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The Crystal Structure of (–)₅₈₉-Bis[(*S,S*)-*trans*-1,2-diaminocyclohexane]-(*R,R*)-*trans*-1,2-diaminocyclohexanecobalt(III) Chloride Pentahydrate

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Crystals of the title compound are hexagonal, space group $P6_1$ with $a = 12.472(1)$, $c = 32.594(2)$ Å and $Z = 6$. The crystal structure has been refined by block-diagonal least-squares calculations to an R value of 0.040 on the basis of 2595 independent reflexions collected by diffractometry. The crystal structure resembles that of the chloride pentahydrate of the lel_3 -isomer. The complex ion takes the lel_3ob conformation, and has an approximate twofold axis of rotation through the central Co atom and bisecting the C–C bond in the ob chelate ring. All the bond distances and angles are normal: the mean Co–N distance is 1.972(5) Å and the mean N–Co–N angle in the chelate ring is 84.5(2)°. The absolute configuration of the complex ion can be designated as $A(\delta\delta\lambda)$ according to the IUPAC convention. The plane formed by Co and two N atoms of the ob ring is inclined at an angle of 35.7° with respect to the pseudo threefold axis of the complex ion, which is larger by about 4° than that of the lel_3 -isomer as well as the ob_3 -isomer. Such a large inclination may be ascribed to the non-bonded H–H interaction between the lel and ob -chelate rings.

Introduction

The isomers of the tris[(±)-*trans*-1,2-diaminocyclohexane]cobalt(III) ion consist of two catoptric series with absolute configurations A and Δ around the Co atom. For each of the configurational series there exist four diastereoisomers: lel_3 , lel_2ob , ob_2lel and ob_3 . These eight isomers were recently isolated and characterized (Harnung, Sørensen, Creaser, Maegaard, Pfenninger & Schäffer, 1976). The crystal structures of the A - lel_3 and A ob_3 -isomers are already reported (Marumo, Utsumi & Saito, 1970; Kobayashi, Marumo & Saito, 1972). This paper deals with the crystal structure of the chloride pentahydrate of the A - lel_2ob -isomer.

Experimental

Crystals were kindly provided by Dr S. E. Harnung. They are orange-red hexagonal bipyramids.

Crystal data: (–)₅₈₉-(lel_2ob)-[Co(chxn)₃]Cl₃·5H₂O. C₁₈H₅₂N₆O₅CoCl₃, F.W. 597.9. Hexagonal, $a = 12.472(1)$, $c = 32.594(2)$ Å, $U = 4391.0$ Å³, $D_m = 1.35$ (floatation, benzene/carbon tetrachloride), $D_x = 1.36$ g cm⁻³, $Z = 6$, μ for Mo $K\alpha$ ($\lambda = 0.7107$ Å) = 9.16 cm⁻¹, space group $P6_1$ (No. 169).

Intensity data were collected on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation monochromated by a graphite plate. A crystal specimen was approximately shaped into a sphere of

Table 1. *Final atomic parameters*

Positional parameters are given as fractional coordinates $\times 10^4$: for H $\times 10^3$. The U_{ij} 's are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots) \times 10^{-3}]$.
 The isotropic temperature factor is defined by $\exp[-8\pi^2U(\sin \theta/\lambda)^2]$. Mean value of U for the hydrogen atoms is 0.05(2) Å².

