Crystal structure of (μ-oxalato)bis[chlorotris(triphenylphosphine oxide-*O*)iron(III)] tetrachloroferrate(III), $[FeCl(C_{18}H_{15}PO)_3][C_2O_4][FeCl_4]$

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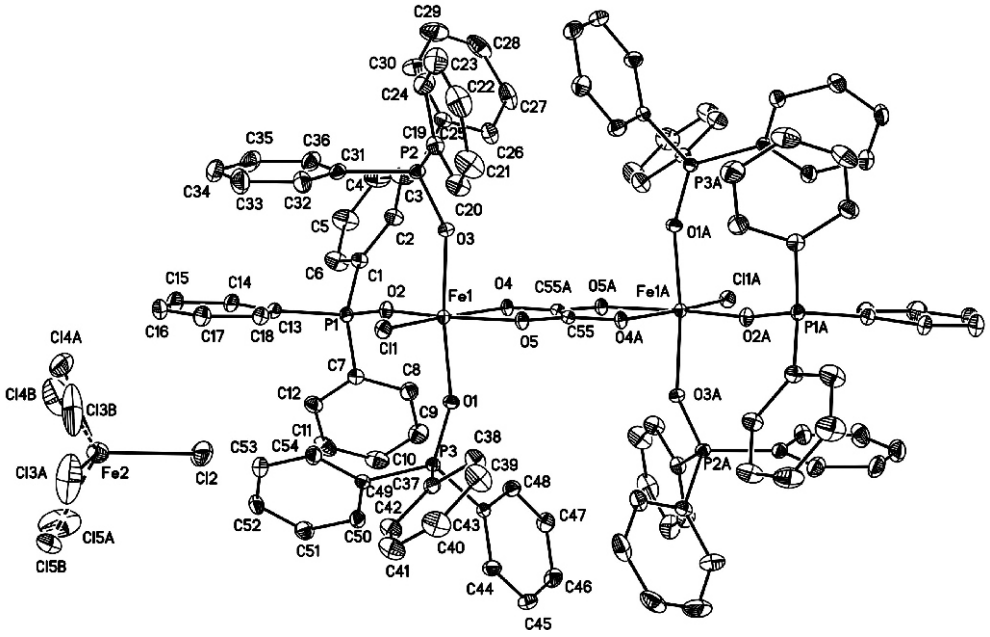

Abstract

$C_{110}H_{90}Cl_{10}Fe_4O_{10}P_6$, triclinic, $P\bar{1}$ (no. 2), a = 10.672(7) Å, b = 15.74(1) Å, c = 16.71(1) Å, α = 78.803(8)°, β = 85.771(9)°, γ = 81.857(9)°, V = 2722.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.055, $wR_{ref}(F^2)$ = 0.148, T = 173 K.

Source of material

Starting materials and solvents for synthesis were purchased commercially and used as received. The mixture of H_3BO_3 (0.062 g, 0.1mmol), $P(C_6H_5)_3$ (0.157 g, 0.06 mmol), $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ (0.147 g, 0.03 mmol), 2.0 ml H_2O, 0.70 ml 37 % HCl and 0.50 ml H_3PO_4 was placed in a thick borosilicate glass tube. The tube was sealed and then kept at 120 °C for two days to give green single crystals.

Elemental analysis — found: C, 56.55 %, H, 3.80 %; calculated for $C_{110}H_{90}Cl_{10}Fe_4O_{10}P_6$: C, 56.57 %, H, 3.88 %.

Experimental details

All H atoms on C atoms were generated geometrically and refined as riding with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(O). Three Cl atoms of the $FeCl_4$ are disordered over two equivalent positions.

Discussion

The preparation of inorganic-organic hybrid coordination complexes has received much attention due to their potential applications as functional materials [1,2]. Solvo(hydro)thermal synthesis has rapidly developed over the past several years due to its effectiveness, simplicity and environmental friendliness [3]. In order to synthetize new inorganic-organic hybrid material, we synthetized the title complex by hydrothermal method and report here.

In the title crystal structure, each Fe of a dimer is coordinated in a distorted octahedron by two oxygen atoms from oxalate, three oxygen atoms from Ph_3PO (triphenylphosphine oxide) and one chlorine atom. The asymmetric unit contains half of a dimer, which is one Fe, half oxalate, one chlorine and three Ph_3PO molecules, and there is one neutral molecule per unit cell. The bond angles ∠O3–Fe1–O5 are less than 90° and ∠Cl–Fe–O are more than 90°. The three Ph_3PO molecules bind to the Fe from the direction nearly perpendicular to the FeOCl plane with the bond angles ∠O–Fe–O (Ph_3PO) being less than 90° and ∠Cl–Fe–O (Ph_3PO) more than 90°.

