$$C_{44}H_{48}O_{10}.2NaClO_4$$

Fig. 3. Vue stéréoscopique de AA55/Na⁺ [programme SNOOPI (Davies, 1983)].

Dans le cristal, les noyaux anthracéniques sont donc parallèles, ils forment des paires 'sandwich faiblement décalé' avec un écart interplanaire correspondant à la distance de van der Waals ($\simeq 3,4$ Å). A température ambiante, le cristal émet une fluorescence dont les spectre est une bande large, non structurée, avec maximum situé à 580 nm. Cette émission correspond à un excimère décalé à fort recouvrement (Ferguson et al., 1976; Bouas-Laurent et al., 1986) La géométrie quasi sandwich observée dans les cristaux AA55.2NaClO₄ est sans doute la situation ultime avant le rapprochement des cycles aromatiques pour conduire à l'excimère.

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Structure of a Mononuclear Ruthenium(II) Complex Containing Carboxylato and Trimethylphosphine Ligands and an Aqua Ligand

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Abstract. Aquabis(trifluoroacetato)tris(trimethylphosphine)ruthenium(II), $[Ru(C_2F_3O_2)_2(C_3H_9P)_3(H_2O)]$, $M_r = 573 \cdot 35$, monoclinic, $P2_1/c$, $a = 15 \cdot 849$ (7), $b = 8 \cdot 760$ (4), $c = 17 \cdot 398$ (3) Å, $\beta = 90 \cdot 21$ (2)°, $U = 2415 \cdot 5$ Å³, $Z = 4$, $D_x = 1 \cdot 58$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 81$ mm⁻¹, $F(000) = 1160$, $T = 295$ K, $R = 0 \cdot 0452$ for 2594 unique reflections with $F_o \geq 4\sigma(F_o)$. The octahedral complex is mononuclear with three trimethylphosphine ligands in a facial configuration. The coordination sphere of the Ru atom is completed by two monodentate trifluoro-acetato ligands and an aqua ligand. The non-coordinated O atoms of the two trifluoroacetato ligands are both strongly hydrogen bonded to the aqua ligand, with O(carboxylate)···O(aqua) distances of $2 \cdot 644$ (8) and $2 \cdot 638$ (8) Å.

Introduction. Transition-metal carboxylate complexes possess some unusual properties which make them particularly interesting from the point of view of both inorganic synthesis and catalysis (Mehrotra & Bohra, 1983). As part of a study concerned with the synthesis, reactivity and the catalytic properties of carboxylate complexes of ruthenium (Albers, Liles, Singleton &

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Yates, 1984; Albers & Singleton, 1985; Albers, Singleton & Viney, 1986) we reported synthetic routes to dinuclear ruthenium(II) complexes based upon the formal equivalence between carboxylato and allyl ligands (see scheme). The diene–hydride complexes $[(\eta^4\text{-}C_8H_{12})RuH(L)_3]PF_6$ (L = phosphine ligand) are known to convert to the η^3-cyclooctenyl complexes $[(\eta^3\text{-}C_8H_{13})Ru(L)_3]PF_6$ in solution (Ashworth, Chalmers, Meintjies, Oosthuizen & Singleton, 1984), and herein we report the structure of one of the products of the reaction of $[(\eta^3\text{-}C_8H_{13})Ru(PMe_3)_3]PF_6$ with trifluoroacetic acid, $[Ru(O_2CCF_3)_2(PMe_3)_3(OH_2)]$ (I).

