

The packing of the structure is such that the centres of the ions are all relatively far apart. The shortest Fe—As distance of 6.53 Å is longer than the corresponding distance in alkaline and alkaline-earth nitroprussides. The crystal field acting on the anion is therefore weak and, though the nitroprusside ion is a somewhat distorted octahedron located in a site of  $C_1$  symmetry, a single peak in the CN stretching region is observed (Gentil & Aymonino, 1977).

The nitrosyl groups are neither oriented in a given specific direction nor are they close to each other, as in  $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$  (Castellano, Piro & Rivero, 1977). This explains the much narrower NO stretching band as compared with the Sr salt (Gentil & Aymonino, 1977).

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### Crystal and Molecular Structures of Trinuclear Rhodium(III) Complexes: *trans*- $\mu_3$ -Oxo-tris[bis(acetato)aquarhodium(III)] Perchlorate Dihydrate and Monohydrate

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The structures of *trans*- $\mu_3$ -oxo-tris[bis(acetato)aquarhodium(III)] perchlorate dihydrate (*A*) and monohydrate (*B*) have been determined by single-crystal X-ray diffraction. *A* is monoclinic, space group  $P2_1/c$ , with  $a = 11.737$  (2),  $b = 14.962$  (4),  $c = 15.200$  (4) Å,  $\beta = 92.11$  (3)°,  $Z = 4$ . *B* is monoclinic, space group  $P2_1$ , with  $a = 8.105$  (3),  $b = 13.959$  (5),  $c = 11.515$  (4) Å,  $\beta = 93.95$  (3)°,  $Z = 2$ . The structures were solved by the heavy-atom technique and refined by full-matrix least squares to  $R = 0.049$  for 2435 counter reflexions (*A*), and 0.055 for 1489 reflexions (*B*), for which  $F > 3.92\sigma(F)$ . The trinuclear complex cation contains three Rh atoms at the vertices of an equilateral triangle with a bridging O atom in the centre. The average Rh—Rh length is 3.33 Å.

#### Introduction

The Rh—carboxylic acid compound which has been most thoroughly examined is the dinuclear complex,  $\text{Rh}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$ . X-ray studies (Poray-Koshits & Antschishkina, 1962; Cotton, De Boer, La Prade, Pipal & Ucko, 1971) have shown that it contains an  $\text{H}_2\text{O}-\text{Rh}-\text{Rh}-\text{H}_2\text{O}$  group with a multiple metal—metal bond (2.385 Å). Uemura, Spencer & Wilkinson (1973) obtained an  $\text{Rh}^{\text{III}}$  complex of formula  $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{ClO}_4\cdot 2\text{H}_2\text{O}$  by ozonization

of the binuclear complex in acetic acid. On the basis of electronic, IR and NMR spectra and from the results of electrochemical reduction, these authors have shown that the complex contains an  $M_3\text{O}$  group, found earlier for Cr (Figgis & Robertson, 1965; Chang & Jeffrey, 1970), Mn (Hessel & Romers, 1969), Fe (Figgis & Robertson, 1965; Anzenhofer & De Boer, 1969) and Ru (Cotton & Norman, 1972) compounds.

Baranovski, Mazo & Dikareva (1971) prepared the same compound by reacting  $\text{Rh}^{\text{III}}$  chloride monohydrate with Ag acetate. From the powder photo-

graphs of the Rh and Cr acetate perchlorates they suggested that these compounds are isomorphous. In order to establish the structure of the Rh<sup>III</sup> complex an X-ray analysis has been carried out.

Table 1. *Crystal data*

[Rh <sub>3</sub> O(CH <sub>3</sub> COO) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ]- ClO <sub>4</sub> ·2H <sub>2</sub> O (A)	[Rh <sub>3</sub> O(CH <sub>3</sub> COO) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ]- ClO <sub>4</sub> ·H <sub>2</sub> O (B)
FW 868.5	FW 850.5
Monoclinic, space group <i>P</i> 2 <sub>1</sub> / <i>c</i>	Monoclinic, space group <i>P</i> 2 <sub>1</sub>
<i>a</i> = 11.737 (2) Å	<i>a</i> = 8.105 (3) Å
<i>b</i> = 14.962 (4)	<i>b</i> = 13.959 (5)
<i>c</i> = 15.200 (4)	<i>c</i> = 11.515 (5)
<i>β</i> = 92.11 (3)°	<i>β</i> = 93.95 (3)°
<i>V</i> = 2667 Å <sup>3</sup>	<i>V</i> = 1299 Å <sup>3</sup>
<i>Z</i> = 4	<i>Z</i> = 2
<i>D<sub>m</sub></i> = 2.17 g cm <sup>-3</sup>	<i>D<sub>m</sub></i> = 2.16 g cm <sup>-3</sup>
<i>D<sub>x</sub></i> = 2.16	<i>D<sub>x</sub></i> = 2.17

