P1—O19^{x}	1.489 (3)	P7—O12^{xiii}	1.588 (3)
P1—O13^{x}	1.490 (2)	P8—O8	1.480 (2)
P1—O15^{x}	1.572 (2)	P8—O14	1.488 (3)
P1—O6^{x}	1.588 (2)	P8—O1	1.571 (3)
P2—O20^{x}	1.480 (2)	P8—O2^{ii}	1.590 (2)
P2—O25^{i}	1.497 (3)	P9—O3^{viii}	1.485 (3)
P2—O12^{x}	1.574 (3)	P9—O4^{viii}	1.491 (3)
P2—O21^{x}	1.580 (2)	P9—O2^{xiv}	1.583 (2)
P3—O5^{viii}	1.480 (2)	P9—O24^{xi}	1.592 (3)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z-1$; (iv) $x, y, z-1$; (v) $x, y, 1+z$; (vi) $x, -y, \frac{1}{2}+z$; (vii) $1+x, 1+y, 1+z$; (viii) $x, 1-y, \frac{1}{2}+z$; (ix) $1+x, 1-y, \frac{1}{2}+z$; (x) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (xi) $x, 1+y, z$; (xii) $1+x, y, 1+z$; (xiii) $1+x, y, z$; (xiv) $x-\frac{1}{2}, \frac{1}{2}+y, z$.

The non-centrosymmetric crystal structure of $Cr(PO_3)_3$ has been refined as a racemic twin using *SHELXL*93 (Sheldrick, 1993) following a procedure described by Flack & Schwarzenbach (1988; Flack, 1983).

Data collection: *STADI*-4 (Stoe & Cie, 1995). Cell refinement: *STADI*-4. Data reduction: *STADI*-4. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995), *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

We thank Mr G. Koch and Dr M. Serafin (Giessen) for the data collection. Continuous support by Professor Dr R. Gruehn (Giessen) is gratefully appreciated.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bagieu-Beucher, M. & Guitel, J. C. (1977). *Acta Cryst.* B**33**, 2529–2533.
Bentama, J., Durand, J. & Cot, L. (1988). *Z. Anorg. Allg. Chem.* **556**, 227–232.
Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.
Domanskii, A. I., Shepelev, Y. F., Smolin, Y. I. & Litvin, B. N. (1982). *Sov. Phys. Crystallogr.* **27**, 140–142.
Dowty, E. (1995). *ATOMS for Windows*. Version 3.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.
Fukuoka, H., Imoto, H. & Saito, T. (1995). *J. Solid State Chem.* **119**, 107–114.
Glaum, R. (1992). *Z. Anorg. Allg. Chem.* **616**, 46–52.
Glaum, R. & Gruehn, R. (1990). *Z. Anorg. Allg. Chem.* **580**, 78–94.
Glaum, R. & Hitchman, M. (1996). *Aus. J. Chem.* Submitted.
Glaum, R., Walter-Peter, M., Özalp, D. & Gruehn, R. (1991). *Z. Anorg. Allg. Chem.* **601**, 145–162.
Gruss, M. (1995). Diploma thesis, University of Giessen, Germany.
Harrison, W. T. A., Gier, T. E. & Stucky, G. D. (1994). *Acta Cryst.* C**50**, 1643–1646.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Meer, H. van der (1976). *Acta Cryst.* B**32**, 2423–2426.
Middlemiss, N., Hawthorne, F. & Calvo, C. (1977). *Can. J. Chem.* **55**, 1673–1679.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rémy, P. & Boullé, A. (1972). *Bull. Soc. Chim. Fr.* pp. 2213–2221.
Rittner, P. & Glaum, R. (1994). *Z. Kristallogr.* **209**, 162–169.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stoe & Cie (1995). *STADI-4 Software Manual*. Stoe & Cie, Darmstadt, Germany.
Watson, I. M., Borel, M. M., Chardon, J. & Leclaire, A. (1994). *J. Solid State Chem.* **111**, 253–256.
Yakubovich, O. V., Dimitrova, O. V. & Savina, G. V. (1991). *Sov. Phys. Crystallogr.* **36**, 267–269.

