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A Highly Solvated Zinc(II) Tetrakis-(pentafluorophenyl)- β -octabromoporphyrin

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Abstract

The title compound, {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}]tetracos-1,3(21),4,6,8(22),9,11,13(23),14,16,18(24),19-dodecene}zinc(II) (carbon tetrachloride, *o*-dichlorobenzene, acetone, methanol, water solvate) has a large tetrahedral distortion, with the Br atoms as much as 1.83 Å from the plane of the N atoms. The distortion affects primarily bond angles and bond torsion angles; bond distances in the molecule are normal. Several different solvents are incorporated into the crystal, providing a close (2.16 Å) O atom as an axial neighbor to Zn and a more distant (3.16 Å) Cl atom, in the opposite axial site.

† Contribution No. 8622.

Comment

The Zn complex was synthesized by published procedures (Lyons & Ellis, 1991) and attempts were made to grow crystals by evaporation and/or solvent diffusion from acetone, methanol, dichloromethane and mixtures of these. Solid materials formed, but no good crystals were found, and the solids were dissolved in new solvent without purification. A satisfactory crystal was finally obtained by evaporation over several weeks at 277 K from a solution in *o*-dichlorobenzene and carbon tetrachloride.

The material crystallizes with the porphyrin plane perpendicular to a crystallographic mirror plane that includes N1, Zn and N3. Fig. 1 is a drawing of the molecule showing the numbering system. The Zn atom is displaced from the plane of the four N atoms (which are planar to ± 0.08 Å) by 0.19 Å toward the O atom of an acetone/methanol solvent position. The porphyrin is ruffled in a tetrahedral distortion: the *meso*-C atoms are close to the 4N plane (± 0.02 Å) but the pyrrole C atoms deviate by ± 0.89 Å on average (maximum 0.97 Å) and the Br atoms by ± 1.67 Å (maximum 1.83 Å). The causes of this distortion are severe steric interactions between the Br atoms and the pentafluorophenyl groups. The shortest of these Br...C distances (average 3.13, closest 3.09 Å) are to the apical C atoms; distances to the *ortho*-C atoms of the phenyl groups are also short, averaging 3.37 Å (van der Waals distance is 3.60 Å). The angles C2—C1—Br1, C4—C5—Br2, C7—C6—Br3 and C9—C10—Br4 are also increased

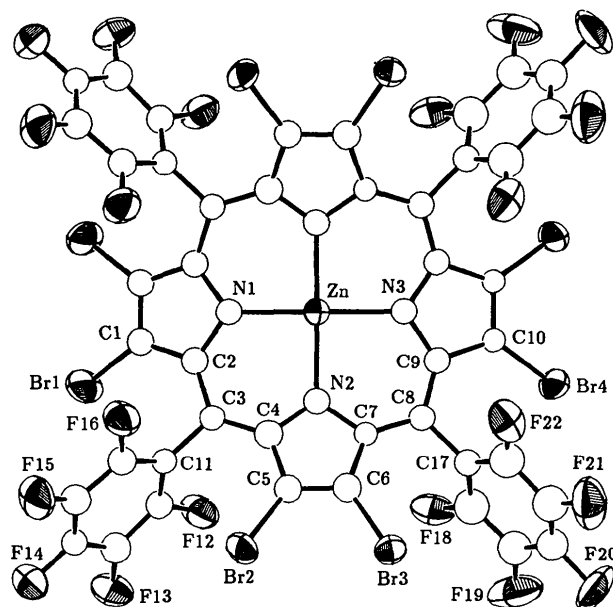


Fig. 1. An ORTEP drawing of the porphyrin molecule with 50% probability ellipsoids showing the numbering system. Unlabelled C atoms on the numbered half of the molecule have the same number as the attached F atom.

by 3° from the 126° expected, as the Br atoms attempt to minimize their steric interactions, but the Br...Br contacts are short, too: 3.387 vs 3.90 Å for a van der Waals contact (a short contact is to be expected, though, where the two Br atoms are bonded to adjacent C atoms). Thus the molecule is highly crowded and the observed structure is apparently the best the molecule can do to minimize these interactions.

