C(23)	0.7129 (6)	0.0411 (5)	0.2644 (4)	4.0 (2)
C(24)	0.7770 (5)	0.1257 (4)	0.3368 (4)	3.6 (2)
C(25)	0.7309 (6)	0.2338 (5)	0.3306 (5)	4.4 (2)
C(26)	0.6211 (6)	0.2583 (5)	0.2502 (5)	4.5 (2)
C(27)	0.9602 (7)	0.1762 (6)	0.4846 (4)	5.2 (3)
C(31)	−0.2537 (6)	−0.0060 (4)	−0.3602 (4)	3.7 (2)
C(32)	−0.3611 (7)	−0.0911 (5)	−0.4172 (5)	5.0 (3)
C(41)	−0.0903 (8)	0.5180 (5)	0.2324 (6)	6.1 (3)
C(42)	−0.068 (1)	0.5904 (7)	0.3313 (8)	9.3 (5)

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

Cd—S(4)	2.606 (2)	N(1)—C(1)	1.323 (6)
Cd—S(1)	2.641 (2)	N(1)—C(11)	1.437 (6)
Cd—S(3)	2.646 (2)	N(2)—C(1)	1.334 (6)
Cd—S(5)	2.710 (2)	N(2)—C(21)	1.430 (6)
Cd—S(2^i)	2.765 (1)	C(11)—C(16)	1.365 (7)
Cd—S(2)	2.831 (2)	C(11)—C(12)	1.380 (8)
S(1)—C(1)	1.699 (5)	C(12)—C(13)	1.380 (8)
S(2)—C(2)	1.714 (5)	C(13)—C(14)	1.373 (7)
S(3)—C(2)	1.655 (5)	C(14)—C(15)	1.378 (8)
S(4)—C(3)	1.701 (5)	C(15)—C(16)	1.380 (7)
S(5)—C(3)	1.673 (5)	C(21)—C(26)	1.369 (8)
O(1)—C(14)	1.373 (6)	C(21)—C(22)	1.378 (8)
O(1)—C(17)	1.415 (8)	C(22)—C(23)	1.367 (7)
O(2)—C(24)	1.373 (5)	C(23)—C(24)	1.379 (7)
O(2)—C(27)	1.405 (7)	C(24)—C(25)	1.366 (7)
O(3)—C(2)	1.329 (5)	C(25)—C(26)	1.384 (7)
O(3)—C(31)	1.461 (6)	C(31)—C(32)	1.495 (8)
O(4)—C(3)	1.319 (6)	C(41)—C(42)	1.43 (1)
O(4)—C(41)	1.451 (6)		
S(1)—Cd—S(2)	150.85 (5)	N(2)—C(1)—S(1)	121.3 (4)
S(1)—Cd—S(3)	85.87 (6)	O(3)—C(2)—S(3)	122.7 (3)
S(1)—Cd—S(5)	98.68 (5)	O(3)—C(2)—S(2)	114.0 (3)
S(3)—Cd—S(2)	65.46 (5)	S(3)—C(2)—S(2)	123.3 (3)
S(3)—Cd—S(5)	98.56 (6)	O(4)—C(3)—S(5)	123.2 (3)
S(4)—Cd—S(1)	103.96 (6)	O(4)—C(3)—S(4)	113.0 (3)
S(4)—Cd—S(2)	105.26 (6)	S(5)—C(3)—S(4)	123.8 (3)
S(4)—Cd—S(3)	164.28 (5)	C(16)—C(11)—C(12)	119.9 (5)
S(4)—Cd—S(5)	68.09 (5)	C(16)—C(11)—N(1)	119.9 (5)
S(5)—Cd—S(2)	91.04 (5)	C(12)—C(11)—N(1)	120.1 (4)
S(1)—Cd—S(2^i)	94.66 (5)	C(11)—C(12)—C(13)	120.1 (5)
S(2)—Cd—S(2^i)	84.63 (5)	C(14)—C(13)—C(12)	119.8 (5)
S(3)—Cd—S(2^i)	97.71 (5)	C(13)—C(14)—O(1)	115.5 (5)
S(4)—Cd—S(2^i)	93.82 (5)	C(13)—C(14)—C(15)	120.0 (5)
S(5)—Cd—S(2^i)	159.63 (4)	O(1)—C(14)—C(15)	124.5 (5)
Cd—S(2)—Cd	95.37 (5)	C(14)—C(15)—C(16)	119.9 (5)
C(1)—S(1)—Cd	110.5 (2)	C(11)—C(16)—C(15)	120.3 (5)
C(2)—S(2)—Cd	98.8 (1)	C(26)—C(21)—C(22)	119.2 (4)
C(2)—S(2)—Cd	81.9 (2)	C(26)—C(21)—N(2)	120.8 (5)
C(2)—S(3)—Cd	89.0 (2)	C(22)—C(21)—N(2)	119.9 (5)
C(3)—S(4)—Cd	85.3 (2)	C(23)—C(22)—C(21)	120.7 (5)
C(3)—S(5)—Cd	82.5 (2)	C(22)—C(23)—C(24)	119.8 (5)
C(14)—O(1)—C(17)	116.7 (5)	C(25)—C(24)—O(2)	124.3 (5)
C(24)—O(2)—C(27)	118.1 (4)	C(25)—C(24)—C(23)	120.1 (4)
C(2)—O(3)—C(31)	118.4 (4)	O(2)—C(24)—C(23)	115.6 (4)
C(3)—O(4)—C(41)	119.0 (4)	C(24)—C(25)—C(26)	119.7 (5)
C(1)—N(1)—C(11)	124.3 (4)	C(21)—C(26)—C(25)	120.5 (5)
C(1)—N(2)—C(21)	126.6 (4)	O(3)—C(31)—C(32)	106.8 (4)
N(1)—C(1)—N(2)	117.6 (4)	C(42)—C(41)—O(4)	107.6 (6)
N(1)—C(1)—S(1)	121.0 (4)		

