Crystal Structure of the Bis-pocket Porphyrin Aquo(tetramesitylporphinato)zinc(II)

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Abstract

The crystal structure of aquo(tetramesitylporphinato)zinc(II) ([Zn(TMP)(OH$_2$)]) is reported. Crystal data for [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O: ZnO$_{1.5}$N$_4$C$_{56}$H$_{55}$, tetragonal, space group *I*4/*m*, *a* = 18.392(10), *c* = 8.804(3) Å, *Z* = 2. The crystal packing of [Zn(TMP)(OH$_2$)] is compared to that of the tetraphenylporphyrin (TPP) analogue which has the same solid state arrangement (space group *I*4/*m*, M. D. Glick, G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc., 89* (1967) 1996). [Zn(TMP)(OH$_2$)] packs with a substantially lower density than [Zn(TPP)(OH$_2$)]. The effect of the bulky mesityl-methyl groups on crystal packing is discussed. Analysis of various assumed arrangements of molecules having only the needed bulky 2- and 6-methyl groups show that the intermolecular contacts are dominated by these substituents. This study suggests that any porphyrin system with *o*-methyl substituted ligands is not likely to form a high-density packing arrangement.

Introduction

Porphyrins with bulky aryl *meso*-substituents are expected to protect both porphyrin faces and thus prevent intermolecular interactions [1]. Tetramesityl porphyrins have been utilized [2] for this purpose in the study of oxygen transfer reactions in model cytochrome P-450 systems. The *ortho* methyl substituents are thought to stabilize reactive oxoferryl porphyrin derivatives by inhibiting the approach of a second molecule that leads to the eventual production of μ-oxo dimers. Even though *meso*-tetramesitylporphyrin (TMP) has been widely used for such studies, only a very few crystal structures have been reported. This seems to suggest that there are real difficulties in growing crystals of TMP derivatives.

We have been investigating M(TMP) π-cation radical derivatives in order to minimize the intermolecular interactions that we have observed in octaethylporphyrin [3] and tetraphenylporphyrin (TPP) [4–6] derivatives. Despite considerable effort, we have been successful thus far in preparing crystals of only one TMP radical complex [7]. In our efforts to grow crystals of the π-cation radical Zn(TMP$\cdot$)ClO$_4$, we obtained crystalline [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O. This material was found to crystallize in the tetragonal system, space group *I*4, *I*$\bar{4}$ or *I*4/*m* and *Z* = 2. The unit cell has certain similarities to the body-centered tetragonal cell of [Zn(TPP)(OH$_2$)] (*Z* = 2). However, the *a*(*b*) cell length in [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O** is significantly longer while *c* is substantially shorter than that of [Zn(TPP)(OH$_2$)] [8]**. Since we had previously examined the lattice packing in a number of related five-coordinate [M(TPP)L] systems [4, 9] the cell length differences immediately suggested that the 4-methyl substituent was probably responsible for a substantial (deleterious?) modification of the crystal packing. We therefore undertook an analysis of the crystal structure and crystal packing in [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O with the expectation that such an analysis might lead to the design of easier-to-crystallize but still hindered porphyrin ligands.

Experimental

Crystals of [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O were obtained in the course of the reaction of Zn(TMP) [10a] and thianthrenium perchlorate. (TMP was prepared following the procedure of ref. 10b.) Crystallization was induced by vapor diffusion of hexane into dichloromethane solution. UV–Vis λ_{max} (CH$_2$Cl$_2$): 419 (Soret), 549 nm.

Preliminary examination of a single crystal of [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O with dimensions of 0.27 × 0.24 × 0.18 mm was carried out on an Enraf-Nonius CAD4 automated diffractometer. Careful examination of axial photographs confirmed the cell lengths and Laue group. The systematic absences and Laue symmetry were consistent with three possible space

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**Crystal data for [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O: ZnO$_{1.5}$N$_4$C$_{56}$H$_{55}$, tetragonal, space group *I*4/*m*, *a* = 18.392(10), *c* = 8.804(3) Å, *Z* = 2. Crystal data for [Zn(TPP)(OH$_2$)]: ZnON$_4$C$_{44}$H$_{30}$, tetragonal, space group *I*4/*m*, *a* = 13.440, *c* = 9.715 Å, *Z* = 2.

