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# Structure of Aqua(tetraphenylporphyrinato)zinc(II) a Redetermination

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**Abstract.** $[Zn(C_{44}H_{28}N_4)(H_2O)]$, $M_r = 693{\cdot}13$, tetragonal, $I4/m$, $a = 13{\cdot}425\ (2)$, $c = 9{\cdot}6934\ (10)$ Å, $V = 1747{\cdot}1\ (7)$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}328$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 7{\cdot}6$ cm$^{-1}$, $F(000) = 720$, $T = 293$ K, final $R = 0{\cdot}043$ for 641 reflections with $I \geq 3\sigma(I)$. The structure has been re-investigated to obtain the accurate zinc displacement from the least-squares plane [0·173 (1) Å] which was poorly determined in previous investigations.

**Introduction.** The original structural investigation of $[Zn^{II}(tpp)(H_2O)]$ ($H_2tpp$ = tetraphenylporphyrin) performed by Fleischer, Miller & Webb (1964) had suggested that the zinc was six-coordinate with two water molecules, the complex having overall $4/m$ symmetry. Later Glick, Cohen & Hoard (1967) reported that, from the same data, they had refined the complex as a disordered five-coordinate species with only one water molecule and the zinc displaced from the mean porphyrin plane by approximately 0·19 Å. However, due to poor data this value was poorly defined. In conjunction with other porphyrin structural studies currently being performed (Golder, Nolan, Povey & Milgrom, 1988), it was decided to re-investigate this structure to obtain a more accurate value for the displacement.

**Experimental.** The method of Thomas & Martell (1959) was used to prepare $[Zn^{II}(tpp)]$ from zinc acetate and $H_2tpp$ (refluxing in acetic acid). Deep-purple square bipyramidal crystals were obtained by crystallization from benzene.

Accurate unit-cell parameters were measured on a CAD-4 diffractometer using 25 accurately centred reflections ($13 \leq \theta \leq 15°$) from a crystal of dimensions $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}7$ mm. Data were collected to a $\theta$ limit of 24° ($0 \leq h \leq 17$, $0 \leq k \leq 17$, $0 \leq l \leq 12$) in an $\omega$–$2\theta$ scan mode, scan speed 3·3° min$^{-1}$, 060 reflection monitored hourly. Variation of its intensity was insignificant during the data-collection period and after data reduction from a total of 731 unique reflections, 641 had $I \geq 3\sigma(I)$. Intensity statistics were below a centric distribution but above acentric. It was assumed this was due to the out-of-plane displacement of the Zn atom and $I4/m$ (No. 87) was chosen as the space group. The structure was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined as a disordered model (after Glick *et al.*, 1967). However, the Zn atom was very unstable and moved substantially during the final refinement.

Space group $I4$ (No. 79) was investigated as an alternative but after anisotropic refinement it was noted that the Zn ion was almost in the porphyrin plane and some thermal ellipsoids were unusual. This is in conflict with all other five-coordinate zinc(II) porphyrin complexes. The disordered model in $I4/m$ was the preferred solution which is in agreement with the solution of Glick *et al.* (1967). A precedent for possible ordered and disordered forms of $[Zn^{II}(tpp)(H_2O)]$ is available in the isomorphous $[Co^{III}Cl(tpp)]$ (Sakurai & Yamamoto, 1976) which was shown to exist in both forms, from the same crystallization.

*MULTAN*78 (Main *et al.*, 1978) had located all the non-H atoms. With the Zn and water O entered with half occupancy and H atoms added in calculated positions, an isotropic least-squares refinement reduced $R$ to 0·077. However, when anisotropic temperature factors were applied to the non-H atoms the $z$ coordinate of the Zn atom changed substantially. This instability was believed to be due to a strong correlation between its $z$ coordinate and the $U_{33}$ temperature factor because of the close proximity of the mirror plane. Fixing $U_{33}$ allowed the structure to be refined normally, convergence occurring at $R = 0{\cdot}043$, $wR = 0{\cdot}059$ $\{w = [\sigma^2(I) + (0{\cdot}06F^2)^2]^{-1/2}$, pwt = 0·04, qwt = 3·0 (Killean & Lawrence, 1969)$\}$, $S = 1{\cdot}054$. The largest shift/e.s.d. was 0·06 and the highest peak in a final difference Fourier calculation was less than 0·25 e Å$^{-3}$. Atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Refinement using *SDP-Plus* (Frenz, 1983).

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**Discussion.** The molecular structure and numbering scheme used are shown in Fig. 1. Atomic coordinates and bond distances and angles are listed in Tables 1 and 2 respectively.* Table 3 lists relevant data for other zinc prophyrins.

Careful refinement and consideration of the other possible space groups has shown that a disordered model in *I*4/*m* is the preferred solution as was used by Glick *et al.* (1967).

