Refinement

Refinement on F^2
$R(F) = 0.0466$
$wR(F^2) = 0.1225$
$S = 1.056$
3383 reflections
208 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.117$ e Å^{-3}
$\Delta\rho_{\min} = -1.548$ e Å^{-3}
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)

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

	x	y	z	$U_{\rm eq}$
W1	0.08068 (5)	0.27828 (4)	0.12315 (6)	0.0332 (2)
Cl1	−0.4299 (4)	0.5992 (3)	0.1666 (5)	0.0744 (11)
O1	−0.0950 (8)	0.2970 (6)	0.2167 (9)	0.040 (2)
O2	0.0194 (8)	0.4375 (7)	0.2056 (9)	0.043 (2)
O3	−0.0015 (9)	0.3083 (6)	−0.0824 (9)	0.040 (2)
O4	0.0651 (8)	0.1372 (7)	0.0035 (8)	0.040 (2)
O5	0.2140 (8)	0.2111 (6)	0.2915 (8)	0.036 (2)
O6	0.2757 (8)	0.2879 (6)	0.1072 (9)	0.040 (2)
C1	−0.1522 (13)	0.4023 (9)	0.3185 (13)	0.042 (3)
C2	−0.1273 (13)	0.4875 (10)	0.2512 (14)	0.045 (3)
C3	−0.2459 (15)	0.5189 (11)	0.1094 (15)	0.053 (3)
C4	−0.1392 (16)	0.2649 (13)	−0.3443 (15)	0.066 (4)
C5	−0.0031 (14)	0.2200 (12)	−0.2192 (14)	0.050 (3)
C6	−0.0268 (12)	0.1275 (10)	−0.1516 (13)	0.039 (3)
C7	0.0334 (17)	0.0085 (11)	−0.2459 (15)	0.057 (3)
C8	0.1499 (16)	0.1863 (13)	−0.2731 (16)	0.063 (4)
C9	−0.1927 (13)	0.1484 (12)	−0.1354 (14)	0.051 (3)
C10	0.4576 (16)	0.1717 (12)	0.4707 (14)	0.058 (3)
C11	0.3803 (13)	0.1772 (9)	0.3013 (13)	0.040 (3)
C12	0.4044 (12)	0.2698 (10)	0.2351 (14)	0.043 (3)
C13	0.5530 (14)	0.2321 (13)	0.1689 (17)	0.064 (4)
C14	0.4257 (15)	0.0604 (11)	0.1991 (16)	0.058 (4)
C15	0.3942 (16)	0.3772 (11)	0.3536 (16)	0.060 (4)

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

W1—O1	1.930 (7)	O1—C1	1.431 (13)
W1—O2	1.930 (8)	O2—C2	1.407 (13)
W1—O4	1.890 (8)	O3—C5	1.433 (15)
W1—O3	1.892 (7)	O4—C6	1.434 (12)
W1—O5	1.897 (7)	O5—C11	1.445 (13)
W1—O6	1.905 (7)	O6—C12	1.438 (13)
Cl1—C3	1.791 (12)		
O1—W1—O2	78.5 (3)	O3—W1—O6	90.0 (3)
O1—W1—O3	106.1 (3)	O4—W1—O5	90.7 (3)
O1—W1—O4	90.0 (3)	O4—W1—O6	106.9 (3)
O1—W1—O5	89.3 (3)	O5—W1—O6	78.3 (3)
O1—W1—O6	158.9 (3)	C1—O1—W1	117.1 (6)
O2—W1—O3	88.4 (3)	C2—O2—W1	118.1 (7)
O2—W1—O4	159.0 (3)	C5—O3—W1	121.6 (7)
O2—W1—O5	106.5 (3)	C6—O4—W1	120.6 (7)
O2—W1—O6	88.7 (3)	C11—O5—W1	120.4 (6)
O3—W1—O4	77.9 (3)	C12—O6—W1	120.2 (6)
O3—W1—O5	160.7 (3)		

Non-H atoms were refined anisotropically. H atoms were included in idealized positions with fixed displacement parameters (1.2 times the displacement parameter of the host atom). The tertiary C—H distances were fixed at 0.98 Å, the secondary C—H distances at 0.97 Å and the methyl group C—H distances at 0.96 Å. The largest maximum and minimum residual electron-density peaks were located about 1 Å from the W atom.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1989). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