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	7059 (1)	3678 (1)	0 (0)	25 (0)	27 (0)	26 (0)	12 (0)	1 (0)	0 (0)
N(1)	5864 (4)	2159 (4)	-283 (1)	37 (2)	32 (2)	29 (2)	18 (2)	3 (2)	-4 (2)
N(2)	6709 (4)	4668 (4)	-388 (1)	30 (2)	33 (2)	26 (2)	14 (2)	-4 (2)	-6 (2)
N(3)	8439 (4)	3786 (4)	-331 (1)	33 (2)	35 (2)	28 (2)	18 (2)	4 (2)	7 (2)
N(4)	5641 (4)	3381 (4)	348 (1)	34 (2)	41 (2)	30 (2)	18 (2)	6 (2)	-2 (2)
N(5)	8167 (4)	5289 (4)	262 (1)	30 (2)	32 (2)	30 (2)	18 (2)	-5 (2)	-2 (2)
N(6)	7528 (4)	2775 (4)	394 (1)	39 (2)	33 (2)	36 (2)	19 (2)	5 (2)	-1 (2)
C(1)	4589 (5)	1831 (5)	-159 (2)	30 (3)	36 (3)	37 (3)	13 (2)	1 (2)	-2 (2)
C(2)	3603 (5)	526 (5)	-277 (2)	40 (3)	40 (3)	56 (4)	11 (3)	-5 (3)	9 (3)
C(3)	2342 (5)	242 (6)	-108 (2)	35 (3)	51 (4)	94 (6)	11 (3)	-3 (3)	-5 (4)
C(4)	2408 (6)	504 (6)	346 (2)	36 (3)	49 (4)	103 (6)	13 (3)	27 (4)	3 (4)
C(5)	3379 (6)	1812 (6)	458 (2)	45 (3)	47 (3)	70 (4)	24 (3)	22 (3)	1 (3)
C(6)	4641 (5)	2087 (5)	290 (2)	36 (3)	36 (3)	49 (3)	15 (2)	9 (2)	4 (3)
C(7)	8776 (5)	2872 (5)	-173 (2)	36 (3)	32 (3)	40 (3)	19 (2)	2 (2)	6 (2)
C(8)	10021 (5)	3068 (6)	-332 (2)	40 (3)	52 (4)	57 (4)	27 (3)	20 (3)	20 (3)
C(9)	10306 (6)	2143 (7)	-127 (2)	54 (4)	71 (4)	82 (5)	48 (4)	22 (4)	22 (4)
C(10)	10282 (6)	2217 (6)	337 (2)	54 (4)	57 (4)	74 (5)	34 (3)	0 (3)	19 (4)
C(11)	9056 (5)	2042 (5)	494 (2)	46 (3)	47 (3)	43 (3)	24 (3)	4 (3)	14 (3)
C(12)	8768 (4)	2958 (4)	288 (2)	30 (3)	26 (2)	37 (3)	12 (2)	-2 (2)	3 (2)
C(13)	7166 (5)	5933 (5)	-224 (2)	38 (3)	34 (3)	38 (3)	19 (2)	-2 (2)	2 (2)
C(14)	7245 (5)	6867 (5)	-537 (2)	46 (3)	40 (3)	36 (3)	26 (3)	-5 (2)	2 (2)
C(15)	7800 (6)	8146 (5)	-338 (2)	76 (5)	40 (3)	55 (4)	38 (3)	-4 (3)	8 (3)
C(16)	9042 (6)	8517 (5)	-147 (2)	64 (4)	35 (3)	66 (4)	18 (3)	-20 (3)	-1 (3)
C(17)	8954 (5)	7591 (5)	168 (2)	47 (3)	34 (3)	53 (3)	16 (3)	-8 (3)	-3 (3)
C(18)	8385 (4)	6300 (4)	-29 (2)	32 (2)	32 (3)	36 (3)	13 (2)	-2 (2)	6 (2)
Cl(1)	4026 (2)	4603 (2)	-187 (1)	55 (1)	89 (1)	152 (2)	47 (1)	12 (1)	16 (1)
Cl(2)	11135 (2)	6324 (2)	15 (1)	40 (1)	62 (1)	133 (2)	21 (1)	-10 (1)	-21 (1)
Cl(3)	5927 (2)	-250 (1)	160 (1)	55 (1)	39 (1)	54 (1)	18 (1)	-3 (1)	2 (1)
O(1)	5737 (5)	9194 (5)	-826 (1)	88 (4)	78 (4)	43 (3)	25 (3)	0 (3)	-16 (3)
O(2)	3497 (6)	6694 (6)	-499 (1)	116 (5)	101 (4)	41 (2)	48 (4)	8 (3)	12 (3)
O(3)	5508 (5)	7249 (5)	602 (2)	88 (4)	69 (3)	60 (3)	37 (3)	1 (3)	13 (3)
O(4)	3274 (4)	8281 (4)	558 (1)	62 (3)	63 (3)	48 (3)	18 (2)	1 (2)	12 (2)
O(5)	2811 (6)	5383 (5)	520 (2)	151 (6)	90 (4)	70 (4)	72 (4)	-44 (4)	-22 (3)