Symmetry code: (i) $-x, -y, -z$.

The structure was solved by the Patterson method and Fourier syntheses and refined by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms. H-atom coordinates were refined with fixed bond distances. All calculatios were performed on a MicroVAX 3100 using *TEXSAN* (Molecular Structure Corporation, 1989).

This work is supported by a Grant for Key Research Project from the State Science and Technology Commission and National Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances involving H atoms and least-squares-planes data have been deposited with the IUCr (Reference: AL1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Casas, J. S., Sanchez, A., Bravo, J., Garcia-Fontan, S., Castellano, E. E. & Jones, M. M. (1989). *Inorg. Chim. Acta*, **158**, 119–126.

Castineiras, A., Arguero, A., Masaguer, J. R., Ruiz-Amil, A., Martinez-Carrera, S. & Garcia-Blanco, S. (1985). *Polyhedron*, **4**, 143–148.

Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Reid, E. E. (1963). *Organic Chemistry of Bivalent Sulfur*, Vol. V, 17–20. New York: Chemical Publishing Co.

Tao, X.-T., Jiang, M.-H., Xu, D. & Shao, Z.-S. (1987). *J. Synth. Cryst.* **16**, 28–32. (In Chinese.)

Thanmaniwong, T., Akimov, V. M., Andrianov, V. G., Struchkov, Y. T. & Molodkin, A. K. (1984). *Zh. Neorg. Khim.* **29**, 1033–1037.

Xing, G.-C., Jiang, M.-H., Shao, Z.-S. & Xu, D. (1987). *Chin. Laser*, **14**, 302–308. (In Chinese.)

Acta Cryst. (1994). C**50**, 1014–1016

[*meso*-5,10,15,20-Tetrakis(4-methoxyphenyl)porphinato]bis(trimethyl phosphito)iron(II)

L. Toupet*

Groupe Matière Condensée et Matériaux, URA 804, CNRS, Université de Rennes, Campus de Beaulieu, 35042 Rennes CEDEX, France

N. Legrand, A. Bondon and G. Simonneaux

Laboratoire de Chimie Organometallique et Biologique, CNRS, URA 415, Université de Rennes, Campus de Beaulieu, 35042 Rennes CEDEX, France

(*Received* 23 *April* 1993; *accepted* 11 *October* 1993)

