

than indicated, or whether the process of recrystallization converts the *cis* form to the *trans* form.

We thank the Natural Science and Engineering Research Council of Canada, the National Cancer Institute of Canada, McMaster University Science and Engineering Research Board and Johnson Matthey, Mallory Ltd for financial support of this work.

### References

- BARNES, J. C., IBALL, J. & WEAKLEY, T. J. R. (1975). *Acta Cryst.* **B31**, 1435–1437.
- BRADDOCK, P. D., CONNORS, T. A., JONES, M., KHOKHAR, A. R., MELZACK, D. H. & TOBE, M. L. (1975). *Chem.-Biol. Interact.* **11**, 145–161.
- CONNORS, T. A., JONES, M., ROSS, W. C. J., BRADDOCK, P. D., KHOKHAR, A. R. & TOBE, M. L. (1972). *Chem.-Biol. Interact.* **5**, 415–424.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, pp. 149–150. Birmingham: Kynoch Press.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A, pp. 72ff. Birmingham: Kynoch Press.
- FAGGIANI, R., LOCK, C. J. L., SPERANZINI, R. A. & TURNER, G. (1976). Abstr. Chem. Inst. Canada Annu. Conf., London, Ontario, June 1976, p. 25.
- HUGHES, R. P., KRISHNAMACHARI, N., LOCK, C. J. L., POWELL, J. & TURNER, G. (1977). *Inorg. Chem.* **16**, 314–319.
- IBALL, J., MACDOUGALL, M. & SCRIMGEOUR, S. N. (1975). *Acta Cryst.* **B31**, 1672–1674.
- IBALL, J. & SCRIMGEOUR, S. N. (1977). *Acta Cryst.* **B33**, 1194–1196.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- LIPPERT, B., LOCK, C. J. L., ROSENBERG, B. & ZVAGULIS, M. (1977). *Inorg. Chem.* **16**, 1525–1529.
- LOCK, C. J. L. & PILON, P. (1980). *Acta Cryst.* In the press.
- LOCK, C. J. L. & ZVAGULIS, M. (1980a). *Acta Cryst.* In the press.
- LOCK, C. J. L. & ZVAGULIS, M. (1980b). In preparation.
- MILBURN, G. H. W. & TRUTER, M. R. (1966). *J. Chem. Soc. A*, pp. 1609–1616.
- ROSENBERG, B. (1976). Private communication.
- ROSENBERG, B., VANCAMP, L., TROSKO, J. E. & MANSOUR, V. H. (1969). *Nature (London)*, **222**, 385–386.
- SLATER, T. F., AHMED, M. & IBRAHIM, S. A. (1977). *J. Clin. Hemat. Oncol.* **7**, 534–546.
- SRIVASTAVA, R. C., FROELICH, J. & EICHHORN, G. L. (1978). *Biochimie*, **60**, 879–891.
- STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- ZANOTTI, G., DEL PRA, A., BOMBIERI, G. & TAMBURRO, A. M. (1978). *Acta Cryst.* **B34**, 2138–2141.

*Acta Cryst.* (1980). **B36**, 1793–1797

## The Structure of the Cytosine–Calcium Chloride (1 : 1) Complex. The First Evidence for Direct Binding of Calcium to Cytosine Base

BY KEIZO OGAWA, MIYOKO KUMIHASHI AND KEN-ICHI TOMITA

*Faculty of Pharmaceutical Sciences, Osaka University, Yamada-kami, Suita, Osaka 565, Japan*

AND SYOICHI SHIROTAKE

*Faculty of Pharmaceutical Sciences, Chiba University, Yayoicho, Chiba, Chiba 260, Japan*

(Received 31 October 1979; accepted 10 March 1980)

