the isomorphous $(Me_4P)Cu_2Cl_5$ structure (Haije, Dobbelaar & Maaskant, 1986). A difference synthesis based on these positions yielded the C-atom positions. H atoms were constrained to ideal positions (C—H = 0.96 Å) and assigned isotropic thermal parameters with magnitudes 1.2 times greater than those of the associated C atoms. Refinement proceeded in a straightforward fashion.

Acknowledgement is made to The Boeing Company and to NSF, through grant CHE-8408407, for the establishment of the X-ray diffraction facility.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71255 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1031]

References

Bond, M. R., Willett, R. D., Haije, W. G. & Maaskant, W. J. A. (1988). *Inorg. Chem.* **27**, 614–620.
Caputo, R. E., Vukosavovich, M. & Willett, R. D. (1976). *Acta Cryst.* **B32**, 2516–2518.
Geiser, U., Willett, R. D., Lindbeck, M. & Emerson, K. (1986). *J. Am. Chem. Soc.* **108**, 1173–1179.
Haije, W. G., Dobbelaar, J. A. L. & Maaskant, W. J. A. (1986). *Acta Cryst.* **C42**, 1485–1487.
Murray, K. & Willett, R. D. (1991). *Acta Cryst.* **C47**, 2660–2662.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Weise, S. & Willett, R. D. (1993). *Acta Cryst.* **B49**, 283–289.

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Heptacarbonylbis(triphenylphosphine)-bis(μ_3-tellurium)-triiron

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Abstract

The heptacarbonyl-1κ^3C,2κ^2C,3κ^2C-bis(μ_3-tellurido)-bis(triphenylphosphine)-2κP,3κP-triiron, $(PPh_3)_2Fe_3(CO)_7(\mu_3\text{-}Te)_2$, structure is a distorted square-pyramid motif with three Fe and two Te atoms at the vertices; Fe(1), Fe(2), Te(1) and Te(2) form the base of the pyramid with Fe(1)—Te(1) = 2.531 (1), Fe(1)—Te(2) = 2.544 (1), Fe(2)—Te(1) = 2.539 (1) and Fe(2)—Te(2) = 2.549 (1) Å. Fe(1) and Fe(2) have two terminal carbonyl ligands and one triphenylphosphine ligand; the phosphine ligands are coordinated equatorially to Fe(1) and axially to Fe(2). The apical Fe(3) atom has three terminal carbonyl ligands.

Comment

The most striking feature of the title complex is the presence of both equatorially and axially coordinated phosphine ligands. This same axial–equatorial coordination scheme was also observed in $(PPh_3)_3Ru_3(CO)_6(\mu_3\text{-}Te)_2$ (Mathur, Thimmappa & Rheingold, 1990) which contains a third phosphine ligand on an apical Ru atom. However, previous reports of structures containing a similar metal-chalcogen cluster framework indicate a preference for equatorial coordination of bulky ligands: $(C_3Ph_2)Fe_3(CO)_8(\mu_3\text{-}S)_2$ (Dettlaf, Hubener, Klimes & Weiss, 1982), $(C_3H_2S_2)Fe_3(CO)_8(\mu_3\text{-}S)_2$ (Benoit, Marouille & Patin, 1982) and $(Me_2NH)Fe_3(CO)_8(\mu_3\text{-}S)_2$ (Adams & Babin, 1986). Comparing the bond lengths of the phosphine ligands reveals, however, that the axial triphenylphosphine ligand has the shorter bond: the axial Fe(2)—P(2) bond is 2.214 (1) Å and the equatorial Fe(1)—P(1) bond is 2.274 (1) Å. The axial Fe(1)—C(2) carbonyl bond length at 1.749 (4) Å is *shorter* than the equatorial Fe(1)—C(1) carbonyl bond at 1.792 (3) Å. [The two Fe(2) carbonyl ligands are statistically identical and of an intermediate length with an averaged bond distance of 1.777 (3) Å.] The structure also shows that equatorial triphenylphosphine ligation places stress on the apical Fe(3) position: the Fe(3)—Fe(1) distance, 2.800 (1) Å, is much longer than the

