

regular O...O separations within the molecular cavity [O(71)...O(101), 2.557 (3); O(72)...O(102), 2.553 (3); O(71)...O(72), 2.450 (3) Å].

The second Li has regular tetrahedral coordination [mean Li—O, 1.946 (5) Å] with the carboxylate O [O(111)], two water molecules and a carboxylate O [O(101')(-x, -y, -z)] forming a dimer across an inversion centre in the cell. This gives an Li(2)...Li(2') separation of 3.457 (8) Å while Li(1)...Li(2) is 3.265 (8) Å. The only other known lithium phenoxyalkanoate structure, anhydrous lithium 2-(carbamoylphenoxy)acetate (Mak *et al.*, 1986), is tetrahedral but forms polymeric bridges *via* both the amide and carboxyl groups.

The dimeric molecules of the title compound appear to be stabilized by the presence of intramolecular hydrogen-bonding interactions involving O(111) and its inversion-related water [Ow(2')] [2.763 (3) Å]. Packing of the molecules in the unit cell involves only two interdimer hydrogen bonds, Ow(1)...Ow(3) [2.989 (3) Å (1 - x, -y, -z)] and O(112)...O(72) [2.913 (3) Å (1 + x, y, z)].

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Structure of Methyltriphenylphosphonium Tetrachloroferrate(III)

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Abstract. [P(CH₃)(C₆H₅)₃][FeCl₄], *M_r* = 474.99, orthorhombic, *P*2₁2₁2₁, *a* = 10.976 (3), *b* = 13.554 (4), *c* = 14.818 (4) Å, *V* = 2204.5 (9) Å³, *Z* = 4, *D_m* = 1.43 (1), *D_x* = 1.431 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 1.25 mm⁻¹, *F*(000) = 964, room temperature, *R* = 0.039 for 2032 reflections. The structure consists of CH₃P(C₆H₅)₃⁺ cations and FeCl₄⁻ anions; the iron(III) atom is tetrahedrally coordinated by four Cl ligands with Fe—Cl distances in the range 2.171 (2)–2.182 (2) Å and Cl—Fe—Cl angles 107.8 (1)–112.4 (1)°. The planes of the phenyl groups

in the cation form dihedral angles of 113.7 (1), 75.2 (1) and 104.9 (2)°.

Introduction. In studies of the oxidation of triphenylphosphine (PPh₃) to triphenylphosphine oxide (OPPh₃) with O₂ catalysed by the [FeCl₂(OPPh₃)₄][FeCl₄] complex considerable influence of various solvents on the course of the reaction was observed: in the reaction between FeCl₃ and PPh₃ in the presence of O₂ in acetonitrile the [FeCl₂(OPPh₃)₄][FeCl₄] complex was formed (Vančová, Ondrejkořová & Ondrejovič, 1984); in ether the FeCl₃(PPh₃)₂ complex was prepared; and from methanol the title compound was

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isolated. However, the formation of the two latter compounds in ether and methanol was also observed in the reaction between FeCl₃ and PPh₃ alone (Naldini, 1960). The crystal structure of the title complex was determined in order to elucidate the quaternization reaction of PPh₃ in the presence of iron(III) chloride.

Experimental. Yellow prisms, 0.4 × 0.4 × 0.6 mm, D_m by flotation (CHCl₃ + C₆H₆), Syntex P₂₁ diffractometer, 15 reflections for lattice-parameters determination, $22 < 2\theta < 30^\circ$, absorption ignored, $2\theta_{\max} = 55^\circ$, hkl range 000 to 13,16,18, two standard reflections every 50 reflections showed no significant decay in intensity, 2896 unique reflections measured, 2032 with $I > 3\sigma(I)$, direct methods using an adapted version of *MULTAN* (Main, Woolfson & Germain, 1976), E map calculated with 312 terms for which $E > 1.5$, methyl-group H atoms located from difference Fourier map, remaining from geometry, full-matrix refinement of positional and anisotropic thermal parameters for non-hydrogen atoms and positional and isotropic thermal parameters for H atoms of CH₃ group (238 parameters refined), refinement based on F , $R = 0.039$, $wR = 0.036$, $S = 2.749$, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0.02 for non-H atoms and 0.1 for H atoms, $\Delta\rho$ in final difference Fourier synthesis $10.45 \text{ e } \text{Å}^{-3}$, calculations performed on the Nova 1200 computer, *XTL* system (Syntex, 1973), scattering factors from *International Tables for X-ray Crystallography* (1962). All calculations performed in the Department of Crystal Structures, Institute of Chemistry, Univ. of Wrocław.