### Abstract

The crystal structure of  $[\text{Ca}(\text{C}_4\text{H}_5\text{N}_3\text{O})\text{Cl}_2] \cdot \text{H}_2\text{O}$  was determined by X-ray diffraction. The complex crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 7.410$  (1),  $b = 16.152$  (2),  $c = 8.351$  (1) Å,  $\beta = 107.60$  (2)° and  $Z = 4$ . The final  $R$  value is 0.070. The  $\text{Ca}^{2+}$  cation is in a pentagonal-bipyramidal environment and is coordinated in the basal plane by two Cl atoms, the N(3) and O(2) atoms of a cytosine base, and

the O(2) atom of an adjacent cytosine base. The axial sites are occupied by a Cl atom and an  $\text{H}_2\text{O}$  molecule. A one-dimensional polymer parallel to the  $c$  axis is generated by cross-linking through  $\text{Ca}-\text{Cl}-\text{Ca}$  and  $\text{Ca}-\text{O}(2)-\text{Ca}$  bridges and two hydrogen bonds,  $\text{N}(4)-\text{H}\cdots\text{Cl}$  and  $\text{N}(1)-\text{H}\cdots\text{Cl}$ , together with direct coordination between Ca and the cytosine bases on the basal plane. The molecular packing is stabilized by base stacking and two  $\text{O}(W)-\text{H}\cdots\text{Cl}$  hydrogen bonds between adjacent one-dimensional polymeric units.

## Introduction

The interactions of biomolecules with metal ions are of great interest in studies on the biological functions of metal ions, especially the alkali and alkaline-earth metals because of their abundant distribution in living bodies. It is known that metal ions can possess a dual action when they interact with nucleic acids; the alkali and alkaline-earth metal ions interact with the negatively charged phosphate group, resulting in the stabilization of the DNA or RNA structure, but several metal ions, including some transition metals, are able to interact with both the phosphate and base moieties, which may cause destabilization of the nucleic acid structure (Eichhorn, 1962). Kinetic studies have been carried out which show that the  $\text{Ca}^{2+}$  cation may selectively bind to the GC-rich DNA fragment (Eichhorn & Shin, 1968), but there is no evidence as to whether the  $\text{Ca}^{2+}$  ion can directly bind to the base moiety.

This paper deals with the X-ray analysis of the title complex crystal, which clearly shows the first evidence of  $\text{Ca}^{2+}$  binding to the cytosine base.

## Experimental

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was added to an aqueous solution of cytosine and the mixture was stirred and heated at 353 K. The mixture was allowed to stand in a thermostat and colorless plate-like crystals were obtained (Shirotake, 1980).

Preliminary X-ray photographs showed the crystal to be monoclinic with the space group  $P2_1/c$ . The density, measured by flotation using a carbon tetrachloride-1,2-dibromoethane mixture, together with the elemental analysis, suggested that a cytosine, a calcium chloride and a water molecule are contained in the asymmetric unit.

The crystal, of  $0.25 \times 0.15 \times 0.35$  mm, was hygroscopic and was therefore sealed in a glass capillary. Three-dimensional intensity data were collected on a Rigaku four-circle diffractometer using

Table 1. *Crystal data*

Formula	$[\text{Ca}(\text{C}_4\text{H}_5\text{N}_3\text{O})\text{Cl}_2] \cdot \text{H}_2\text{O}$
$M_r$	240.10
Crystal system	Monoclinic
$a$	7.410 (1) Å
$b$	16.152 (2)
$c$	8.351 (1)
$\beta$	107.60 (2)°
$V$	952.8 (2) Å <sup>3</sup>
Space group	$P2_1/c$
$Z$	4
$D_m$	1.658 (11) Mg m <sup>-3</sup>
$D_x$	1.674
$\mu(\text{Cu } K\alpha)$	10.4 mm <sup>-1</sup>

Table 2. *The final atomic coordinates with their estimated standard deviations in parentheses*

