varepsilon\lambda\delta\delta$].

Introduction

A series of investigations on the cyclic tetramers of chiral aziridines have been performed in our Institute, and the basic conformations of the molecules have been determined (Tsuboyama, Tsuboyama, Uzawa &

Higashi, 1974; Sakurai, Kobayashi, Tsuboyama & Tsuboyama, 1978a,b; Hiramatsu, Sakurai, Tsuboyama & Tsuboyama, 1979). The 12-membered tetramine ring (cyclen) is known to form a Co^{III} complex as the quadridentate ligand (Collman & Schneider, 1966). The coordination chemistry of complexes of N-containing macrocyclic ligands was reviewed by Busch (1978). The crystal structure analysis of (cyclen)dinitrocobalt(III) chloride has been reported (Iitaka, Shina & Kimura, 1974). We found that the chiral 12-membered tetramine, (2R,5R,8R,11R)-tetraethyl-1,4,7,10-tetra-azacyclododecane (tecyclen), also forms several different Co^{III} complexes in solution, and the title compound was obtained as single crystals. In order to determine the effect of the substituent on the formation of the complex, the crystal structure analysis was performed.

Experimental and structure determination

The ligand tecyclen was prepared as described previously (Tsuboyama, Tsuboyama, Uzawa, Kobayashi & Sakurai, 1977). Air was bubbled through a neutral solution of tecyclen.3HBr (m.p. 540 K, 2 mmol), $CoBr_2.6H_2O$ (3 mmol) and 5% sodium hydroxide for 2 h. The reaction mixture was acidified with HBr and the resulting red solution was allowed to stand for several days, until red crystals separated. Recrystallization from methanol gave red-violet plates of $C_{16}H_{38}Br_3CoN_4O$; $M_r = 601.18$, $\Delta\varepsilon_{602} = +0.84$ (measured 15 days after dissolving in MeOH).

X-ray diffraction data were measured on a Rigaku AFC four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The size of the crystal was $0.2 \times 0.2 \times 0.5$ mm and the absorption coefficient was 5.74 mm^{-1}. The usual Lorentz and polarization corrections were applied, but no absorption correction was made. Within the range $2\theta \leq 55°$, 2101 independent reflections with $|F| \geq 3\sigma(F)$ were observed. The structure was solved by MULTAN (Main, Woolfson & Germain, 1971), and was refined by the block-diagonal least-squares method. Unit weight was given to all reflections. Of the 38 H atoms, 32 were located from the difference Fourier map, and were included in the refinement with isotropic temperature factors. The final R factor was 4.2%.* Atomic parameters are given in Table 1.

Discussion

Fig. 1 is a stereoscopic drawing of the molecule (Johnson, 1965). The free molecule of tecyclen

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35236 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

Positional parameters for non-hydrogen atoms are multiplied by 10^4, and for H atoms by 10^3. The atom-numbering scheme is shown in Figs. 2 and 3, and the H atoms are numbered according to the attached atoms.