Abstract

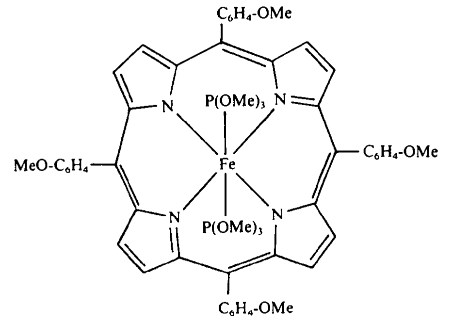
The structure determination of the title compound, {2,7,12,17-tetrakis(4-methoxyphenyl)-21,22,23,24-tetraazapentacyclo[$16.2.1.1^{3,6}.1^{8,11}.1^{16,17}$]tetracosa-1(21),2,4,6,8(23),9,11,13,15,17,19-undecaenediido-N,N',N'',N'''}bis(trimethyl phosphito-*P*)iron(II), $[Fe(C_{48}H_{36}N_4)(C_3H_9O_3P)_2]$, is the first example of a

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

structural study on a model phosphito ferrous porphyrin derivative. The complex crystallizes in a centrosymmetric form. The metal–phosphorus bond lengths [2.255 (2) Å] are shorter than those observed in the analogous iron(II) complex containing dimethylphenylphosphine ligands [2.284 (1) Å].

Comment

During the past few years, we have been investigating the coordination of phosphines both to metalloporphyrins (Sodano, Simonneaux & Toupet, 1988) and to haemoproteins (Simonneaux, Bondon & Sodano, 1987; Simonneaux, Bondon, Brunel & Sodano, 1988). A few phosphite derivatives of haemes (Ohya, Morohoshi & Sato, 1984; Stynes, Fletcher & Chen, 1986) and haemoproteins (Schejter, Plotkin & Vig, 1991) have been described. However, no structural studies on model phosphine ferrous porphyrin derivatives have been reported previously. Herein we report the structural study of [*meso*-5,10,15,20-tetrakis(*p*-methoxyphenyl)porphinato]bis(trimethyl phosphito)iron(II), (1).



(1)

The molecule lies on a centre of symmetry (Fig. 1). The geometry of the porphyrin ring is very similar to that found in other low-spin ferrous porphyrins (Scheidt & Reed, 1981). The bond distances for the two crystallographically non-equivalent pyrrole rings have an average value of 1.996 (4) Å, which is in agreement with those observed in other low-spin iron(II) porphyrin structures (Scheidt & Reed, 1981). This low-spin state has been confirmed by ^{1}H NMR spectroscopy. The spectrum displays two groups of signals corresponding to the porphyrin ring protons (7–9 p.p.m.) and to the phosphite ligand [P(OMe)$_3$ 1.82 p.p.m.] as expected for a diamagnetic iron(II) porphyrin derivative. The axial Fe—P(OCH$_3$) distance [2.255 (2) Å] is shorter than the analogous distance in the bis(dimethylphenylphosphine)iron(II) complex [2.284 (1) Å] (Sodano, Simonneaux & Toupet, 1988). This is consistent with the greater π-acceptor ability of phosphite ligands compared with that of phosphine ligands (Tolman, 1970), and with a concomitant increase in π back bonding from iron to the axial ligand.

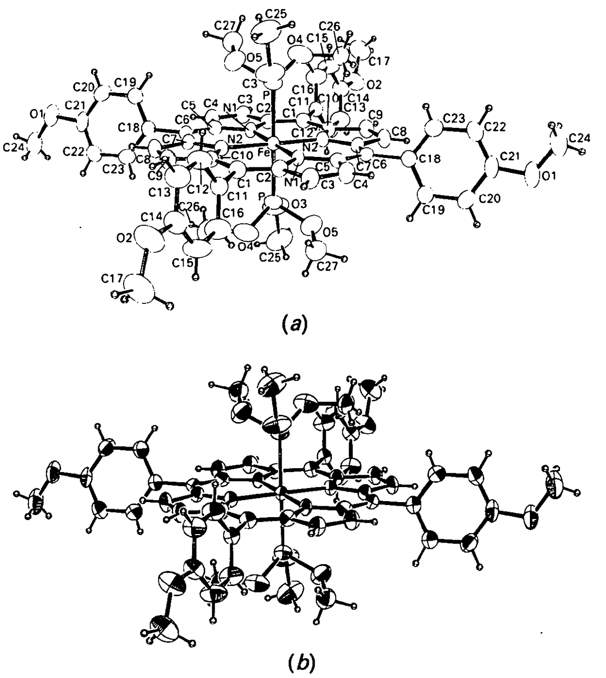


Fig. 1. *ORTEP* (Johnson, 1965) views of the title structure: (*a*) with atomic labels; (*b*) with ellipsoid axes (50% probability).