This work was supported by the NESTE Foundation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Chisholm, M. H., Parkin, I. P., Streib, W. E. & Eisenstein, O. (1994). *Inorg. Chem.* **33**, 812–815.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lehtonen, A. & Sillanpää, R. (1994). *Polyhedron*, **13**, 2519–2524.
Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Single Crystal Structure Analysis Software*. Version 5.0. MSC, 3200 Reseach Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Scherle, J. & Schröder, F. A. (1974). *Acta Cryst.* B**30**, 2772–2775.
Schrock, R. R., DePue, R. T., Feldman, J., Schaverien, C. J., Dewan, J. C. & Liu, A. H. (1988). *J. Am. Chem. Soc.* **110**, 1423–1435.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1995). C**51**, 1271–1275

Diaqua(5,10,15,20-tetraphenylporphinato)iron(III) Perchlorate, $[Fe(C_{44}H_{28}N_4)(H_2O)_2]ClO_4$

BEISONG CHENG AND W. ROBERT SCHEIDT

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

(*Received* 19 *October* 1994; *accepted* 23 *January* 1995)

Abstract

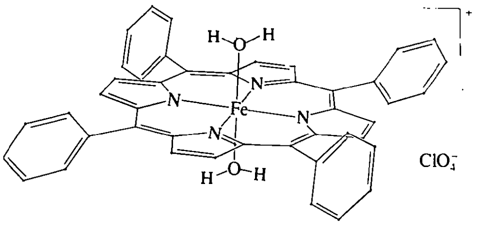
The crystal structure of a new crystal form of $[Fe(TPP)(H_2O)_2]ClO_4$ has been determined. The asymmetric unit contains one molecule in a general position and a half molecule with required inversion symmetry. The two independent molecules have almost identical average values for the equatorial Fe—N$_p$ bond lengths [2.029 (4) and 2.028 (6) Å], and the axial Fe—O bond lengths are 2.140 (2) and 2.121 (3) Å for molecule 1 (in a general position) and 2.126 (2) Å for molecule 2 (in a

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

special position). A brief comparison of the core structure and hydrogen-bonding environment of this molecule with two other crystal forms is described.

Comment

We have recently reported the synthesis and characterization of a five-coordinate aqua(octaethylporphinato)iron(III) complex, $[Fe(OEP)(H_2O)]ClO_4$ (Cheng *et al.*, 1994). In our attempted synthesis of the tetraphenylporphyrin derivative, we isolated the title compound, (I), in a new crystal form (space group $P2_1/n$, $Z = 6$). The structure of tetrahydrofuran solvated $[Fe(TPP)(H_2O)_2]ClO_4$ has been reported (Scheidt, Cohen & Kastner, 1979), and that of a non-solvated form (space group $P2_1/n$, $Z = 2$) has also been determined (Ceccio, 1988).



(I)

*ORTEP*II (Johnson, 1976) diagrams with labeling schemes for 1 and 2 are shown in Fig. 1. The average values for the unique chemical classes of distances and angles in the porphinato cores and the perpendicular displacements of each atom from the mean plane of the 24-atom core are given in Fig. 2. The agreement between chemically equivalent bond distances and angles in the two independent molecules is quite satisfactory. The average Fe—N_p bond lengths for the two molecules are the same [2.029 (4) and 2.028 (6) Å in 1 and 2, respectively] and the axial Fe—O bond lengths are slightly different [2.140 (2) for Fe(1)—O(1), 2.121 (3) for Fe(1)—O(2) and 2.126 (2) Å for Fe(2)—O(7)]. Hydrogen-bonding interaction is found between the aqua ligands and the O atoms of the perchlorate anions with an O···O distance *ca* 2.8 Å.

The coordination geometry of this new crystal form is very close to that of the previously determined non-solvated form (Ceccio, 1988) in which the Fe—N_p and Fe—O bond lengths were found to be 2.024 (7) and 2.142 (5) Å, respectively; however, it is quite different from that of the tetrahydrofuran solvated form (Scheidt, Cohen & Kastner, 1979) which shows a more expanded porphinato core [Fe—N_p 2.045 (8) Å] and a shorter axial Fe—O bond length of 2.095 (2) Å. Another important difference between the non-solvated and the tetrahydrofuran solvated form is the nature of the hydrogen bonding: in both non-solvated forms, each aqua ligand has only one hydrogen-bonding interaction with the perchlorate anion, the O···O distance is 2.8 Å for this new form. However, in the tetrahydrofuran solvated form, two hydrogen bonds were observed for each aqua ligand with an average O···O distance of 2.9 Å. We believe the difference in the core structure is related to the difference in hydrogen bonding. An increase in the hydrogen-bonding interaction (from the non-solvated forms to the tetrahydrofuran solvated form) leads to a decreased axial ligand field, which influences the nature of the spin state of the iron center and consequently leads to porphinato core expansion and shortening of the axial Fe—O bond length.