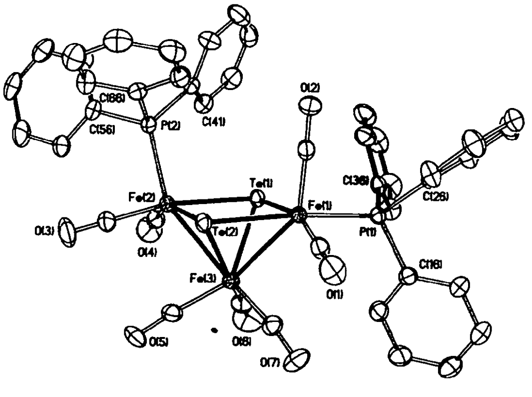

Fig. 1. Diagram for $(PPh_3)_2Fe_3(CO)_7(\mu_3\text{-}Te)_2$ showing the numbering scheme. Thermal ellipsoids are drawn at 35% probability boundaries.

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Fe(3)—Fe(2) distance, 2.707 (1) Å. Looking down on the Fe(3) apex of a space-filling model gives further indication of why the second phosphine ligand is axially coordinated: P(2) would have to be located at the sites labeled O(3) or O(4) causing a phenyl ring to approach either O(5) or O(6) too closely (see Fig. 2). It would be interesting to learn whether disubstitution of ligands less sterically demanding than triphenylphosphine would result in both ligands coordinating in equatorial positions.

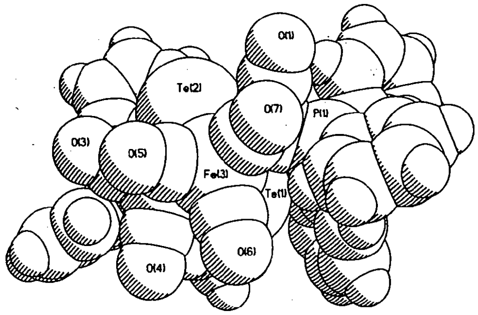

Fig. 2. Space-filling model showing the steric interactions at the apical Fe(3) site.

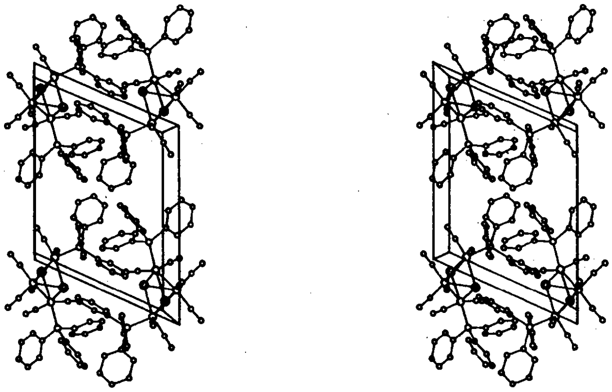

Fig. 3. Unit-cell packing diagram as viewed down the *b* axis.

Experimental

Crystal data

$[Fe_3Te_2(C_{18}H_{15}P)_2(CO)_7]$
M_r = 1143.4
Triclinic
$P\bar{1}$
a = 11.763 (4) Å
b = 13.598 (5) Å
c = 14.635 (4) Å
α = 87.66 (3)°
β = 66.45 (2)°
γ = 86.44 (3)°
V = 2140 (1) Å^3
Z = 2

D_x = 1.77 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–12.5°
μ = 2.54 mm^{-1}
T = 298 K
Block
0.40 × 0.35 × 0.30 mm
Dark red
Crystal source: hexane

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
7862 measured reflections
7541 independent reflections
6299 observed reflections [$F_o > 5.0\sigma(F_o)$]
R_{int} = 0.0209

θ_{max} = 25°
h = −14 → 14
k = −17 → 17
l = 0 → 18
3 standard reflections monitored every 197 reflections intensity variation: <3%

