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The Crystal and Molecular Structure of $HK_8Rh_3Br_{18}.10H_2O$

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The crystal and molecular structure of $HK_8Rh_3Br_{18}.10H_2O$ has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic with space group *Pbam* and 2 molecules in the unit cell of dimensions $a=15{\cdot}32$, $b=16{\cdot}63$ and $c=9{\cdot}30$ Å. Two monomeric $RhBr_6$ octahedra exist which are not related by the crystal symmetry.

Introduction

A series of complexes of formula $K_{3-N}RhBr_{6-N}(H_2O)_N$ ($N=0,1,2,3$) was prepared as a prelude to a kinetic mechanistic study of the anation reactions of aquobromorhodate(III) complexes in aqueous acid medium (Bekker, 1968).

The first experiment was designed to examine the equilibrium hydrolysis,

$$RhBr_5(H_2O)^{2-}+Br^- \rightleftharpoons RhBr_6^{3-}+H_2O\ ,$$

as a logical complement to earlier reported studies on the chloro congeners (Robb & Harris, 1965; Robb, Steyn & Krüger, 1970). The fact that the potassium salt of the $RhBr_6^{3-}$ moiety was isolated from a liquor that yielded two other complexes of formulae $K_3Rh_2Br_9$ and $K_4Rh_2Br_{10}$ served as an indication that the kinetic picture could become rather complicated and also made it necessary that a complete characterization of the complexes be attempted.

The results of the first of these crystallographic investigations form the basis for this report. The complex of formula $K_3Rh_2Br_9$ is expected to be isomorphous with the nonachlorodirhodate(III) complex which was isolated as the quaternary ammonium salt (Work & Good, 1970). The latter complex was in turn found to be isomorphous with the chromium(III) dimeric species which was shown to exist in the solid state as two distorted octahedra coupled face to face. A more recent publication communicated the full X-ray structural analysis of the complexes $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ (Saillant, Jackson, Streib, Folting & Wentworth, 1971).

The complex of formula $K_4Rh_2Br_{10}$ is presently being prepared for crystallographic studies.

Experimental section

Dark brown needles of the complex analysing according to the formula $K_8Rh_3Br_{18}.10H_2O$ were prepared from $Rh(OH)_3.3H_2O$ in the presence of HBr and KBr. The full details of other preparations of all of these aquobromorhodate(III) and bromorhodate(III) complexes, together with their ligand field spectra are to be reported elsewhere with the kinetic results.

Basing the amount of material taken (22 mg) on the formula $K_8Rh_3Br_{18}.10H_2O$, 10 ml of a 1 millimolar solution of the complex was made up in doubly distilled water and immediately subjected to a *p*H measurement at 20°C. The *p*H was found to be 3 hence showing the presence of a single proton for each unit of above formula or, more correctly, $\frac{1}{3}$ of a proton per $RhBr_6^{3-}$ unit.

With the aid of oscillation, Weissenberg and precession photographs the crystals were determined to be orthorhombic with space group *Pbam* ($0kl$ with $k=2n$, $h0l$ with $h=2n$). Unit-cell dimensions were calculated from the accurate spot positions measured on a Hilger & Watts four circle automatic diffractometer.

Crystal data:

$a = 15{\cdot}32 \pm 0{\cdot}02$ Å
$b = 16{\cdot}63 \pm 0{\cdot}02$
$c = 9{\cdot}30 \pm 0{\cdot}01$
$D_m = 3{\cdot}16$ g.cm^{-3} (pycnometrically, using C_6H_5Br)
$D_x = 3{\cdot}14$
Molecular formula: $K_8Rh_3Br_{18}.10H_2O$
Molecular weight: 2241·05
$Z = 2$

A single crystal of almost spherical shape with a diameter of approximately 0·10 mm was selected for the intensity measurements. The diffractometer was used with Mo $K\alpha$ (Zr, β-filtered) radiation to collect a total of 723 independent reflexions according to the ω–2θ scanning technique. Of these intensities 454 were greater than 3σ(I), where $\sigma(I)$ is given by $[I_o + I_b]^{1/2}$. I_o is the total number of counts during the peak scan and I_b the number of counts for the background intensity. Background corrections were made from scans of intensity against θ, parallel to central lattice rows. The standard Lp corrections were made and absorption corrections applied according to *International Tables for X-ray Crystallography* (1962), assuming spherical geometry for the crystal with $\mu R \simeq 1{\cdot}0$.