	$x$	$y$	$z$	$B_{\text{eq}}$ (Å <sup>2</sup> )
Ca	0.1742 (1)	0.2769 (1)	0.1933 (1)	1.136
Cl(1)	0.1942 (2)	0.1404 (1)	0.4024 (2)	2.714
Cl(2)	-0.2040 (2)	0.3062 (1)	0.0994 (2)	2.230
N(1)	0.2343 (8)	0.4572 (3)	0.5891 (6)	2.590
C(2)	0.2109 (7)	0.4012 (3)	0.4723 (6)	1.485
O(2)	0.1828 (6)	0.3259 (2)	0.4886 (5)	2.149
N(3)	0.2164 (7)	0.4253 (3)	0.3103 (6)	1.728
C(4)	0.2440 (9)	0.5052 (4)	0.2842 (8)	2.129
N(4)	0.2520 (9)	0.5264 (3)	0.1328 (7)	3.131
C(5)	0.2649 (10)	0.5664 (4)	0.4115 (8)	2.647
C(6)	0.2599 (10)	0.5394 (4)	0.5624 (8)	2.780
O(W)	0.5039 (6)	0.2697 (3)	0.2838 (6)	3.481
H(1)	0.22 (1)	0.435 (5)	0.71 (1)	
H(4a)	0.24 (1)	0.479 (5)	0.04 (1)	
H(4b)	0.27 (1)	0.582 (6)	0.11 (1)	
H(5)	0.29 (1)	0.630 (5)	0.39 (1)	
H(6)	0.27 (1)	0.579 (5)	0.67 (1)	
H(Wa)	0.55 (1)	0.244 (5)	0.38 (1)	
H(Wb)	0.61 (1)	0.296 (5)	0.25 (1)	

Table 3. *Bond distances (Å) and angles (°) with their estimated standard deviations in parentheses*

Ca-Cl(1)	2.793 (2)	Ca-Cl(2)	2.714 (2)
Ca-O(2)	2.572 (5)	Ca-N(3)	2.571 (5)
Ca-O(W)	2.332 (6)	Ca-Cl(1)*	2.818 (2)
Ca-O(2)*	2.398 (5)	N(1)-C(2)	1.363 (8)
N(1)-C(6)	1.369 (10)	C(2)-O(2)	1.264 (7)
C(2)-N(3)	1.340 (7)	N(3)-C(4)	1.335 (8)
C(4)-N(4)	1.329 (9)	C(4)-C(5)	1.425 (10)
C(5)-C(6)	1.344 (10)	N(1)-H(1)	1.07 (8)
N(4)-H(4a)	1.06 (8)	N(4)-H(4b)	0.95 (9)
C(5)-H(5)	1.08 (9)	C(6)-H(6)	1.06 (8)
O(W)-H(Wa)	0.85 (8)	O(W)-H(Wb)	1.03 (10)
Cl(1)-Ca-Cl(2)	100.00 (6)	Cl(1)-Ca-O(2)	70.3 (1)
Cl(1)-Ca-N(3)	121.5 (1)	Cl(1)-Ca-O(W)	84.6 (1)
Cl(1)-Ca-Cl(1)*	155.38 (7)	Cl(1)-Ca-O(2)*	83.7 (1)
Cl(2)-Ca-O(2)	87.0 (1)	Cl(2)-Ca-N(3)	86.8 (1)
Cl(2)-Ca-O(W)	172.6 (1)	Cl(2)-Ca-Cl(1)*	89.25 (6)
Cl(2)-Ca-O(2)*	99.4 (1)	O(2)-Ca-N(3)	52.0 (2)
O(2)-Ca-O(W)	89.1 (1)	O(2)-Ca-Cl(1)*	133.4 (1)
O(2)-Ca-O(2)	153.9 (2)	N(3)-Ca-O(W)	85.9 (2)
N(3)-Ca-Cl(1)*	81.5 (1)	N(3)-Ca-O(2)*	152.9 (2)
O(W)-Ca-Cl(1)*	88.9 (1)	O(W)-Ca-O(2)*	86.9 (2)
Cl(1)*-Ca-O(2)*	72.3 (1)	Ca-Cl(1)*-Ca*	98.95 (7)
Ca-O(2)-C(2)	95.0 (3)	Ca-N(3)-C(2)	93.1 (3)
Ca-N(3)-C(4)	147.8 (4)	Ca-O(2)*-Ca*	98.95 (7)
Ca-O(2)*-C(2)*	146.3 (4)	C(2)-N(1)-C(6)	120.6 (6)
N(1)-C(2)-O(2)	119.5 (5)	N(1)-C(2)-N(3)	120.7 (5)
O(2)-C(2)-N(3)	119.8 (5)	C(2)-N(3)-C(4)	119.0 (5)
N(3)-C(4)-N(4)	117.2 (6)	N(3)-C(4)-C(5)	122.4 (6)
N(4)-C(4)-C(5)	120.3 (6)	C(4)-C(5)-C(6)	116.6 (7)
C(5)-C(6)-N(1)	120.7 (7)	C(2)-N(1)-H(1)	118 (4)
C(6)-N(1)-H(1)	121 (4)	C(4)-N(4)-H(4a)	118 (5)
C(4)-N(4)-H(4b)	122 (6)	H(4a)-N(4)-H(4b)	120 (7)
C(4)-C(5)-H(5)	123 (5)	C(6)-C(5)-H(5)	120 (5)
C(5)-C(6)-H(6)	123 (4)	N(1)-C(6)-H(6)	116 (4)
H(Wa)-O(W)-H(Wb)	109 (8)		