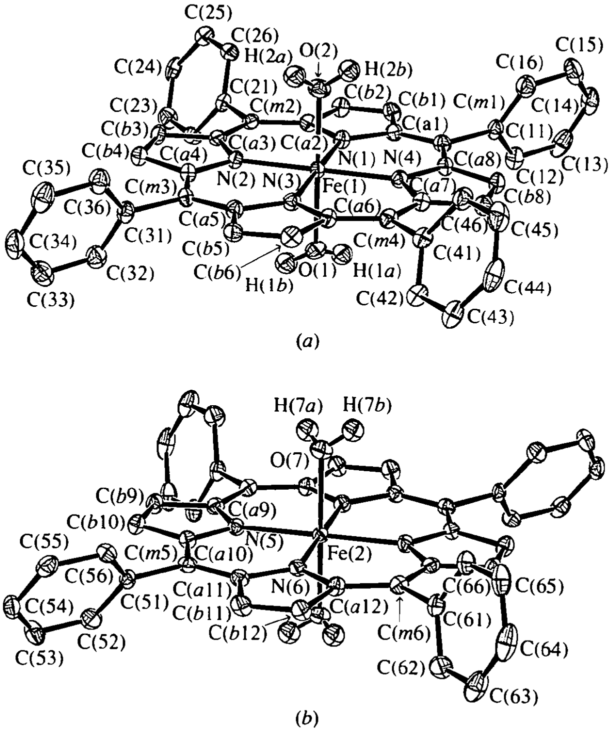


Fig. 1. *ORTEP*II (Johnson, 1976) diagrams of (*a*) molecule 1 and (*b*) molecule 2 of $[Fe(TPP)(H_2O)_2]^+$ with their labeling schemes. Displacement ellipsoids are drawn at the 50% probability level. Porphyrin H atoms are omitted for clarity.

There is an interesting relationship between our cell and that reported by Ceccio (1988), with only the *b* axis showing significant differences. The present cell has $b = 24.092(1)$ Å (127 K) while that of Ceccio (1988) has $b = 7.986(6)$ Å (20 K). Both are in space group $P2_1/n$. The cell of Ceccio (1988) would appear to be an approximate subcell of the current one. Note that the vector between Fe(1) and Fe(2) is (~0, 1/3, ~0). We note that we have obtained the same cell for several crystalline specimens both at room temperature and at 127 K. Strouse (private communications) suggests that the difference in unit cells may arise from the crystalline solvent. He has observed that more polar solvents yield more ordered crystals of metalloporphyrins [Ceccio's

(1988) crystals were obtained from $CHCl_3$, while ours were from CH_2Cl_2]. We also note that reflections of the $k = 3n + 1$ and $3n + 2$ class are systematically weaker than those with $k = 3n$, but all classes are significantly above background.