Table 2. *Final positional parameters* (×10<sup>4</sup>; for Rh ×10<sup>5</sup>), with *e.s.d.*'s in parentheses, of [Rh<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O (A)

	<i>x</i>	<i>y</i>	<i>z</i>
Rh(1)	9480 (12)	36414 (9)	35234 (8)
Rh(2)	33394 (12)	25736 (8)	41076 (8)
Rh(3)	33777 (12)	41164 (8)	25345 (8)
Cl	2678 (5)	6656 (4)	374 (4)
O(1)	1055 (11)	3660 (8)	4864 (8)
O(2)	2733 (11)	3026 (8)	5258 (7)
O(3)	543 (11)	2326 (8)	3454 (9)
O(4)	2144 (12)	1620 (7)	3909 (8)
O(5)	4682 (10)	3357 (8)	4408 (8)
O(6)	4722 (10)	4408 (8)	3350 (8)
O(7)	4101 (10)	1995 (7)	3079 (8)
O(8)	4200 (11)	3047 (8)	2030 (8)
O(9)	2696 (11)	5294 (7)	2880 (8)
O(10)	1104 (12)	5005 (8)	3577 (9)
O(11)	2204 (13)	3919 (9)	1575 (7)
O(12)	551 (11)	3697 (9)	2230 (8)
O( <i>b</i> )	2569 (10)	3449 (8)	3396 (7)
O(1 <i>r</i> )	-828 (10)	3825 (8)	3700 (8)
O(2 <i>r</i> )	4170 (10)	1594 (7)	4932 (7)
O(3 <i>r</i> )	4203 (11)	4849 (8)	1551 (7)
O(1Cl)	3312 (18)	6637 (15)	1173 (13)
O(2Cl)	3455 (15)	6843 (13)	9695 (11)
O(3Cl)	1841 (16)	7311 (11)	323 (11)
O(4Cl)	2152 (18)	5816 (12)	222 (15)
O(1 <i>w</i> )	-3519 (12)	4967 (9)	1436 (9)
O(2 <i>w</i> )	-2421 (17)	3627 (15)	2445 (17)
C(1)	1817 (18)	3445 (12)	5407 (11)
C(2)	1643 (17)	3709 (14)	6343 (11)
C(3)	1156 (20)	1643 (13)	3628 (13)
C(4)	543 (17)	726 (12)	3433 (12)
C(5)	5100 (15)	4023 (12)	4035 (12)
C(6)	6180 (16)	4435 (13)	4494 (14)
C(7)	4404 (15)	2282 (12)	2316 (11)
C(8)	5034 (17)	1643 (12)	1782 (12)
C(9)	1837 (19)	5516 (12)	3286 (13)
C(10)	1634 (19)	6505 (12)	3447 (14)
C(11)	1152 (21)	3776 (11)	1572 (10)
C(12)	502 (19)	3707 (14)	695 (13)