Experimental

Crystal data

[Fe($C_{48}H_{36}N_4$)($C_3H_9O_3P$)$_2$]
M_r = 1036.9
Orthorhombic
Pccn
a = 21.122 (3) Å
b = 20.705 (6) Å
c = 11.610 (7) Å
V = 5078 (2) Å^3
Z = 4
D_x = 1.356 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7–12°
μ = 0.417 mm^{-1}
T = 294 K
Prism
0.35 × 0.30 × 0.22 mm
Red
Crystal source: grown from *o*-dichlorobenzene/pentane solution

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4879 measured reflections
4879 independent reflections
2362 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max}$ = 25°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity variation: 0.2%

Refinement

Refinement on F
R = 0.055
wR = 0.052
S = 1.9

$w = 1/[\sigma^2(I) + (0.04F_o^2)^2]^{1/2}$
$(\Delta/\sigma)_{\max}$ = 0.6
$\Delta\rho_{\max}$ = 0.32 e Å^{-3}
$\Delta\rho_{\min}$ = 0.05 e Å^{-3}

2362 reflections
404 parameters
Only coordinates of H atoms refined

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Fe	0	0	0	1.99 (2)
P	0.02225 (7)	−0.00583 (8)	0.1896 (1)	3.05 (3)
O1	0.3848 (2)	−0.1798 (2)	−0.1424 (4)	4.6 (1)
O2	0.1631 (2)	0.4049 (2)	0.0290 (4)	4.7 (1)
O3	−0.0149 (2)	−0.0598 (2)	0.2545 (4)	5.0 (1)
O4	0.0264 (2)	0.0544 (3)	0.2704 (4)	6.0 (1)
O5	0.0939 (2)	−0.0314 (4)	0.2184 (4)	5.0 (1)
N1	0.0871 (2)	0.0343 (2)	−0.0263 (4)	2.10 (9)
N2	0.0327 (2)	−0.0899 (2)	−0.0166 (4)	2.21 (8)
C1	0.0670 (2)	0.1504 (2)	−0.0053 (5)	2.5 (1)
C2	0.1064 (2)	0.0978 (3)	−0.0247 (5)	2.4 (1)
C3	0.1731 (3)	0.1020 (3)	−0.0488 (5)	2.9 (1)
C4	0.1943 (3)	0.0424 (3)	−0.0649 (5)	3.0 (1)
C5	0.1414 (2)	−0.0011 (3)	−0.0499 (4)	2.5 (1)
C6	0.1451 (2)	−0.0674 (3)	−0.0549 (5)	2.5 (1)
C7	0.0938 (2)	−0.1086 (2)	−0.0379 (5)	2.3 (1)
C8	0.0975 (3)	−0.1778 (3)	−0.0456 (5)	3.0 (1)
C9	0.0390 (3)	−0.2008 (3)	−0.0307 (5)	3.0 (1)
C10	−0.0023 (3)	−0.1463 (2)	−0.0118 (5)	2.54 (9)
C11	0.0963 (2)	0.2166 (2)	0.0015 (5)	2.5 (1)
C12	0.0902 (3)	0.2610 (3)	−0.0862 (5)	3.6 (1)
C13	0.1138 (3)	0.3230 (3)	−0.0746 (6)	3.9 (1)
C14	0.1434 (3)	0.3413 (3)	0.0251 (5)	3.2 (1)
C15	0.1519 (3)	0.2979 (3)	0.1107 (6)	4.4 (2)
C16	0.1275 (3)	0.2362 (3)	0.0986 (6)	4.1 (1)
C17	0.1834 (4)	0.4280 (3)	0.1383 (7)	5.6 (2)
C18	0.2084 (2)	−0.0975 (3)	−0.0803 (5)	2.5 (1)
C19	0.2559 (3)	−0.0978 (3)	0.0009 (6)	3.4 (1)
C20	0.3143 (3)	−0.1257 (3)	−0.0230 (5)	3.7 (1)
C21	0.3256 (3)	−0.1540 (3)	−0.1283 (5)	3.3 (1)
C22	0.2790 (3)	−0.1548 (3)	−0.2089 (6)	3.9 (1)
C23	0.2214 (3)	−0.1266 (3)	−0.1841 (6)	3.6 (1)
C24	0.4018 (3)	−0.1984 (4)	−0.2551 (7)	5.7 (2)
C25	−0.0032 (4)	−0.0753 (4)	0.3754 (6)	6.4 (2)
C26	−0.0314 (3)	0.0911 (5)	0.2976 (7)	6.9 (2)
C27	0.1447 (3)	0.0081 (3)	0.2449 (6)	4.5 (1)