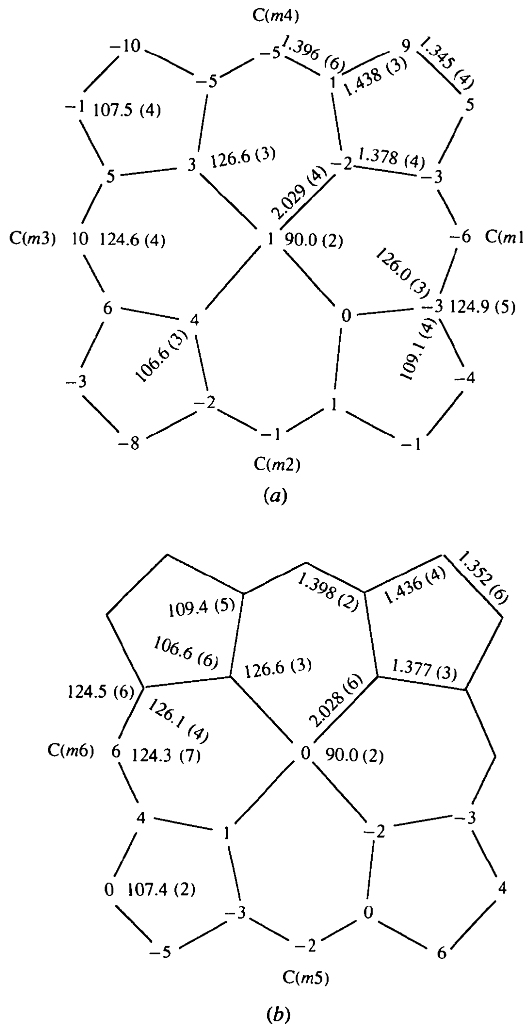


Fig. 2. Formal diagrams of the porphinato cores of $[Fe(TPP)(H_2O)_2]ClO_4$ displaying the average value for the bond parameters. Values for molecules 1 and 2 are given in (*a*) and (*b*), respectively. The numbers in parentheses are the estimated standard deviations calculated on the assumption that the average values were all drawn from the same population. Also displayed are the perpendicular displacements, in units of 0.01 Å, of each atom from the 24-atom mean plane of the core. For 2, only the crystallographically unique values are given in the centrosymmetric diagram.

Experimental

The title compound was synthesized by the reaction of $[Fe(TPP)]_2O$ in dichloromethane solution with an excess amount of aqueous perchloric acid (10%), and crystallized from dichloromethane and hexanes. In our hands, this is the only crystal form isolated.

Crystal data

$[Fe(C_{44}H_{28}N_4)(H_2O)_2]ClO_4$
$M_r = 804.04$
Monoclinic
$P2_1/n$
$a = 10.330\,(1)$ Å
$b = 24.092\,(1)$ Å
$c = 21.543\,(1)$ Å
$\beta = 97.89\,(1)°$
$V = 5310.7\,(6)$ Å^3
$Z = 6$
$D_x = 1.508$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 5.1–20.8°$
$\mu = 0.561$ mm^{-1}
$T = 127\,(2)$ K
Rectangular prism
0.55 × 0.25 × 0.25 mm
Black

Data collection

Enraf–Nonius FAST area-detector diffractometer
'Brute force' scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.617$, $T_{max} = 0.757$

31 873 measured reflections
11 466 independent reflections
7369 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0809$
$\theta_{max} = 28.16°$
$h = -11 \rightarrow 13$
$k = -31 \rightarrow 28$
$l = -21 \rightarrow 28$

Refinement

Refinement on F^2
$R(F) = 0.0684$
$wR(F^2) = 0.1657$
$S = 1.156$
11 453 reflections
840 parameters
Coordinates and U_{iso} of the H atoms of the water ligand refined; porphyrin H atoms idealized (riding model, C—H = 0.95 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 3.4902P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.011$
$\Delta\rho_{max} = 1.051$ e Å^{-3}
$\Delta\rho_{min} = -0.561$ 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 isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for O(3*a*) and O(5*b*); $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{eq}/U_{iso}
Fe(1)	0.98928 (4)	0.16663 (2)	0.99755 (2)	0.01449 (14)
N(1)	0.9424 (2)	0.19501 (11)	0.90855 (12)	0.0170 (6)
N(2)	0.8906 (2)	0.23081 (11)	1.02990 (12)	0.0153 (6)
N(3)	1.0362 (2)	0.13805 (11)	1.08659 (12)	0.0166 (6)
N(4)	1.0881 (2)	0.10280 (11)	0.96491 (12)	0.0167 (6)
C(*a*1)	0.9773 (3)	0.17182 (14)	0.85482 (15)	0.0179 (7)
C(*a*2)	0.8688 (3)	0.24146 (14)	0.89010 (15)	0.0181 (7)
C(*a*3)	0.8297 (3)	0.27355 (14)	0.99518 (15)	0.0173 (7)
C(*a*4)	0.8763 (3)	0.24099 (14)	1.09145 (14)	0.0171 (7)
C(*a*5)	1.0013 (3)	0.16119 (14)	1.14013 (14)	0.0172 (7)
C(*a*6)	1.1149 (3)	0.09283 (14)	1.10500 (15)	0.0165 (7)
C(*a*7)	1.1513 (3)	0.06030 (14)	0.99977 (15)	0.0184 (7)
C(*a*8)	1.1018 (3)	0.09195 (14)	0.90318 (15)	0.0181 (7)
C(*b*1)	0.9220 (3)	0.20406 (15)	0.80130 (15)	0.0206 (7)
C(*b*2)	0.8552 (3)	0.24582 (15)	0.82293 (15)	0.0206 (7)
C(*b*3)	0.7802 (3)	0.31295 (15)	1.0364 (2)	0.0206 (7)
C(*b*4)	0.8081 (3)	0.29266 (14)	1.0950 (2)	0.0197 (7)