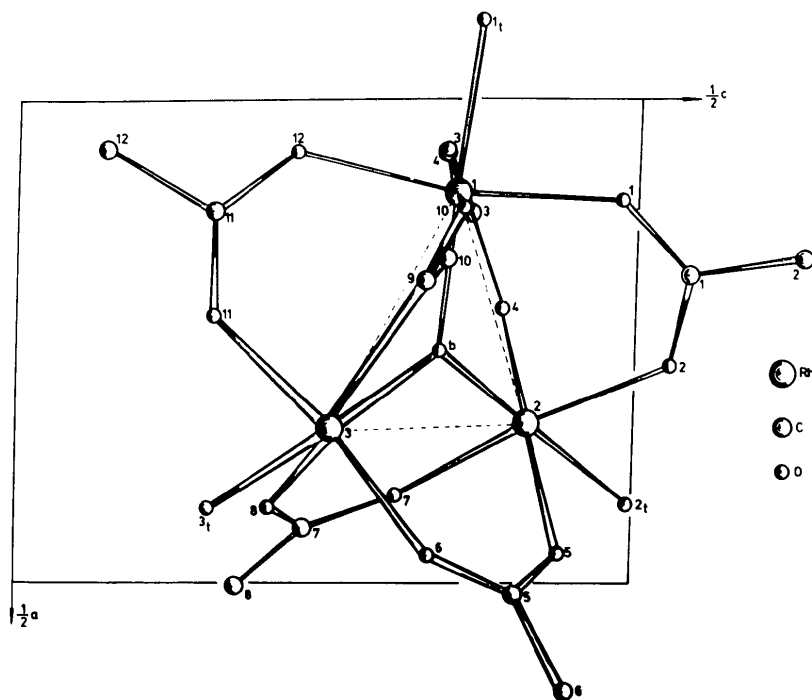
## Experimental

Red-brown monoclinic crystals were prepared by the method of Uemura *et al.* (1973). Preliminary photographic studies showed that during crystallization from aqueous solution two types of crystals were obtained. They do not differ in habit but detailed X-ray studies have shown that they are the dihydrate and monohydrate. Crystal data are given in Table 1.

Weissenberg photographs were used to determine the space groups and approximate cell dimensions. Space group *P*2<sub>1</sub> (for *B*) was chosen on the basis of  $|E|$  statistics. The subsequent structure analysis confirmed this choice. Intensities were measured on a Syntex *P*2<sub>1</sub> four-circle diffractometer equipped with scintillation counter and graphite monochromator. 2927 (*A*) and 1524 (*B*) reflexions were collected with Cu *Kα* radiation by the  $\theta$ -2 $\theta$  scan technique. After each group of 15 reflexions the intensity of a standard was measured and no significant change observed. The in-

Table 3. *Final positional parameters* (×10<sup>3</sup>), with *e.s.d.*'s in parentheses, of [Rh<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (B)

	<i>x</i>	<i>y</i>	<i>z</i>
Rh(1)	-80.6 (3)	173.3 (3)	149.1 (2)
Rh(2)	119.0 (3)	227.6 (2)	402.8 (2)
Rh(3)	82.9 (3)	0	319.6 (2)
Cl	527 (1)	668 (1)	231 (1)
O(1)	-224 (3)	265 (2)	228 (2)
O(2)	-101 (3)	293 (2)	410 (2)
O(3)	88 (3)	274 (2)	110 (2)
O(4)	203 (3)	319 (2)	284 (2)
O(5)	351 (3)	170 (2)	421 (2)
O(6)	318 (3)	14 (2)	390 (2)
O(7)	49 (3)	151 (2)	542 (2)
O(8)	1 (3)	-1 (2)	481 (2)
O(9)	-149 (3)	-51 (2)	260 (2)
O(10)	-265 (3)	74 (2)	158 (2)
O(11)	172 (3)	-26 (2)	163 (2)
O(12)	41 (3)	83 (2)	44 (2)
O( <i>b</i> )	33 (3)	131 (1)	293 (2)
O(1 <i>r</i> )	-207 (3)	217 (2)	-4 (2)
O(2 <i>r</i> )	217 (3)	323 (2)	527 (2)
O(3 <i>r</i> )	132 (3)	-151 (2)	343 (2)
O(1Cl)	593 (6)	218 (4)	724 (4)
O(2Cl)	476 (5)	174 (4)	885 (2)
O(3Cl)	337 (5)	210 (4)	726 (3)
O(4Cl)	466 (9)	73 (3)	742 (5)
O( <i>w</i> )	35 (4)	247 (2)	845 (2)
C(1)	-225 (4)	300 (2)	327 (3)
C(2)	-364 (4)	363 (3)	363 (3)
C(3)	184 (5)	326 (3)	176 (3)
C(4)	299 (5)	388 (3)	110 (4)
C(5)	404 (4)	89 (3)	420 (3)
C(6)	580 (5)	70 (3)	461 (3)
C(7)	2 (4)	66 (2)	557 (3)
C(8)	-61 (4)	41 (3)	675 (3)
C(9)	-262 (4)	-11 (3)	199 (3)
C(10)	-424 (5)	-71 (3)	181 (3)
C(11)	138 (5)	7 (3)	64 (3)
C(12)	222 (5)	-29 (3)	-38 (3)

Fig. 1. A view of the trinuclear cation along *b*.Table 4. *Interatomic distances (Å) for [Rh<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O (A) and [Rh<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (B)*