Discussion. Final atomic parameters for non-H atoms are listed in Table 1, interatomic distances and bond angles in Table 2.*

The packing of the ions in the structure is shown in Fig. 1. The anion shows only small departures from ideal tetrahedral geometry: Fe—Cl distances do not significantly differ and bond angles show only small deviations from the tetrahedral angle (Table 2). Similar small variations in distances and angles were found for the structure of FeCl₄⁻ in chlorobis(triphenylphosphine)tris(4-tolylisocyanide)iron(II) tetrachloroferrate(III): Fe—Cl distances range from 2.172 (3) to 2.180 (4) Å and Cl—Fe—Cl angles from 107.6 (3) to 112.0 (3)° (Pelizzi, Albertin, Bordignon, Orio & Calogero, 1977). In another, for the structure of the FeCl₄ anion in FeCl₃·2½H₂O {i.e. [FeCl₂(H₂O)₄]-[FeCl₄].H₂O}, significant variations in Fe—Cl bonds, from 2.169 (4) to 2.220 (4) Å, were found (Szymański,

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

| | <i>x</i> | <i>y</i> | <i>z</i> | B_{eq} |
|-------|-----------|----------|-----------|-----------------|
| Fe | -1423 (1) | 4818 (1) | 2194 (1) | 4.00 (5) |
| Cl(1) | -2357 (2) | 4966 (2) | 3478 (1) | 6.6 (2) |
| Cl(2) | -2639 (2) | 5227 (2) | 1097 (1) | 8.2 (2) |
| Cl(3) | 170 (2) | 5781 (1) | 2188 (1) | 6.0 (1) |
| Cl(4) | -790 (2) | 3306 (1) | 2081 (2) | 8.2 (2) |
| P | 3556 (2) | 4348 (1) | 307 (1) | 3.7 (1) |
| C(1) | 4864 (7) | 3781 (5) | -220 (5) | 4.9 (6) |
| C(11) | 2208 (6) | 4025 (4) | -305 (4) | 3.9 (5) |
| C(12) | 1086 (6) | 4358 (5) | -14 (4) | 5.3 (6) |
| C(13) | 43 (6) | 4117 (6) | -485 (5) | 6.1 (7) |
| C(14) | 126 (7) | 3566 (5) | -1254 (5) | 6.1 (7) |
| C(15) | 1217 (8) | 3220 (6) | -1542 (5) | 7.4 (8) |
| C(16) | 2258 (7) | 3448 (6) | -1072 (5) | 6.3 (7) |
| C(21) | 3442 (5) | 3908 (4) | 1447 (3) | 3.6 (4) |
| C(22) | 2553 (6) | 3260 (5) | 1719 (4) | 4.8 (6) |
| C(23) | 2545 (6) | 2882 (6) | 2580 (5) | 5.9 (7) |
| C(24) | 3418 (8) | 3173 (6) | 3166 (4) | 6.4 (7) |
| C(25) | 4308 (7) | 3825 (5) | 2914 (5) | 6.2 (7) |
| C(26) | 4327 (6) | 4201 (5) | 2054 (4) | 5.2 (6) |
| C(31) | 3731 (5) | 5658 (4) | 296 (4) | 3.7 (4) |
| C(32) | 4435 (6) | 6119 (5) | -348 (4) | 5.1 (6) |
| C(33) | 4480 (8) | 7130 (5) | -395 (5) | 6.3 (7) |
| C(34) | 3830 (8) | 7690 (5) | 189 (6) | 6.2 (8) |
| C(35) | 3108 (7) | 7245 (5) | 847 (5) | 6.6 (8) |
| C(36) | 3066 (6) | 6225 (5) | 910 (5) | 5.2 (6) |

Table 2. Main interatomic distances (Å) and bond angles (°) with e.s.d.'s in parentheses

| | | | |
|----------------|-----------|---------------|-----------|
| Fe—Cl(1) | 2.171 (2) | P—C(1) | 1.805 (7) |
| Fe—Cl(2) | 2.175 (2) | P—C(11) | 1.790 (6) |
| Fe—Cl(3) | 2.182 (2) | P—C(21) | 1.797 (5) |
| Fe—Cl(4) | 2.171 (2) | P—C(31) | 1.786 (6) |
| Cl(1)—Fe—Cl(2) | 110.0 (1) | C(1)—P—C(11) | 109.5 (3) |
| Cl(1)—Fe—Cl(3) | 109.1 (1) | C(1)—P—C(21) | 108.7 (3) |
| Cl(1)—Fe—Cl(4) | 107.8 (1) | C(1)—P—C(31) | 109.5 (3) |
| Cl(2)—Fe—Cl(3) | 109.7 (1) | C(11)—P—C(21) | 109.7 (3) |
| Cl(2)—Fe—Cl(4) | 112.4 (1) | C(11)—P—C(31) | 109.1 (3) |
| Cl(3)—Fe—Cl(4) | 108.0 (1) | C(21)—P—C(31) | 110.3 (3) |