C(*b*5)	1.0600 (3)	0.13001 (14)	1.1934 (2)	0.0186 (7)
C(*b*6)	1.1306 (3)	0.08901 (15)	1.1722 (2)	0.0211 (7)
C(*b*7)	1.1998 (3)	0.02104 (15)	0.9582 (2)	0.0209 (7)
C(*b*8)	1.1706 (3)	0.04075 (14)	0.8994 (2)	0.0207 (7)
C(*m*1)	1.0532 (3)	0.12427 (15)	0.85172 (14)	0.0187 (7)
C(*m*2)	0.8169 (3)	0.27860 (14)	0.93031 (15)	0.0167 (7)
C(*m*3)	0.9240 (3)	0.20852 (14)	1.14315 (14)	0.0170 (7)
C(*m*4)	1.1686 (3)	0.05662 (14)	1.06547 (15)	0.0178 (7)
C(11)	1.0894 (3)	0.10755 (14)	0.78940 (15)	0.0202 (7)
C(12)	0.9982 (4)	0.0845 (2)	0.7427 (2)	0.0256 (8)
C(13)	1.0341 (4)	0.0706 (2)	0.6848 (2)	0.0351 (10)
C(14)	1.1590 (5)	0.0797 (2)	0.6733 (2)	0.0367 (10)
C(15)	1.2516 (4)	0.1014 (2)	0.7191 (2)	0.0350 (10)
C(16)	1.2165 (4)	0.1148 (2)	0.7773 (2)	0.0268 (8)
C(21)	0.7397 (3)	0.32718 (14)	0.90118 (15)	0.0179 (7)
C(22)	0.6078 (3)	0.3323 (2)	0.9067 (2)	0.0231 (8)
C(23)	0.5370 (3)	0.3772 (2)	0.8804 (2)	0.0279 (8)
C(24)	0.5960 (3)	0.41766 (15)	0.8492 (2)	0.0237 (8)
C(25)	0.7268 (3)	0.4128 (2)	0.8431 (2)	0.0223 (7)
C(26)	0.7991 (3)	0.36768 (14)	0.86910 (14)	0.0191 (7)
C(31)	0.8898 (3)	0.22587 (14)	1.20580 (15)	0.0201 (7)
C(32)	0.7631 (3)	0.2188 (2)	1.2187 (2)	0.0258 (8)
C(33)	0.7301 (4)	0.2321 (2)	1.2768 (2)	0.0335 (9)
C(34)	0.8228 (4)	0.2540 (2)	1.3226 (2)	0.0368 (10)
C(35)	0.9481 (4)	0.2629 (2)	1.3100 (2)	0.0348 (10)
C(36)	0.9826 (4)	0.2488 (2)	1.2518 (2)	0.0268 (8)
C(41)	1.2530 (3)	0.01039 (14)	1.0940 (2)	0.0186 (7)
C(42)	1.2038 (3)	−0.03036 (15)	1.12986 (15)	0.0206 (7)
C(43)	1.2844 (3)	−0.0741 (2)	1.1542 (2)	0.0247 (8)
C(44)	1.4121 (4)	−0.0767 (2)	1.1435 (2)	0.0310 (9)
C(45)	1.4619 (3)	−0.0362 (2)	1.1085 (2)	0.0316 (9)
C(46)	1.3832 (3)	0.0073 (2)	1.0833 (2)	0.0254 (8)
O(1)	0.8135 (2)	0.11860 (11)	0.98893 (13)	0.0217 (6)
O(2)	1.1639 (2)	0.21400 (12)	1.00641 (13)	0.0242 (6)
Cl(1*a*)†	0.4942 (2)	0.18114 (8)	0.99579 (8)	0.0264 (4)
O(3*a*)†	0.3909 (11)	0.1474 (5)	0.9913 (6)	0.134 (4)
O(4*a*)†	0.5805 (5)	0.1733 (2)	0.9501 (2)	0.062 (2)