Refinement

Refinement on F
Final R = 0.0271
wR = 0.0323
S = 0.997
6297 reflections
442 parameters
H-atom parameters not refined
$w = [\sigma^2(F_o) + 0.0010F_o^2]^{-1}$

$(\Delta/\sigma)_{max}$ = 0.332
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Te(1)	0.2242 (1)	0.1939 (1)	0.1131 (1)	0.033 (1)
Te(2)	0.0531 (1)	0.3794 (1)	0.0722 (1)	0.035 (1)
Fe(1)	0.1246 (1)	0.3462 (1)	0.2138 (1)	0.030 (1)
Fe(2)	0.1574 (1)	0.2276 (1)	−0.0306 (1)	0.033 (1)
Fe(3)	−0.0090 (1)	0.2123 (1)	0.1605 (1)	0.033 (1)
P(1)	0.1769 (1)	0.2968 (1)	0.3428 (1)	0.031 (1)
P(2)	0.3391 (1)	0.2665 (1)	−0.1468 (1)	0.034 (1)
C(1)	0.0088 (3)	0.4360 (3)	0.2863 (3)	0.043 (1)
O(1)	−0.0638 (3)	0.4963 (2)	0.3282 (3)	0.071 (1)
C(2)	0.2490 (4)	0.4238 (3)	0.1646 (3)	0.043 (1)
O(2)	0.3286 (3)	0.4766 (2)	0.1317 (2)	0.069 (1)
C(3)	0.0734 (4)	0.2622 (3)	−0.1056 (3)	0.053 (2)
O(3)	0.0189 (3)	0.2870 (3)	−0.1528 (3)	0.086 (2)
C(4)	0.1709 (4)	0.0994 (3)	−0.0537 (3)	0.047 (2)
O(4)	0.1775 (4)	0.0170 (2)	−0.0662 (3)	0.085 (2)
C(5)	−0.1077 (3)	0.2061 (3)	0.0958 (3)	0.047 (2)
O(5)	−0.1777 (3)	0.2030 (2)	0.0597 (2)	0.066 (1)
C(6)	−0.0112 (4)	0.0845 (3)	0.1942 (3)	0.054 (2)
O(6)	−0.0190 (4)	0.0033 (2)	0.2166 (3)	0.097 (2)
C(7)	−0.1177 (4)	0.2527 (3)	0.2783 (3)	0.046 (2)
O(7)	−0.1983 (3)	0.2725 (2)	0.3529 (2)	0.067 (1)
C(11)	−0.0095 (2)	0.1690 (2)	0.4423 (2)	0.048 (2)
C(12)	−0.0971	0.1231	0.5253	0.066 (2)
C(13)	−0.1165	0.1518	0.6211	0.079 (2)
C(14)	−0.0482	0.2264	0.6338	0.077 (2)
C(15)	0.0395	0.2723	0.5508	0.057 (2)
C(16)	0.0588	0.2437	0.4551	0.039 (1)
C(21)	0.3236 (2)	0.3688 (1)	0.4337 (2)	0.049 (2)
C(22)	0.3707	0.4418	0.4711	0.058 (2)
C(23)	0.3316	0.5402	0.4671	0.056 (2)
C(24)	0.2454	0.5657	0.4256	0.060 (2)
C(25)	0.1983	0.4927	0.3882	0.052 (2)
C(26)	0.2375	0.3942	0.3923	0.035 (1)
C(31)	0.2922 (2)	0.1100 (2)	0.3555 (2)	0.055 (2)
C(32)	0.3925	0.0411	0.3262	0.075 (3)
C(33)	0.5059	0.0652	0.2512	0.074 (2)
C(34)	0.5189	0.1582	0.2055	0.069 (2)
C(35)	0.4186	0.2272	0.2347	0.053 (2)
C(36)	0.3052	0.2030	0.3097	0.037 (1)
C(41)	0.4955 (2)	0.1307 (2)	−0.1031 (2)	0.049 (2)
C(42)	0.6021	0.0958	−0.0899	0.061 (2)
C(43)	0.6942	0.1603	−0.0997	0.067 (2)
C(44)	0.6797	0.2596	−0.1227	0.069 (2)