	x	y	z	B/B_{eq} (Å^2)
Co(1)	2173 (1)	0 (0)	1053 (1)	2·0
Br(1)	1261 (1)	1047 (1)	−1285 (1)	3·2
Br(2)	4342 (1)	−80 (2)	−3140 (1)	4·8
Br(3)	644 (1)	−2044 (1)	−2809 (2)	3·6
O(1)	2678 (6)	−994 (6)	−665 (8)	2·5
N(1)	942 (6)	−956 (7)	1409 (10)	2·3
N(4)	1570 (6)	964 (7)	2676 (10)	2·4
N(7)	3527 (6)	886 (8)	1163 (10)	2·6
N(10)	2995 (7)	−855 (7)	2888 (10)	2·4
C(2)	220 (8)	−457 (9)	2675 (14)	2·8
C(3)	901 (8)	349 (8)	3813 (13)	2·6
C(5)	2515 (9)	1648 (8)	3493 (13)	2·7
C(6)	3217 (9)	1916 (9)	2071 (15)	3·1
C(8)	4486 (8)	329 (9)	2206 (12)	2·5
C(9)	4157 (8)	−859 (9)	2382 (13)	2·7
C(11)	2428 (8)	−1875 (8)	3308 (13)	2·5
C(12)	1429 (8)	−2017 (10)	1936 (13)	2·7
C(2)1	−823 (8)	51 (11)	1676 (14)	3·2
C(2)2	−1504 (10)	−725 (11)	504 (17)	4·1
C(5)1	2149 (10)	2620 (10)	4499 (16)	3·7
C(5)2	3097 (11)	3171 (13)	5650 (18)	4·8
C(8)1	5582 (9)	443 (10)	1404 (14)	3·4
C(8)2	5974 (11)	1579 (13)	1324 (19)	4·9
C(11)1	3186 (11)	−2878 (10)	3444 (16)	3·9
C(11)2	2565 (12)	−3863 (11)	3971 (19)	5·2
H(N1)	61 (11)	−87 (12)	41 (17)	6 (4)
H(N7)	374 (9)	101 (11)	−10 (15)	5 (3)
H(N10)	280 (10)	−68 (10)	385 (16)	5 (3)
H(C2)	−8 (8)	−112 (8)	361 (12)	2 (2)
H(C2-1)1	−128 (6)	36 (7)	267 (10)	1 (2)
H(C2-1)2	−61 (7)	65 (7)	85 (10)	1 (2)
H(C2-2)1	−181 (10)	−128 (11)	120 (16)	5 (3)
H(C2-2)2	−121 (7)	−88 (8)	−65 (12)	2 (2)
H(C2-2)3	−227 (12)	−34 (14)	18 (19)	8 (4)
H(C3)1	46 (6)	80 (7)	442 (10)	1 (2)
H(C3)2	135 (7)	4 (9)	461 (11)	2 (2)
H(C5)1	285 (6)	125 (6)	429 (9)	0 (1)
H(C5-1)1	187 (10)	309 (14)	389 (17)	6 (3)
H(C5-1)2	155 (7)	243 (8)	554 (11)	2 (2)
H(C5-2)1	364 (8)	334 (8)	486 (12)	3 (2)
H(C6)1	388 (8)	224 (8)	234 (13)	3 (2)
H(C6)2	288 (12)	236 (14)	143 (20)	8 (4)
H(C8)	450 (11)	44 (12)	357 (17)	7 (4)
H(C8-1)1	639 (10)	2 (13)	235 (16)	6 (3)
H(C8-1)2	557 (7)	13 (9)	50 (12)	3 (2)
H(C8-2)1	589 (8)	203 (9)	215 (13)	3 (2)
H(C8-2)2	676 (8)	166 (9)	95 (13)	3 (2)
H(C8-2)3	588 (12)	197 (14)	8 (19)	9 (4)
H(C9)1	435 (9)	−111 (10)	117 (15)	4 (3)
H(C9)2	461 (9)	−110 (10)	334 (14)	4 (3)
H(C11)	216 (7)	−190 (9)	458 (11)	2 (2)
H(C111)1	347 (9)	−308 (10)	233 (14)	3 (3)
H(C112)1	201 (10)	−410 (11)	301 (16)	5 (3)
H(C112)2	312 (11)	−458 (12)	426 (17)	7 (4)
H(C112)3	199 (12)	−391 (14)	528 (19)	8 (4)
H(C12)1	172 (10)	−240 (11)	101 (16)	5 (3)
H(C12)2	95 (8)	−239 (9)	242 (13)	3 (2)