O(5*a*)†	0.5821 (7)	0.1756 (3)	1.0526 (3)	0.078 (2)
O(6*a*)†	0.4498 (4)	0.2374 (2)	0.9891 (2)	0.0423 (11)
Cl(1*b*)‡	0.4920 (6)	0.1548 (3)	0.9990 (4)	0.073 (2)
O(3*b*)‡	0.3922 (9)	0.1559 (4)	1.0370 (6)	0.036 (3)
O(4*b*)‡	0.3993 (14)	0.1490 (5)	0.9418 (6)	0.062 (4)
O(5*b*)‡	0.567 (5)	0.198 (2)	0.997 (3)	0.29 (3)
O(6*b*)‡	0.548 (2)	0.1015 (11)	1.0106 (10)	0.141 (10)
Fe(2)	1	1/2	1	0.0140 (2)
N(5)	0.9025 (2)	0.56412 (12)	1.03285 (12)	0.0160 (6)
N(6)	0.9564 (2)	0.52982 (12)	0.91132 (12)	0.0157 (6)
C(*a*9)	0.8870 (3)	0.57437 (14)	1.09415 (14)	0.0161 (7)
C(*a*10)	0.8411 (3)	0.60721 (14)	0.99818 (14)	0.0164 (7)
C(*a*11)	0.8826 (3)	0.57613 (14)	0.89319 (14)	0.0160 (7)
C(*a*12)	0.9925 (3)	0.50682 (14)	0.85784 (14)	0.0162 (7)
C(*b*9)	0.8188 (3)	0.62566 (14)	1.09840 (15)	0.0189 (7)
C(*b*10)	0.7907 (3)	0.64601 (15)	1.03941 (15)	0.0201 (7)
C(*b*11)	0.8719 (3)	0.58159 (15)	0.82614 (14)	0.0203 (7)
C(*b*12)	0.9394 (3)	0.53960 (15)	0.80461 (15)	0.0198 (7)
C(*m*5)	0.8293 (3)	0.61277 (14)	0.93314 (15)	0.0167 (7)
C(*m*6)	1.0669 (3)	0.45871 (14)	0.85414 (14)	0.0165 (7)
C(51)	0.7507 (3)	0.66080 (14)	0.90453 (14)	0.0160 (7)
C(52)	0.6184 (3)	0.6653 (2)	0.9099 (2)	0.0235 (8)
C(53)	0.5465 (3)	0.7101 (2)	0.8842 (2)	0.0279 (8)
C(54)	0.6044 (3)	0.7511 (2)	0.8535 (2)	0.0264 (8)
C(55)	0.7355 (3)	0.7474 (2)	0.8478 (2)	0.0233 (8)
C(56)	0.8087 (3)	0.70200 (14)	0.87245 (15)	0.0192 (7)
C(61)	1.1020 (3)	0.44186 (14)	0.79174 (15)	0.0186 (7)
C(62)	1.0097 (3)	0.4197 (2)	0.7453 (2)	0.0254 (8)
C(63)	1.0455 (4)	0.4057 (2)	0.6874 (2)	0.0309 (9)
C(64)	1.1726 (4)	0.4139 (2)	0.6755 (2)	0.0328 (9)
C(65)	1.2641 (4)	0.4355 (2)	0.7221 (2)	0.0298 (9)
C(66)	1.2293 (3)	0.44907 (15)	0.7799 (2)	0.0217 (7)
O(7)	1.1761 (2)	0.54675 (12)	1.01032 (13)	0.0222 (6)
Cl(2)	1.5056 (2)	0.51573 (7)	1.00138 (11)	0.0273 (5)
O(8)	1.558 (2)	0.4984 (8)	0.9527 (6)	0.182 (11)
O(9)	1.4626 (6)	0.5719 (3)	0.9916 (3)	0.0453 (15)
O(10)	1.6048 (8)	0.5119 (3)	1.0535 (5)	0.067 (2)
O(11)	1.3994 (7)	0.4849 (4)	1.0227 (9)	0.116 (7)