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
H(N1)1	591 (5)	151 (5)	-25 (2)	H(C9)2	975 (5)	141 (5)	-20 (2)
H(N1)2	591 (4)	222 (4)	-54 (1)	H(C10)1	1087 (6)	296 (6)	45 (2)
H(N2)1	596 (4)	432 (5)	-44 (1)	H(C10)2	1039 (5)	164 (5)	46 (2)
H(N2)2	704 (4)	468 (4)	-64 (1)	H(C11)1	906 (4)	223 (4)	76 (1)
H(N3)1	908 (4)	448 (4)	-33 (2)	H(C11)2	839 (4)	121 (4)	47 (1)
H(N3)2	825 (4)	364 (4)	-59 (1)	H(C12)	938 (5)	378 (5)	38 (1)
H(N4)1	584 (4)	354 (4)	58 (2)	H(C13)	662 (5)	587 (5)	0 (2)
H(N4)2	539 (5)	393 (5)	26 (2)	H(C14)1	635 (5)	651 (5)	-63 (2)
H(N5)1	787 (4)	540 (4)	48 (1)	H(C14)2	769 (4)	691 (4)	-73 (1)
H(N5)2	887 (4)	536 (4)	32 (1)	H(C15)1	725 (5)	814 (5)	-12 (2)
H(N6)1	696 (6)	200 (6)	39 (2)	H(C15)2	795 (5)	882 (5)	-52 (2)
H(N6)2	750 (5)	297 (5)	63 (2)	H(C16)1	946 (5)	923 (4)	-5 (2)
H(C1)	433 (4)	236 (4)	-30 (1)	H(C16)2	955 (5)	862 (5)	-42 (2)
H(C2)1	383 (5)	-7 (5)	-18 (2)	H(C17)1	963 (5)	782 (5)	24 (2)
H(C2)2	361 (4)	44 (4)	-55 (1)	H(C17)2	847 (4)	752 (4)	38 (1)
H(C3)1	183 (6)	-53 (6)	-17 (2)	H(C18)	889 (5)	625 (5)	-24 (2)
H(C3)2	204 (6)	71 (6)	-23 (2)	H(O1)1	567 (5)	924 (5)	-62 (2)
H(C4)1	169 (6)	31 (6)	45 (2)	H(O1)2	643 (7)	1000 (7)	-90 (2)
H(C4)2	250 (6)	-12 (6)	50 (2)	H(O2)1	292 (6)	642 (6)	-38 (2)
H(C5)1	340 (5)	179 (5)	77 (2)	H(O2)2	396 (7)	644 (8)	-46 (2)
H(C5)2	319 (4)	237 (4)	37 (1)	H(O3)1	510 (6)	683 (6)	43 (2)
H(C6)	484 (4)	154 (4)	43 (1)	H(O3)2	570 (6)	788 (5)	48 (2)
H(C7)	814 (4)	207 (4)	-25 (1)	H(O4)1	391 (5)	871 (5)	44 (2)
H(C8)1	1061 (4)	386 (4)	-27 (2)	H(O4)2	282 (6)	772 (5)	42 (2)
H(C8)2	993 (5)	292 (5)	-64 (2)	H(O5)1	219 (5)	540 (5)	47 (2)
H(C9)1	1107 (5)	226 (6)	-19 (2)	H(O5)2	290 (6)	502 (6)	36 (2)