Acta Cryst. (1996). C**52**, 2650–2652

Tetracarbonyl(tetraphosphorus hexaoxide)iron

Martin Jansen* and Jürgen Clade

Institut für Anorganische Chemie, Universität Bonn,
Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany

(*Received 1 February 1996; accepted 1 April 1996*)

Abstract

The title $[Fe(CO)_4(P_4O_6)]$ molecule consists of a trigonal-bipyramidally coordinated Fe atom, with the adamantane-like P_4O_6 cage in an axial position. As a consequence of the electronic effects of the iron–carbonyl group on the P_4O_6 cage, the P—O bond lengths show distortions similar to those observed within the series $P_4O_7 \rightarrow P_4O_6S \rightarrow P_4O_6Se$, but the effects are slightly less pronounced.

Comment

$P_4O_6Fe(CO)_4$ is the first transition metal complex of P_4O_6 to be investigated by single-crystal X-ray diffraction. An earlier structural investigation of the complex $P_4O_6[Ni(CO)_3]_4$ by means of powder diffraction (Pierron, Wheatley & Riess, 1966) did not reveal accurate bond lengths and angles, and more recent structural data on P_4O_6–transition metal complexes are not available.

The goal of the present work was to compare the influences of group VIA substituents and the isolobal iron–tetracarbonyl group on the distortion of the P_4O_6 unit (for crystal structures of the compounds P_4O_6X, where X is O, S and Se, see Jansen & Voss, 1981; Jost & Schneider, 1981; Jansen & Möbs, 1984*a*; Frick, Jansen, Bruna & Peyerimhoff, 1991; Clade, Jansen, Engels & Marian, 1995). The Fe atom is coordinated trigonal bipyramidally by four carbonyl groups and the P_4O_6 cage, the cage being in an axial position. The C_{ax}—Fe—C_{eq} and C_{eq}—Fe—P_{coord} angles are almost 90°. This means that the P_4O_6 cage, due to the considerably long

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

Fe—P1 distance of 2.1233 (12) Å, does not have any steric influence on the equatorial CO groups. The Fe—C bond distances do not differ significantly from those observed in $Fe(CO)_5$ (Braga, Grepioni & Orpen, 1993), while the average C—O distance is about 0.01 Å shorter in the present case. This difference, however, already approaches the range of experimental error. Within the P_4O_6 cage, the bond distances and angles show the same tendencies that have already been observed in the series P_4O_6X (X = O, S, Se; Jansen & Voss, 1981; Jost & Schneider, 1981; Jansen & Möbs, 1984*a*; Frick, Jansen, Bruna & Peyerimhoff, 1991; Clade, Jansen, Engels & Marian, 1995). The P_{coord}—$O(P_{uncoord})$ distances [average 1.603 (2) Å] are significantly shorter than the average P—O distance found in P_4O_6 [1.656 (3) Å; Jansen, Voss & Deiseroth, 1981; Jansen & Möbs, 1984*b*], while the $P_{uncoord}$—$O(P_{coord})$ distances [average 1.663 (2) Å] are slightly longer. Also, the O—P_{coord}—O bond angles [average 101.4 (1)°] are slightly stretched [in P_4O_6, the O—P—O angle is 99.8 (1)°; Jansen, Voss & Deiseroth, 1981; Jansen & Möbs, 1984*b*]. It has been shown that the amount of distortion of the P_4O_6 cage is correlated with the charge transfer from the pentavalent P atom to the terminally bound substituent (Mühlhäuser, Engels, Marian, Peyerimhoff, Bruna & Jansen, 1994). As one would expect, this effect is slightly less pronounced in $P_4O_6Fe(CO)_4$ than in the analogous chalcogen derivatives. In contrast to our expectations, the 'staggered' conformation of the iron-carbonyl group with respect to the P_4O_6 cage does not occur in the crystal. The dihedral angle between the planes defined by atoms C2, Fe, P1 and Fe, P1, O1 is 35.1°. Thus, the molecule belongs to C_3 point symmetry, the configuration being half-staggered.