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groups: $I4$, $I\bar{4}$ and $I4/m$. Intensity data were measured at the ambient laboratory temperature using graphite-monochromated Mo Kα radiation and θ–2θ scanning. Four standard reflections were monitored periodically during data collection with no significant deviations noted. Intensity data were reduced using the Blessing suite of data reduction programs [11]. A total of 666 reflections having $\sin\theta/\lambda < 0.65$ Å^{-1} and $F > 3\sigma(F)$ were taken as observed.

The structure was solved by the direct methods program DIRDIF [12]. Attempts to interpret the structures in space group $I4$ or $I\bar{4}$ were not satisfactory. Thus, the choice of $I4/m$ was made. All subsequent developments of structure solution and refinement were consistent with this choice of space group. After least-squares refinement was carried to convergence, all hydrogen atoms were idealized as fixed contributors (C–H = 0.95 Å and $B(\mathrm{H}) = 1.2 \times B(\mathrm{C})$). Final cycles of full-matrix least-squares used anisotropic temperature factors for all heavy atoms except the Zn atom*. At convergence, $R_1 = 0.0986$ and $R_2 = 0.130$, the error of fit was 2.680 and the final data/parameter ratio was 7.4. The final difference map was featureless with a highest peak of 0.4 e/Å^3. Fractional coordinates and isotropic thermal parameters are given in Table 1. See also 'Supplementary

TABLE 1. Fractional coordinates[a]

Atom	x	y	z
Zn	0.0000	0.0000	0.0226(11)
O(1)	0.0000	0.0000	0.275(5)
O(2)	0.0000	0.0000	0.5000
N(1)	−0.1057(7)	0.0314(6)	0.0000
C(a1)	−0.1325(9)	0.1010(9)	0.0000
C(a2)	−0.1645(10)	−0.0126(9)	0.0000
C(b1)	−0.2084(9)	0.1001(10)	0.0000
C(b2)	−0.2305(9)	0.0310(9)	0.0000
C(m1)	−0.1645(9)	−0.0884(9)	0.0000
C(1)	−0.2340(11)	−0.1272(11)	0.0000
C(2)	−0.2684(9)	−0.1463(8)	0.134(3)
C(3)	−0.3352(9)	−0.1844(9)	0.130(4)
C(4)	−0.3677(16)	−0.2045(18)	0.0000
C(Me1)	−0.2349(13)	−0.1279(11)	0.281(3)
C(Me2)	−0.4388(15)	−0.2466(21)	0.0000

[a] The e.s.d.s of the least significant digits are given in parentheses.

Results and Discussion

The molecular structure of [Zn(TMP)(OH$_2$)] is illustrated in Fig. 1. In space group $I4/m$, the molecule has required $4/m$ symmetry which can be only achieved in a statistical fashion. Such statistical disorder has been described for a number of M(TPP)L derivatives [9]. The porphyrin plane lies on the crystallographically required mirror plane at $z = 0$. Zinc and oxygen atoms are disordered with two equally possible orientations as shown in Fig. 1, e.g. half-atoms of zinc and oxygen lie on the four-fold axis at $0, 0, \pm z$ and $0, 0, \pm z'$, respectively. The two orientations of the molecule leads to a statistically averaged molecule having a planar porphinato core. The mesityl group planes are perpendicular to the porphyrin plane as required by the imposed symmetry. A well-protected ligand binding pocket is thus formed by the 2- and 6-methyl substituents (Fig. 1). This ligand binding pocket has an approximate depth of 2.48 Å comparable to the 2.3 Å reported for the free base *meso*-tetra(2,4,6-trimethoxyphenyl)porphyrin [13] and 2.6 Å for [tetrakis-(2,6-dichlorophenyl)porphinato)]zinc(II) [14].

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*Because of the small displacement of the half atom of zinc, the z coordinate and β_{33} cannot both be refined. We have chosen to best define the atomic coordinates of zinc.