about 0.33 mm in diameter. It was mounted nearly along the a axis on the diffractometer, the ω scan technique being employed with a scanning rate of 2° min^{-1} . Three standard reflexions were measured every 50 reflexions. They showed a slight intensity decrease of about 3% during the course of data collection owing to dehydration and radiation damage. Data were corrected for this effect and the Lorentz and polarization factors as usual. No correction was applied for absorption and extinction. Cell dimensions were derived by a least-squares method on the basis of 2θ values of 51 high-angle reflexions. 3423 independent reflexions were measured up to $2\theta = 55^\circ$, of which 2595 reflexions with $|F| > 3\sigma(|F|)$ were used for the structure determination and refinement.

Structure determination

The structure was solved by routine application of the heavy-atom method. The three-dimensional Patterson function revealed that the Co atom was situated nearly on the threefold screw axis like that in the le_3 analogue (Marumo *et al.*, 1970). All other non-hydrogen atoms could be located by successive Fourier syntheses of electron density. The structure was then refined by the least-squares method with a block-diagonal approximation, with anisotropic thermal factors. At a later stage of the refinement, at $R = 0.057$, the positions of all the H atoms were obtained from a difference Fourier synthesis. Further refinement was carried out including the H atoms with isotropic thermal factors. The final R and R_2 values were 0.040 and 0.033 respectively for all the 2595 observed reflexions. In the last cycle of the refinement, all the parameter shifts were less than one third of the corresponding standard deviations. The atomic scattering factors for all atoms and the corrections for anomalous dispersion of Co and Cl atoms were taken from *International Tables for X-ray*

Crystallography (1974). A weighting scheme, $w = 0.5$ for $|F_o| < 15$ and $w = 1.0$ for all other $|F_o|$'s, was employed. The positional and thermal parameters with their estimated standard deviations are listed in Table 1.*

Determination of the absolute configuration

In order to determine the absolute structure, Weissenberg photographs were taken around the a axis with Cu $K\alpha$ radiation up to the third layer. In Table 2 are compared the observed intensity relations and calculated intensities of hkl and $hk\bar{l}$ reflexions, which differed by more than 40%. The agreement in the table rejects the possibility of the space group $P6_3$. Accordingly the absolute configuration of the complex ion, $(-)\text{_{589}}\text{-}[\text{Co}(\text{chxn})_3]^{3+}$, can be designated in full as $A(-)\text{_{589}}\text{-}[\text{Co}\{(S,S)(+)\text{chxn}\}_2\{(R,R)(-)\text{chxn}\}\delta\delta\lambda]^{3+}$ (IUPAC, 1972), in agreement with the assignment based on a circular dichroism spectrum (Harnung *et al.*, 1976).

