

ditions, but at higher temperatures, *i.e.* 35°C. Even if some small amount of hydrolysis did occur one would expect the aquo-acid, $\text{RhBr}_3(\text{H}_2\text{O})^{2-}$, to have a $pK_a > 8$ when compared to $\text{RhCl}_3(\text{H}_2\text{O})^{2-}$ where the $pK_a > 8$.

References

- BEKKER, P. V. Z. (1968). M.Sc. Thesis, Pretoria University.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 DUNNING, A. J. & VAND, V. (1969). *Acta Cryst.* A25, 489.

- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040.
International Tables for X-ray Crystallography (1962). Vol. II. Birmingham: Kynoch Press.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
 PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*. p. 260. London: Freeman.
 ROBB, W. & HARRIS, G. M. (1965). *J. Amer. Chem. Soc.* 87, 4472.
 ROBB, W., STEYN, M. M. DE V. & KRUGER, H. (1969). *Inorg. Chim. Acta*, 3, 383.
 SAILLANT, R., JACKSON, R. B., STREIB, W. E., FOLTING, K. & WENTWORTH, R. A. D. (1971). *Inorg. Chem.* 10, 1453.
 WORK, R. A. & GOOD, M. L. (1970). *Inorg. Chem.* 9, 956.

Acta Cryst. (1972). B28, 3591

The Crystal Structure of (+)₅₄₆-Tris-(*R,R*-2,4-diaminopentane)cobalt(III) Chloride Monohydrate, (+)₅₄₆-[Co(*R,R*-ptn)₃]Cl₃·H₂O

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(+)₅₄₆-Tris(*R,R*-2,4-diaminopentane)cobalt(III) chloride monohydrate has been studied by X-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$, $a = 17.516$, $b = 13.537$, $c = 11.048$ Å and $Z = 4$. Three-dimensional intensity data collected by the diffractometer method gave a final R value of 0.076 for the 701 observed reflexions. The complex cation has an approximate symmetry D_3 . The six-membered chelate ring has a twisted-boat form. The two methyl groups are in equatorial positions with respect to the average plane of the chelate ring. The average NCoN angle is $87.9 \pm 1.3^\circ$. The absolute configuration of the complex ion is A , as expected from its circular dichroism spectra. The conformation of the three chelate rings can be designated as λ , providing the helicity is defined by the line joining the two coordinating nitrogen atoms and by the line joining the two asymmetric carbon atoms.

Introduction

Two isomers have been isolated of tris(*R,R*-2,4-diaminopentane)cobalt(III) salts (Mizukami, Ito, Fujita & Saito, 1970). One of the isomers, (+)₅₄₆-tris(*R,R*-2,4-diaminopentane)cobalt(III) chloride monohydrate (+)₅₄₆-[Co(*R,R*-ptn)₃]Cl₃·H₂O, was expected to have the absolute configuration A from the positive circular dichroism band in the first transition region. The other, (-)₅₄₆-[Co(*R,R*-ptn)₃]Cl₃·2H₂O, was assigned as a Δ isomer. The crystals of these isomers have been subjected to X-ray crystal analysis in order to gain a greater understanding of the relation between the circular dichroism spectra and the absolute configuration of transition metal complexes. This paper deals with the crystal structure of (+)₅₄₆-[Co(*R,R*-ptn)₃]Cl₃·H₂O.

Experimental

Crystals of (+)₅₄₆-[Co(*R,R*-ptn)₃]Cl₃·H₂O were kindly supplied by Professor J. Fujita of Tohoku University.

Lath-shaped crystals, orange-red in colour, were used for X-ray analysis. The cell dimensions determined from higher order reflexions recorded on Weissenberg photographs were later refined by employing data obtained on a single-crystal diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

Crystal data are: (+)₅₄₆-Co(C₅H₁₄N₂)₃Cl₃·H₂O, F.W. 489.9; orthorhombic, $a = 17.516 \pm 0.003$, $b = 13.537 \pm 0.003$, $c = 11.048 \pm 0.002$ Å, $U = 2620$ Å³; $D_m = 1.230$ g.cm⁻³, $Z = 4$, $D_x = 1.242$ g.cm⁻³. Space group $P2_12_12_1$ (D_3^4 , No. 19). Linear absorption coefficient for Mo $K\alpha$, $\mu = 11.5$ cm⁻¹.