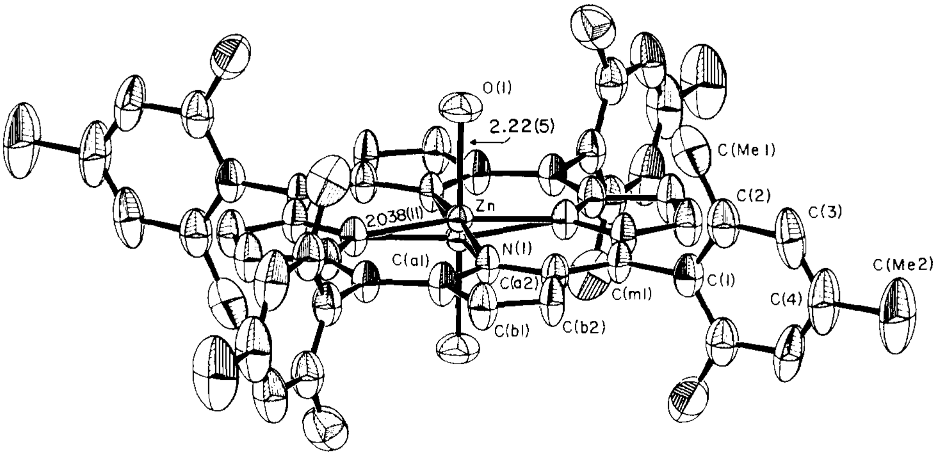

Fig. 1. ORTEP diagram of the [Zn(TMP)(OH$_2$)] molecule showing the atom labeling scheme. 20% probability surfaces are used.

The Zn–N (2.038(12) Å) and Zn–O (2.22(5) Å) bond lengths are comparable to those for [Zn(TPP)(OH$_2$)] (2.05(1) and 2.21(6) Å, respectively). The out-of-plane displacement of the zinc ion (0.20 Å) is comparable to that for [Zn(TPP)(OH$_2$)] but is somewhat smaller than those observed for several other five-coordinate zinc(II) porphyrinates having a neutral donor ligand [14, 15]. Table 2 gives individual values for bond lengths and bond angles.

[Zn(TMP)(OH$_2$)] crystallizes in the same body-centered tetragonal lattice as [Zn(TPP)(OH$_2$)] (see footnote on p. 37). Comparative views of the crystal packing arrangement are shown in Fig. 2 (*ab* face) and Fig. 3 (*ac* face). Figure 2 shows that the orientation of the porphyrin molecule with respect to the crystal axes is almost identical; there is a 2.8° rotational difference in the two compounds. Furthermore, an examination of Fig. 2 is in basic agreement with the notion that the crystal packing in [Zn(TMP)(OH$_2$)] is much more open than that in [Zn(TPP)(OH$_2$)] as a result of the 4-methyl substituent. We have compared the size of vacancies in the crystalline lattices of [Zn(TMP)(OH$_2$)] and [Zn(TPP)(OH$_2$)] by using the program CAVITY [16]. (The cavity program computes the distances from the points inside the required volume to all the atoms present in it and to those distant from its faces by an amount chosen by the user.) In [Zn(TMP)(OH$_2$)], there

TABLE 2. Bond lengths and bond angles in [Zn(TMP)(OH$_2$)]·$\frac{1}{2}$H$_2$O

Bond lengths (Å)			
Zn–O	2.22(5)	Zn–N(1)	2.038(12)
O(1)–O(2)	1.98(5)	N(1)–C(a2)	1.350(20)
N(1)–C(a1)	1.371(20)	C(a1)–C(b1)	1.397(24)
C(a1)–C(m1′)	1.422(23)	C(a2)–C(b2)	1.456(25)
C(a2)–C(m1)	1.394(22)	C(b1)–C(b2)	1.333(23)
C(m1)–C(1)	1.463(27)	C(1)–C(2)	1.387(24)
C(2)–C(Me1)	1.47(3)	C(2)–C(3)	1.414(23)
C(3)–C(4)	1.340(28)	C(4)–C(Me2)	1.52(4)
Bond angles (°)			
N(1)ZnO(1)	95.59(27)	ZnN(1)C(a2)	126.4(11)
ZnN(1)C(a1)	127.4(11)	C(a2)N(1)C(a1)	105.8(12)
N(1)C(a1)C(b1)	110.3(14)	N(1)C(a1)C(m1′)	124.2(15)
C(b1)C(a1)C(m1′)	125.5(15)	N(1)C(a2)C(m1)	126.9(16)
N(1)C(a2)C(b2)	109.7(13)	C(m1)C(a2)C(b2)	123.4(15)
C(b2)C(b1)C(a1)	108.5(16)	C(b1)C(b2)C(a2)	105.6(15)
C(a2)C(m1)C(1)	119.3(16)	C(a1)C(m1)C(1)	116.0(15)
C(a2)C(m1)C(a1′)	124.7(15)	C(2)C(1)C(m1)	121.5(13)
C(2)C(1)C(2′)	117.1(25)	C(1)C(2)C(3)	119.7(26)
C(3)C(2)C(Me1)	120.3(24)	C(1)C(2)C(Me1)	120.0(15)
C(4)C(3)C(2)	123.3(29)	C(3)C(4)C(Me2)	121.6(14)
C(3)C(4)C(3′)	116.7(28)		