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

Fe—P	2.255 (2)	C2—C3	1.438 (7)
Fe—N1	1.996 (4)	C3—C4	1.326 (8)
Fe—N2	1.995 (4)	C4—C5	1.445 (8)
N1—C2	1.376 (6)	C5—C6	1.376 (8)
N1—C5	1.388 (7)	C6—C7	1.393 (8)
N2—C7	1.370 (7)	C6—C18	1.505 (7)
N2—C10′	1.382 (6)	C7—C8	1.439 (7)
C1—C2	1.390 (7)	C8—C9	1.335 (8)
C1—C10′	1.384 (8)	C9—C10	1.442 (7)
C1—C11	1.505 (7)		
P—Fe—N1	88.6 (1)	C3—C4—C5	107.6 (5)
P—Fe—N1′	91.4 (1)	N1—C5—C4	109.4 (5)
P—Fe—N2	88.4 (1)	N1—C5—C6	125.6 (5)
P—Fe—N2′	91.6 (1)	C4—C5—C6	125.0 (5)
N1—Fe—N2	89.9 (2)	C5—C6—C7	124.1 (5)
N1—Fe—N2′	90.1 (2)	N2—C7—C6	125.9 (5)
C2—N1—C5	105.2 (4)	N2—C7—C8	110.1 (5)
C7—N2—C10	105.8 (4)	C6—C7—C8	124.0 (5)
C2—C1—C10′	124.5 (5)	C7—C8—C9	107.2 (5)
N1—C2—C1	125.0 (5)	C8—C9—C10	107.5 (5)
N1—C2—C3	110.2 (5)	N2—C10—C1′	125.8 (5)
C1—C2—C3	124.8 (5)	N2—C10—C9	109.4 (5)
C2—C3—C4	107.5 (5)	C1′—C10—C9	124.8 (5)

All the calculations were performed with a Digital MicroVAX 3100 using the *MolEN* package (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71728 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1063]

References

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

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

Ohya, T., Morohoshi, H. & Sato, M. (1984). *Inorg. Chem.* **23**, 1303–1305.

Scheidt, W. R. & Reed, C. A. (1981). *Chem. Rev.* **61**, 543–555.

Schejter, A., Plotkin, B. & Vig, I. (1991). *FEBS Lett.* **280**, 199–201.

Simonneaux, G., Bondon, A., Brunel, C. & Sodano, P. (1988). *J. Am. Chem. Soc.* **110**, 7637–7640.

Simonneaux, G., Bondon, A. & Sodano, P. (1987). *Inorg. Chem.* **26**, 3636–3638.

Sodano, P., Simonneaux, G. & Toupet, L. (1988). *J. Chem. Soc. Dalton Trans.* pp. 2615–2620.

Stynes, D. V., Fletcher, D. & Chen, X. (1986). *Inorg. Chem.* **25**, 3483–3488.

Tolman, C. A. (1970). *J. Am. Chem. Soc.* **92**, 2953–2965.

Acta Cryst. (1994). C**50**, 1016–1019

1,4,7,10,13-Pentaoxacyclopentadecane (15-Crown-5) Sodium Iodide Complex, $C_{10}H_{20}O_5.NaI$

G. W. Buchanan, M. Gerzain and C. Bensimon

Ottawa-Carleton Chemistry Institute,
Department of Chemistry, Carleton University, Ottawa,
Canada K1S 5B6

(*Received* 13 *May* 1993; *accepted* 14 *December* 1993)

Abstract

The Na cation forms a 1/1 complex with 15-crown-5 ether. In this complex, Na^+ is six-coordinated to the five macrocyclic O atoms (average Na—O 2.42 Å) and the I^- ion. The coordination geometry is pentagonal pyramidal. The Na^+ ion lies 0.798 (3) Å above the least-squares plane of the ether O atoms. All structural parameters of the crown ether are similar to those of related complexes.

Comment

To date, only one crystal structure for a sodium complex of 15-crown-5 ether has been published,

Acta Crystallographica Section C
ISSN 0108-2701 ©1994