The intensity data were collected on a Rigaku automated four-circle diffractometer. The specimen was mounted with the b axis parallel to the ϕ axis of the diffractometer. The ω -scan technique was employed.

The scan range was calculated from the formula, $2.0^\circ + 1.0^\circ \times \tan \theta$. The scan speed was 1° per min in ω and background counts each of 10 sec duration were taken at both limits of the scan. Mo $K\alpha$ radiation monochromated by an LiF crystal was used. As the cry-

stal was small and unsuitable for X-ray analysis, two of the independent reflexions, hkl and $hk\bar{l}$, were measured in order to improve the accuracy of the measurement. A set of standard reflexions was measured every fifty reflexions during the data collection to check the electronic stability of the instrument as well as any deterioration of the crystal. A total of about 4500 intensities were measured up to $2\theta = 55^\circ$. Reflexions for which the intensities were less than three times their standard deviations were regarded as 'unobserved' and were not included in subsequent calculations. For the observed reflexions, the structure amplitudes of hkl and $hk\bar{l}$ were averaged. Thus, 701 independent reflexions were selected and used for the structure analysis. The intensities were corrected for Lorentz and polarization effects, but corrections for absorption and extinction were not applied.

Determination of the structure

The structure was solved by the heavy-atom method. The positions of the cobalt atoms and chloride ions were deduced from three-dimensional Patterson maps. The cobalt atoms lie close to the twofold screw axis. The Weissenberg photographs of the zero layer around the b axis showed that the structure projected along the b axis has a pseudo-sixfold symmetry. This fact was of great help in locating the chloride ions. The positions of the other lighter atoms, except hydrogen, were determined by routine application of the heavy-atom method. Electron-density maps showed broader and slightly lower peaks at the positions of the oxygen atoms. Block-

diagonal least-squares refinement using anisotropic temperature factors reduced the R value (defined by $\sum ||F_o| - |F_c|| / \sum |F_o|$) to 0.09. At this stage a difference Fourier synthesis was carried out which revealed the positions of all the hydrogen atoms of the complex ions, but the positions of several of them were adjusted

Table 1. Final positional parameters and their standard deviations in parentheses ($\times 10^4$)

	x	y	z
Co	5017 (5)	5942 (4)	2568 (8)
Cl(1)	4268 (7)	8426 (12)	253 (10)
Cl(2)	6590 (6)	8424 (11)	2686 (14)
Cl(3)	4042 (7)	8463 (12)	4597 (12)
N(1)	4467 (21)	5063 (38)	3699 (37)
N(2)	4073 (15)	6757 (31)	2445 (44)
N(3)	4666 (17)	5088 (26)	1236 (26)
N(4)	5501 (22)	6816 (28)	1257 (37)
N(5)	5934 (17)	5085 (24)	2643 (48)
N(6)	5459 (17)	6792 (22)	3815 (30)
C(1)	3986 (37)	5619 (52)	4615 (59)
C(2)	3256 (23)	5925 (46)	4026 (47)
C(3)	3327 (22)	6258 (37)	2742 (47)
C(4)	3820 (36)	5009 (50)	5721 (59)
C(5)	2718 (25)	6935 (36)	2282 (45)
C(6)	4371 (25)	5610 (46)	157 (47)
C(7)	5099 (37)	5948 (40)	-564 (43)
C(8)	5798 (33)	6294 (33)	171 (36)
C(9)	3923 (30)	4951 (54)	-740 (69)
C(10)	6095 (35)	7064 (48)	-690 (53)
C(11)	6685 (23)	5612 (31)	2963 (50)
C(12)	6664 (32)	5903 (44)	4287 (52)
C(13)	5891 (29)	6287 (28)	4792 (42)
C(14)	7404 (26)	5025 (40)	2779 (33)
C(15)	6222 (35)	6932 (56)	5733 (53)
O	481 (47)	1425 (113)	2668 (79)