The packing of this material is complicated. Disorder and partial occupancy of some sites have prevented us from least-squares refinement of all the atoms, but we have fitted the difference map with solvents known to have been used in the crystallization to the best of our ability. We had insufficient material for a chemical analysis. Our final model comprised the following solvents:

(1) CCl_4 . This region of the structure could be modelled very well with a pair of half-occupancy CCl_4 molecules, each on a mirror plane and forming approximately a tetrahedron-antitetrahedron array, except that the two central C atoms are not coincident. The Cl atoms (C11a-3a, C11b-3b) were refined with anisotropic U_{ij} parameters; the C atoms (Ca, Cb) were fixed at the centers of the two tetrahedra.

(2) *o*-Dichlorobenzene. This region is also quite clear, and contains two sets of half-populated sites related to one another by the mirror plane. Because of overlap, only the coordinates of one atom could be freely refined – those of C11o. Cl2o, which serves as a weak axial ligand of the Zn atom, lies close to the mirror plane and its y parameter was fixed; all the C atoms (C1o-C6o) were idealized to a benzene ring, with the help of a difference map in their plane. All atoms were treated as isotropic.

(3) Acetone, water and (probably) methanol. These regions of the structure are more complex, and our interpretation less unambiguous. There is surely an O atom, O(a), in an apical position about 2.16 Å from Zn, and Fourier maps strongly suggest that, at least some of the time, this atom is part of an acetone molecule. However, peaks corresponding to the methyl groups are weak and are impossibly close to other weak peaks in an adjoining solvent area. Our representation was to assign a population factor of 0.5 to the acetone molecule, with the other 0.5 taken as a methanol molecule; when acetone is present, the adjoining area is occupied by two water molecules, while when methanol is present the adjoining area accommodates a second acetone molecule. The only one of these atoms whose coordinates were included in the refinement was C2b – half the time a water molecule, half the time a methyl group of acetone (we assigned it the form factor of nitrogen).

Thus the total complement of solvent per zinc porphyrin molecule is: one CCl_4 group, disordered

between two sites; one dichlorobenzene molecule, again disordered between two mirror-related sites; one acetone molecule, in two half-occupied sites; one water molecule, in two half-occupied sites; and one-half a methanol molecule. We make no representations that this interpretation is correct in all details; however, it explains the difference maps quite well and is consistent with the various solvents known to have been present during the various crystallization attempts.

The packing in the crystal shows normal contact distances with perhaps four exceptions. Br2 and Br4 have encounters with Cl atoms of the CCl_4 molecule of 3.44 and 3.49 Å, where 3.75 Å is a van der Waals distance, and they also approach F atoms of other porphyrin molecules, with distances 3.17 and 3.20 Å (3.30 Å expected). Figs. 2 and 3 show the packing, with the solvent molecules more easily seen in Fig. 2, but their interactions with the porphyrin clearer from Fig. 3.

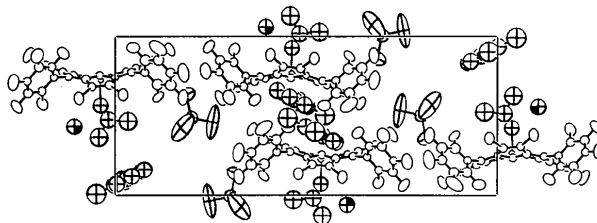


Fig. 2. An ORTEP projection down the b axis with 50% probability ellipsoids. Water molecules are shown with shaded quadrants, other solvent atoms with outlined quadrants; the porphyrin atoms are not shaded or outlined. The c axis is horizontal.

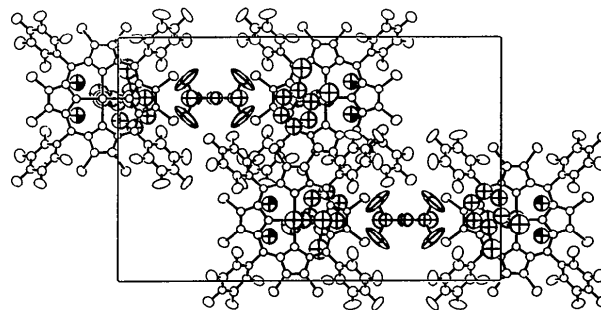


Fig. 3. An ORTEP projection down a , with the c axis horizontal; other details the same as for Fig. 2.