(I)
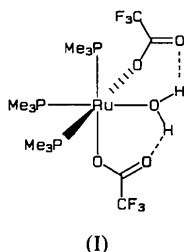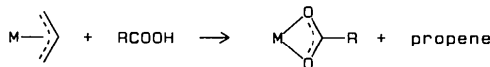
Experimental. The reaction of $[(\eta^3\text{-}C_8H_{13})\text{-}Ru(PMe_3)_3]PF_6$ (Ashworth et al., 1984) with trifluoroacetic acid in boiling acetone gives a purple solution from which a purple solid of stoichiometry $[\{Ru(O_2CCF_3)\text{-}(PMe_3)_3\}_2(O)](PF_6)_2$ (II) can be isolated. Crystallization from moist ethanol solution deposits colourless crystals of the title compound (I). Crystal: $0.30 \times 0.15 \times 0.15$ mm cut from a larger crystal; Philips PW 1100 four-circle diffractometer, graphite-crystal-monochromatized Mo $K\alpha$ radiation; lattice parameters: 25 reflections $10.48 \le \theta \le 16.04°$, least-squares refinement; $\omega/2\theta$ scan mode, scan width $1.20°$ in ω, scan speed $0.040°$ s^{-1} in ω, 15 s stationary background at each end of the scan; 4226 unique reflections with $3 \le \theta \le 23°$ measured in the quadrant $\pm h$, $+k$, $+l$, three standard reflections measured every 60 min showed no significant deviations from their mean intensities, no absorption corrections were applied: 2594 reflections with $F_o \ge 4\sigma(F_o)$ used in the analysis; structure solved by normal heavy-atom methods and refined using SHELX (Sheldrick, 1978); all hydrogen atoms located and refined with separate common isotropic temperature factors for the methyl and aqua H-atoms; one CF_3 group disordered, two positions refined for each of the three F atoms with a site occupation factor of 0.5 and isotropic temperature factors for each positon; all other non-H atoms anisotropic; least-squares refinement, $\sum w(\Delta F)^2$ minimized, $w = \sigma^{-2}(F_o)$ with the matrix blocked so that parameters for the ruthenium atom refined in every cycle and those for the PMe_3 ligands and the O_2CCF_3

and aqua ligands refined in alternate cycles, converged to give $R = 0.0452$ and $wR = 0.0419$; all reductions in wR significant at the 99.5% level (Hamilton, 1965); complex neutral-atom scattering factors used for all atoms (Cromer & Waber, 1974); in final cycles 339 parameters varied, comprising 180 positional parameters, 150 anisotropic temperature factor components, eight isotropic temperature factors and one overall scale, $\Delta\rho$ $+0.91$ to -0.53 e Å^{-3}, max. shift/ e.s.d. in final LS cycles 0.934.

(II)

(III)
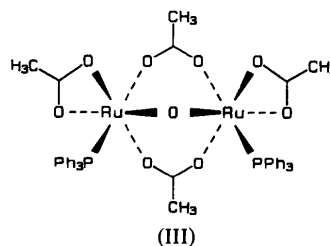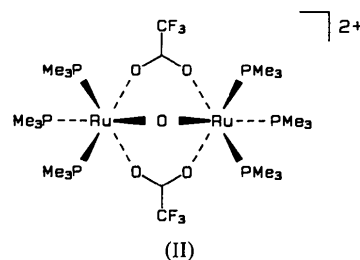
Discussion. The final atomic coordinates are given in Table 1.* Selected bond lengths and angles are given in Table 2. Fig. 1 is a perspective view of the complex showing the atom-numbering scheme; Fig. 2 shows the unit-cell contents.

The structure consists of isolated molecules occupying general positions in the unit cell. The octahedral complex is monomeric with the three trimethylphosphine ligands in a facial configuration. The coordination sphere is completed by two monodentate trifluoroacetato ligands and one aqua ligand. The non-coordinated oxygen atoms of the two trifluoroacetato ligands are both strongly hydrogen bonded to the aqua ligand with O(trifluoroacetate)$\cdots$O(aqua) distances of 2.644 (8) and 2.638 (8) Å and O(trifluoroacetato)$\cdots$H(aqua) distances of 1.95 (9) and 1.61 (9) Å. Similar strong hydrogen-bonding effects between monodentate carboxylato ligands and bridging aqua ligands have been observed in the dinuclear ruthenium(II) complexes $[\{L_2Ru(O_2CR)\}(\mu\text{-}O_2CR)_2\text{-}(\mu\text{-}OH_2)]$ $\{L_2 = $ cycloocta-1,5-diene (COD), $R = CF_3$