The core size, 2·043 Å, as measured by the $C_t\cdots$N distance (where $C_t$ is the centroid of the nitrogen least-squares plane), is almost the same as that for the four-coordinate [Zn(tpp)] and the $\pi$-bonded toluene/[Zn(tpp)] complex [Zn(tpp)].2$C_6H_5CH_3$ (Table 3). The displacement of the Zn atom from the least-squares plane [0·173 (1) Å] through the four N atoms ($C_t\cdots$Zn) is close to the 0·19 Å suggested by Glick *et al.* (1967). They, however, thought that this was a minimum value because of their non-spherical data set. The bonded water molecule has a Zn—O bond of 2·228 (12) Å which is intermediate between that found for the six-coordinate [Zn(tpp)(thf)$_2$], Zn—O = 2·380 (2) Å (Schauer, Anderson, Eaton & Eaton, 1985) and the Zn—O(water) bond distance in the [Zn(acac)$_2$($H_2O$)] complex (Montgomery & Lingafelter, 1963) where Zn—O = 2·00 Å, the latter value being indicative of a much more tightly bound aqua ligand (thf = tetrahydrofuran, acac = acetylace-

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

|  | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Zn | 1·000 | 1·000 | 1·0179 (1) | 2·252 (6) |
| O | 1·000 | 1·000 | 0·248 (1) | 6·0 (2) |
| N | O·8521 (2) | 0·9642 (2) | 1·00 | 2·85 (7) |
| C(1) | O·8123 (3) | 0·8699 (3) | 1·000 | 3·02 (8) |
| C(2) | 0·7052 (3) | 0·8770 (3) | 1·000 | 3·57 (9) |
| C(3) | 0·6815 (3) | 0·9741 (3) | 1·000 | 3·64 (9) |
| C(4) | 0·7737 (3) | 1·0294 (3) | 1·000 | 2·99 (8) |
| C(5) | 0·7808 (3) | 1·1338 (3) | 1·000 | 2·94 (8) |
| C(21) | 0·6850 (3) | 1·1916 (3) | 1·000 | 2·94 (8) |
| C(22) | 0·6397 (3) | 1·2179 (3) | 1·1209 (4) | 4·93 (8) |
| C(23) | 0·5507 (3) | 1·2708 (3) | 1·1202 (5) | 5·68 (9) |
| C(24) | 0·5075 (3) | 1·2967 (4) | 1·000 | 4·5 (1) |

Table 2. *Bond lengths* (Å) *and angles* (°)

|  |  |  |  |
|---|---|---|---|
| Zn—O | 2·228 (12) | O—Zn—N | 94·84 (4) |
| Zn—N | 2·050 (3) | Zn—N—C(1) | 126·32 (4) |
| N—C(1) | 1·374 (5) | Zn—N—C(4) | 126·55 (4) |
| N—C(4) | 1·369 (5) | C(1)—N—C(4) | 106·8 (3) |
| C(1)—C(2) | 1·441 (6) | N—C(1)—C(2) | 109·1 (4) |
| C(2)—C(3) | 1·341 (6) | C(1)—C(2)—C(3) | 107·5 (4) |
| C(3)—C(4) | 1·443 (6) | C(2)—C(3)—C(4) | 107·2 (4) |
| C(4)—C(5) | 1·405 (6) | C(3)—C(4)—N | 109·3 (4) |
| C(5)—C(21) | 1·502 (6) | N—C(4)—C(5) | 125·8 (4) |
| C(21)—C(22) | 1·367 (4) | C(4)—C(5)—C(21) | 117·2 (3) |
| C(22)—C(23) | 1·390 (5) | C(5)—C(21)—C(22) | 121·0 (2) |
| C(23)—C(24) | 1·347 (5) | C(21)—C(22)—C(23) | 120·7 (4) |
|  |  | C(22)—C(23)—C(24) | 120·4 (4) |
|  |  |  |  |
|  |  | N—Zn—N$^{\text{i}}$ | 89·6 (2) |
|  |  | N—Zn—N$^{\text{ii}}$ | 170·3 (2) |
|  |  | C(4)—C(5)—C(1$^{\text{i}}$) | 125·1 (2) |

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

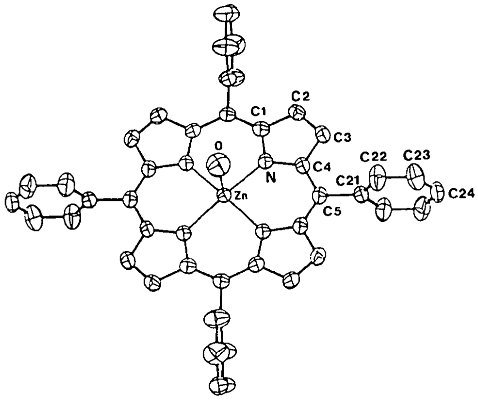

Fig. 1. The molecular structure of aqua(tetraphenylporphyrinato)zinc(II). Thermal ellipsoids are shown at 50% probability.