Table 2. Final thermal parameters, with their standard deviations in parentheses

The values have been multiplied by 10^4 and refer to the expression:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	11 (1)	22 (2)	23 (4)	-1 (2)	-1 (5)	5 (6)
Cl(1)	28 (5)	41 (7)	57 (11)	6 (7)	5 (6)	-10 (12)
Cl(2)	26 (4)	42 (7)	69 (15)	-0 (7)	3 (7)	-2 (15)
Cl(3)	22 (4)	36 (7)	88 (13)	-2 (7)	7 (7)	-10 (12)
N(1)	9 (13)	108 (46)	71 (43)	9 (21)	-7 (22)	-73 (42)
N(2)	7 (9)	103 (36)	18 (25)	-5 (17)	-7 (27)	-25 (48)
N(3)	7 (11)	27 (23)	7 (27)	8 (14)	1 (4)	-19 (24)
N(4)	26 (15)	34 (31)	97 (48)	-20 (18)	-18 (24)	55 (33)
N(5)	11 (10)	30 (21)	72 (48)	-14 (13)	27 (26)	-56 (39)
N(6)	5 (10)	1 (21)	65 (38)	7 (12)	-15 (18)	14 (22)
C(1)	56 (34)	88 (59)	113 (76)	11 (37)	-11 (44)	52 (58)
C(2)	3 (13)	89 (45)	88 (54)	-14 (26)	5 (25)	45 (52)
C(3)	8 (13)	78 (47)	75 (63)	8 (18)	8 (25)	29 (46)
C(4)	51 (30)	68 (50)	131 (79)	-8 (33)	43 (45)	27 (60)
C(5)	24 (17)	57 (39)	39 (54)	-15 (19)	9 (24)	-31 (42)
C(6)	11 (19)	93 (53)	79 (55)	14 (23)	-24 (26)	-67 (46)
C(7)	40 (26)	35 (29)	82 (46)	22 (28)	6 (38)	49 (41)
C(8)	59 (27)	30 (35)	10 (33)	-18 (25)	-12 (28)	24 (29)
C(9)	20 (21)	101 (60)	203 (101)	7 (33)	29 (42)	13 (78)
C(10)	50 (30)	70 (48)	87 (63)	0 (33)	-31 (38)	6 (52)
C(11)	2 (13)	11 (26)	168 (85)	-18 (16)	-4 (26)	-11 (36)
C(12)	45 (26)	47 (39)	106 (66)	31 (32)	15 (36)	-5 (51)
C(13)	32 (20)	1 (26)	73 (47)	5 (18)	-7 (28)	62 (32)
C(14)	21 (16)	67 (37)	2 (48)	0 (21)	3 (19)	-56 (38)
C(15)	44 (28)	137 (82)	74 (60)	6 (38)	18 (36)	-20 (62)
O	180 (64)	1034 (301)	173 (97)	41 (130)	-10 (84)	273 (98)

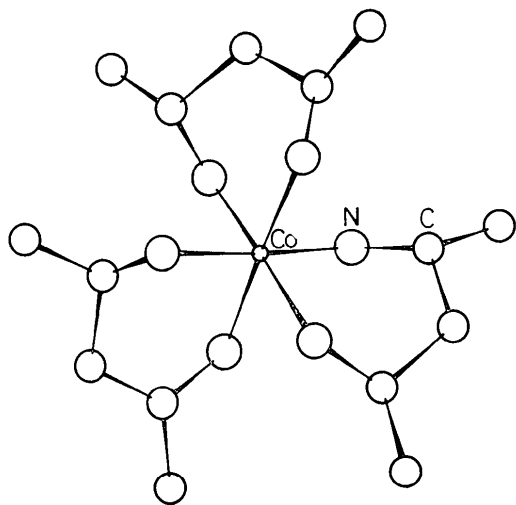


Fig. 1. A perspective drawing of the complex ion, (+)₅₄₆[Co(R,R-2,4-ptn)₃]³⁺.