Description of the structure and discussion

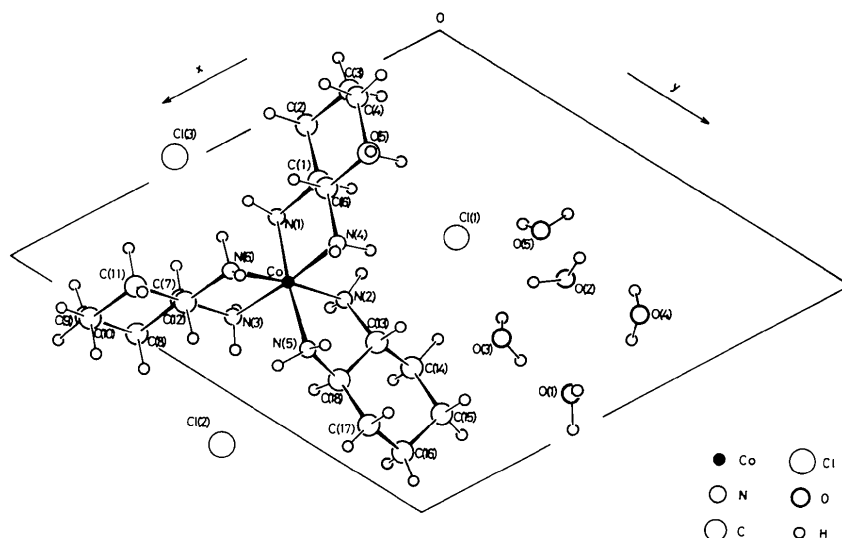
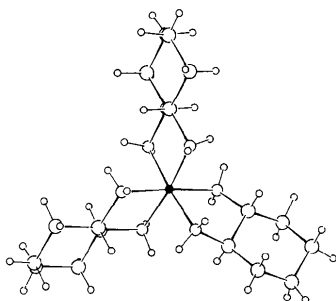
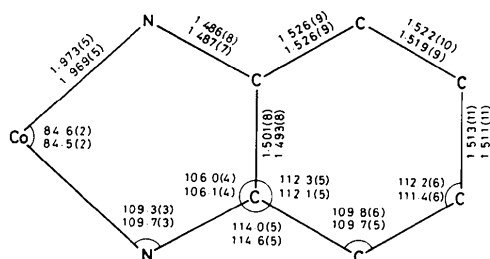
Fig. 1 shows a partial projection of the structure along c , where only one asymmetric unit is illustrated. The numbering scheme of the atoms is basically the same as that of the le_3 analogue, since the two structures are closely related. A perspective drawing of the complex ion is shown in Fig. 2, where the ion is viewed along the normal to the plane through the midpoints of the line joining the two N atoms of each ligand. Hereafter this line will be called the axis of the complex ion. Two of the C—C bonds in the chelate rings are inclined at a mean angle of 3.9° with respect to the axis of the complex ion, while the remaining one is at an angle of 64.4° . Thus the complex ion takes the ' le_2ob ' conformation. The ion has an approximately twofold axis of rotation, through the central Co atom and bisecting the C—C bond in the ob chelate ring.

The interatomic distances and bond angles within the chelate rings are listed in Table 3. Mean values of the bond lengths and angles in the ligands are presented in Fig. 3. There are no significant differences between the le_1 and ob Co—chxn moieties. The overall average values are: Co—N 1.972 (5), N—C 1.486 (7), C—C 1.498 (8) Å; N—Co—N $84.5(2)$, Co—N—C $109.4(3)$, N—C—C $106.0(4)^\circ$. The bond distances reported for the le_3 -isomer are slightly longer than those of the present work probably owing to omission of the H atoms in the former analysis.

Table 2. Observed and calculated intensity relations between some hkl and $hk\bar{l}$ reflexions

hkl	$ F_c(hkl) ^2$	Observed	$ F_c(hk\bar{l}) ^2$
0 2 2	50	<	222
0 2 3	49	<	1731
0 3 1	1436	<	2621
0 4 3	2153	>	967
0 5 3	1866	>	686
0 6 5	605	>	102
1 3 4	108	<	462
1 3 9	2992	<	5446
2 1 3	7726	>	3410
2 1 4	942	>	296
2 2 1	2520	>	1096
2 5 1	328	<	1482
3 2 3	847	>	137
3 4 2	207	<	745

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32123 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. A partial projection of the structure along *c*.Fig. 2. A perspective drawing of the complex ion, $A(-)_{389}-(lel_2ob)-[Co(chxn)_3]^{3+}$.Fig. 3. Mean bond lengths (Å) and angles (°) within the complex ion. The values are separately indicated for the ligand molecules of *lel* (upper value) and *ob* (lower value) conformations.Table 3. *Interatomic distances (Å) and bond angles (°) in the chelate rings with their standard deviations in parentheses*