Structure refinement

The trial structure was deduced using three-dimensional Patterson and Fourier techniques. Subsequent refinement thereof was done by the full-matrix least-squares program of Busing, Martin & Levy (1962) which minimizes the function $\sum w(|F_o| - |kF_c|)^2$. With individual isotropic thermal parameters for all the atoms an R index of 0·090, $[R = (\sum |F_o| - |F_c||)/\sum|F_o|]$, was obtained. An equivalent set of atomic parameters was obtained with no change in the R index when the

Table 1. *Refined atomic parameters (fractional coordinates and isotropic temperature factors)*

Standard deviations are given in parentheses.

	x	y	z	B(Å^2)
Rh(1)	0·0	0·0	0·0	3·7 (3)
Rh(2)	0·1808 (7)	0·3068 (7)	0·5	4·2 (2)
Br(1)	0·1550 (8)	−0·0484 (7)	0·0	4·4 (3)
Br(2)	0·0	0·0	0·2682 (14)	4·8 (3)
Br(3)	0·0521 (8)	0·1438 (7)	0·0	4·1 (3)
Br(4)	0·3060 (9)	0·2069 (8)	0·5	5·0 (3)
Br(5)	0·1841 (6)	0·3046 (6)	0·2322 (15)	5·5 (3)
Br(6)	0·0755 (8)	0·1923 (8)	0·5	4·5 (3)
Br(7)	0·2856 (9)	0·4220 (8)	0·5	4·4 (3)
Br(8)	0·0571 (10)	0·4021 (9)	0·5	6·2 (4)
K(1)	0·4032 (12)	0·3240 (11)	0·2592 (22)	4·7 (5)
K(2)	0·1964 (14)	0·0918 (12)	0·2570 (26)	6·4 (6)
O(1)	0·2924 (77)	0·1682 (70)	0·0	11·6 (3·7)
O(2)	0·3674 (40)	0·0252 (34)	0·2340 (77)	8·3 (1·9)
O(3)	0·4643 (41)	0·1715 (37)	0·1556 (78)	9·7 (2·0)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations are given in parentheses.

Rh(1)–Br(1)	2·51 (1)	Br(1)–Rh(1)–Br(3)	90·3 (4)
Rh(1)–Br(2)	2·50 (1)	Br(1)–Rh(1)–Br(2)	90·0
Rh(1)–Br(3)	2·52 (1)	Br(5)–Rh(1)–Br(3)	90·0
Rh(2)–Br(4)	2·54 (2)	Br(2)–Rh(2)–Br(6)	89·4 (5)
Rh(2)–Br(5)	2·49 (1)	Br(2)–Rh(2)–Br(7)	90·9 (5)
Rh(2)–Br(6)	2·50 (2)	Br(6)–Rh(2)–Br(8)	89·6 (6)
Rh(2)–Br(7)	2·50 (2)	Br(7)–Rh(2)–Br(8)	90·1 (6)
Rh(2)–Br(8)	2·47 (2)	Br(4)–Rh(2)–Br(5)	88·6 (4)
		Br(5)–Rh(2)–Br(6)	90·1 (4)
O(1)···O(1)	2·90 (8)	Br(5)–Rh(2)–Br(8)	91·4 (4)
[mirror image]		Br(5)–Rh(2)–Br(7)	89·9 (4)
O(1)···O(3)	3·00 (12)		
O(2)···O(3)	2·94 (8)		
K(1)···O(2)	2·85 (6)		
K(1)···O(3)	2·87 (7)		