	<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>
Rh(1)—O( <i>b</i> )	1.941 (12)	1.93 (2)	C(9)—O(9)	1.25 (2)	1.25 (4)
Rh(2)—O( <i>b</i> )	1.906 (11)	1.94 (2)	C(9)—O(10)	1.24 (2)	1.28 (5)
Rh(3)—O( <i>b</i> )	1.924 (12)	1.90 (2)	C(11)—O(11)	1.25 (3)	1.25 (4)
Rh(1)—O(1 <i>t</i> )	2.129 (12)	2.07 (2)	C(11)—O(12)	1.25 (2)	1.33 (5)
Rh(2)—O(2 <i>t</i> )	2.140 (11)	2.08 (2)	C(1)—C(2)	1.50 (3)	1.50 (5)
Rh(3)—O(3 <i>t</i> )	2.117 (1)	2.16 (2)	C(3)—C(4)	1.57 (3)	1.51 (6)
Rh(1)—O(1)	2.037 (12)	1.99 (2)	C(5)—C(6)	1.55 (3)	1.50 (5)
Rh(1)—O(3)	2.026 (13)	2.03 (2)	C(7)—C(8)	1.47 (3)	1.52 (5)
Rh(1)—O(10)	2.050 (12)	2.04 (2)	C(9)—C(10)	1.52 (3)	1.56 (5)
Rh(1)—O(12)	2.005 (12)	2.05 (2)	C(11)—C(2)	1.51 (3)	1.48 (5)
Rh(2)—O(2)	2.028 (11)	2.01 (2)	Rh(1)···Rh(2)	3.322 (2)	3.329 (3)
Rh(2)—O(4)	2.016 (13)	2.03 (2)	Rh(1)···Rh(3)	3.348 (2)	3.333 (3)
Rh(2)—O(5)	2.003 (12)	2.04 (2)	Rh(2)···Rh(3)	3.325 (2)	3.325 (3)
Rh(2)—O(7)	2.024 (12)	2.04 (2)	O(1)···O(2)	2.25 (2)	2.29 (3)
Rh(3)—O(6)	2.019 (12)	2.03 (2)	O(3)···O(4)	2.24 (2)	2.24 (3)
Rh(3)—O(8)	2.033 (12)	2.02 (2)	O(5)···O(6)	2.25 (2)	2.22 (4)
Rh(3)—O(9)	2.013 (12)	2.08 (2)	O(7)···O(8)	2.25 (2)	2.26 (3)
Rh(3)—O(11)	1.991 (13)	2.02 (2)	O(9)···O(10)	2.22 (2)	2.28 (3)
C(1)—O(1)	1.24 (2)	1.24 (4)	O(11)···O(12)	2.24 (2)	2.27 (3)
C(1)—O(2)	1.27 (2)	1.34 (4)	O(1)···O(3)	2.97 (2)	2.95 (3)
C(3)—O(3)	1.27 (2)	1.28 (5)	O(1)···O(10)	2.81 (2)	2.80 (3)
C(3)—O(4)	1.22 (3)	1.25 (4)	O(1)···O(1 <i>t</i> )	2.79 (2)	2.77 (3)
C(5)—O(5)	1.26 (2)	1.21 (4)	Cl—O(1Cl)	1.40 (2)	1.33 (5)
C(5)—O(6)	1.26 (2)	1.29 (4)	Cl—O(2Cl)	1.43 (2)	1.34 (3)
C(7)—O(7)	1.30 (2)	1.27 (4)	Cl—O(3Cl)	1.39 (2)	1.31 (5)
C(7)—O(8)	1.24 (2)	1.27 (4)	Cl—O(4Cl)	1.41 (2)	1.36 (4)

Table 5. Bond angles ( $^{\circ}$ ) for  $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{ClO}_4$  dihydrate (*A*) and monohydrate (*B*)