Co—N(1)	1.960 (4)	N(1)—Co—N(4)	85.0 (2)
Co—N(2)	1.962 (5)	N(2)—Co—N(5)	84.3 (2)
Co—N(3)	1.979 (5)	N(3)—Co—N(6)	84.1 (2)
Co—N(4)	1.974 (5)	Average	84.5 (2)
Co—N(5)	1.975 (4)	Co—N(1)—C(1)	109.2 (4)
Co—N(6)	1.980 (5)	Co—N(2)—C(13)	110.5 (3)
Average	1.972 (5)	Co—N(3)—C(7)	109.1 (3)
N(1)—C(1)	1.488 (7)	Co—N(4)—C(6)	108.6 (4)
N(2)—C(13)	1.482 (7)	Co—N(5)—C(18)	108.9 (3)
N(3)—C(7)	1.490 (9)	Co—N(6)—C(12)	110.1 (3)
N(4)—C(6)	1.478 (6)	Average	109.4 (3)
N(5)—C(18)	1.491 (7)	N(1)—C(1)—C(6)	106.4 (4)
N(6)—C(12)	1.486 (8)	N(2)—C(13)—C(18)	105.7 (5)
Average	1.486 (7)	N(3)—C(7)—C(12)	106.0 (5)
C(1)—C(6)	1.494 (8)	N(4)—C(6)—C(1)	106.3 (4)
C(7)—C(12)	1.507 (7)	N(5)—C(18)—C(13)	106.5 (4)
C(13)—C(18)	1.493 (8)	N(6)—C(12)—C(7)	105.3 (4)
Average	1.498 (8)	Average	106.0 (4)

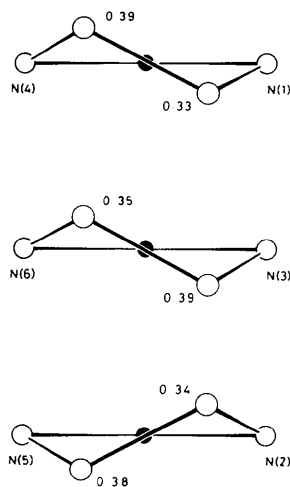


Fig. 4. Conformations of the chelate rings. Figures attached to each carbon atom indicate the distances from the coordination plane.

The chelate rings are puckered and chiral. Each chelate ring has an unsymmetrical skew conformation as shown in Fig. 4. The dihedral angles about the C—C bond of the rings are 53.8 and 52.8° for the *lel* and *ob* rings respectively.

The CoN_6 chromophore is slightly deformed from a regular octahedral disposition. The upper triangle formed by the three N atoms is rotated counterclockwise by about 6.4° with respect to the lower triangle of the three remaining N atoms from the position expected for a regular octahedron. The planes of the two triangles make an angle of about 1.9° . The Co—N bonds make an angle of 55.6 and 57.0° on average with respect to the axis of the complex ion in the rings of *lel* and *ob* conformations respectively.

Non-bonded short H—H contacts occur between NH_2 and CH groups in adjacent chelate rings. The average H...H distances are $2.46(9)$ Å between the *lel* rings and $2.33(8)$ Å between the *lel* and the *ob* rings. The angle of inclination between the coordination plane of the *ob* ring and the axis of the ion, 35.7° , is significantly larger than those of the *lel*, and *ob*₃-isomers (31.8 and 31.5° respectively). This difference is certainly to alleviate the non-bonded H...H interaction. In fact, if the *ob*₃ complex were formed with the same inclination angle of 35.7° , retaining the geometry of the ligand molecule, the H...H distance would become as short as 2.22 Å.

The cyclohexane ring adopts a chair conformation. All the bond distances and angles within the ring are

Table 4. Relevant interatomic distances (Å) less than 3.6 Å outside the complex ion with their standard deviations in parentheses

Key to symmetry operations: (i) $x + y, -x + y, -\frac{1}{6} + z$; (ii) $1 + x - y, x + y, \frac{1}{6} + z$; (iii) $x, -1 + y, z$; (iv) $x, 1 + y, z$; (v) $-1 + x, y, z$.