Table 1. Data collection and handling.

Crystal:	green block, size 0.11 × 0.13 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.13 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16701, 1046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6711
$N(param)_{refined}$:	658
Programs:	SHELXS-97, SHELXL-97, SHELXTL [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2)	2*i*	–0.0933	0.9742	0.2896	0.063
H(3)	2*i*	–0.1939	1.0841	0.3561	0.088
H(4)	2*i*	–0.3551	1.0559	0.4533	0.099
H(5)	2*i*	–0.4206	0.9189	0.4847	0.108
H(6)	2*i*	–0.3222	0.8070	0.4190	0.088
H(8)	2*i*	–0.2648	0.8367	0.1687	0.072
H(9)	2*i*	–0.4353	0.7825	0.1262	0.089
H(10)	2*i*	–0.5071	0.6579	0.2012	0.093
H(11)	2*i*	–0.4052	0.5834	0.3173	0.094
H(12)	2*i*	–0.2295	0.6345	0.3591	0.070
H(14)	2*i*	–0.1531	0.7025	0.4693	0.080
H(15)	2*i*	–0.0296	0.5973	0.5596	0.104
H(16)	2*i*	0.1758	0.5466	0.5205	0.110
H(17)	2*i*	0.2632	0.6017	0.3934	0.091
H(18)	2*i*	0.1438	0.7095	0.3029	0.066
H(20)	2*i*	0.3683	0.9538	0.1014	0.078
H(21)	2*i*	0.5750	0.9766	0.0551	0.106
H(22)	2*i*	0.6898	1.0527	0.1209	0.107
H(23)	2*i*	0.6043	1.1045	0.2368	0.099
H(24)	2*i*	0.4022	1.0784	0.2872	0.080
H(26)	2*i*	0.0080	1.1130	0.1768	0.070
H(27)	2*i*	–0.1104	1.2384	0.2158	0.101
H(28)	2*i*	–0.0638	1.2805	0.3354	0.113

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(29)	2*i*	0.0988	1.2057	0.4122	0.118
H(30)	2*i*	0.2172	1.0836	0.3741	0.088
H(32)	2*i*	0.4106	0.8522	0.2921	0.074
H(33)	2*i*	0.4498	0.7498	0.4110	0.104
H(34)	2*i*	0.3078	0.7432	0.5217	0.108
H(35)	2*i*	0.1216	0.8376	0.5149	0.100
H(36)	2*i*	0.0778	0.9444	0.3973	0.075
H(38)	2*i*	0.2015	0.7908	–0.0517	0.074
H(39)	2*i*	0.3955	0.7487	–0.1160	0.102
H(40)	2*i*	0.4725	0.6007	–0.1048	0.098
H(41)	2*i*	0.3639	0.4957	–0.0241	0.089
H(42)	2*i*	0.1709	0.5370	0.0410	0.070
H(44)	2*i*	–0.0187	0.6124	–0.0855	0.059
H(45)	2*i*	–0.1788	0.6219	–0.1762	0.071
H(46)	2*i*	–0.3593	0.7220	–0.1711	0.073
H(47)	2*i*	–0.3790	0.8185	–0.0807	0.071
H(48)	2*i*	–0.2191	0.8120	0.0089	0.061
H(50)	2*i*	–0.1846	0.5904	0.0858	0.059
H(51)	2*i*	–0.2228	0.4767	0.1942	0.077
H(52)	2*i*	–0.0874	0.4369	0.3017	0.080
H(53)	2*i*	0.0914	0.5072	0.2991	0.080
H(54)	2*i*	0.1325	0.6177	0.1912	0.064