Table 3. Observed and calculated structure amplitudes

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
2	0	0	230	261	12	2	1	34	46	11	2	2	44	50	7	0	0	44	47	14	4	0	76	72
4	0	0	83	85	16	2	1	37	38	10	2	2	44	50	7	0	0	44	47	14	4	0	76	72
6	0	0	31	25	18	2	1	41	27	8	2	2	34	29	10	0	0	44	50	12	2	0	56	56
8	0	0	90	90	1	3	1	21	27	9	2	2	37	37	12	0	0	44	47	14	4	0	76	72
10	0	0	131	130	2	3	1	101	109	10	2	2	35	35	14	0	0	44	47	14	4	0	76	72
12	0	0	28	30	4	3	1	95	88	11	2	2	36	35	15	0	0	44	47	14	4	0	76	72
14	0	0	71	80	18	3	1	75	78	12	2	2	36	35	16	0	0	44	47	14	4	0	76	72
16	0	0	39	43	3	4	1	88	93	13	2	2	36	35	17	0	0	44	47	14	4	0	76	72
18	0	0	71	87	5	4	1	100	90	14	2	2	36	35	18	0	0	44	47	14	4	0	76	72
20	0	0	48	54	7	4	1	110	107	15	2	2	36	35	19	0	0	44	47	14	4	0	76	72
22	0	0	152	107	2	4	1	22	22	16	2	2	36	35	20	0	0	44	47	14	4	0	76	72
24	0	0	84	74	3	4	1	25	20	17	2	2	36	35	21	0	0	44	47	14	4	0	76	72
26	0	0	97	83	7	4	1	55	41	18	2	2	36	35	22	0	0	44	47	14	4	0	76	72
28	0	0	82	80	8	4	1	53	41	19	2	2	36	35	23	0	0	44	47	14	4	0	76	72
30	0	0	46	36	9	4	1	93	81	20	2	2	36	35	24	0	0	44	47	14	4	0	76	72
32	0	0	115	104	10	4	1	105	107	21	2	2	36	35	25	0	0	44	47	14	4	0	76	72
34	0	0	53	55	11	4	1	31	37	22	2	2	36	35	26	0	0	44	47	14	4	0	76	72
36	0	0	89	90	12	4	1	44	42	23	2	2	36	35	27	0	0	44	47	14	4	0	76	72
38	0	0	43	46	13	4	1	44	42	24	2	2	36	35	28	0	0	44	47	14	4	0	76	72
40	0	0	36	36	14	4	1	24	20	25	2	2	36	35	29	0	0	44	47	14	4	0	76	72
42	0	0	54	57	15	4	1	24	20	30	2	2	36	35	30	0	0	44	47	14	4	0	76	72
44	0	0	36	36	16	4	1	24	20	31	2	2	36	35	31	0	0	44	47	14	4	0	76	72
46	0	0	57	57	17	4	1	24	20	32	2	2	36	35	32	0	0	44	47	14	4	0	76	72
48	0	0	36	36	18	4	1	24	20	33	2	2	36	35	33	0	0	44	47	14	4	0	76	72
50	0	0	57	57	19	4	1	24	20	34	2	2	36	35	34	0	0	44	47	14	4	0	76	72
52	0	0	36	36	20	4	1	24	20	35	2	2	36	35	35	0	0	44	47	14	4	0	76	72
54	0	0	57	57	21	4	1	24	20	36	2	2	36	35	36	0	0	44	47	14	4	0	76	72
56	0	0	36	36	22	4	1	24	20	37	2	2	36	35	37	0	0	44	47	14	4	0	76	72
58	0	0	57	57	23	4	1	24	20	38	2	2	36	35	38	0	0	44	47	14	4	0	76	72
60	0	0	36	36	24	4	1	24	20	39	2	2	36	35	39	0	0	44	47	14	4	0	76	72
62	0	0	57	57	25	4	1	24	20	40	2	2	36	35	40	0	0	44	47	14	4	0	76	72
64	0	0	36	36	26	4	1	24	20	41	2	2	36	35	41	0	0	44	47	14	4	0	76	72
66	0	0	57	57	27	4	1	24	20	42	2	2	36	35	42	0	0	44	47	14	4	0	76	72
68	0	0	36	36	28	4	1	24	20	43	2	2	36	35	43	0	0	44	47	14	4	0	76	72