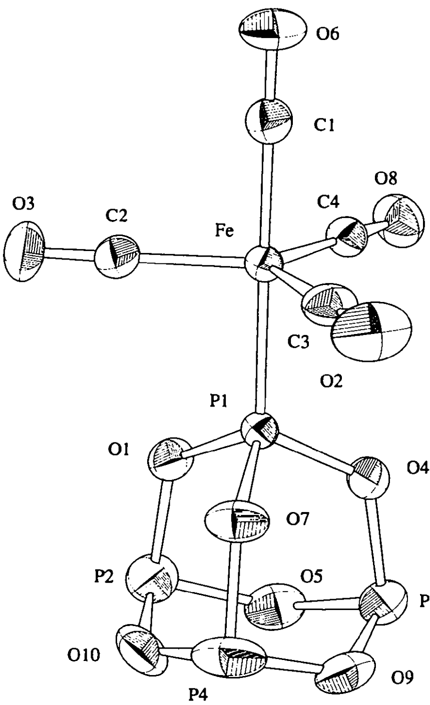

Fig. 1. The molecular structure of $P_4O_6Fe(CO)_4$ with ellipsoids plotted at the 50% probability level.

Experimental

All operations were carried out under inert conditions. $P_4O_6Fe(CO)_4$ was prepared from P_4O_6 and $Fe(CO)_5$ according to a photochemical method described in the literature (Walker & Mills, 1975). Single crystals were obtained by subliming the yellowish residue which remained after evaporation of the solvent (vacuum, 323 to 293 K). Since the crystals were found to be light sensitive, data collection was performed at 223 K under exclusion of light.

Crystal data

$[Fe(CO)_4(P_4O_6)]$
M_r = 387.77
Monoclinic
$P2_1/n$
a = 9.264 (5) Å
b = 12.768 (6) Å
c = 10.177 (5) Å
β = 94.19 (2)°
V = 1200.6 (11) Å^3
Z = 4
D_x = 2.145 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9–10.5°
μ = 1.833 mm^{-1}
T = 223 (2) K
Irregular
0.4 × 0.3 × 0.2 mm
Transparent yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.48, T_{max} = 0.69
3449 measured reflections
2630 independent reflections
2399 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0338
θ_{max} = 30.06°
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 16$
$l = -12 \rightarrow 12$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0377
$wR(F^2)$ = 0.1046
S = 1.068
2627 reflections
172 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 2.9315P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 1.182 e Å^{-3}
$\Delta\rho_{min}$ = −1.121 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe	0.09742 (4)	0.82104 (3)	0.69086 (4)	0.02422 (13)
P1	−0.08345 (8)	0.91426 (6)	0.73254 (7)	0.0229 (2)
P2	−0.22696 (11)	1.01899 (8)	0.94061 (9)	0.0406 (2)

P3	−0.39733 (10)	0.91804 (9)	0.72381 (12)	0.0491 (3)
P4	−0.23517 (13)	1.10963 (8)	0.67693 (12)	0.0531 (3)
C1	0.2516 (4)	0.7417 (3)	0.6571 (3)	0.0345 (7)
O1	−0.0947 (2)	0.9479 (2)	0.8837 (2)	0.0343 (5)
O2	−0.0656 (3)	0.7393 (3)	0.4553 (3)	0.0543 (8)
O3	0.0827 (3)	0.7173 (2)	0.9471 (2)	0.0445 (6)
O4	−0.2393 (2)	0.8629 (2)	0.6993 (3)	0.0377 (5)
O5	−0.3650 (3)	0.9538 (2)	0.8765 (3)	0.0442 (6)
O6	0.3487 (3)	0.6915 (2)	0.6370 (3)	0.0521 (7)
O7	−0.1007 (3)	1.0253 (2)	0.6599 (3)	0.0403 (6)
C2	0.0878 (3)	0.7570 (2)	0.8477 (3)	0.0296 (6)
C3	−0.0031 (4)	0.7712 (3)	0.5470 (3)	0.0343 (7)
O8	0.2673 (3)	1.0133 (2)	0.6737 (4)	0.0630 (9)
C4	0.2015 (4)	0.9390 (3)	0.6812 (4)	0.0370 (7)
O9	−0.3720 (3)	1.0286 (3)	0.6504 (3)	0.0544 (8)
O10	−0.2257 (3)	1.1160 (2)	0.8382 (3)	0.0444 (6)