	<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>
Rh(1)—O( <i>b</i> )—Rh(2)	119.4 (6)	118 (1)	O(2 <i>t</i> )—Rh(2)—O(2)	83.7 (5)	88.7 (9)
Rh(1)—O( <i>b</i> )—Rh(3)	120.1 (6)	121 (1)	O(2 <i>t</i> )—Rh(2)—O(4)	84.4 (5)	85.9 (9)
Rh(2)—O( <i>b</i> )—Rh(3)	120.5 (6)	120 (1)	O(2 <i>t</i> )—Rh(2)—O(5)	85.9 (5)	82.9 (9)
O( <i>b</i> )—Rh(1)—O(1 <i>t</i> )	178.1 (5)	178.8 (9)	O(2 <i>t</i> )—Rh(2)—O(7)	87.4 (5)	84.9 (9)
O( <i>b</i> )—Rh(2)—O(2 <i>t</i> )	178.5 (5)	176.3 (9)	O(2)—Rh(2)—O(4)	95.8 (5)	94.5 (9)
O( <i>b</i> )—Rh(3)—O(3 <i>t</i> )	177.5 (4)	178.3 (9)	O(2)—Rh(2)—O(5)	84.6 (5)	170.9 (9)
O( <i>b</i> )—Rh(1)—O(1)	94.4 (5)	93.6 (9)	O(2)—Rh(2)—O(7)	171.0 (5)	84.8 (9)
O( <i>b</i> )—Rh(1)—O(3)	94.5 (5)	96.4 (9)	O(4)—Rh(2)—O(5)	170.2 (5)	88.3 (9)
O( <i>b</i> )—Rh(1)—O(10)	93.7 (5)	93.5 (9)	O(4)—Rh(2)—O(7)	84.6 (5)	170.7 (9)
O( <i>b</i> )—Rh(1)—O(12)	95.8 (5)	95.7 (9)	O(5)—Rh(2)—O(7)	93.4 (5)	90.9 (9)
O(1 <i>t</i> )—Rh(1)—O(1)	84.1 (5)	86.0 (9)	O( <i>b</i> )—Rh(3)—O(6)	95.0 (5)	99.0 (9)
O(1 <i>t</i> )—Rh(1)—O(3)	84.5 (5)	84.7 (9)	O( <i>b</i> )—Rh(3)—O(8)	95.8 (5)	94.4 (9)
O(1 <i>t</i> )—Rh(1)—O(10)	87.3 (5)	85.4 (9)	O( <i>b</i> )—Rh(3)—O(9)	93.8 (5)	95.7 (9)
O(1 <i>t</i> )—Rh(1)—O(12)	85.7 (5)	84.6 (9)	O( <i>b</i> )—Rh(3)—O(11)	94.4 (5)	96.4 (9)
O(1)—Rh(1)—O(3)	94.1 (5)	94.5 (9)	O(3 <i>t</i> )—Rh(3)—O(6)	87.4 (4)	82.7 (9)
O(1)—Rh(1)—O(10)	86.8 (5)	87.9 (9)	O(3 <i>t</i> )—Rh(3)—O(8)	84.6 (4)	85.4 (8)
O(3)—Rh(1)—O(12)	86.8 (5)	86.2 (9)	O(3 <i>t</i> )—Rh(3)—O(9)	85.8 (4)	82.5 (9)
O(10)—Rh(1)—O(12)	90.8 (5)	89.8 (9)	O(3 <i>t</i> )—Rh(3)—O(11)	83.2 (4)	83.7 (8)
O(1)—Rh(1)—O(12)	169.6 (5)	170.5 (9)	O(6)—Rh(3)—O(8)	91.8 (5)	89.3 (9)
O(3)—Rh(1)—O(10)	171.6 (5)	170.1 (9)	O(6)—Rh(3)—O(9)	87.7 (5)	165.0 (9)
O( <i>b</i> )—Rh(2)—O(2)	94.9 (5)	93.7 (9)	O(6)—Rh(3)—O(11)	170.5 (5)	89.5 (9)
O( <i>b</i> )—Rh(2)—O(4)	95.1 (5)	96.7 (9)	O(8)—Rh(3)—O(9)	170.4 (5)	87.4 (9)
O( <i>b</i> )—Rh(2)—O(5)	94.6 (5)	94.6 (9)	O(8)—Rh(3)—O(11)	86.1 (5)	96.0 (9)
O( <i>b</i> )—Rh(2)—O(7)	94.0 (5)	92.6 (9)	O(9)—Rh(3)—O(11)	92.8 (5)	91.0 (9)
C(1)—O(1)—Rh(1)	132 (1)	136 (2)	C(2)—C(1)—O(1)	116 (2)	122 (3)
C(1)—O(2)—Rh(2)	130 (1)	129 (2)	C(2)—C(1)—O(2)	116 (2)	113 (3)
C(3)—O(3)—Rh(1)	130 (1)	131 (2)	C(4)—C(3)—O(3)	114 (2)	114 (3)
C(3)—O(4)—Rh(2)	133 (1)	134 (2)	C(4)—C(3)—O(4)	117 (2)	120 (3)
C(5)—O(5)—Rh(2)	133 (1)	134 (2)	C(6)—C(5)—O(5)	116 (2)	120 (3)
C(5)—O(6)—Rh(3)	131 (1)	131 (2)	C(6)—C(5)—O(6)	116 (2)	115 (3)
C(7)—O(7)—Rh(2)	134 (1)	134 (2)	C(8)—C(7)—O(7)	116 (2)	117 (3)
C(7)—O(8)—Rh(3)	133 (1)	130 (2)	C(8)—C(7)—O(8)	120 (2)	117 (3)
C(9)—O(9)—Rh(3)	134 (1)	130 (2)	C(10)—C(9)—O(9)	118 (2)	115 (3)
C(9)—O(10)—Rh(1)	131 (1)	131 (2)	C(10)—C(9)—O(10)	115 (2)	117 (3)
C(11)—O(11)—Rh(3)	133 (1)	133 (2)	C(12)—C(11)—O(11)	118 (2)	121 (3)
C(11)—O(12)—Rh(1)	132 (1)	134 (2)	C(12)—C(11)—O(12)	115 (2)	115 (3)
O(1)—C(1)—O(2)	127 (2)	125 (3)	O(1Cl)—Cl—O(1Cl)	107 (1)	113 (3)
O(3)—C(3)—O(4)	128 (2)	125 (3)	O(1Cl)—Cl—O(3Cl)	114 (1)	104 (3)
O(5)—C(5)—O(6)	127 (2)	125 (3)	O(1Cl)—Cl—O(4Cl)	110 (1)	116 (3)
O(7)—C(7)—O(8)	124 (1)	126 (3)	O(2Cl)—Cl—O(3Cl)	107 (1)	108 (3)
O(9)—C(9)—O(10)	126 (2)	128 (3)	O(2Cl)—Cl—O(4Cl)	110 (1)	106 (3)
O(11)—C(11)—O(12)	127 (2)	123 (3)	O(3Cl)—Cl—O(4Cl)	108 (1)	109 (3)