70	0	0	57	57	29	4	1	24	20	44	2	2	36	35	44	0	0	44	47	14	4	0	76	72
72	0	0	36	36	30	4	1	24	20	45	2	2	36	35	45	0	0	44	47	14	4	0	76	72
74	0	0	57	57	31	4	1	24	20	46	2	2	36	35	46	0	0	44	47	14	4	0	76	72
76	0	0	36	36	32	4	1	24	20	47	2	2	36	35	47	0	0	44	47	14	4	0	76	72
78	0	0	57	57	33	4	1	24	20	48	2	2	36	35	48	0	0	44	47	14	4	0	76	72
80	0	0	36	36	34	4	1	24	20	49	2	2	36	35	49	0	0	44	47	14	4	0	76	72
82	0	0	57	57	35	4	1	24	20	50	2	2	36	35	50	0	0	44	47	14	4	0	76	72
84	0	0	36	36	36	4	1	24	20	51	2	2	36	35	51	0	0	44	47	14	4	0	76	72
86	0	0	57	57	37	4	1	24	20	52	2	2	36	35	52	0	0	44	47	14	4	0	76	72
88	0	0	36	36	38	4	1	24	20	53	2	2	36	35	53	0	0	44	47	14	4	0	76	72
90	0	0	57	57	39	4	1	24	20	54	2	2	36	35	54	0	0	44	47	14	4	0	76	72
92	0	0	36	36	40	4	1	24	20	55	2	2	36	35	55	0	0	44	47	14	4	0	76	72
94	0	0	57	57	41	4	1	24	20	56	2	2	36	35	56	0	0	44	47	14	4	0	76	72
96	0	0	36	36	42	4	1	24	20	57	2	2	36	35	57	0	0	44	47	14	4	0	76	72
98	0	0	57	57	43	4	1	24	20	58	2	2	36	35	58	0	0	44	47	14	4	0	76	72
100	0	0	36	36	44	4	1	24	20	59	2	2	36	35	59	0	0	44	47	14	4	0	76	72
102	0	0	57	57	45	4	1	24	20	60	2	2	36	35	60	0	0	44	47	14	4	0	76	72
104	0	0	36	36	46	4	1	24	20	61	2	2	36	35	61	0	0	44	47	14	4	0	76	72
106	0	0	57	57	47	4	1	24	20	62	2	2	36	35	62	0	0	44	47	14	4	0	76	72
108	0	0	36	36	48	4	1	24	20	63	2	2	36	35	63	0	0	44	47	14	4	0	76	72
110	0	0	57	57	49	4	1	24	20	64	2	2	36	35	64	0	0	44	47	14	4	0	76	72
112	0	0	36	36	50	4	1	24	20	65	2	2	36	35	65	0	0	44	47	14	4	0	76	72
114	0	0	57	57	51	4	1	24	20	66	2	2	36	35	66	0	0	44	47	14	4	0	76	72
116	0	0	36	36	52	4	1	24	20	67	2	2	36	35	67	0	0	44	47	14	4	0	76	72
118	0	0	57	57	53	4	1	24	20	68	2	2	36	35	68	0	0	44	47	14	4	0	76	72
120	0	0	36	36	54	4	1	24	20	69	2	2	36	35	69	0	0	44	47	14	4	0	76	72
122	0	0	57	57	55	4	1	24	20	70	2	2	36	35	70	0	0	44	47	14	4	0	76	72
124	0	0	36	36	56	4	1	24	20	71	2	2	36	35	71	0	0	44	47	14	4	0	76	72
126	0	0	57	57	57	4	1	24	20	72	2	2	36	35	72	0	0	44	47	14	4	0	76	72
128	0	0	36	36	58	4	1	24	20	73	2	2	36	35	73	0	0	44	47	14	4	0	76	72
130	0	0	57	57	59	4	1	24	20	74	2	2	36	35	74	0	0	44	47	14	4	0	76	72
132	0	0	36	36	60	4	1	24	20	75	2	2	36	35	75	0	0	44	47	14	4	0	76	72
134	0	0	57	57	61	4	1	24	20	76	2	2	36	35	76	0	0	44	47	14	4	0	76	72
136	0	0	36	36	62	4	1	24	20	77	2	2	36	35	77	0	0	44	47	14	4	0	76	72
138	0	0	57	57	63	4	1	24	20	78	2	2	36	35	78	0	0	44	47	14	4	0	76	72
140	0																							