\* Atoms at the position  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ .

Ni-filtered  $\text{Cu } K\alpha$  radiation. With the  $\omega$ - $2\theta$  scan technique, a scan speed of  $4^\circ \text{ min}^{-1}$  ( $2\theta$ ) and 10 s background measurements at each end of the scan, the intensities of 1280 independent non-zero reflections were measured in the range  $\sin \theta/\lambda < 0.57 \text{ \AA}^{-1}$ . The

crystallographic data are given in Table 1. Because of the large linear absorption coefficient of the crystal and the use of a glass capillary, an absorption correction (Furnas, 1957) was applied.

### Structure determination and refinement

The structure was solved by the heavy-atom method and refined first by a full-matrix least-squares method with isotropic temperature factors for all non-hydrogen atoms. Six reflections having large discrepancies between  $F_o$  and  $F_c$ , probably due to extinction, were omitted from the refinement. All the H atoms were located from a difference Fourier map. The final refinement was made by a block-diagonal least-squares procedure with anisotropic temperature factors for all the non-hydrogen atoms and isotropic ones for all the H atoms; the following weighting scheme was used:  $w = 0.0$  for  $F_o = 0.0$ , and  $w = \{[\sigma(|F_o|)]^2 + 0.103|F_o| + 0.03|F_o|^2\}^{-1}$  for  $F_o > 0.0$ . Neutral-atom scattering factors were used for Ca and Cl. The final  $R$  value is 0.070 for 1274 independent non-zero reflections. All the calculations were carried out on an ACOS Series NEAC ACOS-700 computer of the Crystallographic Research Center, Institute for Protein Research, Osaka University.

### Result and discussion

The final positional parameters are listed in Table 2.\* The bond distances and angles are given in Table 3.

#### Ca<sup>2+</sup> coordination sphere

The Ca<sup>2+</sup> cation is in a pentagonal-bipyramidal environment; it is coordinated in the basal plane by two Cl atoms related by the  $c$ -glide symmetry, Cl(1) and

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35271 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

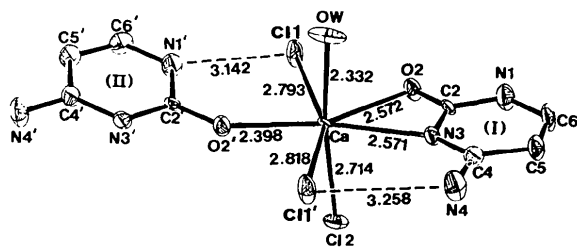


Fig. 1. The coordination geometry around the Ca<sup>2+</sup> ion together with bond distances (Å) and interligand hydrogen bonds (Å) shown by dashed lines. Primes indicate atoms at the position  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$  translated by the  $c$ -glide symmetry.