Experimental

Crystal data

$[\text{Zn}(\text{C}_{44}\text{Br}_8\text{F}_{20}\text{N}_4)] \cdot$
 $\text{CCl}_4 \cdot \text{C}_6\text{H}_4\text{Cl}_2 \cdot$
 $(\text{C}_3\text{H}_6\text{O}, \text{CH}_4\text{O})_{1/2} \cdot$
 $[\text{C}_3\text{H}_6\text{O}, 2(\text{H}_2\text{O})]_{1/2}$
 $M_r = 2062.03$

$D_x = 2.10 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 19
 reflections

Orthorhombic
Pnma
a = 12.053 (4) Å
b = 18.453 (6) Å
c = 29.259 (10) Å
V = 6508 (4) Å³
Z = 4

$\theta = 6-12^\circ$
 $\mu = 5.60 \text{ mm}^{-1}$
T = 295 K
 Elongated hexagonal prism
 0.30 × 0.12 × 0.11 mm
 Purple

Data collection

Enraf-Nonius CAD-4
 diffractometer
 ω scans
 Absorption correction:
 none
 6539 measured reflections
 3151 independent reflections
 3151 observed reflections
 [all reflections used]

$R_{\text{int}} = 0.067$ for 2057 du-
 plicates (GOF = 0.95 for
 2948 multiples)
 $\theta_{\text{max}} = 20^\circ$
 $h = -11 \rightarrow 11$
 $k = 0 \rightarrow 17$
 $l = 0 \rightarrow 28$
 3 standard reflections
 frequency: 120 min
 intensity variation: within
 counting statistics

Refinement

Refinement on F^2
 Final *R* = 0.066 (on *F*)
 for 1398 data with
 $F_o^2 > 3\sigma(F_o^2)$
 $wR = 0.020$ (on F^2)
 $S = 1.74$
 3151 reflections
 294 parameters

No H atoms included in
 model
 $w = 1/\sigma^2(F_o^2)$
 $(\Delta/\sigma)_{\text{max}} = 0.01$ for por-
 phyrin, 0.10 for solvents
 $\Delta\rho_{\text{max}} = 2.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.65 \text{ e \AA}^{-3}$

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

Isotropic *B* values are given for N and C atoms and Cl1*o* and Cl2*o*; for other atoms $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Cl atoms have population parameters of 0.5.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> or U_{eq}
Zn	0.2496 (3)	0.2500	0.5394 (1)	0.0535 (11)
Br1	0.3871 (2)	0.3419 (1)	0.7258 (1)	0.0859 (9)
Br2	0.1145 (2)	0.5433 (1)	0.5949 (1)	0.0694 (8)
Br3	0.1366 (2)	0.5459 (1)	0.4795 (1)	0.0647 (8)
Br4	0.4192 (2)	0.3416 (1)	0.3570 (1)	0.0666 (8)
N1	0.2609 (17)	0.2500	0.6087 (7)	3.0 (5)
N2	0.2583 (11)	0.3611 (7)	0.5400 (6)	3.0 (3)
N3	0.2829 (16)	0.2500	0.4714 (7)	2.9 (5)
C1	0.3234 (14)	0.2866 (9)	0.6799 (6)	3.2 (5)
C2	0.2805 (15)	0.3104 (10)	0.6361 (6)	3.2 (5)
C3	0.2502 (15)	0.3813 (10)	0.6216 (6)	2.8 (4)
C4	0.2347 (15)	0.4021 (11)	0.5770 (7)	3.4 (5)
C5	0.1866 (15)	0.4701 (11)	0.5607 (7)	3.3 (5)
C6	0.1975 (15)	0.4691 (11)	0.5147 (7)	3.6 (5)
C7	0.2428 (14)	0.4021 (10)	0.5009 (6)	2.3 (4)
C8	0.2780 (14)	0.3823 (9)	0.4578 (7)	2.9 (4)
C9	0.3041 (14)	0.3112 (10)	0.4462 (6)	2.9 (5)
C10	0.3547 (13)	0.2866 (8)	0.4029 (5)	2.4 (4)
C11	0.2450 (15)	0.4355 (10)	0.6592 (6)	2.7 (5)
C12	0.3133 (17)	0.4891 (12)	0.6647 (7)	3.3 (5)
C13	0.3121 (18)	0.5422 (12)	0.6987 (7)	4.1 (5)
C14	0.2221 (16)	0.5353 (11)	0.7292 (7)	2.9 (4)
C15	0.1475 (18)	0.4830 (12)	0.7269 (7)	4.0 (5)
C16	0.1598 (16)	0.4350 (12)	0.6907 (7)	3.5 (5)
C17	0.2761 (16)	0.4389 (11)	0.4222 (6)	3.0 (5)
C18	0.3532 (20)	0.4929 (14)	0.4207 (8)	5.3 (6)
C19	0.3532 (19)	0.5443 (13)	0.3868 (8)	4.9 (6)