N(1)...Cl(3)	3.370 (6)*	C(1)...O(5 ⁱ)	3.357 (8)
N(2)...Cl(1)	3.370 (6)*	C(4)...O(4 ⁱⁱⁱ)	3.511 (11)
N(3)...Cl(2)	3.458 (4)*	C(7)...O(3 ⁱ)	3.373 (7)
N(4)...Cl(1)	3.534 (6)*	C(13)...O(1 ⁱⁱ)	3.537 (7)
N(5)...Cl(2)	3.351 (5)*	C(17)...O(1 ⁱⁱ)	3.499 (8)
N(6)...Cl(3)	3.358 (4)*	C(18)...O(1 ⁱⁱ)	3.492 (8)
N(1)...O(3 ⁱ)	3.261 (8)	O(1)...Cl(3 ^{iv})	3.272 (5)*
N(1)...O(5 ⁱ)	2.974 (8)*	O(2)...Cl(1)	3.161 (9)*
N(2)...O(4 ⁱ)	2.953 (7)*	O(2)...Cl(2 ^v)	3.217 (7)*
N(2)...O(5 ⁱ)	3.371 (8)	O(3)...Cl(3 ^{iv})	3.233 (6)*
N(3)...O(3 ⁱ)	3.262 (7)	O(4)...Cl(2 ^v)	3.113 (4)*
N(3)...O(4 ⁱ)	3.014 (7)*	O(4)...Cl(3 ^{iv})	3.150 (5)*
N(4)...O(1 ⁱⁱ)	3.027 (7)	O(5)...Cl(1)	3.166 (8)*
N(4)...O(2 ⁱⁱ)	3.008 (8)*	O(5)...Cl(2 ^v)	3.304 (9)
N(5)...O(1 ⁱⁱ)	3.017 (9)*	O(1)...O(2)	3.155 (7)
N(5)...O(2 ⁱⁱ)	3.577 (6)	O(3)...O(5)	2.955 (8)*
N(6)...O(2 ⁱⁱ)	2.967 (8)*	O(3)...O(1 ⁱⁱ)	2.874 (11)*
C(13)...Cl(1)	3.407 (6)	O(4)...O(5)	3.366 (9)
C(18)...Cl(2)	3.417 (6)		

* Hydrogen bonding.

normal. The average N—H and C—H bond lengths are $0.851(5)$ and $0.931(5)$ Å respectively. They are apparently shorter than the values obtained by neutron diffraction studies, as is well known.

The packing modes of the complex ions are very much like hexagonal close-packing (see Fig. 1). The Co atom is 0.46 Å off the threefold screw axis: the *ob* chelate ring is oriented away from the screw axis. The axis of the complex ion is inclined by 8.1° with respect to the *c* axis. Interatomic distances outside the complex ion are listed in Table 4. There seem to exist weak hydrogen bonds between N and Cl atoms: the N...Cl contacts range from $3.351(5)$ to $3.534(6)$ Å with a mean value of $3.407(5)$ Å.

Fig. 5 shows a projection of the structure along *a*, where some atoms are omitted to simplify the aspect. Water molecules are arranged between the complex ions around the screw axis. There exist hydrogen bonds between N atoms and the water molecules and between the water molecules. They are indicated by broken lines in the figure. Dotted lines indicate O—H...Cl hydrogen bonds. The complex ions, Cl⁻ ions and the water molecules are linked by hydrogen bonds to form a three-dimensional network.

The structure analysis of the *ob*₂*lel*-isomer is now in progress.

The calculations were performed on a FACOM 270-48 computer of this Institute with a local version of the Universal Crystallographic Computation Program System UNICS (Crystallographic Society of Japan). A part of the calculations was carried out on a HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo.

