

$[CuCl_4]^{2-}$ anions are distinctly distorted. The Cl—Cu—Cl angles vary from 98.72 (4) to 134.32 (5)° and Cu—Cl bond lengths from 2.221 (1) to 2.272 (1) Å owing to different crystal environments.

The work was performed under research project RP.II.10 from the Polish Ministry of National Education.

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Acta Cryst. (1989). **C45**, 410–412

Structure of Dichloro[tetrakis(triphenylphosphine oxide)]iron(III) Tetrachloroferrate(III)

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(Received 1 September 1987; accepted 29 September 1988)

Abstract. $C_{72}H_{60}Cl_2FeO_4P_4^+Cl_4Fe^-$, $M_r = 1437.53$, monoclinic, $P2_1/c$, $a = 14.002$ (4), $b = 27.718$ (7), $c = 18.317$ (5) Å, $\beta = 104.48$ (5)°, $V = 6883$ (4) Å³, $Z = 4$, $D_m = 1.389$ (1), $D_x = 1.387$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 7.47$ cm⁻¹, $F(000) = 2952$, room temperature, $R = 0.0643$ for 6807 reflections. The structure consists of $[FeCl_2(OPPh_3)_4]^+$ cations (Ph = phenyl group) and $FeCl_4^-$ anions; the iron(III) atom in the complex cation is octahedrally coordinated by four O atoms from $OPPh_3$ ligands and by two Cl ligands with Fe—O interatomic distances in the range 2.005 (4)–2.019 (4) Å, and Fe—Cl distances 2.347 (2) and 2.353 (2) Å. The Cl—Fe—O bond angles in the cation are near to 90°, the Cl—Fe—Cl angle is

177.7 (1)°. The iron(III) atom in the anion is tetrahedrally coordinated by four Cl ligands with Fe—Cl distances in the range 2.111 (5)–2.217 (5) Å and Cl—Fe—Cl angles ranging from 104.3 (2) to 113.8 (2)°.

Introduction. Oxidation of triphenylphosphine (PPh_3) to triphenylphosphine oxide ($OPPh_3$) with O_2 in the presence of Fe compounds has been studied for $Fe^{2+} + X^- + PPh_3 + O_2 + \text{solvent}$ systems ($z = 0, 2$ or 3; $X = Cl, Br$ and NCS) (Ondrejkořová, 1984). With acetonitrile as solvent, PPh_3 was oxidized to $OPPh_3$ (Vančová, Ondrejkořová & Ondrejkoř, 1984) and $FeX_3(OPPh_3)_2$ compounds were formed showing

different catalytic activity in the oxidation process involving the systems above. The crystal structure determination of $\text{FeCl}_3(\text{OPPh}_3)_2$, i.e. $[\text{FeCl}_2(\text{OPPh}_3)_4] \cdot [\text{FeCl}_4]$ (title complex) was undertaken as a continuation of the study on the structure of the reaction products of the above systems (Głowiak, Đurčanská, Ondrejkořičová & Ondrejovič, 1986) as well as on the relationship between structure and different catalytic activity of the $\text{FeX}_3(\text{OPPh}_3)_2$ compounds (Ondrejkořičová, Vančová & Ondrejovič, 1983).

Experimental. Yellow plates, $0.5 \times 0.6 \times 0.2$ mm; D_m by flotation ($\text{CHCl}_3 + \text{C}_6\text{H}_6$); Syntex $P2_1$ diffractometer; 15 reflections for lattice-parameter determination, $22 < 2\theta < 30^\circ$; absorption neglected; $2\theta_{\text{max}} = 50^\circ$; hkl range 0,0,-21 to 12, 32, 21; two standard reflections every 50 reflections showed no significant intensity variation; 6807 independent reflections with $I > 1.96\sigma(I)$ (29 unobserved); Patterson and Fourier methods; H-atom positions from geometry; anisotropic full-matrix refinement (except H atoms) based on F ; $R = 0.0643$, $wR = 0.0707$, $w^{-1/2} = \sigma^2(F) + (0.0012F_o)^2$; $(\Delta/\sigma)_{\text{max}}$ in final least-squares cycle 0.33 for non-H atoms [except for 0.86 for C(12) atom]; $\Delta\rho$ in final difference Fourier synthesis $|0.59| \text{ e } \text{Å}^{-3}$; calculations performed on a Nova 1200 computer; XTL system (Syntex, 1973) (Patterson and Fourier), EC 1055 computer (SHELX86; Sheldrick, 1986) (least-squares refinement, interatomic distances and bond angles) and M 4030 computer (PARST; Nardelli, 1983) (dihedral angles and intermolecular contacts). Scattering factors for Fe from *International Tables for X-ray Crystallography* (1962). Calculations by XTL system performed in the Department of Crystal Structures, Institute of Chemistry, University of Wrocław, Poland.*