Table 2. *Selected geometric parameters (Å, °)*

Fe—C2	1.801 (3)	P2—O5	1.623 (3)
Fe—C1	1.805 (3)	P2—O1	1.663 (2)
Fe—P1	2.1233 (12)	O3—C2	1.136 (4)
P1—O1	1.608 (2)		
C2—Fe—C1	90.31 (15)	O5—P2—O1	99.16 (13)
C2—Fe—P1	89.22 (10)	P1—O1—P2	125.43 (14)
O1—P1—Fe	116.61 (9)	P2—O5—P3	127.8 (2)
O10—P2—O5	100.14 (15)		

Data collection: Enraf–Nonius diffractometer software. Cell refinement: Enraf–Nonius diffractometer software. Data reduction: *CADSHEL* (Kopf & Rübcke, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for kindly supporting this work.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Braga, D., Grepioni, F. & Orpen, A. G. (1993). *Organometallics*, **12**, 1481–1483.

Clade, J., Jansen, M., Engels, B. & Marian, C. M. (1995). *Z. Anorg. Allg. Chem.* **621**, 2065–2069.

Frick, F., Jansen, M., Bruna, P.-J. & Peyerimhoff, S. D. (1991). *Chem. Ber.* **124**, 1711–1714.

Jansen, M. & Möbs, M. (1984*a*). *Z. Anorg. Allg. Chem.* **514**, 39–48.

Jansen, M. & Möbs, M. (1984*b*). *Inorg. Chem.* **23**, 4486–4488.

Jansen, M. & Voss, M. (1981). *Angew. Chem.* **93**, 120–121.

Jansen, M., Voss, M. & Deiseroth, H.-J. (1981). *Angew. Chem.* **93**, 1023–1024.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Jost, K.-H. & Schneider, M. (1981). *Acta Cryst.* **B37**, 222–224.

Kopf, J. & Rübcke, H.-C. (1993). *CADSHEL. Program for Reduction of Enraf–Nonius CAD-4 Data.* Version 3.1. University of Hamburg, Germany.

Mühlhäuser, M., Engels, B., Marian, C. M., Peyerimhoff, S. D., Bruna, P.-J. & Jansen, M. (1994). *Angew. Chem.* **106**, 578–581.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Pierron, E. D., Wheatley, P. J. & Riess, J. G. (1966). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Walker, M. L. & Mills, J. L. (1975). *Inorg. Chem.* **14**, 2438–2440.

Acta Cryst. (1996). **C52**, 2652–2655

A New Quaternary Borocarbide, $GdRh_2B_2C$

Jinhua Ye,[a] Toetsu Shishido,[b] Takashi Kimura,[a]
Takehiko Matsumoto[a] and Tsuguo Fukuda[b]

[a]*National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan, and* [b]*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980, Japan. E-mail: ye@nrim.go.jp*

(*Received 17 April 1996; accepted 31 May 1996*)

Abstract

A new quaternary borocarbide, gadolinium dirhodium diboron carbide, has been synthesized by the flux method and its structure has been analyzed using single-crystal X-ray diffraction. The compound crystallizes as a derivative of the $ThCr_2Si_2$ structure type, as do many newly discovered superconducting compounds in the RT_2B_2C system (R = rare earth, T = transition metal). The structure consists of thick tetrahedrally coordinated Rh_2B_2 layers and GdC NaCl-type layers. These two atomic layers stack alternately along [001] *via* strong B—C bonds to form a three-dimensional network.

Comment

Since the discovery of superconductivity with $T_c = 23$ K in the Y–Pd–B–C system (Cava *et al.*, 1994), the interest in intermetallic compounds has been renewed and in the search for new quaternary borocarbides many new materials have been found for a variety of rare earth elements (R) and transition metals (T). Our group has studied the crystal chemistry and magnetic properties of the R–T–B ternary systems for many years, particularly for T = Co and Rh (Niihara, Shishido & Yajima, 1973; Shishido, Higashi, Kitazawa, Bernhard, Takei & Fukuda, 1994). Recently, we extended our search from the R–T–B ternary system to the R–T–B–C quaternary system and succeeded in the crystal growth of a new quaternary borocarbide, $GdRh_2B_2C$, using a copper flux.

The crystal structure of $GdRh_2B_2C$ is shown in Fig. 1. It may be viewed as a layered structure containing GdC NaCl-type layers and Rh_2B_2 slabs. Within the

Acta Crystallographica Section C
ISSN 0108-2701 © 1996