Cl(1)', the N(3) and O(2) atoms of a cytosine base and the O(2)' atom of an adjacent cytosine base, as shown in Fig. 1. Therefore, the O(2) of one cytosine base is coordinated to two Ca<sup>2+</sup> ions through a lone-electron pair. The two axial positions are occupied by the Cl(2) and the water oxygen atom O(W). As shown in Table 3, the Cl(2)–Ca–O(2)' angle (99.4°) deviates considerably from a right-angle, indicating that the Cl(2) position is shifted from an apex of a regular pentagonal bipyramid. Such a coordination geometry around the Ca<sup>2+</sup> ion was also observed in CaHPO<sub>4</sub> (MacLennan & Beevers, 1955) and Ca–5'-TMP (Trueblood, 1961).

A classification of the possible binding mode of a metal ion ( $M$ ) with base atoms in cytosine, cytidine and CMP under various conditions could be considered as follows: (1) unidentate binding,  $M-N(3)$ , (2) unidentate binding,  $M-O(2)$ , and (3) bidentate binding,  $M \begin{smallmatrix} \swarrow N(3) \\ \searrow O(2) \end{smallmatrix}$ . Most of the structures of metal complexes so far determined by X-rays belong to category (3), except for [Pt{1-( $\beta$ -D-arabinofuranosyl)cytosine}(ethylenediamine)Cl] (Neidle, Taylor & Robins, 1978), *trans*-[Pt(cytosine)(Me<sub>2</sub>SO)Cl<sub>2</sub>] (Melanson & Rochon, 1977), and *cis*-[Pt(3'-CMP)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] (Wu & Bau, 1979) which belong to category (1), and [Ag(1-methylcytosine)(NO<sub>3</sub>)] (Marzilli, Kistenmacher & Rossi, 1977) and [Mn(5'-CMP)(H<sub>2</sub>O)]<sub>n</sub> (Aoki, 1976) in category (2). In the present Ca complex, the Ca<sup>2+</sup> ion binds to the cytosine base through Ca–O(2)' and Ca  $\begin{smallmatrix} \swarrow N(3) \\ \searrow O(2) \end{smallmatrix}$ , *i.e.* the binding mode belongs to two

Table 4. *Least-squares planes, deviations of atoms and dihedral angles between the planes*

In each equation  $X$ ,  $Y$  and  $Z$  are the coordinates (Å) referred to the orthogonal axes  $a$ ,  $b$  and  $c^*$ .

Plane 1: basal plane around the Ca<sup>2+</sup> ion

$$\text{Plane equation: } 0.9561X - 0.0161Y + 0.2972Z - 1.2912 = 0.0$$

Cl(1)	0.014 (3) Å	O(2)	-0.122 (5) Å
N(3)	0.105 (6)	Cl(1) <sup>a</sup>	-0.001 (3)
O(2) <sup>a</sup>	-0.040 (5)	Ca <sup>b</sup>	-0.146 (2)

Plane 2: cytosine molecule at  $(x, y, z)$

$$\text{Plane equation: } 0.9482X - 0.1462Y + 0.2822Z - 0.4711 = 0.0$$

N(1)	0.008 (7) Å	C(2)	-0.006 (7) Å
O(2) <sup>b</sup>	-0.029 (8)	N(3)	-0.001 (6)
C(4)	0.008 (8)	N(4) <sup>b</sup>	0.037 (10)
C(5)	-0.008 (9)	C(6)	-0.993 (9)

Plane 3: cytosine molecule at  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$

$$\text{Plane equation: } 0.9482X + 0.1462Y + 0.2822Z - 1.7259 = 0.0$$

Dihedral angles

Between plane 1 and plane 2	7.5 (1)°
Between plane 1 and plane 3	16.8 (2)
Between plane 2 and plane 3	9.3 (2)

(a) Atoms excluded from the plane calculation.