diaminopropane)cobalt(III) ion (Nomura, Marumo & Saito, 1969), are all less than 90°, the average being $87.9 \pm 1.3^\circ$. The distortion of an octahedron formed by the six nitrogen atoms is opposite to that observed in Λ -[Co(tn)₃]³⁺. The upper triangle defined by the three nitrogen atoms is rotated counterclockwise around the threefold axis of *D*₃ by about 4° with respect to the lower triangle of the remaining three nitrogen atoms from the position expected for a regular octahedron (Fig. 1). This distortion is similar to that observed in Λ -[Co(en)₃]³⁺.

The two methyl groups are in equatorial positions with respect to the average plane of the chelate ring. The conformation of the chelate rings can be designated as *ob*₃, since the line joining the two asymmetric carbon atoms is inclined at about 70° with respect to the quasi-threefold axis of the complex ion. The six-membered chelate ring is chiral and its absolute configuration can be designated as λ , providing the helicity is defined by the line joining the two nitrogen atoms and the line joining the two asymmetric carbon atoms that are neighbours to each of the coordinating atoms. The crystal structure projected along the *b* axis is shown in Fig. 2. A central metal atom lies a little off the twofold screw axis parallel to the *b* axis, with the

Table 5. Interatomic distances and angles within the complex ions with their estimated standard deviations

Co—N(1)	1.98 (5) Å	N(1)—C(1)	1.52 (8) Å
Co—N(2)	1.99 (3)	N(2)—C(3)	1.51 (5)
Co—N(3)	1.97 (3)	N(3)—C(6)	1.48 (6)
Co—N(4)	2.05 (4)	N(4)—C(8)	1.49 (6)
Co—N(5)	1.98 (3)	N(5)—C(11)	1.54 (5)
Co—N(6)	1.96 (3)	N(6)—C(13)	1.49 (6)
C(1)—C(2)	1.49 (8)	C(6)—C(7)	1.57 (8)
C(2)—C(3)	1.49 (7)	C(7)—C(8)	1.54 (8)
C(1)—C(4)	1.50 (9)	C(6)—C(9)	1.55 (9)
C(3)—C(5)	1.50 (6)	C(8)—C(10)	1.50 (8)
C(11)—C(12)	1.52 (8)	C(11)—C(14)	1.50 (6)
C(12)—C(13)	1.55 (8)	C(13)—C(15)	1.48 (8)
N(1)—Co—N(2)	88 (1)°	N(1)—C(1)—C(4)	112 (3)°
N(3)—Co—N(4)	87 (1)	N(2)—C(3)—C(5)	106 (2)
N(5)—Co—N(6)	90 (1)	N(3)—C(6)—C(9)	115 (2)
N(1)—C(1)—C(2)	109 (4)	N(4)—C(8)—C(10)	108 (2)
N(2)—C(3)—C(2)	114 (4)	N(5)—C(11)—C(14)	116 (2)
N(3)—C(6)—C(7)	105 (4)	N(6)—C(13)—C(15)	116 (2)
N(4)—C(8)—C(7)	107 (4)	C(1)—C(2)—C(3)	115 (4)
N(5)—C(11)—C(12)	109 (4)	C(6)—C(7)—C(8)	118 (4)
N(6)—C(13)—C(12)	110 (4)	C(11)—C(12)—C(13)	117 (5)
Co—N(1)—C(1)	113 (2)	C(7)—C(6)—C(9)	105 (4)
Co—N(2)—C(3)	117 (3)	C(7)—C(8)—C(10)	99 (4)
Co—N(3)—C(6)	116 (2)	C(4)—C(1)—C(2)	110 (5)
Co—N(4)—C(8)	116 (3)	C(2)—C(3)—C(5)	117 (4)
Co—N(5)—C(11)	116 (2)	C(12)—C(13)—C(15)	96 (4)
Co—N(6)—C(13)	116 (3)	C(12)—C(11)—C(14)	107 (4)