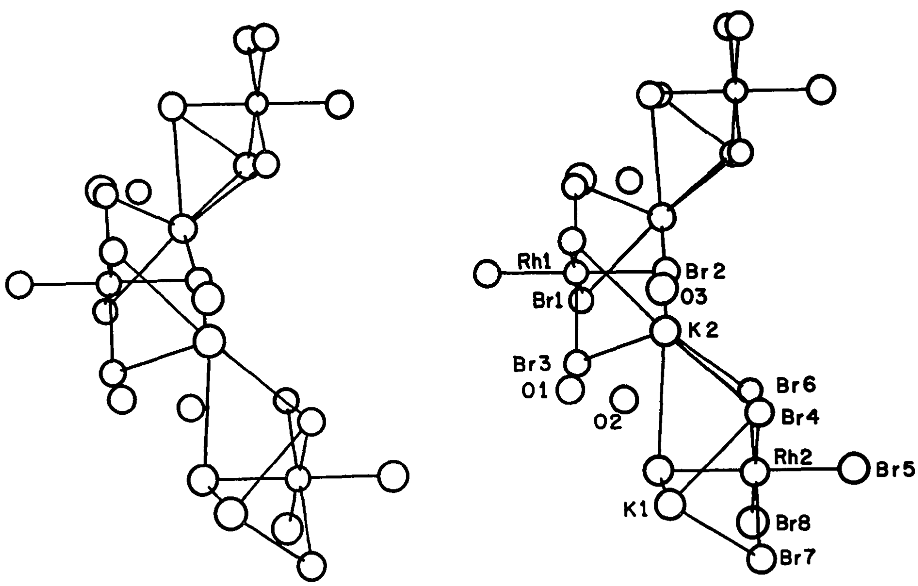
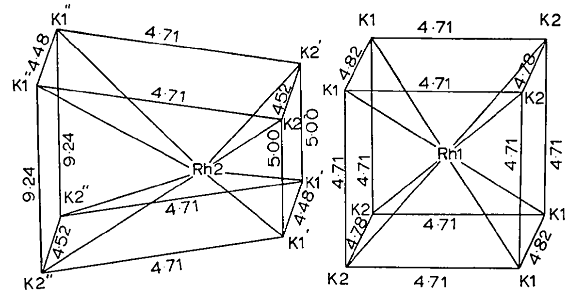


Fig. 1. Stereoscopic drawing showing the atomic numbering used.



Rh2 – K1' = 4·09 Å
Rh2 – K1'' = 5·28
Rh2 – K2' = 4·24
Rh2 – K2'' = 5·58

Rh1 – K1 = 4·07 Å
Rh1 – K2 = 4·14

Fig. 2. Diagram showing the dissimilar arrangement of K atoms about the two rhodium atoms, Rh(1) and Rh(2). (The standard deviations for Rh–K and K–K interatomic distances are 0·02 and 0·03 Å respectively.)

refinement was carried out using the alternative non-centric space group *Pba*2. The form factors used were those of Hanson, Herman, Lea & Skillman (1964). The 454 non-zero intensities were included in the refinement with equal weight. All others (the unobserved) were omitted (Dunning & Vand, 1969). The final atomic parameters are listed in Table 1. Bond lengths and angles (Table 2) were calculated with the aid of the crystallographic program *ORFFE* of Busing, Martin & Levy (1964). The values for the observed and calculated structure factors are given in Table 3.

Discussion

The stereoscopic pair in Fig. 1 shows the molecular geometry and the atomic numbering used. The Rh, Br and K atoms form a layered arrangement stacked normal to the *c* axis with an interval of *c*/4. Each rhodium is octahedrally surrounded by six bromine atoms at a distance of 2·50 Å [sum of covalent radii for Rh(III) and Br is 2·46 Å, (Pauling, 1960)]. Two non-equivalent octahedra exist, however. These involve the atoms Rh(1) and Rh(2) respectively.

The Rh(1) atom occupies the special position (0,0,0) while the other Rh(2) lies on the mirror plane $(x,y,\frac{1}{2})$.

Table 3. *Observed and calculated structure factors*

The columns are k, l, F_{obs}, and F_{calc}.