(b) Atoms at the position  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ .

categories, (2) and (3), which is the first such case observed for metal-cytosine complexes. Moreover, in all metal-cytosine complexes belonging to category (3), the metal-ligand distance,  $M-N(3)$ , is shorter than the  $M-O(2)$  distance, but in this complex, the  $Ca-N(3)$  and  $Ca-O(2)$  distances are almost equal.

The equations of the least-squares planes are given in Table 4. The five atoms occupying the basal plane of the pentagonal bipyramid are almost in a plane, but the  $Ca^{2+}$  cation deviates slightly towards the apical  $Cl(2)$  atom (0.146 Å). The dihedral angle between two cytosine rings related by the  $c$ -glide is  $16.8 (2)^\circ$ .

One example of a metal-nucleotide complex having a pentagonal-bipyramidal coordination geometry was reported in  $Cd-5'$ -CMP (Shiba & Bau, 1978), in which the  $N(3)$  and  $O(2)$  atoms of the cytosine base moiety occupy the basal positions along with three phosphate O atoms, and the binding mode belongs to category (3).

Provided that the two different binding modes of  $Ca^{2+}$  with cytosine observed in this complex may also occur in  $Ca$ -polynucleotide interactions, the bidentate chelation by  $N(3)$  and  $O(2)$  might be found in the interaction of  $Ca^{2+}$  with a single-stranded DNA or RNA, and the unidentate binding through  $O(2)$  might stabilize the GC-rich regions of a double-stranded polynucleotide *via* bridges between two chains, in a similar manner to the  $Na^+$  ion in the ApU structure (Seeman, Rosenberg, Suddath, Kim & Rich, 1976).

Two nucleotide structures containing the  $Ca^{2+}$  ion have been solved,  $Ca-GpC$  (Hingerty, Subramanian, Stellman, Sato, Broyde & Langridge, 1976) and  $Ca-5'$ -TMP (Trueblood, 1961), but in these cases the  $Ca^{2+}$  cation binds to the phosphate moiety as a counterion. Therefore, the present complex is the first example of direct binding of  $Ca^{2+}$  to cytosine base.

There are two interligand  $N-H \cdots Cl$  hydrogen bonds, as shown in Fig. 1 and Table 5, of which the  $N(4)-H \cdots Cl$  bond formation was predicted from PMR spectra (Shirotake, 1980).

### Cytosine molecule

The bond angles are normal in comparison with those in cytosine monohydrate (Jeffrey & Kinoshita, 1963; Neidle, 1976). On the other hand, the  $C(2)-N(3)$  and  $C(4)-N(4)$  bonds are slightly shorter and the  $C(2)-O(2)$  and  $N(1)-C(6)$  bonds slightly longer than those in cytosine monohydrate. However, considering the structural features of the cytosine or cytosinium rings found in cytosinium hemitetrachlorozincate-cytosine and dicytosinium tetrachlorocuprate (Ogawa, Nishitani, Fujiwara, Shirotake & Tomita, 1979; Fujinami, Ogawa, Arakawa, Shirotake, Fujii & Tomita, 1979), the cytosine molecule in this complex can be assumed to be in the neutral form. The longer  $C(2)-O(2)$  distance (1.264 Å) may be due to the coordination of  $O(2)$  to two  $Ca^{2+}$  ions. Except for the