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	2*i*		0.07617(5)	0.86965(3)	0.13044(3)	0.0291(3)	0.0290(3)	0.0282(3)	–0.0030(2)	–0.0023(2)	–0.0025(2)
O(1)	2*i*		0.0051(2)	0.7899(2)	0.0718(2)	0.039(2)	0.033(1)	0.047(2)	–0.005(1)	–0.009(1)	–0.012(1)
O(2)	2*i*		–0.0241(2)	0.8306(2)	0.2317(2)	0.038(2)	0.046(2)	0.034(2)	–0.005(1)	0.001(1)	0.003(1)
O(3)	2*i*		0.1355(3)	0.9625(2)	0.1795(2)	0.043(2)	0.040(2)	0.040(2)	–0.009(1)	–0.007(1)	–0.011(1)
O(4)	2*i*		–0.0816(2)	0.9624(2)	0.0915(1)	0.031(2)	0.034(1)	0.030(1)	–0.000(1)	0.004(1)	0.003(1)
O(5)	2*i*		0.1444(2)	0.9337(2)	0.0161(2)	0.026(1)	0.036(1)	0.035(1)	0.003(1)	–0.000(1)	0.001(1)
P(1)	2*i*		–0.1094(1)	0.79240(7)	0.30129(6)	0.0391(6)	0.0374(6)	0.0311(5)	–0.0092(5)	0.0023(5)	–0.0023(4)
P(2)	2*i*		0.2104(1)	0.98949(7)	0.24140(6)	0.0351(6)	0.0405(6)	0.0355(6)	–0.0103(5)	0.0007(5)	–0.0100(5)
P(3)	2*i*		0.0129(1)	0.70210(6)	0.04577(6)	0.0348(6)	0.0314(5)	0.0360(6)	–0.0047(4)	–0.0043(5)	–0.0069(4)
C(1)	2*i*		–0.1934(4)	0.8781(3)	0.3499(3)	0.040(2)	0.047(2)	0.045(2)	–0.007(2)	0.007(2)	–0.014(2)
C(2)	2*i*		–0.1588(4)	0.9619(3)	0.3301(3)	0.046(3)	0.051(3)	0.062(3)	–0.011(2)	0.007(2)	–0.016(2)
C(3)	2*i*		–0.2192(5)	1.0273(3)	0.3692(4)	0.064(4)	0.059(3)	0.103(4)	–0.013(3)	0.008(3)	–0.034(3)
C(4)	2*i*		–0.3148(5)	1.0108(4)	0.4263(4)	0.066(4)	0.087(4)	0.107(5)	–0.012(3)	0.020(4)	–0.056(4)
C(5)	2*i*		–0.3533(6)	0.9296(4)	0.4452(4)	0.075(4)	0.101(5)	0.102(5)	–0.021(4)	0.048(4)	–0.048(4)
C(6)	2*i*		–0.2941(5)	0.8629(3)	0.4067(3)	0.066(3)	0.071(3)	0.087(4)	–0.025(3)	0.037(3)	–0.027(3)
C(7)	2*i*		–0.2315(4)	0.7406(3)	0.2682(3)	0.035(2)	0.045(2)	0.045(2)	–0.006(2)	0.002(2)	–0.012(2)
C(8)	2*i*		–0.2927(5)	0.7847(3)	0.1990(3)	0.054(3)	0.063(3)	0.064(3)	–0.012(3)	–0.014(3)	–0.007(3)
C(9)	2*i*		–0.3943(5)	0.7528(4)	0.1742(4)	0.055(3)	0.083(4)	0.087(4)	–0.008(3)	–0.025(3)	–0.016(3)
C(10)	2*i*		–0.4361(5)	0.6790(4)	0.2182(4)	0.043(3)	0.075(4)	0.123(5)	–0.006(3)	–0.014(3)	–0.038(4)
C(11)	2*i*		–0.3759(5)	0.6349(3)	0.2869(4)	0.065(4)	0.053(3)	0.119(5)	–0.020(3)	0.002(4)	–0.012(3)
C(12)	2*i*		–0.2720(5)	0.6654(3)	0.3121(3)	0.060(3)	0.051(3)	0.068(3)	–0.018(2)	–0.007(3)	–0.008(2)
C(13)	2*i*		–0.0179(4)	0.7149(3)	0.3756(2)	0.058(3)	0.043(2)	0.033(2)	–0.012(2)	–0.008(2)	–0.001(2)
C(14)	2*i*		–0.0686(6)	0.6821(3)	0.4533(3)	0.095(4)	0.066(3)	0.039(3)	–0.025(3)	–0.006(3)	0.001(2)
C(15)	2*i*		0.0047(8)	0.6197(4)	0.5069(3)	0.140(6)	0.074(4)	0.046(3)	–0.036(4)	–0.026(4)	0.016(3)