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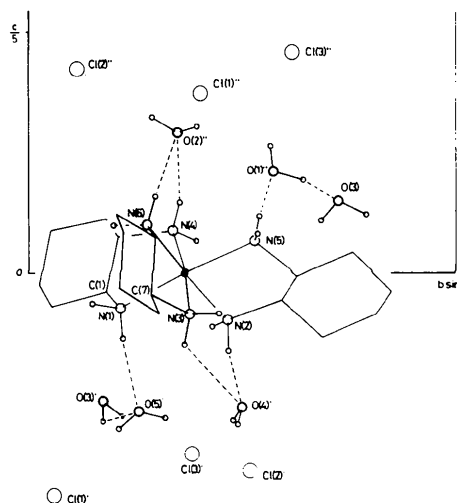


Fig. 5. A partial projection of the structure along *a*.

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Transition-Metal–Nucleoside Complexes. The Crystal and Molecular Structure of (Glycylglycinato)(cytidine)copper(II) Dihydrate

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Details of the molecular and crystal structure of the nucleoside complex (glycylglycinato)(cytidine)copper(II) are reported. The complex crystallizes in the monoclinic system, space group $P2_1$, with crystal data: $a = 4.710(4)$, $b = 26.99(3)$, $c = 14.99(2)$ Å, $\beta = 90.1(1)^\circ$; $D_m = 1.67(2)$, $D_c = 1.64$ g cm $^{-3}$. There are two independent, but closely related, complexes and four waters of crystallization per asymmetric volume. Intensities for 2190 symmetry-independent reflections were collected by counter methods with the θ – 2θ scan technique and graphite-monochromatized Mo $K\alpha$ radiation. The structure was solved by standard heavy-atom Patterson and Fourier methods. Full-matrix least-squares refinement, based on F , led to final R values of 0.144 (all data) and 0.127 [the 1852 reflections with $F_o \geq 3\sigma(F_o)$]. The coordination geometry about the Cu is pseudo-square pyramidal with the tridentate glycylglycinato dianion and N(3) of the cytidine ligand occupying the equatorial plane, and O(2) of cytidine approximately in an axial position. The cytidine ligand is thus chelated to the Cu^{II} center employing an equatorial position *via* N(3) and an axial position *via* O(2). The two complexes in the asymmetric unit have nearly identical molecular conformations and are related by a local twofold axis parallel to **a**. The conformation of the cytidine ligand is very similar to that found in uncomplexed cytidine. The complete crystal structure is maintained by an extensive hydrogen-bonding network and columnar stacking of the complexes along **a**.

Introduction

Solution (Marzilli, 1977) and crystallographic (Hodgson, 1977) studies on the binding of metal ions and metal complexes to nucleic acids and nucleic acid constituents have recently been comprehensively reviewed. The crystallographic work (Hodgson, 1977) has centered on the binding of metal species to purines, pyrimidines, alkylated purines and pyrimidines, nucleosides and nucleotides. Of these ligand types, the nucleosides have been the least studied by crystallographic techniques, primarily because of synthetic difficulties, very low stability constants, and the low solubility of the nucleosides themselves.

In fact we know of only four crystallographic studies on metal–nucleoside complexes: (1) the bispyridine osmate ester of adenosine (Conn, Kim, Suddath, Blattmann & Rich, 1974); (2) the present cytidine complex (Szalda, Marzilli & Kistenmacher, 1975a); (3) the [(ethylenediamine)bis(guanosine)platinum(II)]²⁺ complex cation (Gellert & Bau, 1975); (4) the deoxyadenosine complex of bis(acetylacetonato)nitrocobalt(III) (Sorrell, Epps, Kistenmacher & Marzilli, 1977).

Perhaps the most interesting feature which has emerged from the crystallographic studies on metal–nucleoside complexes is the chelation of cytidine *via* N(3) and O(2) to Cu^{II} (Szalda, Marzilli & Kistenmacher, 1975a). Verification of the importance of such