tensities were corrected for Lorentz and polarization effects but not for absorption.

Both structures were solved by the heavy-atom method and refined by full-matrix least squares. The Rh atom was found from a Patterson function and the remaining non-hydrogen atoms in successive Fourier syntheses. Isotropic refinement gave  $R = 0.065$  for (*A*) and  $0.063$  for (*B*). Anisotropic thermal parameters were then introduced, but, because of the limited data available for (*B*), the C atoms were kept isotropic. Final refinement converged to  $R_1 = 0.049$  and  $R_2 = 0.064$  for (*A*), and  $R_1 = 0.055$  and  $R_2 = 0.075$  for (*B*), where  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2(F)$ . Scattering factors for neutral atoms were taken from Cromer & Waber (1974).

All calculations were performed with the Syntex XTL structure determination system (Nova 1200 computer and additional external disc memory) with the Syntex crystallographic programs. The final parameters are listed in Tables 2 and 3.\* In Tables 4 and 5 the interatomic distances and valence angles are given. The atom numbering is shown in Figs. 1 and 3. Table 6 contains the equations of planes passing through certain groups of atoms and the distances of atoms from these planes.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32318 (88 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 6. *Least-squares planes in*  
 $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  (A)

Values are given in the following order: atoms defining the plane, equation of plane, deviations of atoms from the plane ( $\text{\AA}$ ).

Plane 1: Rh(1), Rh(2), Rh(3)

$$-0.2161X - 0.7005Y - 0.6801Z + 7.6610 = 0$$

O(b) -0.016, O(1t) 0.009, O(2t) -0.004, O(3t) 0.070

Plane 2: O(1), O(3), O(10), O(12)

$$0.9770X - 0.1540Y - 0.1473Z + 0.6972 = 0$$

Rh(1) 0.1647, O(1) -0.016, O(3) 0.018, O(10) 0.019, O(12) -0.017

Plane 3: O(1), O(2), C(1), C(2)

$$0.4631X + 0.8693Y - 0.1727Z - 4.0690 = 0$$

O(1) 0.0, O(2) 0.0, C(1) 0.004, C(2) 0.0,

Rh(1) 0.268, Rh(2) 0.048

Plane 4: O(3), O(4), C(3), C(4)