(Sakurai *et al.*, 1978*a*) has fourfold symmetry. However, on formation of the title complex, the molecule bends about the line connecting N(1) and N(7), thus forming the *cis* coordination for the other two ligands [Br(1) and O]. The coordination to the Co atom is octahedral. The distances between the Co and the ligand atoms are shown in Fig. 2. The mean Co⋯N distance, 1·947 Å, is almost the same as those found in the cyclen complex (1·949 Å) and other similar complexes (Buckingham *et al.*, 1974). On the other hand, the Co⋯O distance of 1·948 Å is significantly longer than the 1·91 ∼ 1·92 Å found in other complexes (Buckingham *et al.*, 1974; Freeman, Marzilli & Maxwell, 1970; Mitsui *et al.*, 1976). This is due to the formation of O—H⋯Br hydrogen bonds. Although the H atoms attached to the O atom were not well observed on the difference Fourier synthesis, the distances and the angle between O⋯Br(2) and O⋯Br(3) (Fig. 2*a*) indicate that hydrogen bonds exist between these atoms. The minimum intermolecular distances between these Br atoms and other atoms are 3·457 Å for Br(2)⋯N(10), and 3·522 Å for Br(3)⋯C(5)1 (Fig. 4). Therefore, these Br atoms form part of the neutral complex *via* the hydrogen bonds. The bond angles about the Co atom are shown in Table 2. Some deviate considerably from the regular octahedral value. In particular, N(1)—Co—N(7) is 168·7°. A similar deviation of this angle is also found in the cyclen complex. On the other hand, three mean planes through Co, Br(1), O, N(10), N(4); Co, Br(1), N(1), N(10),
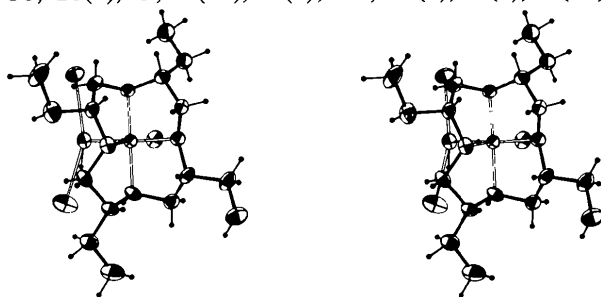

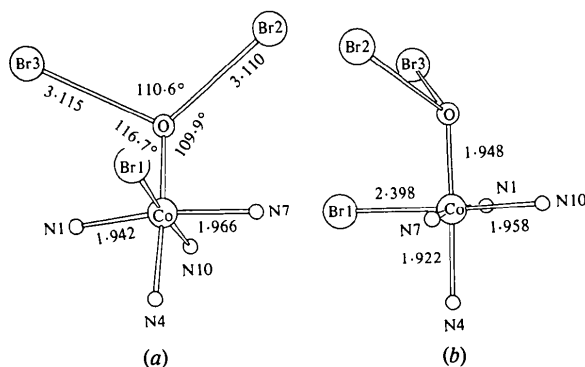Fig. 1. A stereoscopic drawing of the molecule.

(a)   (b)

Fig. 2. Coordination about the Co atom. The standard deviations are: Co—Br 0·002, Co—O 0·007, Co—N 0·008, O—Br 0·007 Å; Br—O—Br 0·2, Co—O—Br 0·3°.

Table 2. *Bond angles* (°) *about the* Co *atom*

Br(1)—Co—O	89·1 (2)	O—Co—N(7)	93·8 (3)
Br(1)—Co—N(1)	97·7 (2)	O—Co—N(10)	88·7 (3)
Br(1)—Co—N(4)	88·6 (2)	N(1)—Co—N(4)	86·7 (4)
Br(1)—Co—N(7)	92·9 (2)	N(1)—Co—N(7)	168·7 (3)
Br(1)—Co—N(10)	176·7 (2)	N(1)—Co—N(10)	84·9 (4)
O—Co—N(1)	90·3 (3)	N(4)—Co—N(7)	89·6 (4)
O—Co—N(4)	176·0 (3)	N(4)—Co—N(10)	93·7 (3)
		N(7)—Co—N(10)	84·8 (4)

Table 3. *Mean planes through the* Co *atom*

Listed are atoms defining the planes and their deviations from the mean planes (Å).

Plane (1)

Co	0·004 (1)	N(10)	0·053 (8)
Br(1)	0·045 (1)	N(4)	−0·050 (8)
O	−0·052 (7)		

Plane (2)

Co	0·011 (1)	N(10)	0·064 (8)
Br(1)	0·043 (1)	N(7)	−0·060 (8)
N(1)	−0·058 (8)		

Plane (3)

Co	0·056 (1)	N(4)	0·101 (8)
O	0·091 (7)	N(7)	−0·121 (8)
N(1)	−0·128 (8)		

Dihedral angles between the planes (°)

(1)–(2)	89·9 (4)	(2)–(3)	89·2 (4)
(1)–(3)	91·3 (4)		

N(7); and Co, O, N(1), N(4), N(7) are almost orthogonal to each other, as shown in Table 3. The Co atom is always located near the mean plane, and the other atoms form the saddle shape.