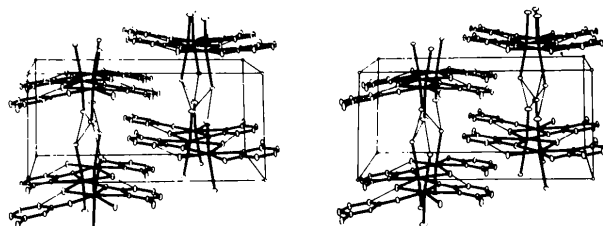


Fig. 2. A stereoscopic view of the molecular packing. Thin lines indicate hydrogen bonds. The origin of the coordinate system lies at the upper-left back corner. The positive  $a$  axis is down the page. The positive  $b$  axis runs towards the right and the  $c$  axis towards the reader.

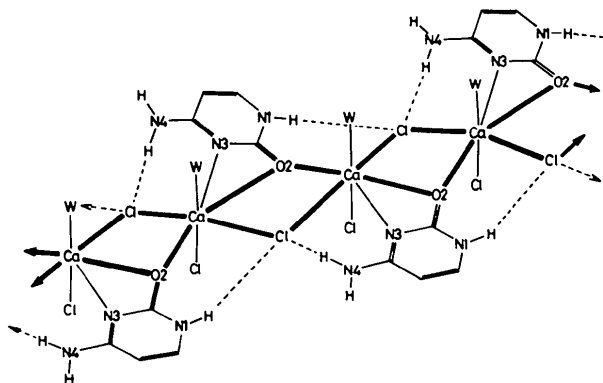


Fig. 3. A schematic representation of the linearly polymerized complex molecules.

Table 5. *Hydrogen bonds*

Donors (D)—H	Acceptors (A)	$D \cdots A$	$A \cdots H$	$\angle DHA$
$N(1)-H(1)$	$Cl(1)^a$	3.142 (6) Å	2.10 (8) Å	164 (6)°
$N(4)-H(4a)$	$Cl(1)^b$	3.258 (7)	2.22 (8)	166 (7)
$O(W)-H(Wa)$	$Cl(2)^c$	3.112 (6)	2.33 (8)	152 (7)
$O(W)-H(Wb)$	$Cl(2)^d$	3.069 (6)	2.11 (10)	154 (8)

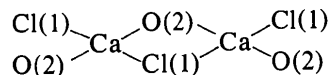
Symmetry operations for acceptors

- (a)  $x, \frac{1}{2} - y, \frac{1}{2} - z$       (c)  $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$   
 (b)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$       (d)  $1 + x, y, z$

exocyclic atoms,  $O(2)$  and  $N(4)$ , all the atoms in the cytosine ring lie approximately in a plane, as shown in Table 4.

### Crystal structure

A stereoview of the molecular packing is shown in Fig. 2. The complex units related by the  $c$ -glide symmetry are joined together by polymeric bridges formed through  $O(2)$  and  $Cl(1)$ ; *i.e.* as shown in Fig. 3, the unit forms a



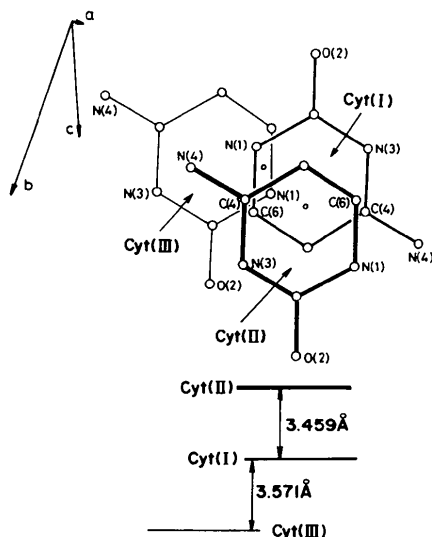


Fig. 4. The stacking of the cytosine molecules. The symmetry operations for Cyt(I), Cyt(II) and Cyt(III) are  $(x, y, z)$ ,  $(-x, 1 - y, 1 - z)$  and  $(1 - x, 1 - y, 1 - z)$ , respectively.

chain parallel to the  $c$  axis. The apical Cl(2) and water oxygen O(W) form O(W)—H...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).