		H = 0	
0	1	264.5	-285.8
0	2	352.2	322.2
0	3	301.9	-306.0
0	4	1124.7	1121.4
0	5	160.9	-156.6
0	6	243.3	246.0
0	7	123.6	-100.7
0	8	423.7	384.2
2	0	127.7	-152.7
2	1	359.8	317.2
2	3	421.8	383.3
2	4	76.5	-67.3
2	5	128.1	130.1
2	7	221.4	194.3
4	0	52.1	28.8
4	2	102.4	-104.5
4	3	58.0	46.4
6	0	331.9	328.0
6	1	188.9	183.3
6	2	131.5	-128.5
6	3	112.6	113.6
6	4	181.6	176.8
6	5	88.4	88.2
8	0	372.3	-374.8
8	1	273.5	269.9
8	2	92.8	-94.1
8	3	290.1	313.1
8	4	246.4	-239.5
8	5	133.7	132.5
8	7	163.9	170.7
10	0	385.7	390.9
10	1	316.9	-331.6
10	3	280.7	-289.3
10	4	263.1	267.3
10	5	182.8	-199.9
10	7	138.7	-142.3
12	0	72.1	22.3
12	2	75.1	-91.8
16	0	94.2	90.5
		H = 1	
1	0	253.7	288.3
1	1	228.5	256.5
1	3	317.9	315.8
1	4	207.3	216.0
1	5	76.8	96.3
1	7	162.8	149.2
1	8	88.2	83.3
2	0	231.6	217.6
2	1	141.4	-134.0
2	2	60.4	59.8
2	3	144.1	-143.9
2	4	165.3	155.3
3	0	165.0	168.6
3	2	62.5	-30.6
3	4	82.1	54.6
4	0	86.2	-94.2
4	2	587.9	561.3
4	4	87.7	-45.1
4	6	233.2	234.6
5	0	138.3	139.9
5	1	81.8	-63.5
5	2	97.0	90.8
7	3	131.4	147.3
7	7	92.4	94.8
8	0	354.5	369.6
8	2	94.2	81.8
8	4	255.7	266.9
9	0	176.7	188.8
9	1	112.1	-95.3
9	3	118.6	-120.4
9	4	102.4	123.4
10	3	84.9	76.9
11	0	113.4	-132.7
11	3	70.7	75.5
11	4	77.4	-90.6
11	5	85.5	34.6
12	0	125.1	129.8
12	4	85.0	84.3
14	1	94.3	117.1
5	3	57.2	59.5
5	4	111.3	122.1
5	5	65.7	-73.9
6	0	276.7	255.0
6	1	154.9	138.6
6	2	98.1	-88.4
6	4	181.0	168.9
6	5	114.2	109.1
7	0	265.3	252.0
7	1	96.5	82.5
7	3	94.9	99.0
7	4	194.7	179.9
7	5	70.1	46.8
7	8	85.6	65.2
8	3	80.5	74.7
9	1	76.6	64.8
9	2	86.3	-96.0
10	0	133.3	-152.6
10	1	86.7	103.9
10	3	84.2	96.0
10	4	96.5	-112.0
11	2	124.9	-121.2
13	0	80.7	113.9
13	4	82.2	80.8
14	0	77.8	-87.5
		H = 2	
0	0	76.2	-95.9
0	1	281.0	259.6
0	2	49.0	45.6
0	3	287.1	262.7
0	4	73.7	-93.2
0	5	81.1	82.6
0	7	209.9	180.4
1	0	268.0	-256.5
1	1	126.5	131.7
1	2	71.2	-76.2
1	3	175.7	152.3
1	4	186.0	-181.0
1	7	123.9	94.0
2	0	274.6	265.7
2	1	37.7	-52.8
2	4	202.2	183.7
2	8	93.9	49.8
3	0	94.3	101.5
3	1	41.8	44.7
3	2	53.6	63.3
3	4	93.5	70.4
4	2	203.5	-179.7
4	3	111.6	95.6
4	6	76.0	-79.7
5	0	187.9	188.5
5	1	60.6	72.8
5	2	252.3	249.4
5	4	149.5	144.2
5	6	110.3	130.4
6	0	282.0	282.9
6	1	79.6	90.8
6	3	119.2	116.0
6	4	169.9	165.9
6	7	87.4	90.8
7	1	109.1	135.3
7	2	62.1	-51.1
		H = 3	
1	0	114.4	111.5
1	2	141.5	-119.8
1	4	85.6	79.8
2	0	57.4	-53.6
2	2	189.0	-191.5
3	0	226.7	-229.3
3	1	111.8	122.4
3	2	270.5	-261.4
3	3	153.1	167.2
3	4	203.3	-189.2
3	6	114.0	-114.0
3	7	146.0	128.1