C(45)	0.5731	0.2945	−0.1359	0.058 (2)
C(46)	0.4810	0.2300	−0.1261	0.038 (1)
C(51)	0.5020 (2)	0.2315 (2)	−0.3437 (2)	0.050 (2)
C(52)	0.5382	0.1959	−0.4398	0.063 (2)
C(53)	0.4558	0.1439	−0.4642	0.070 (2)
C(54)	0.3373	0.1275	−0.3925	0.075 (2)
C(55)	0.3011	0.1631	−0.2963	0.055 (2)
C(56)	0.3834	0.2150	−0.2719	0.040 (1)
C(61)	0.3257 (3)	0.4367 (2)	−0.2561 (2)	0.049 (2)
C(62)	0.3216	0.5383	−0.2726	0.061 (2)
C(63)	0.3367	0.6018	−0.2063	0.059 (2)
C(64)	0.3560	0.5637	−0.1234	0.058 (2)
C(65)	0.3602	0.4620	−0.1069	0.049 (2)
C(66)	0.3450	0.3985	−0.1732	0.038 (1)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Te(1)—Fe(1)	2.531 (1)	Te(1)—Fe(2)	2.539 (1)
Te(1)—Fe(3)	2.545 (1)	Te(2)—Fe(1)	2.544 (1)
Te(2)—Fe(2)	2.549 (1)	Te(2)—Fe(3)	2.565 (1)
Fe(1)—Fe(3)	2.800 (1)	Fe(1)—P(1)	2.274 (1)
Fe(1)—C(1)	1.792 (3)	Fe(1)—C(2)	1.749 (4)
Fe(2)—Fe(3)	2.707 (1)	Fe(2)—P(2)	2.214 (1)
Fe(2)—C(3)	1.779 (5)	Fe(2)—C(4)	1.775 (4)
Fe(3)—C(5)	1.775 (5)	Fe(3)—C(6)	1.786 (4)
Fe(3)—C(7)	1.771 (3)		
Fe(1)—Te(1)—Fe(2)	98.9 (1)	P(2)—Fe(2)—C(4)	97.6 (1)
Fe(2)—Te(1)—Fe(3)	64.3 (1)	Te(1)—Fe(3)—Te(2)	80.9 (1)
Fe(1)—Te(2)—Fe(3)	66.5 (1)	Te(1)—Fe(3)—Fe(2)	57.7 (1)
Te(1)—Fe(1)—Te(2)	81.5 (1)	Te(1)—Fe(3)—C(6)	86.0 (1)
Te(1)—Fe(1)—P(1)	94.0 (1)	Te(2)—Fe(3)—Fe(1)	56.4 (1)
Te(1)—Fe(1)—C(2)	99.4 (1)	Te(2)—Fe(3)—C(5)	86.8 (1)
Te(2)—Fe(1)—P(1)	172.4 (1)	Te(2)—Fe(3)—C(7)	99.8 (1)
Te(2)—Fe(1)—C(2)	94.5 (1)	Fe(1)—Fe(3)—C(5)	141.4 (1)
Fe(3)—Fe(1)—C(1)	104.2 (1)	Fe(1)—Fe(3)—C(7)	77.5 (1)
P(1)—Fe(1)—C(1)	93.6 (1)	Fe(2)—Fe(3)—C(6)	106.7 (1)
C(1)—Fe(1)—C(2)	97.8 (2)	C(5)—Fe(3)—C(6)	95.7 (2)
Te(1)—Fe(2)—Fe(3)	57.9 (1)	C(6)—Fe(3)—C(7)	95.7 (2)
Fe(1)—Te(1)—Fe(3)	67.0 (1)	Te(1)—Fe(2)—C(4)	89.9 (2)
Fe(1)—Te(2)—Fe(2)	98.3 (1)	Te(2)—Fe(2)—P(2)	109.1 (1)
Fe(2)—Te(2)—Fe(3)	63.9 (1)	Te(2)—Fe(2)—C(4)	152.8 (1)
Te(1)—Fe(1)—Fe(3)	56.8 (1)	Fe(3)—Fe(2)—C(3)	107.7 (1)
Te(1)—Fe(1)—C(1)	160.9 (1)	P(2)—Fe(2)—C(3)	94.2 (1)
Te(2)—Fe(1)—Fe(3)	57.1 (1)	C(3)—Fe(2)—C(4)	96.5 (2)
Te(2)—Fe(1)—C(1)	88.9 (1)	Te(1)—Fe(3)—Fe(1)	56.3 (1)
Fe(3)—Fe(1)—P(1)	115.3 (1)	Te(1)—Fe(3)—C(5)	135.2 (1)
Fe(3)—Fe(1)—C(2)	143.0 (1)	Te(1)—Fe(3)—C(7)	124.0 (2)
P(1)—Fe(1)—C(2)	92.3 (1)	Te(2)—Fe(3)—Fe(2)	57.7 (1)
Te(1)—Fe(2)—Te(2)	81.3 (1)	Te(2)—Fe(3)—C(6)	163.5 (1)
Te(1)—Fe(2)—P(2)	98.5 (1)	Fe(1)—Fe(3)—Fe(2)	88.7 (1)
Te(1)—Fe(2)—C(3)	164.9 (1)	Fe(1)—Fe(3)—C(6)	122.8 (2)
Te(2)—Fe(2)—Fe(3)	58.3 (1)	Fe(2)—Fe(3)—C(5)	79.3 (1)
Te(2)—Fe(2)—C(3)	86.9 (1)	Fe(2)—Fe(3)—C(7)	157.5 (1)
Fe(3)—Fe(2)—P(2)	153.2 (1)	C(5)—Fe(3)—C(7)	100.4 (2)
Fe(3)—Fe(2)—C(4)	95.2 (1)		