*Acta Cryst.* (1980). B36, 1797–1801

## The Structure of *cis*-(SSSR)-{Bromo[dibromoqua(2-)][(2*R*,5*R*,8*R*,11*R*)-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*

(Received 17 December 1979; accepted 25 February 1980)

### Abstract

[CoBr(Br<sub>2</sub>H<sub>2</sub>O)(C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>)], monoclinic,  $P2_1$ ,  $a = 12.089$  (10),  $b = 12.384$  (14),  $c = 7.698$  (5) Å,  $\beta = 95.59$  (7)°,  $U = 1147$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.72$ ,  $D_c = 1.740$  (3) Mg m<sup>-3</sup>. The structure was refined to a final  $R$  of 4.2%. The 12-membered tetramine ring is coordinated to Co<sup>III</sup> 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

0567-7408/80/081797-05\$01.00

### References

- AOKI, K. (1976). *J. Chem. Soc. Chem. Commun.* pp. 748–749.
- EICHHORN, G. L. (1962). *Nature (London)*, **194**, 474–475.
- EICHHORN, G. L. & SHIN, Y. A. (1968). *J. Am. Chem. Soc.* **90**, 7323–7328.
- FUJINAMI, F., OGAWA, K., ARAKAWA, Y., SHIROTAKE, S., FUJII, S. & TOMITA, K. (1979). *Acta Cryst.* **B35**, 968–970.
- FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. General Electric Co., Milwaukee.
- HINGERTY, B., SUBRAMANIAN, E., STELLMAN, S. D., SATO, T., BROYDE, S. B. & LANGRIDGE, R. (1976). *Acta Cryst.* **B32**, 2998–3013.
- JEFFREY, G. A. & KINOSHITA, Y. (1963). *Acta Cryst.* **16**, 20–28.
- MACLENNAN, G. & BEEVERS, C. A. (1955). *Acta Cryst.* **8**, 579–583.
- MARZILLI, L. G., KISTENMACHER, T. J. & ROSSI, M. (1977). *J. Am. Chem. Soc.* **99**, 2797–2798.
- MELANSON, R. & ROCHON, F. D. (1977). *Inorg. Chem.* **17**, 679–681.
- NEIDLE, S. (1976). *Acta Cryst.* **B32**, 2050–2053.
- NEIDLE, S., TAYLOR, G. L. & ROBINS, A. B. (1978). *Acta Cryst.* **B34**, 1838–1841.
- OGAWA, K., NISHITANI, K., FUJIWARA, T., SHIROTAKE, S. & TOMITA, K. (1979). *Acta Cryst.* **B35**, 965–967.
- SEEMAN, N. C., ROSENBERG, J. M., SUDDATH, F. L., KIM, J. J. P. & RICH, A. (1976). *J. Mol. Biol.* **104**, 109–144.
- SHIBA, J. K. & BAU, R. (1978). *Inorg. Chem.* **17**, 3484–3488.
- SHIROTAKE, S. (1980). *Chem. Pharm. Bull.* In preparation.
- TRUEBLOOD, K. N. (1961). *Acta Cryst.* **14**, 965–982.
- WU, S. & BAU, R. (1979). *Biochem. Biophys. Res. Commun.* **88**, 1435–1442.

1*S*, 4*S*, 7*S* and 10*R*. The complex formed can be written as *cis*- $\Lambda\Lambda(-)_{589}$ -(SSSR)-[CoBr(OH<sub>2</sub>...Br<sub>2</sub>)-(2*R*,5*R*,8*R*,11*R*-Et<sub>4</sub>-[12]-ane-1,4,7,10-N<sub>4</sub>) $\epsilon\lambda\delta\delta$ ].

### 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 &

© 1980 International Union of Crystallography