Discussion. Positional and equivalent isotropic thermal parameters for non-H atoms are given in Table 1; Table 2 gives the main bond distances and angles. The complex ions with atom numbering are shown in Fig. 1. The Fe^{III} atom in the complex cation is pseudo-octahedrally coordinated by four O atoms forming the equatorial plane of the coordination polyhedron and by two Cl atoms in axial positions. The remaining four Cl atoms are tetrahedrally coordinated to a second Fe^{III} atom thus forming the complex anion. No significant differences were found between the Fe—O distances (Table 2) that show only small differences with those (average 2.062 Å) found for $[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2][\text{FeCl}_4]$.

Table 1. Final atomic coordinates ($\times 10^4$; $\times 10^5$ for Fe) and equivalent isotropic thermal parameters, U_{eq} [$\text{Å}^2 \times 10^3$; $\text{Å}^2 \times 10^4$ for Fe(1)] with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i U_{ii} \text{ (} U_{ii} \text{ orthogonalized).}$$

	x	y	z	U_{eq}
Fe(1)	780 (6)	9858 (3)	27014 (4)	305 (3)
Fe(2)	53256 (9)	34825 (5)	31915 (8)	82 (1)
Cl(1)	387 (1)	991 (1)	4025 (1)	50 (1)
Cl(2)	-175 (1)	1001 (1)	1386 (1)	49 (1)
Cl(3)	5007 (2)	4240 (1)	3288 (2)	104 (1)
Cl(4)	6907 (2)	3361 (1)	3480 (2)	114 (1)
Cl(5)	4762 (3)	3131 (2)	4087 (3)	180 (2)
Cl(6)	4580 (3)	3186 (2)	2142 (2)	225 (3)
P(1)	-2318 (1)	738 (1)	2755 (1)	36 (1)
P(2)	-383 (1)	2216 (1)	2478 (1)	36 (1)
P(3)	303 (1)	-216 (1)	2349 (1)	35 (1)
P(4)	2620 (1)	1131 (1)	3127 (1)	44 (1)
O(1)	-1374 (3)	911 (1)	2615 (2)	40 (2)
O(2)	-87 (3)	1705 (1)	2688 (2)	43 (2)
O(3)	219 (3)	263 (1)	2694 (2)	46 (2)
O(4)	1542 (3)	1073 (2)	2829 (2)	48 (2)
C(11)	-2773 (5)	1156 (2)	3336 (4)	51 (3)
C(12)	-2443 (13)	1599 (3)	3412 (8)	152 (8)
C(13)	-2860 (17)	1946 (4)	3821 (9)	205 (12)
C(14)	-3573 (10)	1807 (4)	4129 (6)	107 (5)
C(15)	-3817 (7)	1340 (5)	4164 (5)	98 (4)
C(16)	-3460 (6)	1000 (3)	3740 (5)	80 (4)
C(21)	-3221 (4)	702 (2)	1868 (3)	39 (2)
C(22)	-2989 (5)	901 (3)	1240 (4)	52 (3)
C(23)	-3662 (5)	895 (3)	542 (4)	63 (3)
C(24)	-4566 (5)	669 (3)	459 (4)	67 (3)
C(25)	-4814 (5)	477 (3)	1071 (4)	64 (3)
C(26)	-4164 (5)	505 (3)	1781 (4)	54 (3)
C(31)	-2236 (4)	169 (2)	3248 (3)	40 (2)
C(32)	-2729 (5)	-244 (2)	2965 (4)	52 (3)