C20	0.2736 (18)	0.5398 (13)	0.3554 (8)	4.3 (5)
C21	0.1958 (20)	0.4894 (14)	0.3552 (9)	5.4 (5)
C22	0.2001 (20)	0.4359 (14)	0.3895 (9)	5.3 (5)
F12	0.3972 (10)	0.4977 (6)	0.6349 (4)	0.0757 (38)
F13	0.3822 (11)	0.5941 (7)	0.7030 (4)	0.0938 (47)
F14	0.2156 (11)	0.5844 (7)	0.7642 (4)	0.0989 (51)
F15	0.0637 (11)	0.4799 (7)	0.7559 (4)	0.0904 (45)
F16	0.0811 (10)	0.3822 (7)	0.6893 (4)	0.0801 (41)
F18	0.4313 (9)	0.4962 (6)	0.4530 (5)	0.0747 (40)
F19	0.4281 (12)	0.5974 (7)	0.3880 (5)	0.1230 (62)
F20	0.2727 (14)	0.5938 (8)	0.3219 (5)	0.1362 (63)
F21	0.1181 (13)	0.4888 (8)	0.3230 (4)	0.1200 (57)
F22	0.1219 (10)	0.3869 (7)	0.3876 (4)	0.0786 (41)
Cl1 <i>a</i>	0.1358 (20)	0.2500	0.3140 (9)	0.1546 (100)
Cl2 <i>a</i>	-0.0361 (50)	0.2500	0.2455 (9)	0.2865 (255)
Cl3 <i>a</i>	-0.0688 (35)	0.1737 (18)	0.3230 (11)	0.3416 (198)
Cl1 <i>b</i>	-0.2042 (27)	0.2500	0.2899 (16)	0.2321 (187)
Cl2 <i>b</i>	-0.0488 (26)	0.2500	0.3610 (11)	0.1774 (128)
Cl3 <i>b</i>	-0.0092 (26)	0.1774 (15)	0.2828 (10)	0.2243 (137)
C2 <i>b</i>	-0.0606 (18)	0.1829 (12)	0.6066 (7)	10.8 (7)
Cl1 <i>o</i>	0.0958 (16)	0.1295 (11)	0.0229 (7)	17.6 (8)
Cl2 <i>o</i>	0.0090 (14)	0.2300	-0.0488 (6)	18.0 (7)

Table 2. Selected bond lengths (Å) and angles (°)

Zn—N1	2.03 (2)	Br1—C1	1.853 (17)
Zn—N2	2.053 (14)	Br2—C5	1.891 (19)
Zn—N3	2.03 (2)	Br3—C6	1.90 (2)
Zn—O(<i>a</i>)	2.158	Br4—C10	1.854 (15)
Zn—Cl2 <i>o</i>	3.167		
N1—Zn—N2	89.4 (7)	N2—Zn—N3	89.8 (7)
N1—Zn—N3	164.8 (8)	N2—Zn—N2'	174.1 (6)

The structure was solved by interpreting a Patterson map to obtain coordinates for Zn and Br atoms. The porphyrin molecule atoms were then found with little difficulty, but three regions of disordered solvent were hard to explain. The material did not crystallize easily, so it had been moved from one solvent to another, without purification in between, in the hope of obtaining crystals. Evidently the solvents remained with the solid material and found their way into the crystal. Final crystallization was from a carbon tetrachloride/*o*-dichlorobenzene solution, but we also found it necessary to include acetone, methanol and water in the model; the material had been exposed to all three of these. The disorder and partial occupancies made least-squares refinement of all the solvent impossible, but we refined what we could and positioned other atoms on the basis of difference maps. No H atoms were included in the structure factors. All of these are on disordered solvent molecules. The weights were taken as $1/\sigma^2(F_o^2)$; variances [$\sigma^2(F_o^2)$] were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014I)^2$. Atomic scattering factors and values for f' were taken from Cromer & Waber (1974) and Cromer (1974); the programs used were those of *CRYM* (Duchamp, 1964) and *ORTEP* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71014 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1024]