3	8	86.6	-69.1
4	0	154.7	141.8
4	2	112.8	115.7
4	4	76.6	73.9
4	6	71.8	70.4
5	0	696.3	716.5
5	1	259.8	-252.0
5	3	220.7	-215.3
5	4	472.8	475.8
5	5	121.0	-126.7
5	7	108.6	-108.7
5	8	166.9	157.8
6	0	76.3	-85.0
6	1	182.7	176.3
6	3	170.2	176.6
6	5	80.3	91.8
6	7	85.3	89.2
7	0	93.9	98.3
7	1	196.1	196.1
7	3	228.6	240.9
7	4	75.9	75.1
7	5	81.4	77.6
7	7	152.7	138.7
8	3	67.6	-11.6
9	0	178.1	192.3
9	1	63.6	69.2
9	4	125.3	125.6
10	1	87.0	-100.7
10	2	91.1	116.5
10	3	102.0	-107.7
11	0	120.3	124.0
13	1	139.8	151.5
13	3	137.7	171.2
15	0	136.0	173.1
		H = 4	
0	0	98.8	90.0
0	2	65.4	70.5
1	0	75.8	64.0
1	1	93.8	80.9
1	2	616.2	-572.8
1	5	78.9	68.3
1	6	238.4	-234.2
2	0	187.1	198.1
2	1	115.0	-102.6
2	2	86.8	-62.1
2	4	134.0	148.0
2	5	95.2	-86.9
2	8	88.2	51.9
3	0	268.7	-255.7
3	2	190.2	-183.9
3	3	60.8	57.0
3	4	157.8	-168.9
3	6	84.2	-94.6
4	0	63.3	46.2
4	1	84.0	27.0
3	3	71.5	57.0
4	7	85.6	50.0
5	0	95.6	-109.0
5	1	90.1	98.4
5	3	101.2	107.2
5	8	81.0	-21.6
6	1	168.1	179.8
6	3	144.4	158.0
6	5	68.1	89.5
6	7	85.9	90.6
7	0	141.1	140.8
7	1	101.9	-112.6
7	2	66.5	-77.6
7	3	131.6	-146.7
7	4	73.0	75.3
8	0	207.6	207.3
8	1	74.9	81.5
8	3	93.0	111.0
8	4	144.0	153.5
9	0	132.8	-156.4
9	1	193.5	-195.5
9	2	163.1	190.0
9	3	142.4	-129.6
9	4	115.8	-97.9
9	5	130.5	-145.2
10	0	105.2	111.0
10	4	97.1	80.1
11	0	90.3	72.1
11	5	77.7	55.7
12	0	120.7	125.2
12	4	81.9	86.6
14	0	91.5	122.0
		H = 5	
1	0	196.7	172.5
1	1	50.4	41.4
1	3	116.7	100.6
1	4	126.6	117.2
2	0	198.7	-181.9
2	1	232.4	-216.3
2	3	135.5	-125.4
2	4	93.6	-101.5
2	5	145.2	-130.4
3	0	676.1	675.0
3	1	109.6	-118.7
3	3	117.1	-120.0
3	4	417.6	423.7
3	8	172.5	150.3
4	0	284.2	292.0
4	1	216.3	-218.5
4	3	234.2	-244.0
4	4	163.3	164.6
4	5	108.5	-115.3
4	7	126.3	-111.8
5	0	423.4	-449.4
5	1	317.1	336.6
5	2	69.2	-69.2
5	3	346.0	349.7
5	4	284.4	-291.2
5	5	155.2	169.2
5	7	192.0	185.6
6	0	161.4	-178.0
6	1	76.7	87.7
6	2	73.0	-72.1
6	3	93.0	96.1
6	4	104.6	-119.4
7	0	189.8	220.7
7	4	145.2	153.5
8	0	137.4	-136.7
8	2	146.7	-174.5
9	0	111.5	131.6
9	2	106.3	-107.7
9	3	70.1	84.6
9	4	77.0	82.2
10	3	80.5	-42.7
12	5	91.4	58.8
13	0	203.0	230.2
13	1	83.8	-87.4
13	4	102.0	167.1
14	0	80.9	117.4
		H = 6	
0	0	315.6	319.0
0	1	137.9	129.5
0	2	106.6	-81.9
0	3	73.0	70.0
0	4	216.6	196.8
0	5	95.5	93.1
1	0	223.6	-242.2
1	2	110.3	89.7
1	4	183.4	-183.8
1	5	71.4	-62.1
2	0	86.7	108.4
2	1	174.7	187.2
2	3	237.3	240.6
2	5	69.5	61.8
2	7	158.6	140.6
3	0	90.6	-81.5
3	3	90.0	-81.1
4	0	273.3	287.8
4	3	65.7	59.8
4	4	177.5	198.2