C(33)	-2663 (6)	-656 (3)	3405 (4)	66 (3)
C(34)	-2086 (6)	-648 (2)	4142 (4)	57 (3)
C(35)	-1563 (6)	-246 (3)	4419 (4)	61 (3)
C(36)	-1651 (5)	168 (3)	3985 (4)	57 (3)
C(41)	-338 (5)	2556 (2)	3325 (4)	45 (2)
C(42)	-69 (10)	2336 (3)	3982 (4)	114 (6)
C(43)	-35 (15)	2589 (4)	4646 (5)	181 (10)
C(44)	-149 (9)	3058 (4)	4645 (6)	105 (5)
C(45)	-459 (10)	3286 (3)	3991 (6)	106 (5)
C(46)	-557 (8)	3036 (3)	3314 (5)	90 (4)
C(51)	-1586 (5)	2275 (2)	1862 (4)	45 (3)
C(52)	-1747 (6)	2100 (3)	1124 (4)	66 (3)
C(53)	-2663 (8)	2129 (3)	645 (5)	81 (4)
C(54)	-3439 (6)	2328 (3)	870 (6)	82 (4)
C(55)	-3309 (6)	2491 (4)	1594 (6)	83 (4)
C(56)	-2383 (6)	2467 (3)	2079 (4)	70 (3)
C(61)	444 (5)	2498 (2)	1999 (3)	38 (2)
C(62)	283 (7)	2955 (3)	1698 (5)	81 (4)
C(63)	973 (7)	3181 (3)	1396 (6)	85 (4)
C(64)	1816 (6)	2951 (3)	1384 (5)	71 (4)
C(65)	1955 (7)	2488 (4)	1622 (7)	107 (5)
C(66)	1266 (7)	2261 (3)	1929 (5)	81 (4)
C(71)	885 (5)	-627 (2)	3087 (3)	50 (2)
C(72)	1603 (5)	-954 (2)	3008 (4)	62 (3)
C(73)	1994 (8)	-1271 (3)	3627 (7)	99 (4)
C(74)	1647 (11)	-1258 (4)	4270 (7)	123 (6)
C(75)	943 (10)	-939 (4)	4317 (5)	97 (5)
C(76)	559 (6)	-622 (3)	3736 (4)	66 (3)
C(81)	-865 (4)	-472 (2)	1905 (3)	42 (2)
C(82)	-1592 (5)	-189 (2)	1429 (4)	51 (3)
C(83)	-2479 (5)	-387 (3)	1057 (4)	64 (3)
C(84)	-2666 (6)	-875 (3)	1145 (5)	71 (3)
C(85)	-1984 (7)	-1149 (3)	1633 (6)	84 (4)
C(86)	-1083 (6)	-951 (3)	2000 (5)	72 (3)
C(91)	1022 (5)	-218 (2)	1664 (3)	43 (3)
C(92)	1992 (7)	-95 (3)	1906 (5)	80 (4)
C(93)	2592 (7)	-114 (4)	1417 (6)	93 (5)
C(94)	2231 (9)	-249 (4)	691 (6)	92 (5)
C(95)	1265 (8)	-378 (4)	438 (4)	87 (5)
C(96)	647 (6)	-354 (3)	934 (4)	64 (3)
C(101)	2935 (5)	1552 (3)	3901 (4)	61 (3)
C(102)	3661 (8)	1469 (4)	4533 (5)	100 (4)
C(103)	3920 (9)	1806 (5)	5083 (6)	128 (6)
C(104)	3470 (10)	2216 (5)	5057 (7)	121 (6)
C(105)	2670 (14)	2302 (5)	4474 (9)	168 (8)
C(106)	2456 (11)	1964 (5)	3890 (7)	166 (7)
C(111)	3149 (6)	1327 (3)	2377 (5)	62 (3)
C(112)	2662 (7)	1196 (3)	1656 (5)	81 (4)
C(113)	3089 (11)	1321 (5)	1064 (6)	119 (6)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes, phenyl interatomic distances and shortest interionic contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51447 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1 (cont.)