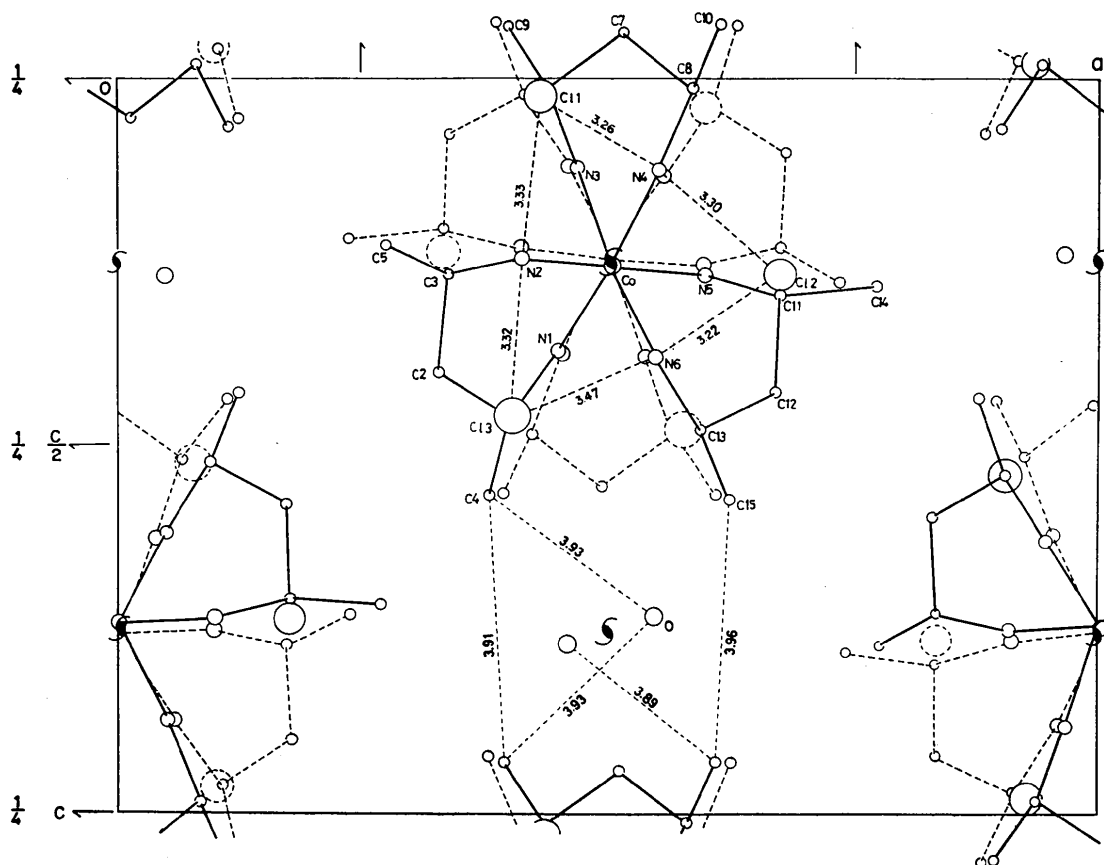


Fig. 2. A projection of the structure along the *b* axis. Broken lines indicate close contacts.