The structure was solved by direct methods. The phenyl rings were constrained as rigid groups. All H atoms were included in idealized riding positions, with fixed isotropic *U*. The *SHELXTL-Plus* (Sheldrick, 1990) program library was used throughout.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71208 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1039]

References

Adams, R. D. & Babin, J. E. (1986). *Inorg. Chem.* **25**, 3418–3422.

Benoit, A., Marouille, J. L. & Patin, C. M. H. (1982). *J. Organomet. Chem.* **233**, C51–C54.

Dettlaf, G., Hubener, P., Klimes, J. & Weiss, E. (1982). *J. Organomet. Chem.* **229**, 63–75.

Mathur, P., Thimmappa, B. H. S. & Rheingold, A. L. (1990). *Inorg. Chem.* **29**, 4658–4665.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.21/V. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Copper(II) and Nickel(II) Octabromo-tetrakis(pentafluorophenyl) Porphyrin Complexes

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Abstract

The copper and nickel complexes of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ({4,5,9,10,14,15,19,20-octabromo-2,7,12,17-tetrakis(pentafluorophenyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1,3(22),4,6,8(23),9,11,13(24),14,16,18(21),19-dodecaene}copper(II) 0.5-dichloromethane solvate and {4,5,9,10,14,15,19,20-octabromo-2,7,12,17-tetrakis(pentafluorophenyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1,3(22),4,6,8(23),9,11,13(24),14,16,18(21),19-dodecaene}nickel(II) 0.5-dichloromethane solvate) form isostructural crystals. There is significant distortion from planarity of the porphyrin ring caused by the octabromo substituents interacting with the *meso*-pentafluorophenyl groups and with each other, with departures of the Br atoms from the plane defined by the four N atoms of up to 2.36 Å. This tetrahedral distortion of the molecule does not result in any significant changes in bond distances from those in non-halogenated tetraphenylporphyrin complexes.

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† Contribution No. 8624.

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