C(16)	2*i*		0.1267(8)	0.5901(4)	0.4838(4)	0.139(7)	0.052(3)	0.084(5)	–0.017(4)	–0.061(5)	0.011(3)
C(17)	2*i*		0.1786(6)	0.6225(3)	0.4085(4)	0.088(4)	0.059(3)	0.081(4)	0.003(3)	–0.044(4)	–0.006(3)
C(18)	2*i*		0.1071(5)	0.6859(3)	0.3545(3)	0.064(3)	0.048(3)	0.053(3)	–0.005(2)	–0.017(3)	–0.006(2)
C(19)	2*i*		0.3642(4)	1.0130(3)	0.1996(3)	0.034(2)	0.049(2)	0.051(3)	–0.010(2)	0.003(2)	–0.004(2)
C(20)	2*i*		0.4162(5)	0.9837(3)	0.1300(3)	0.061(3)	0.066(3)	0.071(3)	–0.018(3)	0.026(3)	–0.021(3)
C(21)	2*i*		0.5386(6)	0.9981(4)	0.1021(4)	0.068(4)	0.083(4)	0.112(5)	–0.015(3)	0.046(4)	–0.027(4)
C(22)	2*i*		0.6066(5)	1.0425(4)	0.1411(5)	0.037(3)	0.090(5)	0.127(6)	–0.010(3)	0.017(4)	0.008(4)
C(23)	2*i*		0.5564(5)	1.0731(4)	0.2098(4)	0.044(3)	0.109(5)	0.092(4)	–0.038(3)	–0.010(3)	0.008(4)
C(24)	2*i*		0.4364(5)	1.0580(3)	0.2392(3)	0.057(3)	0.088(4)	0.058(3)	–0.033(3)	–0.003(3)	–0.004(3)
C(25)	2*i*		0.1238(4)	1.0858(3)	0.2715(3)	0.047(3)	0.039(2)	0.050(3)	–0.011(2)	0.005(2)	–0.013(2)
C(26)	2*i*		0.0271(5)	1.1315(3)	0.2248(3)	0.067(3)	0.044(3)	0.056(3)	0.000(2)	0.014(3)	–0.002(2)
C(27)	2*i*		–0.0439(6)	1.2059(4)	0.2481(4)	0.092(5)	0.055(3)	0.085(4)	0.013(3)	0.020(4)	0.014(3)
C(28)	2*i*		–0.0152(8)	1.2310(4)	0.3187(5)	0.126(6)	0.045(3)	0.108(6)	–0.010(4)	0.053(5)	–0.028(4)
C(29)	2*i*		0.0799(8)	1.1868(5)	0.3642(5)	0.114(6)	0.092(5)	0.106(5)	–0.022(4)	0.021(5)	–0.063(4)
C(30)	2*i*		0.1499(5)	1.1145(4)	0.3416(3)	0.070(4)	0.080(4)	0.083(4)	–0.008(3)	–0.001(3)	–0.046(3)
C(31)	2*i*		0.2398(4)	0.9089(3)	0.3331(2)	0.044(3)	0.050(3)	0.038(2)	–0.017(2)	–0.004(2)	–0.007(2)
C(32)	2*i*		0.3511(5)	0.8503(3)	0.3374(3)	0.058(3)	0.058(3)	0.064(3)	–0.010(3)	–0.008(3)	0.003(3)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(33)	2*i*		0.3737(6)	0.7896(4)	0.4081(4)	0.084(5)	0.070(4)	0.097(5)	–0.004(3)	–0.036(4)	0.013(4)
C(34)	2*i*		0.2901(8)	0.7852(4)	0.4735(4)	0.119(6)	0.083(4)	0.068(4)	–0.038(4)	–0.042(4)	0.017(3)
C(35)	2*i*		0.1809(7)	0.8413(4)	0.4694(3)	0.113(5)	0.104(5)	0.037(3)	–0.051(4)	–0.001(3)	–0.001(3)
C(36)	2*i*		0.1540(5)	0.9048(3)	0.3992(3)	0.066(3)	0.079(3)	0.043(3)	–0.022(3)	0.000(3)	–0.009(3)
C(37)	2*i*		0.1646(4)	0.6679(3)	0.0007(2)	0.040(2)	0.040(2)	0.043(2)	0.001(2)	–0.007(2)	–0.011(2)
C(38)	2*i*		0.2336(5)	0.7306(3)	–0.0462(3)	0.059(3)	0.051(3)	0.069(3)	–0.004(2)	0.013(3)	–0.008(2)
C(39)	2*i*		0.3485(5)	0.7057(4)	–0.0846(4)	0.066(4)	0.075(4)	0.106(5)	–0.007(3)	0.032(3)	–0.013(3)
C(40)	2*i*		0.3949(5)	0.6178(4)	–0.0770(4)	0.052(3)	0.088(4)	0.104(5)	0.004(3)	0.020(3)	–0.035(4)