† Occupancy factor = 0.712 (5).
‡ Occupancy factor = 0.288 (5).

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

O(1)—H(1*a*)	0.73 (7)	Fe(1)—N(3)	2.033 (3)
O(1)—H(1*b*)	0.95 (7)	Fe(1)—N(4)	2.025 (3)
O(2)—H(2*a*)	0.74 (7)	O(7)—H(7*a*)	0.70 (6)
O(2)—H(2*b*)	0.95 (8)	O(7)—H(7*b*)	0.89 (6)
Fe(1)—O(1)	2.140 (2)	Fe(2)—O(7)	2.126 (2)
Fe(1)—O(2)	2.121 (3)	Fe(2)—N(5)	2.024 (3)
Fe(1)—N(1)	2.031 (3)	Fe(2)—N(6)	2.033 (3)
Fe(1)—N(2)	2.027 (3)		
Fe(1)—O(1)—H(1*a*)	108. (5)	N(1)—Fe(1)—O(2)	89.63 (10)
Fe(1)—O(1)—H(1*b*)	124. (4)	N(2)—Fe(1)—O(2)	91.14 (11)
Fe(1)—O(2)—H(2*a*)	122. (5)	N(3)—Fe(1)—O(2)	90.44 (10)
Fe(1)—O(2)—H(2*b*)	128. (5)	N(4)—Fe(1)—O(2)	88.66 (11)
H(1*a*)—O(1)—H(1*b*)	110. (6)	O(1)—Fe(1)—O(2)	179.74 (10)
H(2*a*)—O(2)—H(2*b*)	98. (6)	Fe(2)—O(7)—H(7*a*)	111. (5)
N(1)—Fe(1)—N(2)	90.10 (11)	Fe(2)—O(7)—H(7*b*)	126. (4)
N(1)—Fe(1)—N(3)	179.88 (6)	H(7*a*)—O(7)—H(7*b*)	104. (6)
N(1)—Fe(1)—N(4)	89.67 (11)	N(5)—Fe(2)—N(5^i)	179.996 (1)
N(2)—Fe(1)—N(3)	89.99 (11)	N(5)—Fe(2)—N(6^i)	89.88 (11)
N(2)—Fe(1)—N(4)	179.69 (11)	N(5)—Fe(2)—N(6)	90.12 (11)
N(3)—Fe(1)—N(4)	90.25 (11)	N(5)—Fe(2)—O(7)	91.09 (11)
N(1)—Fe(1)—O(1)	90.60 (10)	N(6)—Fe(2)—O(7)	89.27 (10)
N(2)—Fe(1)—O(1)	88.96 (11)	N(5)—Fe(2)—O(7^i)	88.92 (11)
N(3)—Fe(1)—O(1)	89.32 (10)	N(6)—Fe(2)—O(7^i)	90.73 (10)
N(4)—Fe(1)—O(1)	91.24 (11)		

Symmetry code: (i) $2 - x, 1 - y, 2 - z$.

Cell determination and intensity data collection were performed on an Enraf–Nonius FAST area-detector diffractometer with an Mo rotating anode source, using *MADNES* (Messerschmitt & Pflugrath, 1987). Our detailed methods and procedures for small molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). The structure was solved by *SHELXS*86 (Sheldrick, 1985) and refined by *SHELXL*93 (Sheldrick, 1993). One and a half molecules were found in an asymmetric cell with the first molecule in a general position and the second molecule possessing a symmetry center imposed on its iron(III) atom. Two sets of geometries (*a* and *b*) were resolved for the first perchlorate anion, their occupancy factors [0.712 (5) and 0.288 (5)] were refined by the least-squares process; another perchlorate anion was disordered around an inversion center. Since the two disordered groups for the first perchlorate anion were very close, O(3*a*) and O(5*b*) could not be refined anisotropically and thus were included as isotropic contributors. All H atoms of the porphyrin macrocycles were idealized with the standard methods in *SHELXL*93 and included in the least-squares process as fixed contributors; however, the H atoms of the aqua ligands were located from difference Fourier synthesis and isotropically refined in the least-squares process.

Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

We thank the National Institutes of Health for support of this research under grant GM-38401. Funds for the purchase of the FAST area detector diffractometer were provided through NIH grant RR-06709. We thank Professor Strouse for an interesting discussion.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ceccio, S. M. (1988). MS thesis, Univ. of California, Los Angeles, USA.

Cheng, B., Safo, M. K., Orosz, R. D., Reed, C. A., Debrunner, P. G. & Scheidt, W. R. (1994). *Inorg. Chem.* **33**, 1319–1324.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Messerschmitt, A. & Pflugrath, J. W. (1987). *J. Appl. Cryst.* **20**, 306–315.

Scheidt, W. R., Cohen, I. A. & Kastner, M. E. (1979). *Biochemistry*, **18**, 3546–3552.

Scheidt, W. R. & Reed, C. A. (1981). *Chem. Rev.* **81**, 543–555.