The stable conformation of the 12-membered ring is the square [3333] form (Bixon & Lifson, 1967; Dale, 1976). However, because of the formation of the complex, the ring conformation becomes rectangular [2424]. The bond lengths, angles and torsion angles are shown in Fig. 3. The chiralities of the N atoms are assigned as 1*S*, 4*S*, 7*S* and 10*R*.*

The overall conformation of the 12-membered ring is similar to that of cyclen, and has approximate mirror symmetry with respect to the plane passing through Co, Br(1), O, N(4) and N(10). However, the present molecule is more irregular. The bond lengths C(3)—N(4), 1·462 Å, and C(5)—C(6), 1·487 Å, are possibly significantly shorter than the usual values of 1·496 and 1·518 Å respectively. The main difference in conformation from that of cyclen involves the N(10), C(11) and C(12) part. The bond angle of 121·3° for

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* Since tecyclen was derived from (*R*)-2-ethylaziridine with complete retention of configuration, the known absolute configuration of the four asymmetric C atoms was used as the internal reference.
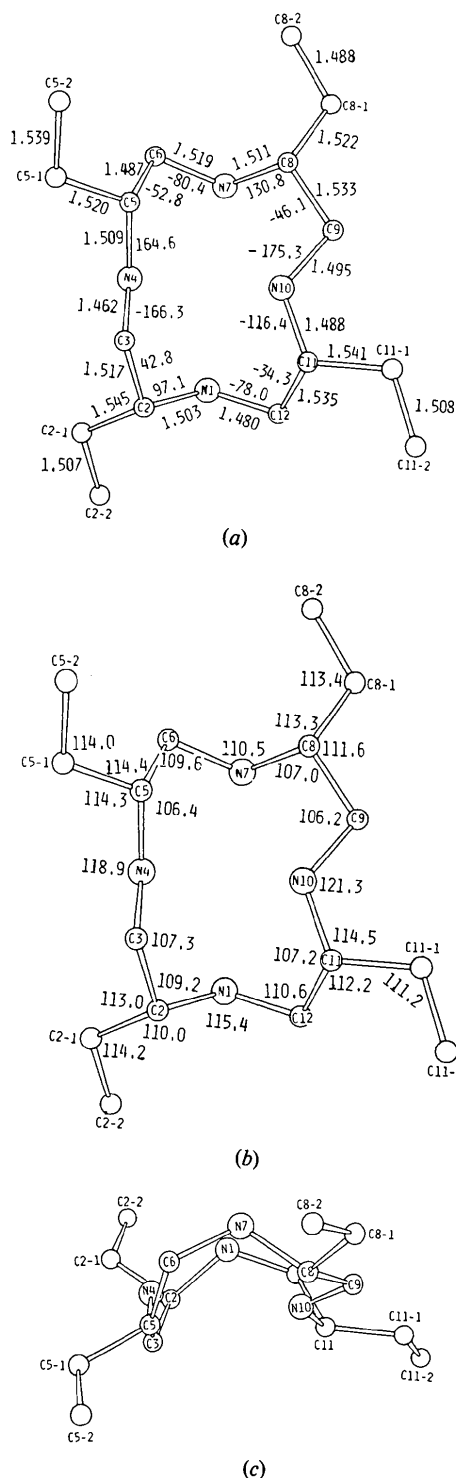
C(9)—N(10)—C(11) is considerably larger than the stable value of *ca* 113°. The torsion angles about this part differ ~60% from those obtained in cyclen, and the mirror symmetry is not satisfied (Fig. 3c). This is due to the effect of the ethyl group at C(11). It can easily be shown that if the conformation at this part were similar to that of cyclen, a large repulsion would result between the ethyl group and O···Br(3).

The five-membered chelate ring Co—N—C—C—N is known to have twist forms λ, δ, or the envelope form ε. However, these notations are not sufficient to describe the conformation of the heterocyclic ring unless the atom is explicitly specified. The most satisfactory description was given by Altona & Sundaralingam (1972). According to their notation and the following numbering scheme,
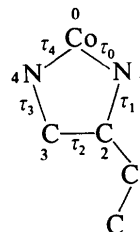

Fig. 3. The bond parameters in the tecyclen group. (a) Bond lengths (Å) and torsion angles (°). Torsion angles around the ring are given by the figures inside the ring. Other values are bond lengths. The standard deviations are: N—C 0·013, C—C(ring) 0·015, C—C(ring–ethyl) 0·016, C—C(ethyl) 0·019 Å. The standard deviation for the torsion angles is 1·0°. (b) Bond angles (°). The standard deviations are: in the ring 0·8, in the ring—ethyl 0·9, in the ethyl 1·0°. (c) Side view of tecyclen.