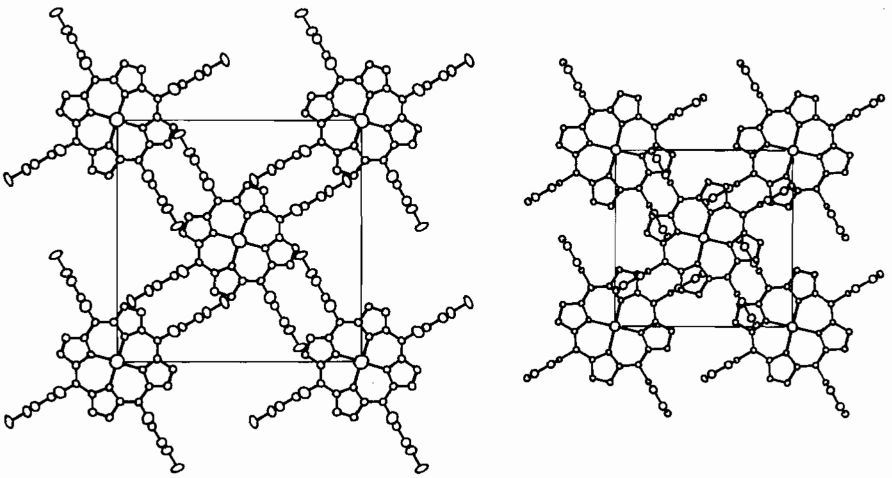

Fig. 2. Comparative diagrams of the packing [Zn(TMP)(OH$_2$)] (left) and [Zn(TPP)(OH$_2$)] (right) viewed down the *c* axis.

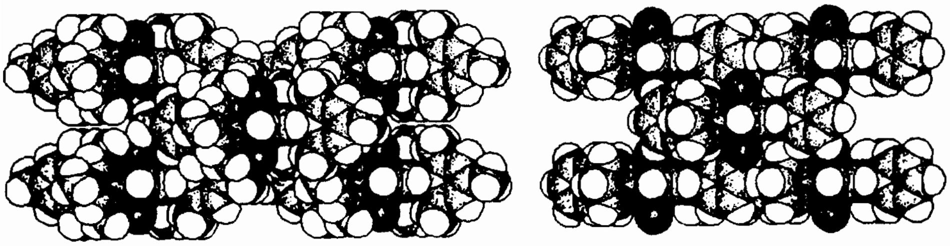

Fig. 3. Comparative packing diagrams (SCHAKAL86) viewed down the b axis of the two cells: [Zn(TMP)(OH$_2$)] (left), [Zn(TPP)(OH$_2$)] (right). van der Waals radii of all atoms are displayed.