Table 1. *Fractional coordinates* ($\times 10^4$, $\times 10^5$ *for* Ru, $\times 10^3$ *for* H) *and equivalent isotropic temperature factors* (Å^2, $\times 10^3$, $\times 10^4$ *for* Ru) *for* (I)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U$_{eq}$
Ru	24856 (3)	1798 (4)	21080 (3)	375 (2)
P(1)	3690 (1)	26 (2)	1437 (1)	53 (1)
C(11)	4082 (5)	−1925 (9)	1373 (5)	75 (5)
C(12)	4576 (5)	958 (11)	1895 (7)	87 (6)
C(13)	3792 (6)	663 (12)	443 (6)	86 (7)
P(2)	2466 (1)	2753 (2)	2192 (1)	52 (1)
C(21)	1429 (6)	3558 (10)	2301 (6)	84 (6)
C(22)	3008 (7)	3406 (9)	3062 (6)	82 (6)
C(23)	2894 (7)	3995 (9)	1464 (6)	83 (6)
P(3)	1616 (1)	21 (2)	1083 (1)	61 (1)
C(31)	507 (5)	−107 (12)	1347 (6)	95 (6)
C(32)	1755 (7)	−1714 (11)	522 (6)	90 (7)
C(33)	1571 (7)	1438 (12)	310 (6)	94 (7)
O(41)	1470 (2)	280 (4)	2929 (3)	58 (2)
O(42)	1040 (3)	−2106 (5)	3108 (3)	81 (3)
C(41)	1083 (4)	−758 (7)	3265 (4)	58 (4)
C(42)	621 (5)	−221 (9)	3976 (5)	74 (5)
F(41)	1162 (4)	145 (7)	4522 (3)	133 (5)
F(42)	172 (4)	937 (7)	3871 (4)	130 (6)
F(43)	158 (3)	−1264 (6)	4300 (3)	110 (4)
O(51)	3232 (3)	98 (4)	3162 (2)	60 (3)
O(52)	3466 (4)	−2352 (5)	3380 (3)	89 (4)
C(51)	3510 (4)	−998 (8)	3516 (4)	60 (4)
C(52)	3994 (7)	−554 (11)	4271 (6)	99 (7)
F(51)	3666 (8)	442 (15)	4641 (7)	133 (4)*
F(52)	4792 (6)	−178 (10)	4051 (5)	98 (3)*
F(53)	4145 (7)	−1845 (12)	4698 (6)	118 (4)*
F(54)	3438 (8)	−659 (15)	4853 (7)	139 (4)*
F(55)	4151 (7)	949 (12)	4323 (7)	118 (3)*
F(56)	4586 (8)	−1424 (16)	4440 (8)	145 (5)*
O(6)	2386 (3)	−2348 (4)	2223 (3)	52 (3)
H(61)	190 (5)	−235 (10)	232 (5)	135 (25)*
H(62)	287 (5)	−244 (9)	263 (5)	135 (25)*

* Isotropic temperature factor.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* (I)