5	0	94.6	97.8
5	2	93.1	98.5
5	4	75.3	94.8
6	4	100.0	73.8
9	2	124.5	-148.7
9	3	74.5	-53.3
10	0	136.9	140.3
10	4	105.6	95.4
		H = 7	
1	0	81.8	72.9
1	1	128.3	122.5
1	2	64.4	42.2
1	3	137.2	128.5
1	5	77.7	63.8
1	7	129.0	73.2
2	1	123.4	-121.8
2	3	131.1	-132.2
2	7	112.7	-87.7
3	0	192.7	205.9
3	1	116.1	115.5
3	3	153.0	152.3
3	4	134.5	152.7
3	7	112.1	93.6
4	0	69.0	-54.2
4	1	79.1	93.9
4	2	105.2	109.1
4	3	101.7	114.3
4	7	95.0	86.7
5	0	154.6	161.0
5	1	78.6	70.4
5	3	80.4	78.5
5	4	113.0	110.5
6	0	164.4	190.1
6	1	77.2	66.4
6	4	125.0	133.4
6	5	74.2	69.6
7	0	69.5	65.7
7	5	86.4	-71.5
8	0	69.9	-70.1
9	0	107.2	120.0
9	4	75.8	86.2
12	0	105.5	101.9
12	4	84.1	74.9
		H = 8	
1	0	120.5	-121.6
1	4	94.9	-100.3
2	0	344.1	379.3
2	3	79.7	-73.4
2	4	257.7	256.7
3	1	100.5	113.1
3	2	62.8	-76.2
3	3	87.8	98.3
4	0	188.7	192.4
4	1	80.6	90.8
4	3	100.4	111.6
4	4	128.3	129.6
5	0	84.8	94.1
5	1	122.8	139.4
5	3	134.7	137.4
5	4	97.4	77.0
7	2	116.2	129.1
8	0	251.6	263.2
8	1	112.4	-110.8
8	3	111.8	-110.6
8	4	163.2	183.0
8	5	93.0	-64.9
10	0	148.8	-126.0
10	1	180.1	189.0
10	3	187.4	200.5
10	5	105.8	98.6
12	0	107.3	111.1
		H = 9	
1	0	168.0	169.0
1	1	158.3	-159.3
1	3	114.0	-116.6
1	4	118.5	111.4
1	5	115.0	-113.9
2	2	80.5	68.3
2	6	80.4	26.2
3	3	133.1	123.7
4	0	116.2	124.4
4	1	106.5	120.4
4	2	165.4	-173.9
4	3	74.2	73.9
4	4	78.4	70.4
4	6	97.3	-75.5
5	0	108.8	120.5
5	1	118.2	103.0
5	2	134.4	-126.3
5	3	86.4	90.2
5	4	89.5	79.7
5	6	91.3	-50.9
6	2	178.2	170.3
6	6	84.1	81.8
7	0	77.3	-55.8
7	2	80.3	-79.5
9	0	110.3	103.6
9	3	88.1	62.6
11	0	174.5	201.2
		H = 10	
0	0	183.9	192.5
0	1	140.6	-149.7
0	2	171.9	-175.3
0	3	103.4	-105.0
0	4	145.2	135.4
0	5	135.2	-111.0
1	0	211.9	223.8
1	1	113.2	-115.2
1	3	168.1	-139.5
1	4	161.1	148.7
1	5	79.4	-56.0
2	3	87.7	77.5
4	0	123.1	130.2
4	4	86.2	93.2
6	0	90.4	96.0
6	4	82.7	70.7
7	0	73.5	85.1
7	3	83.3	-71.7
8	0	91.9	-54.8
8	1	123.7	86.8
8	3	92.4	94.5
9	0	147.4	-156.2
9	1	103.4	100.1
9	2	78.8	-55.8
9	3	109.2	106.0
9	4	100.7	-113.0
10	0	195.9	188.5
		H = 11	
1	2	106.0	-88.7
3	0	173.3	188.3
3	4	144.2	138.9
4	0	83.0	-83.2
4	3	83.9	-53.7
4	4	80.2	-63.7
5	1	100.4	88.1
5	3	115.1	116.6
6	1	79.3	-68.2
7	0	139.1	130.8
7	3	80.7	-54.8
7	4	84.2	90.8
		H = 12	
0	0	75.2	66.0
2	1	135.6	110.2
2	3	102.3	112.0
4	0	142.7	129.8
4	4	129.5	93.6
6	0	138.1	130.0
6	1	84.4	-71.8
6	4	91.4	98.7
		H = 13	
1	0	116.6	125.0
3	1	147.2	125.5
3	3	145.8	141.5
4	0	164.4	-153.6
4	1	100.4	72.2
5	0	221.4	192.3
		H = 14	
2	0	152.2	141.5
3	0	95.3	71.5