	x	y	z	U _{eq}
C(114)	3954 (16)	1575 (6)	1193 (11)	148 (9)
C(115)	4417 (10)	1694 (5)	1902 (12)	145 (9)
C(116)	4017 (7)	1586 (3)	2509 (6)	92 (5)
C(121)	3211 (5)	573 (2)	3487 (4)	47 (3)
C(122)	2799 (6)	309 (3)	3965 (4)	61 (3)
C(123)	3240 (7)	-117 (3)	4278 (5)	79 (4)
C(124)	4089 (7)	-282 (3)	4095 (6)	86 (4)
C(125)	4488 (6)	-26 (3)	3612 (6)	88 (4)
C(126)	4055 (6)	408 (3)	3299 (5)	65 (3)

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

Fe(1)—Cl(1)	2.353 (2)	P(1)—C(11)	1.795 (7)
Fe(1)—Cl(2)	2.347 (2)	P(1)—C(21)	1.794 (5)
Fe(1)—O(1)	2.010 (4)	P(1)—C(31)	1.805 (6)
Fe(1)—O(2)	2.005 (4)	P(2)—C(41)	1.803 (7)
Fe(1)—O(3)	2.013 (4)	P(2)—C(51)	1.785 (6)
Fe(1)—O(4)	2.019 (4)	P(2)—C(61)	1.795 (7)
Fe(2)—Cl(3)	2.164 (3)	P(3)—C(71)	1.800 (6)
Fe(2)—Cl(4)	2.171 (3)	P(3)—C(81)	1.781 (6)
Fe(2)—Cl(5)	2.217 (5)	P(3)—C(91)	1.795 (8)
Fe(2)—Cl(6)	2.111 (5)	P(4)—C(101)	1.803 (8)
P(1)—O(1)	1.488 (5)	P(4)—C(111)	1.799 (9)
P(2)—O(2)	1.500 (4)	P(4)—C(121)	1.801 (6)
P(3)—O(3)	1.488 (4)		
P(4)—O(4)	1.479 (4)		
Cl(1)—Fe(1)—Cl(2)	177.7 (1)	O(2)—P(2)—C(41)	109.0 (3)
Cl(1)—Fe(1)—O(1)	90.2 (1)	O(2)—P(2)—C(51)	113.9 (3)
Cl(1)—Fe(1)—O(2)	89.9 (1)	O(2)—P(2)—C(61)	111.4 (3)
Cl(1)—Fe(1)—O(3)	91.2 (1)	C(41)—P(2)—C(51)	108.7 (3)
Cl(1)—Fe(1)—O(4)	87.7 (1)	C(41)—P(2)—C(61)	107.7 (3)
Cl(2)—Fe(1)—O(1)	91.8 (1)	C(51)—P(2)—C(61)	105.9 (3)
Cl(2)—Fe(1)—O(2)	89.0 (1)	O(3)—P(3)—C(71)	108.4 (3)
Cl(2)—Fe(1)—O(3)	90.0 (1)	O(3)—P(3)—C(81)	112.8 (3)
Cl(2)—Fe(1)—O(4)	90.3 (1)	O(3)—P(3)—C(91)	114.7 (3)
O(1)—Fe(1)—O(2)	89.5 (2)	C(71)—P(3)—C(81)	106.4 (3)
O(1)—Fe(1)—O(3)	89.8 (2)	C(71)—P(3)—C(91)	107.2 (3)
O(1)—Fe(1)—O(4)	177.7 (2)	C(81)—P(3)—C(91)	106.9 (3)
O(2)—Fe(1)—O(3)	178.7 (2)	O(4)—P(4)—C(101)	112.8 (3)
O(2)—Fe(1)—O(4)	89.6 (2)	O(4)—P(4)—C(111)	109.2 (3)
O(3)—Fe(1)—O(4)	91.2 (2)	O(4)—P(4)—C(121)	111.9 (3)
Cl(3)—Fe(2)—Cl(4)	110.5 (1)	C(101)—P(4)—C(111)	109.8 (4)
Cl(3)—Fe(2)—Cl(5)	104.3 (2)	C(101)—P(4)—C(121)	105.6 (3)
Cl(3)—Fe(2)—Cl(6)	112.8 (2)	C(111)—P(4)—C(121)	107.4 (3)
Cl(4)—Fe(2)—Cl(5)	106.4 (1)	Fe(1)—O(1)—P(1)	160.8 (3)
Cl(4)—Fe(2)—Cl(6)	113.8 (2)	Fe(1)—O(2)—P(2)	165.0 (2)
Cl(5)—Fe(2)—Cl(6)	108.4 (2)	Fe(1)—O(3)—P(3)	155.4 (3)
O(1)—P(1)—C(11)	110.9 (3)	Fe(1)—O(4)—P(4)	165.5 (3)
O(1)—P(1)—C(21)	108.5 (3)		
O(1)—P(1)—C(31)	114.8 (3)		

