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 (~3,4 Å). À température ambiante, le cristal émet une fluorescence dont le spectre est une bande large, non structuré, avec maximum situé ~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 AA5.2NaC104 est sans doute la situation ultime avant le rapprochement des cycles aromatiques pour conduire à l’excimère.

Références


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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(C2F3O2)2(C3HgP)3(H2O)], Mr = 573.35, monoclinic, P21/c, a = 15.849 (7), b = 8.760 (4), c = 17.398 (3) Å, β = 90.21 (2)°, U = 2415.5 Å3, Z = 4, Dc = 1.58 Mg m−3, Mo Ka radiation, λ = 0.71069 Å, μ = 0.81 mm−1, F(000) = 1160, T = 295 K, R = 0.0452 for 2594 unique reflections with Fo ≥ 4σ(Fo). 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 trifluoroacetato 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(carboxylato)···O(aqua) distances of 2.644 (8) and 2.638 (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 &
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 \( \{(\eta^3-C_8H_13)RuH(L)\}_2PF_6 \) (\( L = \) phosphine ligand) are known to convert to the \( \eta^3 \)-cyclooctenyl complexes \( \{(\eta^3-C_8H_13)Ru(L)\}_2PF_6 \) in solution (Ashworth, Chalmers, Meintjies, Oosthuizen & Singleton, 1984), and herein we report the structure of one of the products of the reaction of \( \{(\eta^3-C_8H_13)Ru(PMe_3)\}_2PF_6 \) with trifluoroacetic acid, \([Ru(O_2CCF_3)(PMe_3)(OH_2)] \) (I).

**Experimental.** The reaction of \( \{(\eta^3-C_8H_13)Ru(PMe_3)\}_2PF_6 \) (Ashworth et al., 1984) with trifluoroacetic acid in boiling acetone gives a purple solution from which a purple solid of stoichiometry \( \{[Ru(O_2CCF_3)(PMe_3)(OH_2)]\}_2PF_6 \) (II) can be isolated. Crystallization from moist ethanol solution deposits colourless crystals of the title compound (I). Crystal: 0·30 × 0·15 × 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 ≤ \( \theta \) ≤ 16·04°, least-squares refinement; \( \omega/2\theta \) scan mode, scan width 1·20° in \( \omega \), scan speed 0·040° s\(^{-1}\) in \( \omega \), 15 s stationary background at each end of the scan; 4226 unique reflections with 3 ≤ \( \theta \) ≤ 23° measured in the quadrant \( +h, +k, +l \), three standard reflections measured every 60 min showed no significant deviations from their mean intensities, no absorption corrections were applied: 2594 reflections with \( F_o \geq 4\sigma(F_o) \) used in the analysis; structure solved by 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 position; all other non-H atoms anisotropic; least-squares refinement, \( \Sigma w(\Delta F)^2 \) 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.

**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 \( O(\text{trifluoroacetate})...O(\text{aqua}) \) distances of 2·644 (8) and 2·638 (8) Å and \( O(\text{trifluoroacetato})...H(\text{aqua}) \) 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 \( \{[L_2Ru(O_2CR)](\mu-O_2CR)(\mu-OH_2)] \) \( L_2 = \) cycloocta-1,5-diene (COD), \( R = CF_3 \)

* Lists of structure factors, H-atom coordinates, anisotropic temperature factors and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43635 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
Table 1. Fractional coordinates (x 10^4, x 10^3 for Ru, x 10^2 for H) and equivalent isotropic temperature factors (Å^2, x 10^4 for Ru) for (I)

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<td>1.943</td>
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<tr>
<td>P(3)</td>
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<td>0.765</td>
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<tr>
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<td>O(3)</td>
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<td>1.943</td>
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</table>

* Isotropic temperature factor.

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

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</tr>
<tr>
<td>O(2)-P(2)</td>
<td>1.235</td>
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<tr>
<td>O(3)-P(3)</td>
<td>1.235</td>
<td>96.0</td>
</tr>
</tbody>
</table>

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 H₂O) and 2.245 (2) and 2.259 (2) Å (trans to O₂⁻-CCF₃) 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(O₂⁻-CCF₃)₂(CO)(PPh₃)₂(MeOH)] (Dobson & Robinson, 1977). The Ru–O(trifluoroacetato) bond lengths are longer than those of Ru–O(trifluoroacetato) in (I) are all within the range of previously reported 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 [{Ru(O₂CC F₃)₂}₂(O₂CC F₃)(µ-O)] [L₂ = cycloocta-1,5-diene (Albers et al., 1984); L = PPh₃ (Albers, Liles, Singleton & Stead, 1986a)], thus displaying the trans influence of the tertiary phosphine ligands.

The reaction of [Ru₂(O₂CC F₃)₂(PPh₃)₂(MeOH)] (Dobson & Robinson, 1977) with trifluoroacetic acid in air is a purple compound of stoichiometry [{Ru(O₂CC F₃)₂(PPh₃)₂(MeOH)}] (II), the precursor to (I). (II) is an analogue of the ruthenium(III) complex [{Ru(PPh₃)₂O(CO)(η¹-CCF₃)}₂] (Albers, Liles, Singleton, & Stead, 1986a) and is also related to the recently reported dinuclear oxo-bridged diiron(III) hemerythrin models (Armstrong, Spool, Papaeftymiou, Frankel, R. B. & Lippard, S. J. (1984). J. Am. Chem. Soc. 106, 3653–3667).

Structure of Bis(1-butane-thiolato)mercury(II)

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Abstract. [Hg(C₄H₉S)₂], M_r = 378.95, tetragonal, I4₁/a, a = 27.10 (1), c = 13.28 (1) Å, V = 9754 (8) Å³, Z = 32, D_x = 2.06 g cm⁻³, λ(Mo Kα) = 0.71069 Å, µ = 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 HgS₄ tetrahedra share corners and edges forming spirals running parallel to e and with the organic residues in the cavities.

Introduction. When Zeise (1834a,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–e) their extreme affinity towards mercuric compounds to yield very stable, © 1987 International Union of Crystallography

References