$$0.3119X + 0.0124Y - 0.9500Z + 4.7137 = 0$$

O(3) 0.001, O(4) 0.001, C(3) -0.007,

C(4) 0.001, Rh(1) 0.094, Rh(2) 0.234

Plane 5: O(1), O(2), O(5), O(6), O(9), O(10)

$$-0.2262X - 0.7019Y - 0.6754Z + 9.1376 = 0$$

O(1) 0.03, O(2) -0.056, O(5) 0.024, O(6) -0.005,

O(9) 0.010, O(10) -0.040, Rh 1.46, O(b) 1.45,

O(t) 1.48

Plane 6: O(3), O(4), O(7), O(8), O(11), O(12)

$$-0.2248X - 0.6871Y - 0.6909Z + 6.2096 = 0$$

O(3) 0.070, O(4) -0.042, O(7) 0.004, O(8) 0.001,

O(11) 0.031, O(12) -0.06

Dihedral angles ( $^\circ$ )

1-2	90.2	1-5	0.6
1-4	55.2	1-6	1.1

### Description and discussion of the structure

These studies have shown that the occurrence of two crystalline forms of the trinuclear  $\text{Rh}^{\text{III}}$  acetate results from the presence of different amounts of water of crystallization. The results in Tables 4 and 5 indicate no significant differences in the geometry of the cation; hence, the following description pertains to both complexes.

The elements of the crystal structure are the complex cation  $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$ , perchlorate anions and uncoordinated water molecules. In the cation three Rh atoms linked through the bridging pairs of acetate ligands form an almost equilateral triangle. The trigonally coordinated O at the centre of the triangle and the water molecule at the terminal position complete the octahedral environment of Rh atoms. The complexation structure is similar to that found for Cr, Fe, Mn and Ru compounds. In the  $\text{Rh}_3\text{O}$  group the central O lies in a plane formed by the Rh atoms and is 1.92  $\text{\AA}$  from each of them. The Rh atoms form an almost equilateral triangle with a 3.33  $\text{\AA}$  side. Hence, the Rh-Rh distance is too long for any significant direct interaction to occur. The Rh-O(b) bond is shorter than all the other Rh-O bonds. The Rh-O(ac) length is almost identical to that found in  $\text{Rh}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$  but is shorter than the Rh-O( $\text{H}_2\text{O}$ ) distance in both trinuclear complexes. The Rh-O( $\text{H}_2\text{O}$ ) length, 2.12  $\text{\AA}$ , is much shorter than that, 2.31  $\text{\AA}$ , in the binuclear com-