are channels centered at $\frac{1}{2}$, 0, z and 0, $\frac{1}{2}$, z. The radii of these channels range from 3.8 to 4.3 Å along the z axis. However, in [Zn(TPP)(OH$_2$)] the radius of the biggest hole is only 3.3 Å (centered at $\frac{1}{2}$, 0, $\frac{1}{4}$ and 0, $\frac{1}{2}$, $\frac{1}{4}$) and channels are not formed. It is surprising that the crystal lattice of [Zn(TMP)(OH$_2$)] is able to support the large cavities that are observed. It could have been expected that the [Zn(TMP)(OH$_2$)] lattice would have incorporated solvent molecules in these channels but there was no evidence for the presence of methylene chloride solvates in difference Fourier maps. A density measurement, which could be expected to define the possible presence of any solvent molecules, could not be performed satisfactorily because the apparent density of the crystal changed continuously during the measurement. The changing density might have resulted from solvent trapped in the channels during the density measurement. The calculated density of [Zn(TMP)(OH$_2$)] is lower than that of [Zn(TPP)(OH$_2$)], even with incorporated solvent. The calculated densities of [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O, [Zn(TMP)(OH$_2$)]$\cdot\frac{1}{2}$H$_2$O$\cdot$2CH2C12, and [Zn(TPP)(OH$_2$)] are 0.97, 1.13 and 1.32 g/cm^3, respectively. A decreased density is also observed in Cu(TMP)SbCl$_6$ [7] compared to its TPP analogue [5] (1.44 and 1.63 g/cm^3, respectively). A very low density is also observed in Ru(TMP)(N$_2$)(THF) (1.07 g/cm^3) [17].

The view of the ac face (Fig. 3) suggests that the tight contacts between molecules in [Zn(TPP)(OH$_2$)] are those involving body-centered molecules while those in [Zn(TMP)(OH$_2$)] might be those between c-translation related pairs. However, the closest intermolecular contacts in [Zn(TMP)(OH$_2$)] are between C(3) of the body-centered neighbors and 2- and 6-methyl substituents (3.77(3) Å); the o-methyl substituents intermolecular contacts along the c axis are slightly longer (3.85(6) Å).

We have attempted to determine whether removal of the 4-methyl substituent could yield more efficiently packed crystalline species (higher density) than the native ZnTMP derivative. However, within the general packing constraints of a tetragonal body-centered lattice of the ZnTMP (or ZnTPP) type, and contrary to our original expectations, tetrakis-(2,6-dimethylphenyl)porphyrin species do not pack more efficiently than the ZnTMP molecules. The closest intermolecular contacts for tetrakis-(2,4,6-trimethylphenyl)porphyrin is a 3.77 Å contact between an o-methyl carbon and C(3) of a body-centered neighbor. Calculated intermolecular contacts following removal of the 4-methyl substituent did not allow for any significant decrease in the 18.392 Å $a(b)$ cell length. Other strategies used to model potentially more efficient packing arrangements for tetrakis-(2,6-dimethylphenyl)porphyrin species included attempts to find packing arrangements in which the closest intermolecular contacts were not between the 2,6-methyl groups with the body-centered neighbors. This involved allowing increases in the c translation with concomitant decreases in $a(b)$ from the original ZnTMP cell constants. Different rotational positions of the ZnTMP molecule were also allowed. Intermolecular contacts are apparently always dominated by contacts involving the o-methyl substituents. It is presumably this poor crystal packing of [Zn(TMP)(OH$_2$)] that leads to the rather large thermal motion of the porphyrin core and the mesityl groups perpendicular to the mean plane (Fig. 1). Interestingly, when we attempted to collect data on this crystalline substance at low temperature, the crystal shattered on cooling. Presumably, this results from the poor packing.

Conclusions

Although [Zn(TMP)(OH$_2$)] crystallizes with the same solid state arrangement as [Zn(TPP)(OH$_2$)], it packs with a substantially lower density. An analysis of the crystal packing for various assumed arrangements of molecules having only the needed bulky 2- and 6-methyl groups shows that the intermolecular contacts are dominated by these substituents. We therefore conclude that any porphyrin system with o-methyl substituted ligands is not likely to form a high-density packing arrangement. We further conclude that the difficulties of obtaining crystalline TMP derivatives are unlikely to be solved by any other similar derivative. Obtaining the needed crystals of these bulky porphyrin ligand complexes will simply require much effort to find the (probably) limited appropriate conditions.

Supplementary Material

Table SI, complete crystal data; Table SII, anisotropic thermal parameters; and Table SIII, fractional coordinates and isotropic thermal parameters for the fixed atoms (3 pages) and listings of observed and calculated structure factors (X10) (3 pages) are available from the authors upon request.

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