A dissimilar arrangement of the potassium ions is observed about the two Rh atoms. The potassiums K(1) and K(2) are transformed by the centre at (0,0,0) and the mirror plane $(x,y,0)$ into a cubic configuration about the Rh(1) atom with the Rh(1)–K(1) and Rh(2)–K(2) interatomic distances of 4·07 and 4·14 Å respectively (Fig. 2).

The eight potassium atoms surrounding the Rh(2) atom form a trapezoid as shown in Fig. 2. In this arrangement two 'long' and two 'short' Rh(2)–K(1) and Rh(2)–K(2) interatomic distances are observed. The Rh(2)–K(1) distances are 5·28 and 4·09 Å respectively, and those for Rh(2)–K(2) are 5·58 and 4·24 Å respectively.

The oxygen atoms cluster about the mirror plane $(x,y,0)$ which is suggestive of hydrogen bonding and the possible existence of a delocalized proton charge. The respective distances between O(1) and its mirror image, O(2) and O(3), and O(1) and O(3), viz. 2·90 ± 0·08, 2·94 ± 0·08 and 3·00 ± 0·12 Å, indicate hydrogen bonding (Pimentel & McClellan, 1960).

Equation (1) in Table 4 gives the least-squares plane which passes through the atomic arrangement Rh(2), Br(4), Br(5), Br(8) and the mirror image of Br(5), while equation (2) represents the plane orthogonal to the first and passing through the atoms Rh(2), Br(5), Br(6), Br(7) and the mirror image of Br(5). The maximum deviations are 0·01 and 0·04 Å respectively, showing both the arrays to be planar.

The molecular packing in the unit cell is illustrated by the stereopair in Fig. 3. The closest approach of two Rh atoms is 7·44 ± 0·01 Å, observed between Rh(1) and Rh(2). Br(3) and Br(5), each forming part of a separate octahedron, show the shortest non-bonded approach distance of 3·99 ± 0·01 Å for this species.

The presence of one proton for each molecule of stoichiometry $K_8Rh_3Br_{18}.10H_2O$ suggests that the complete formula is $HK_8Rh_3Br_{18}.10H_2O$ hence showing all rhodium atoms to be in the +3 oxidation state. This is, of course, to be expected because the mode of preparation precluded any higher oxidation state from being achieved. The single question that remains to be answered concerns the possibility that the proton could arise from a hydrolysis of $RhBr_6^{3-}$ to give $RhBr_5(H_2O)^{2-}$ which could in turn deprotonate to $RhBr_5(OH)^{3-} + H^+$. The time taken to record the pH was no more than 60 seconds after dissolution of the complex whilst the measured half-time for hydrolysis of $RhBr_6^{3-}$ is of the order or 10^4 sec according to the kinetic measurements made under similar con-

Table 4. *Equations for least-squares planes*

Atoms	Equation	Maximum deviation from plane	
Rh(2), Br(4), Br(8), Br(5), Br(5) mirror image	$0.6482X + 0.7616Y = 5.6738$*	0·01	(1)
Rh(2), Br(6), Br(7), Br(5), Br(5) mirror image	$0.7647Z - 0.6444Y = -1.1473$	0·04	(2)

* X, Y and Z (in Å units) refer to the crystallographic axes a, b and c respectively.