Table 3. *Comparison with other zinc*(II) *porphyrin complexes*

| Complex | (Zn···N)$_{av}$ (Å) | $C_t\cdots$N (Å) | $C_t\cdots$Zn (Å) | Reference |
|---|---|---|---|---|
| [Zn(tpp)($H_2O$)] | 2·050 (3) | 2·043 | 0·173 (1) | This work |
| [Zn(tpp)($H_2O$)] | 2·05 (1) | 2·042 | 0·19 | Glick *et al.* (1967) |
| [Zn{triphenyl{2-{[2-(3-pyridyl)ethyl]carbonylamino}-phenyl}porphyrinato}].$C_6H_6$.0·5$C_2H_5OH$ | 2·059 (10) | 2·033 | 0·33 | Bobrik & Walker (1980) |
| [Zn(tpp)].2$C_6H_5CH_3$ | 2·036 (6) | 2·036 | 0 | Scheidt, Kastner & Hatano (1978) |
| [Zn(tpp)($ClO_4$)]* | 2·076 (9) | 2·045 | 0·25 | Spaulding *et al.* (1974) |
| [Zn(tpp)] | 2·037 (2)† | 2·037 | 0 | Scheidt, Mondal, Eigenbrot, Adler, Radonovich & Hoard (1986) |
| [Zn(octaethylporphyrinato)(py)] | 2·067 (6) | 2·043 | 0·31 | Cullen & Meyer (1976) |
| [Zn{$\alpha,\beta,\gamma,\delta$-tetrakis(4-pyridyl)porphyrinato}(py)] | 2·073 (8) | 2·047 | 0·33 | Collins & Hoard (1970) |
| [Zn(tpp)(thf)$_2$] | 2·057 (2) | 2·057 | 0 | Schauer *et al.* (1985) |

* A radical cation species.

† The average of two non-equivalent bonds, 2·029 (2) and 2·045 (2) Å.

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* Lists of observed and calculated structure factors, anisotropic temperature factors, calculated hydrogen positions and associated C—H distances, and a selection of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52690 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tonato). Two other zinc porphyrins with an oxygen-bound axial ligand have been reported, the cation radical [Zn(tpp)($ClO_4$)] [Spaulding, Eller, Bertrand & Felton, 1974; Zn—O = 2·079 (8) Å] and the disordered [Zn(tpp)($H_2O$)] (Glick *et al.*, 1967; Zn—O ≃ 2·00 Å). All atoms in the macrocycle core are in the mirror plane and hence planar. The phenyl ring, as expected, is also planar.

Other bond distances and angles do not differ significantly from those in other metalloporphyrins (Scheidt, 1978). The phenyl rings are perpendicular to the plane (by symmetry), the $C_m$—$C_p$ bond [C(5)—C(21)] being a true single bond and showing no interaction between the phenyl and porphyrin aromatic systems (Masuda, Tage, Osaki, Sugimoto & Mori, 1982). We note that our data for the dihedral angle and $C_m$—$C_p$ bond do not fit on the line of Fig. 6 of Masuda *et al.* (1982). Nor do the data for the other zinc porphyrins listed in Table 3. However, if the line passes through 1·51 Å ($C_m$—$C_p$) at a dihedral angle of 90° then the fit is fairly good, but it should be noted that there is no theoretical need for the line to be linear. Also, it has been stated (Bastiansen & Trætteberg, 1962) that for a C—C bond where both C atoms are $sp^2$ hybrids the expected length is around 1·48 Å and longer values as found for biphenyls (Hargreaves & Rizvi, 1962; Fowweather & Hargreaves, 1950; Smare, 1948) are due to steric repulsion of the H atoms on the ring. Obviously such steric repulsions are present in tetraphenylporphyrins and would mask mesomeric effects.

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# Structure of Piperazinium Tetrachlorocobaltate Monohydrate

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**Abstract.** $C_4H_{12}N_2^{2+}.CoCl_4^{2-}.H_2O$, $M_r = 304{\cdot}9$, monoclinic, $P2_1/a$, $a = 14{\cdot}017\,(2)$, $b = 12{\cdot}706\,(2)$, $c = 6{\cdot}559\,(1)$ Å, $\beta = 87{\cdot}21\,(2)°$, $V = 1166{\cdot}8\,(5)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}736$ Mg m$^{-3}$, $\lambda$(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 2{\cdot}356$ mm$^{-1}$, $F(000) = 612$, $T = 298$ K, $R = 0{\cdot}047$, $wR = 0{\cdot}05$ for 2509 reflexions $> 2\sigma(F)$. The structure