Ru—P(1)	2·245 (2)	Ru—P(2)	2·259 (1)
Ru—P(3)	2·254 (2)	Ru—O(4)	2·158 (4)
Ru—O(51)	2·179 (4)	Ru—O(6)	2·229 (4)
P(1)—C(11)	1·823 (8)	P(1)—C(12)	1·806 (10)
P(1)—C(13)	1·825 (1)	P(2)—C(21)	1·800 (10)
P(2)—C(22)	1·829 (11)	P(2)—C(23)	1·803 (10)
P(3)—C(31)	1·822 (8)	P(3)—C(32)	1·819 (10)
P(3)—C(33)	1·832 (10)	O(41)—C(41)	1·244 (8)
O(42)—C(41)	1·214 (8)	C(41)—C(42)	1·514 (11)
O(51)—C(51)	1·222 (8)	O(52)—C(51)	1·211 (9)
C(51)—C(52)	1·568 (13)		
O(6)—H(61)	0·79 (8)	O(6)—H(62)	1·05 (8)
P(1)—Ru—P(2)	96·0 (1)	P(1)—Ru—P(3)	95·9 (1)
P(2)—Ru—P(3)	96·0 (1)	P(1)—Ru—O(41)	169·9 (1)
P(2)—Ru—O(41)	94·6 (1)	P(3)—Ru—O(41)	94·0 (1)
P(1)—Ru—O(51)	88·6 (1)	P(2)—Ru—O(51)	89·2 (1)
P(3)—Ru—O(51)	172·7 (1)	O(41)—Ru—O(51)	81·3 (2)
P(1)—Ru—O(6)	92·7 (1)	P(2)—Ru—O(6)	169·9 (1)
P(3)—Ru—O(6)	88·1 (1)	O(41)—Ru—O(6)	85·9 (2)
O(51)—Ru—O(6)	86·0 (2)	Ru—P(1)—C(11)	112·3 (3)
Ru—P(1)—C(12)	113·8 (4)	C(11)—P(1)—C(12)	100·7 (4)
Ru—P(1)—C(13)	123·6 (3)	C(11)—P(1)—C(13)	101·4 (4)
C(12)—P(1)—C(13)	102·1 (5)	Ru—P(2)—C(21)	114·2 (3)
Ru—P(2)—C(22)	111·1 (3)	C(21)—P(2)—C(22)	102·5 (5)
Ru—P(2)—C(23)	123·5 (3)	C(21)—P(2)—C(23)	100·6 (5)
C(22)—P(2)—C(23)	102·4 (5)	Ru—P(3)—C(31)	113·1 (3)
Ru—P(3)—C(32)	113·6 (3)	C(31)—P(3)—C(32)	101·7 (5)
Ru—P(3)—C(33)	124·1 (3)	C(31)—P(3)—C(33)	101·0 (5)
C(32)—P(3)—C(33)	100·2 (5)	Ru—O(41)—C(41)	130·7 (4)
O(41)—C(41)—O(42)	129·2 (7)	O(41)—C(41)—C(42)	113·5 (6)
O(42)—C(41)—C(42)	117·3 (6)	C(41)—C(42)—F(41)	110·4 (7)
C(41)—C(42)—F(42)	114·1 (7)	Ru—O(51)—C(51)	130·1 (4)
O(51)—C(51)—O(52)	130·6 (7)	O(51)—C(51)—C(52)	113·7 (6)
O(52)—C(51)—C(52)	115·7 (7)	Ru—O(6)—H(61)	95 (6)
Ru—O(6)—H(62)	95 (4)	H(61)—O(6)—H(62)	125 (8)

(Albers, Liles, Singleton & Yates, 1984); $L = $ PMe$_2$Ph, $R = $ CF$_3$ (Albers, Liles, Singleton & Stead, 1986a); $L_2 = $ bicyclo[2.2.1]hepta-2,5-diene, $R = $ CCl$_3$ (Albers, Liles, Singleton & Stead, 1986b)} where the O(carboxylato)···O(aqua) and O(carboxylato)··· H(aqua) distances are in the ranges 2·48 (1) to 2·54 (1) Å and 1·31 (8) to 1·57 (8) Å respectively. The hydrogen bonding in (I) is also related to that observed in [Ru(O$_2$CCF$_3$)$_2$(CO)(PPh$_3$)$_2$(MeOH)] {the methanol solvate of [Ru(O$_2$CCF$_3$)$_2$(CO)(PPh$_3$)$_2$] and a proposed intermediate in the catalytic homogeneous dehydrogenation of alcohols} where one of the monodentate trifluoroacetato ligands is hydrogen bonded to the coordinated methanol with an O(trifluoroacetato)··· O(methanol) distance of 2·55 Å (Dobson & Robinson, 1977).
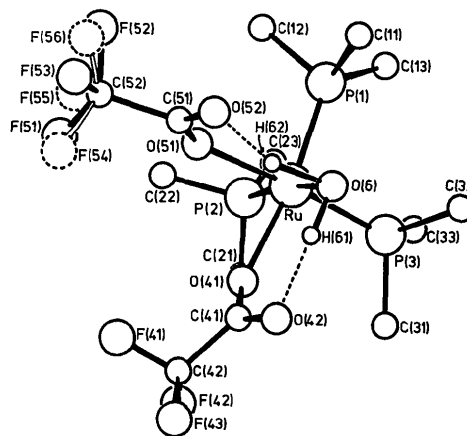