pseudo-threefold axis of the complex ion nearly parallel to the *b* axis. Three chloride ions are arranged approximately in one plane perpendicular to the *b* axis, approximately forming an equilateral triangle. A complex ion is surrounded by six chloride ions, nearly octahedrally. Hydrogen bonds of the type N-H...Cl seem to exist between the chloride ions and the nitrogen atoms of the cation. Intermolecular contacts less than 3.5 Å are given in Table 6.

Table 6. *Interatomic distances less than 3.5 Å outside the complex ions*

Cl(1)···N(2)	3.33 (5) Å
Cl(2)···N(4)	3.30 (4)
Cl(3)···N(6)	3.47 (3)
Cl(1)···N(4)	3.26 (4)
Cl(2)···N(6)	3.22 (3)
Cl(3)···N(2)	3.32 (5)

The complex cations and triangles of three chloride ions are stacked alternately to form a column along the *b* axis. These columns are packed laterally by van der Waals forces. Close approach distances of 3.91 and 3.96 Å occur between C(4) and C(9) and between C(10) and C(15) respectively. Water molecules are enclosed in a hollow space between the columns composed of complex ions and chloride ions. The packing of the water molecules is analogous to the packing in other solvated crystals (see for example, McPhail & Sim, 1968). The separation between the oxygen atom and neighbouring carbon atoms of the complex ions are all greater than 3.8 Å. Interatomic distances less than 4.0 Å are drawn by broken lines in Fig. 2. The absence of any strong intermolecular force apparently permits the observed large thermal motion of the water molecules.

The complex cation has the absolute configuration *A*, in agreement with the assignment from the positive sign of the circular dichroism (CD) band in the first absorption region (Mizukami, Ito, Fujita & Saito, 1970). From this it may be concluded that in the six-membered chelate complexes with the NCoN angles less than 90°, the same relationship holds relating the absolute configuration and the sign of the CD band in the first absorption region, as in the case of the complexes with five-membered chelate rings.

The six-membered chelate ring seems to be more flexible than the five-membered chelate ring. Its conformation may easily be affected by the specific intermolecular forces in the crystal. Woldbye (1965) was the first to predict the skew-boat conformations of the six-membered chelate ring and calculate energy differences of the various conformers. More recently, Gollogly & Hawkins (1972) and Gene & Snow (1972) carried out conformational analyses of the six-membered chelate rings in more detail; however, the results are not always consistent. Beddoe, Harding, Mason & Peart (1971) found that the solution CD of (+)₅₈₉-[Co(tn)₃]³⁺ changes with temperature. They also measured the solid-state CD of (+)₅₈₉-[Co(tn)₃]Br₃·H₂O. These results, combined with the result of the present structure analysis, indicate the conformational equilibrium in solution between a tris-skew boat and a tris-chair form, the latter being more stable by about 0.5 kcal.

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References

- BEDDOE, P. G., HARDING, M. J., MASON, S. F. & PEART, B. J. (1971). *Chem. Commun.* p. 1283.
 GENE, R. J. & SNOW, M. R. (1972). *J. Chem. Soc. (A)*. To be published.
 GOLLOGLY, J. R. & HAWKINS, C. J. (1972). To be published. *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
IUPAC Information Bulletin (1968). No. 33, p. 68-77.
 MCPHAIL, A. T. & SIM, G. A. (1968). *J. Chem. Soc. (B)*, p. 962.
 MIZUKAMI, F., ITO, H., FUJITA, J. & SAITO, K. (1970). *Bull. Chem. Soc. Japan*, **43**, 3633, 3973.
 NOMURA, T., MARUMO, F. & SAITO, Y. (1969). *Bull. Chem. Soc. Japan*, **42**, 1016.
 WOLDBYE, F. (1965). Transcript of Lecture on ORD and CD held at Bonn.