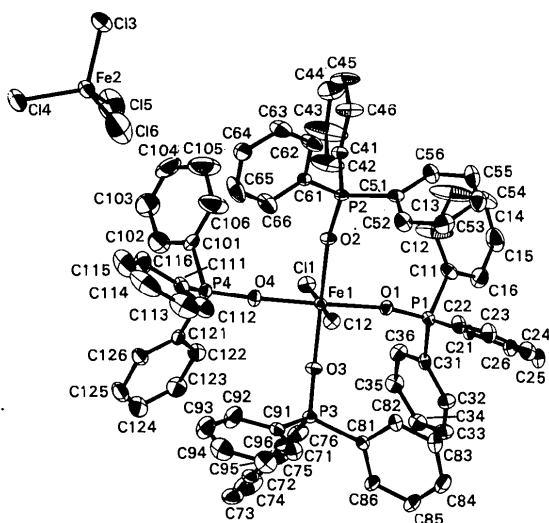


Fig. 1. View of the ions showing the atomic numbering (H atoms omitted).

H₂O (Szymański, 1979). The FeCl₄ anion has a distorted tetrahedral geometry: the Fe—Cl distances range from 2.111 (5) to 2.217 (5) Å and the Cl—Fe—Cl angles from 104.3 (2) to 113.8 (2)° (Table 2). These deviations from the ideal tetrahedral geometry are greater than those found for the FeCl₄ anion in methyltriphenylphosphonium tetrachloroferrate(III), where the Fe—Cl distances range from 2.171 (2) to 2.182 (2) Å and the Cl—Fe—Cl angles from 107.8 (1) to 112.4 (1)° (Głowiak, Ďurčanská, Ondrejkočová & Ondrejovič, 1986) or in chlorotris(4-tolylisocyanide)-bis(triphenylphosphine)iron(II) tetrachloroferrate(III) where the Fe—Cl distances range from 2.172 (3) to 2.180 (4) Å and the Cl—Fe—Cl angles from 107.6 (3) to 112.0 (3)° (Pelizzi, Albertin, Bordignon, Orio & Calogero, 1977). These differences can be explained by different interactions of the FeCl₄ anion with the cation.

The shortest Cl...H interionic distances between the Cl ligands of the anion and phenyl-group H atoms have values from 2.786 (5) to 2.976 (3) Å.

The catalytic activity of FeX₃(OPPh₃)₂ compounds in oxidation of PPh₃ to OPPh₃ by dioxygen depends on the nature of the X ligands: it increases in the order Cl ≪ NCS < Br. The proposed mechanism of catalysis involves the change Fe^{III} ⇌ Fe^{II} (Ondrejkočová, 1984) and the rapid exchange OPPh₃ ⇌ PPh₃ which

is directly influenced by the properties of the X ligands coordinated in the complex. As far as we know the title compound is the first of the FeX₃(OPPh₃)₂ complexes whose crystal structure has been determined. Further structure investigation should lead to the determination of the [Fe(NCS)₃(OPPh₃)₂] crystal structure and thus to the possibility of finding the structural differences responsible for the different catalytic activity.

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