C(41)	2*i*		0.3304(5)	0.5557(3)	–0.0302(4)	0.053(3)	0.055(3)	0.113(5)	0.016(3)	0.001(3)	–0.029(3)
C(42)	2*i*		0.2157(4)	0.5805(3)	0.0085(3)	0.045(3)	0.051(3)	0.079(4)	–0.001(2)	0.000(3)	–0.016(3)
C(43)	2*i*		–0.1031(4)	0.7111(2)	–0.0288(2)	0.038(2)	0.032(2)	0.033(2)	–0.007(2)	–0.002(2)	–0.004(2)
C(44)	2*i*		–0.0916(4)	0.6545(3)	–0.0843(3)	0.053(3)	0.047(3)	0.052(3)	–0.004(2)	–0.005(2)	–0.019(2)
C(45)	2*i*		–0.1870(5)	0.6598(3)	–0.1377(3)	0.071(4)	0.061(3)	0.054(3)	–0.018(3)	–0.015(3)	–0.020(2)
C(46)	2*i*		–0.2934(5)	0.7198(3)	–0.1352(3)	0.055(3)	0.073(3)	0.059(3)	–0.018(3)	–0.022(3)	–0.007(3)
C(47)	2*i*		–0.3056(5)	0.7766(3)	–0.0813(3)	0.044(3)	0.060(3)	0.069(3)	0.005(2)	–0.021(3)	–0.007(3)
C(48)	2*i*		–0.2109(4)	0.7727(3)	–0.0283(3)	0.051(3)	0.051(3)	0.053(3)	–0.002(2)	–0.011(2)	–0.016(2)
C(49)	2*i*		–0.0222(4)	0.6150(2)	0.1285(2)	0.042(2)	0.033(2)	0.040(2)	–0.002(2)	–0.005(2)	–0.010(2)
C(50)	2*i*		–0.1281(4)	0.5733(3)	0.1291(3)	0.055(3)	0.046(2)	0.045(3)	–0.014(2)	–0.006(2)	0.000(2)
C(51)	2*i*		–0.1509(5)	0.5062(3)	0.1938(3)	0.079(4)	0.058(3)	0.058(3)	–0.030(3)	0.008(3)	–0.007(2)
C(52)	2*i*		–0.0704(6)	0.4821(3)	0.2572(3)	0.104(5)	0.041(3)	0.047(3)	–0.006(3)	–0.004(3)	0.006(2)
C(53)	2*i*		0.0351(6)	0.5239(3)	0.2557(3)	0.090(4)	0.055(3)	0.051(3)	–0.007(3)	–0.016(3)	0.003(2)
C(54)	2*i*		0.0592(5)	0.5895(3)	0.1919(3)	0.056(3)	0.051(3)	0.053(3)	–0.012(2)	–0.014(2)	0.001(2)
C(55)	2*i*		0.0652(3)	0.9924(2)	–0.0217(2)	0.028(2)	0.028(2)	0.032(2)	–0.005(2)	0.000(2)	–0.008(2)
Cl(1)	2*i*		0.26062(9)	0.77905(6)	0.15236(6)	0.0327(6)	0.0446(6)	0.0523(6)	0.0055(5)	–0.0104(5)	–0.0054(5)
Fe(2)	2*i*		0.46563(7)	0.37050(5)	0.34839(5)	0.0549(5)	0.0617(4)	0.0670(5)	–0.0125(4)	–0.0023(4)	–0.0141(4)
Cl(2)	2*i*		0.3823(2)	0.4696(1)	0.2475(1)	0.095(1)	0.093(1)	0.093(1)	0.0203(9)	–0.049(1)	–0.0184(9)
Cl(3A)	2*i*	0.50	0.6511(5)	0.3185(4)	0.3075(3)	0.099(4)	0.228(6)	0.098(3)	0.065(4)	0.035(3)	0.041(4)
Cl(4A)	2*i*	0.50	0.4670(7)	0.4256(3)	0.4564(3)	0.244(7)	0.089(3)	0.094(3)	0.031(4)	–0.094(4)	–0.041(3)
Cl(5A)	2*i*	0.50	0.3576(7)	0.2624(5)	0.3733(4)	0.277(8)	0.203(7)	0.138(4)	–0.200(7)	0.045(5)	–0.038(4)
Cl(3B)	2*i*	0.50	0.6630(4)	0.3869(4)	0.3486(4)	0.052(2)	0.191(5)	0.196(6)	–0.040(3)	–0.031(3)	0.132(4)
Cl(4B)	2*i*	0.50	0.3843(6)	0.3906(4)	0.4693(3)	0.208(6)	0.134(5)	0.090(3)	0.053(4)	0.076(4)	0.006(3)
Cl(5B)	2*i*	0.50	0.4637(9)	0.2350(3)	0.3396(4)	0.38(1)	0.052(2)	0.197(6)	0.001(4)	–0.180(7)	–0.033(3)

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