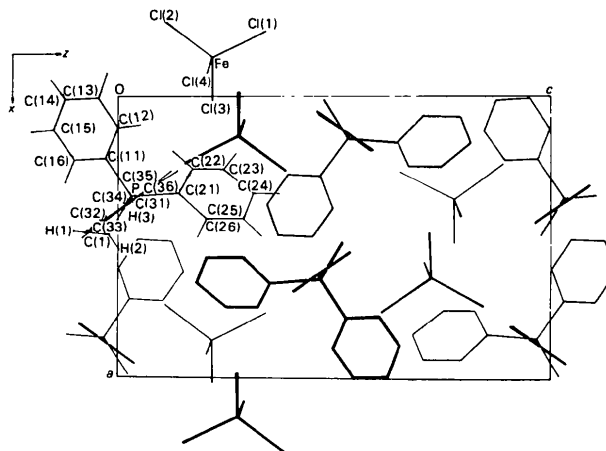


Fig. 1. Projection of the structure along **b** with atom numbering. Unnumbered H atoms follow the numbering of the attached C atom.

* Lists of structure factors, anisotropic thermal parameters, H-atom and phenyl-ring parameters, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43045 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1979), but the Cl—Fe—Cl angles varied from 106.6 (1) to 110.7 (2)°, similar to those found for the present structure. A possible explanation of the differences in Fe—Cl distances lies in the different interactions of the FeCl₄ anion with the cation and the solvate water molecules.

The methyltriphenylphosphonium cation was found to have a nearly regular tetrahedral arrangement about the P atom (Table 2). The phenyl C atom planes show only minimal deviations from the P—C bond directions; the P atom lies practically in the C(11)—C(16) plane (1) [0.032 (1) Å] and is displaced by 0.119 (2) and 0.154 (2) Å from the C(21)—C(26) (2) and the C(31)—C(36) (3) planes, respectively. The C—C distances for the phenyl groups range from 1.36 (1) to 1.40 (1) Å. The phenyl-group planes form dihedral angles of 113.7 (1) (1,2), 75.2 (1) (1,3) and 104.9 (2)° (2,3), respectively.

The structure determination of the title compound contributed to the explanation of the course of the reaction in one system of Fe^{III} + PPh₃ + O₂ + solvent: when methanol was used as solvent, PPh₃ was not oxidized to OPPh₃, but was quaternized by the CH₃ group of methanol to a CH₃PPh₃⁺ cation. On the other

hand, with acetonitrile as solvent, PPh₃ was oxidized to OPPh₃ and FeCl₃(OPPh₃)₂ was formed [*i.e.* [FeCl₂(OPPh₃)₄][FeCl₄]]. While the title compound did not show any catalytic properties, the FeCl₃(OPPh₃)₂ catalysed the oxidation in the above system. Structural investigation of the last complex as well as of other FeX₃(OPPh₃)₂ compounds (X = Cl, Br or NCS) should contribute to the explanation of the relationship between the structures and their different catalytic activity (the next object of our structural study).

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Structure of Bis(4-hydroxy-L-prolinato-N,O)palladium(II) Trihydrate

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Abstract. [Pd(C₅H₈NO₃)₂].3H₂O, *M_r* = 420.4, m.p. = 483 K (dec.), monoclinic, *P*2₁, *a* = 9.780 (8), *b* = 7.682 (5), *c* = 11.044 (9) Å, β = 114.36 (3)°, *V* = 755.9 (15) Å³, *Z* = 2, *D_m* = 1.83 (solvents CCl₄ and 1,2-dibromoethane), *D_x* = 1.86 g cm⁻³, Mo *K*α, Zr filter, λ = 0.7107 Å, μ = 12.27 cm⁻¹, *F*(000) = 428, *R* = 0.044 and *wR* = 0.063 for 2036 unique reflections. Palladium has a near-planar coordination with the imino nitrogens and carboxyl oxygens in the *cis* configuration. The Pd—N and Pd—O distances are normal [Pd—N(1),N(2) = 2.016 (5), 2.022 (5) and Pd—O(1),O(4) = 2.000 (5), 2.008 (5) Å]. The proline rings are in envelope conformations with the hydroxy-substituted C(4) and C(9) atoms lying 0.65 (2) and

0.58 (2) Å out of the least-squares planes of the other four atoms of pyrrolidine rings *A* and *B*, respectively. An elaborate network of hydrogen bonds interlinks the molecules.

Introduction. In continuation of our studies on the structure of palladium(II) complexes (Padmanabhan, Patel & Ranganathan, 1985), the crystal-structure determination of the present complex was undertaken. Preliminary findings on the structure have been reported (Sinh, Padmanathan, Patel, Ranganathan & Rao, 1982). As optically active proline and related amino acids are stereospecific (coordinating in the *cis* configuration) (Haines & Reimer, 1973), it was