Table 4. *Conformations of the five-membered rings*

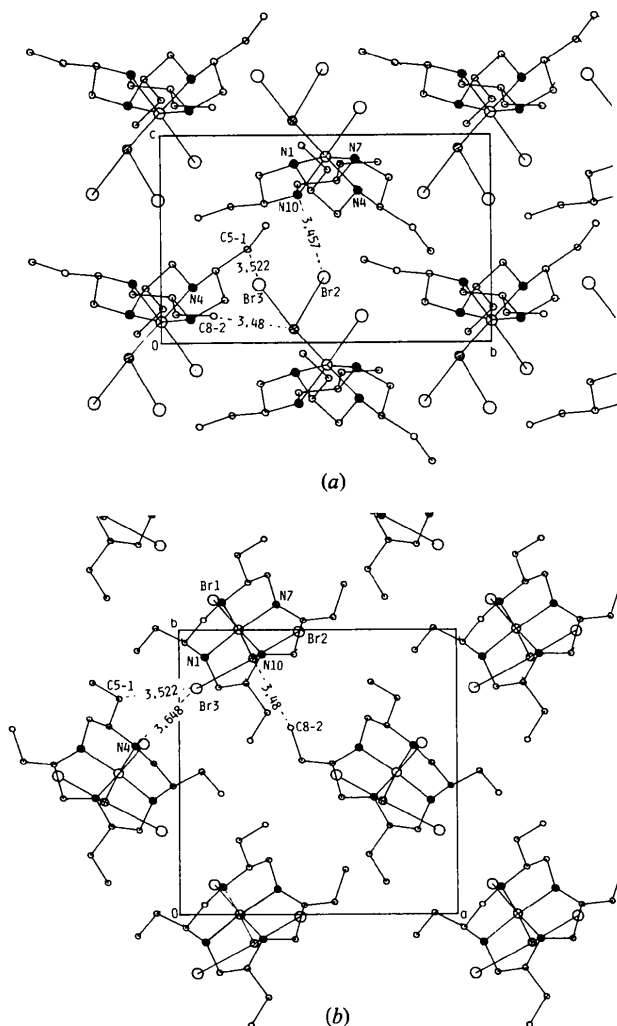| Ring	Conformation	Pseudorotation angle P [in units of $(2\pi/20)$ radian]	
		Present complex	Cyclen
0·57 Å C(3), N(4)--------Co---C(2)—N(1)	^3E (ε)	0	1
0·37 Å C(5), N(7)--------Co--------N(4), C(6), −0·32 Å	^4_3T (λ)	10	10
0·42 Å N(10), Co--------N(7)--------C(8), C(9), −0·39 Å	^9_8T (δ)	12	12
0·43 Å N(1), Co--------N(10)--------C(11), C(12), −0·29 Å	$^{12}_{11}T$ (δ)	18	12

(a)

(b)

Fig. 4. Views of the packing of the crystal structure. (a) a-axis projection; (b) c-axis projection.

the five-membered-ring conformation is expressed as given in Table 4. The main difference from cyclen is again found to involve the ring including C(11), C(12).

Thus, the basic conformation of tecyclen is similar to that of cyclen, but it is deformed in order to avoid the repulsion between the C(11) ethyl group and the O···Br(3) ligand.

The electronic, circular dichroism and NMR spectra in methanol and water reveal high dependency on the solvent used. The latter two spectra also show time dependency. These behaviors may be based on the fact that the coordinated anion or water can be partially replaced by another unidentate ligand. The above assumption is supported by the result of molecular-weight measurement in methanol 72 h after dissolution

$\{M_r$ (measured) $= 295 \cdot 3$; this value corresponds to that of one half of the formulation $[CoBr_2$-(tecyclen)]$^+$.Br$^-$ (Tsuboyama, Tsuboyama, Sakurai & Uzawa, 1980)$\}$.

The packing of the complex in the crystal is shown in Fig. 4. There are no particularly short intermolecular distances. The main interactions are between Br(2) and C(9), N(10) of the molecule translated along the c axis, and between Br(3) and C(5)1, N(4) of the screw-related molecule.

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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