Fig. 1. A perspective view of (I) showing the atom-numbering scheme.
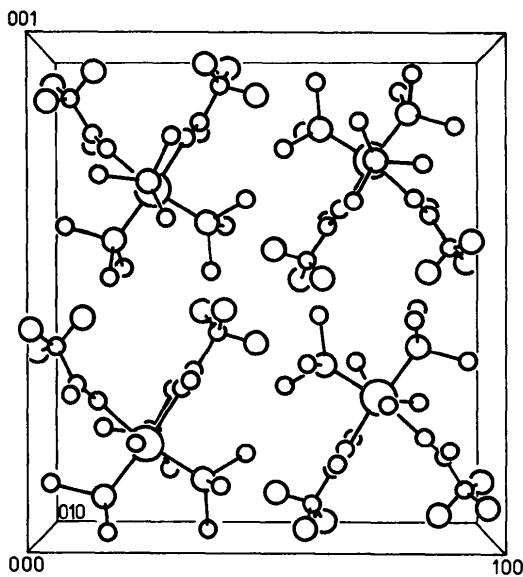

Fig. 2. The unit cell viewed perpendicular to the *ac* plane.

The Ru—P bond lengths of 2·254 (2) Å (*trans* to H_2O) and 2·245 (2) and 2·259 (2) Å (*trans* to O_2-CCF_3) in (I) are all within the range of previously reported Ru—P bond lengths *trans* to oxygen donor ligands (Albers, Liles, Singleton & Stead, 1986a; Ashworth, Nolte & Singleton, 1976, 1977; Jones, Wilkinson, Galas, Hursthouse & Malik, 1980; Skapski & Stephens, 1974), but are shorter than those reported as unexpectedly long (2·339–2·361 Å) for [Ru(O_2-CCF_3)$_2$(CO)(PPh$_3$)$_2$(MeOH)] (Dobson & Robinson, 1977). The Ru—O(trifluoroacetato) bond lengths of 2·158 (4) and 2·179 (4) Å are longer than those of 2·092 (6) to 2·104 (6) Å for the monodentate trifluoroacetato ligands *trans* to oxygen donor ligands in [{L_2Ru(O_2CCF$_3$)}$_2$(μ-O_2CCF$_3$)$_2$(μ-OH$_2$)] [L_2 = cycloocta-1,5-diene (Albers *et al.*, 1984); L = PMe$_2$Ph (Albers, Liles, Singleton & Stead, 1986a)], thus displaying the *trans* influence of the tertiary phosphine ligands. In contrast, no particular *trans* influence was observed in the structure of [Ru(O_2CCF$_3$)$_2$(CO)-(PPh$_3$)$_2$(MeOH)] (Dobson & Robinson, 1977). The reason for this is not immediately apparent.

The reaction of [(η^3-C_8H_{13})Ru(PMe$_3$)$_3$]PF$_6$ (Ashworth *et al.*, 1984) with trifluoroacetic acid in air gives a purple compound of stoichiometry [{Ru(O_2-CCF_3)(PMe$_3$)$_3$}$_2$O] (II), the precursor to (I). (II) is an analogue of the ruthenium(III) complex [{Ru(PPh$_3$)-(O_2CCH$_3$)$_2$}$_2$(μ-O)] (III) proposed to have the structure shown (Mitchell, Spencer & Wilkinson, 1973), and is also related to the recently reported dinuclear oxo-bridged diiron(III) hemerythrin models (Armstrong, Spool, Papefthymiou, Frankel & Lippard, 1984). (II) converts slowly in ethanol solution to the colourless crystalline (I), but we have as yet been unable to determine the mechanism of this unusual conversion.

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Structure of Bis(1-butanethiolato)mercury(II)

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Abstract. [Hg(C_4H_9S)$_2$], $M_r = 378·95$, tetragonal, $I4_1/a$, $a = 27·10$ (1), $c = 13·28$ (1) Å, $V = 9754$ (8) Å^3, $Z = 32$, $D_x = 2·06$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 129$ cm^{-1}, $F(000) = 5696$, $T = 207$ K, $R = 0·036$ for 1533 unique observed reflections. The two independent Hg atoms are tetrahedrally coordinated by the thiolate ligands. The HgS$_4$ tetrahedra share corners and edges forming spirals running parallel to c and with organic residues in the cavities.

Introduction. When Zeise (1834*a,b*) synthesized ethanethiol, he recognized immediately that it was the first member of a new class of compounds, closely related to alcohols, the so-called thioalcohols RSH, or thiols. He also discovered (Zeise, 1834*c–e*) their extreme affinity towards mercuric compounds to yield very stable,

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