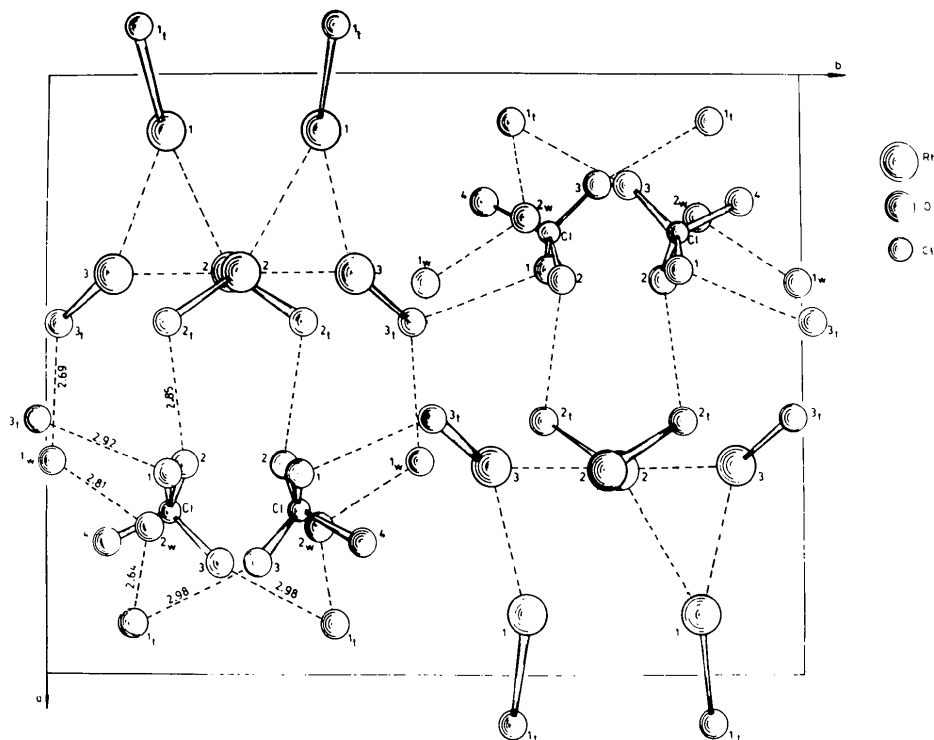


Fig. 2. Arrangement of the trinuclear cations, perchlorate anions and water molecules of crystallization in the crystal of  $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$  (A). Possible  $\text{OH} \cdots \text{O}$  hydrogen bonds are shown as broken lines.

plex. The latter contains, however, a very strong, triple Rh—Rh bond (2.385 Å) which makes the water molecules weakly coordinated *trans* to that bonding. The lack of an Rh—Rh interaction also results in an increase in the Rh—O—C angles in the trinuclear complexes (132° *versus* 119° in the binuclear complex).

The O atoms form somewhat distorted octahedra around the Rh atoms. All O(*b*)—Rh—O(*ac*) angles exceed 90° whereas O(*ac*)—Rh—O(H<sub>2</sub>O) are all smaller. The distortion results from the fact that each Rh is displaced from the plane of the four acetate O towards the bridging O atom.

The acetate groups are almost planar and inclined at an average of 55° to the plane formed by the Rh atoms. All C—C and C—O distances and O—C—O and O—C—C angles are similar to those in the binuclear complex. The planes running through the O atoms situated above and below the plane of the Rh atoms are almost parallel to it and to each other.

Tables 4 and 5 show that the cation has roughly *D*<sub>3h</sub> symmetry. In both trinuclear complexes the uncoordinated water molecules are arranged so as to be capable of hydrogen-bond formation between the complex cations and perchlorate anions. The intermolecular contacts marked in Figs. 2 and 3 indicate the probable occurrence of hydrogen bonds. Although it was not possible to establish the positions of the H atoms and, hence, an accurate hydrogen-bonding scheme, one may

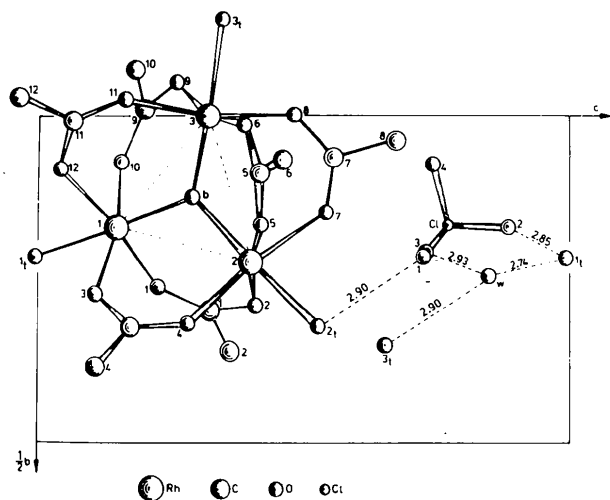


Fig. 3. Projection of the structure of  $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$  (B) along *a*. Only one of the two structure units has been plotted.

presume that the different schemes account for the different cell parameters and space groups. The OH...O distances marked in the figures are consistent with the hydrogen-bond lengths reported by Hamilton & Ibers (1968).

Simultaneously with the structure analysis, magnetic susceptibility measurements, and visible and IR spectra were also recorded. The results are consistent with the trinuclear structure. The compounds appeared to be diamagnetic over the entire temperature range from 77 to 292K, a result of the low-spin *d*<sup>6</sup> electron configuration.

The electronic spectra of octahedral Rh<sup>III</sup> compounds may be expected to exhibit two bands corresponding to the transitions  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ . In the complexes under investigation, these bands were observed at 19 000 and 28 000 cm<sup>-1</sup>, respectively.

The IR spectra exhibit two strong bands at 1425 and 1598 cm<sup>-1</sup> which may be assigned to symmetric and antisymmetric vibration of the COO group in the bridging acetates, and also at 175 and 622 cm<sup>-1</sup>, assigned to symmetric and antisymmetric vibration of the Rh<sub>3</sub>O group.

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