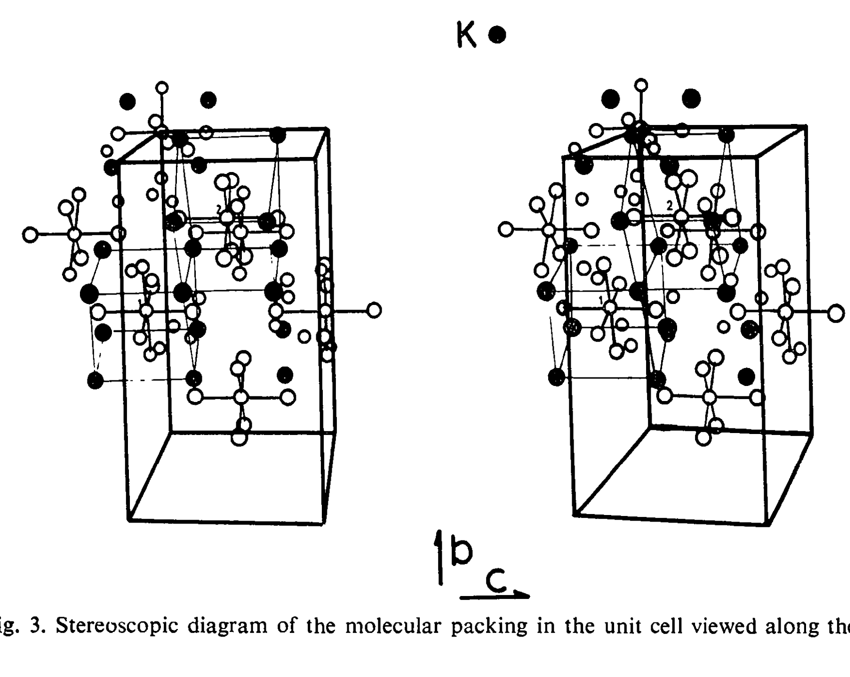


Fig. 3. Stereoscopic diagram of the molecular packing in the unit cell viewed along the a axis.

ditions, but at higher temperatures, *i.e.* 35 °C. Even if some small amount of hydrolysis did occur one would expect the aquo-acid, $RhBr_5(H_2O)^{2-}$, to have a $pK_a > 8$ when compared to $RhCl_5(H_2O)^{2-}$ where the $pK_a > 8$.

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The Crystal Structure of $(+)_{546}$-Tris-(*R*,*R*-2,4-diaminopentane)cobalt(III) Chloride Monohydrate, $(+)_{546}$-[Co(*R*,*R*-ptn)$_3$]$Cl_3.H_2O$

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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 $87·9 \pm 1·3°$. The absolute configuration of the complex ion is Λ, 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)$_3$]$Cl_3.H_2O$, was expected to have the absolute configuration Λ from the positive circular dichroism band in the first transition region. The other, $(-)_{546}$-[Co(*R*,*R*-ptn)$_3$]Cl_3 $2H_2O$, 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)$_3$]$Cl_3.H_2O$.

Experimental

Crystals of $(+)_{546}$-[Co(*R*,*R*-ptn)$_3$]$Cl_3.H_2O$ 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($C_5H_{14}N_2$)$_3Cl_3$ H_2O, F.W. 489·9; orthorhombic, $a = 17·516 \pm 0·003$, $b = 13·537 \pm 0·003$, $c = 11·048 \pm 0·002$ Å, $U = 2620$ Å^3; $D_m = 1·230$ g.cm^{-3}, $Z = 4$, $D_x = 1·242$ g.cm^{-3}. Space group $P2_12_12_1$ (D_2^4, 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, $2·0° + 1·0° \times \tan\theta$. 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-