Scheidt, W. R. & Turowska-Tyrk, I. (1994). *Inorg. Chem.* **33**, 1314–1318.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

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

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1995). C**51**, 1275–1278

A Hexacobalt Sulfide Cluster Compound, $[Co_6(\mu\text{-}S)_8(PPh_3)_6].2PPh_3.2C_2H_4Cl_2.H_2O$

Feilong Jiang,* Xiaoying Huang, Rong Cao,
Maochun Hong and Hanqin Liu

State Key Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

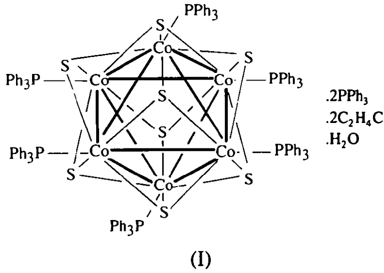
(*Received* 1 *June* 1994; *accepted* 20 *December* 1994)

Abstract

The title compound, octa-μ_3-thio-hexakis(triphenylphosphine)-*octahedro*-hexacobalt–triphenylphosphine–1,2-dichloroethane–water (1/2/2/1), $[Co_6S_8(C_{18}H_{15}P)_6]$.-$2C_{18}H_{15}P.2C_2H_4Cl_2.H_2O$, was prepared by the reaction of $CoCl(PPh_3)_3$ with Na(mpo) (mpo = 2-mercaptopyridine *N*-oxide) or NaS^tBu. The molecular structure consists of discrete cluster units interspersed with molecules of free triphenylphosphine and solvent. The neutral cluster contains a slightly distorted Co_6 octahedron with each triangular face symmetrically capped by a μ_3-S ligand. The molecular structure possesses a crystallographic inversion centre. The average Co—Co, Co—S and Co—P bond distances are 2.87 (6), 2.24 (1) and 2.162 (7) Å, respectively. The hexacobalt sulfide cluster compound was formed *via* the capture of S atoms from thiolate reactants.

Comment

The title hexacobalt cluster compound, (I), consists of discrete $[Co_6(\mu_3\text{-}S)_8(PPh_3)_6]$ cluster units interspersed with molecules of free triphenylphosphine, dichloroethane and water. The neutral cluster contains a slightly distorted Co_6 octahedron with each triangular face symmetrically capped by a μ_3-S ligand. The six Co atoms are each terminally coordinated by one triphenylphosphine ligand. Therefore, each Co atom is surrounded by four S atoms and one P atom in a distorted square-pyramidal environment, along with another four Co atoms. The cluster could also be described as a slightly distorted S_8 cube with the Co atoms in face-centred positions. The molecular structure possesses a crystallographic inversion centre within the Co_6 core.



(I)

The mean Co—Co distance in the title complex, 2.87 (6) Å, is longer than in the cation $[Co_6S_8(PPh_3)_6]^+$ (2.81 Å; Fenske, Hachgenei & Ohmer, 1985) or in $[Co_6S_8(PEt_3)_6]$ (2.81 Å; Cecconi, Ghilardi, Midollini & Orlandini, 1983), while the mean Co—S distance [2.24 (1) Å] is similar to that in $[Co_6S_8(PPh_3)_6]^+$ (2.22 Å) and $[Co_6S_8(PEt_3)_6]$ (2.23 Å). It seems that the Co—Co bond lengths are affected by a change in the cluster charge or the phosphine ligands. The Co—S bonds also appear to make an important contribution to the stability of the cluster framework. The Co—Co—Co bond angles fall within the ranges 59.15 (5)–60.56 (5) and 88.87 (6)–91.13 (6)°, and are comparable with the values of 60 and 90° for perfect octahedral symmetry. It is interesting that the uncoordinated triphenylphosphine molecules act as solvate molecules and lie outside the neutral $[Co_6S_8(PPh_3)_6]$ units, as shown in Fig. 2.

The title compound was synthesized *via* a novel route in which the sulfide ligands were obtained indirectly. To date, polynuclear metal sulfides have been prepared by using inorganic sulfur salts as the sulfide source (Fenske, Hachgenei & Ohmer, 1985). Recently, we have found that using Co^{1+} and thiolates or dithiolates leads to the isolation of polycobalt sulfides such as $[Co_4S(SCH_2CH_2S)_3(PPh_3)_3Cl]$ (Jiang, Huang, Wu, Kang, Hong & Liu, 1993) or $[Co_7S_6(PPh_3)_{7-n}X_n]$ (n = 1, 3; X = Br, Cl) (Jiang, Lei, Hong, Huang, Kang & Liu, 1993). These reactions are of particular interest where the sulfide ligands are obtained indirectly. Substitution of mpo^- (2-mercaptopyridine *N*-oxide) or S^tBu for the thiolates leads to the title compound. This reaction also shows that under appropriate conditions (long reaction times, for instance) the S atoms dissociate completely from the thiolates and are incorporated into the