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Copper(II) Tetrakis(pentafluorophenyl)- β -octachloroporphyrin

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Abstract

The title compound, {4,5,9,10,14,15,19,20-octachloro-2,7,12,17-tetrakis(pentafluorophenyl)-20,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosane-1,3(21),4,6,8(22),9,11,13(23),14,16,18(24),19-dodecane}copper(II) (CuTFPPCl₈) dichloromethane solvate, shows a large tetrahedral distortion or ruffling, with pairs of Cl atoms alternately averaging +1.20 and -1.18 Å out of the plane of the four N atoms; the Cu atom is 0.01 Å out of the plane and the N atoms show a slight (± 0.12 Å) tetrahedral distortion. A Cl atom of the solvent, at 3.515 (6) Å in an approximately axial position, is the closest non-bonded neighbor of the Cu atom.

† Contribution No. 8623.

Comment

Derivatives of halogenated porphyrins are active catalysts for oxygenation of light alkanes, requiring no added co-reductants or sacrificial O-atom donors for their activity (Lyons, Ellis, Wagner, Thompson, Hughes, Hodge & Gray, 1992). The CuTFPPCl₈ derivative was synthesized from the metal-free porphyrin and copper acetate in methanol solution and purified by elution from silica gel with hexane/dichloromethane. Reddish prisms were grown by evaporation of CH₂Cl₂ solutions of the complex at room temperature over 7–10 d. The Cu atom has approximately square-planar coordination. The four N atoms show a slight tetrahedral distortion (± 0.12 Å from their plane) and the nearest axial neighbor atom is a Cl of the solvent, 3.515 (5) Å on one side of the plane. On the other side, C13 of an adjacent molecule is 2.968 (4) Å distant. The molecule is shown in Fig. 1.

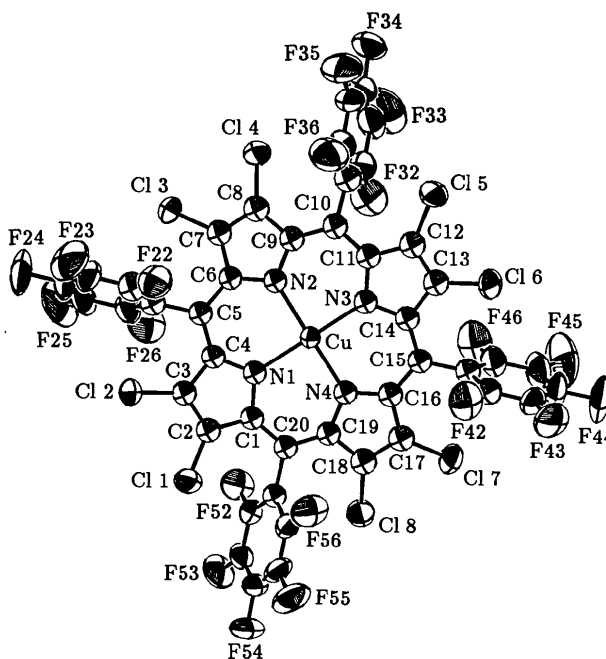


Fig. 1. An ORTEPII drawing of the porphyrin molecule with 75% probability ellipsoids showing the numbering system.

The porphyrin molecule shows a strong tetrahedral distortion, reaching ± 0.7 Å for the pyrrole C atoms and ± 1.19 Å for the Cl atoms (Fig. 2). This appears to be a steric effect caused by crowding between the pentafluorophenyl groups and the Cl atoms on the periphery of the porphyrin. The β C atoms have planar coordination, but the angles to Cl atoms at them are altered to move the Cl atoms away from the phenyl rings. The tetrahedral distortion accomplishes the same effect, but even the combination of the two leaves exceedingly close