Inorganica Chimic Acta, 123 (1986) L11–L14

The Crystal and Molecular Structure of a Monohydrated Dipicoline Magnesium Tetraphenylporphyrin Complex

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Received October 10, 1985

We report the X-ray structure of a five-coordinated Mg tetraphenylporphyrin (TPP) complex, $MgTPP(H_2O)(2\text{-picoline})_2$. The overall coordination geometry of the Mg atom in this complex is similar to that observed for $MgTPP(H_2O)$ [1]. The differences that are observed may be related to the effect of solvate hydrogen bonding to the axially coordinated water molecule that exists in the 2-picoline complex.

Also of interest is the close similarity of the molecular structure of the solvated complex to those of the ethyl chlorophyllide dihydrate derivatives of chlorophyll a and b [2, 3] and of $MgPc(H_2O)(py)_4$ [4], (Pc = phthalocyanin, py = pyridine). This suggests that the observed conformation corresponds to a favourable electronic and bonding arrangement for magnesium porphyrin complexes. In each case displacement of Mg from planar rings is apparently enhanced by hydrogen bonding to a coordinated water molecule. Such an arrangement could readily arise in a protein environment through favourable orientation of amino acid side chain groups.

Experimental

$(TPP)H_2$ was prepared by the condensation of pyrrole and benzaldehyde, and purified according to the procedure adapted from Barnett and coworkers [5]. Mg^{2+} was inserted into $(TPP)H_2$ using $MgCl_2 \cdot 6H_2O$ [6]. The product was heated in 2-picoline. Crystals suitable for X-ray structure determination were obtained from an air-exposed 2-picoline–chloroform solution of the product. Intensity data were collected at room temperature on a computer-controlled Nicolet R3m four-circle diffractometer using graphite monochromated Mo Kα radiation. The cell parameters were determined by least squares refinement using 25 accurately centered reflections ($28° < 2\theta < 32°$). Machine parameters, crystal data and data collection parameters are summarised in Table I. Crystal stability was monitored by recording three standard reflections every 100 reflections and no significant variation was observed.

TABLE I. Summary of Crystal Data, Intensity Collection and Structure Solution

Formula	$C_{59}N_{6.5}H_{47.5}OMg$
Crystal colour, form	red, needles
a (Å)	10.247(2)
b (Å)	13.325(3)
c (Å)	17.700(3)
α (deg)	87.23(2)
β (deg)	88.69(2)
γ (deg)	86.88(2)
Crystal system	triclinic
Space group	$P\bar{1}$
V (Å^3)	2409.9(8)
D_c (g/cm^3)	1.22
D_o (g/cm^3)	1.22
Z	2
Crystal dimensions (mm)	0.35 × 0.125 × 0.163
Absorbance coefficient (μ) (cm^{-1})	0.85
Radiaton, λ (Å)	Mo Kα, 0.71069 graphite monochromator
Scan speed (deg/min)	3.9–29 ($\theta/2\theta$ scan)
Scan range (deg)	2.0
2θ range (deg)	$3 < 2\theta < 45$
Index ranges	h −12 → 12 k −15 → 15 l 0 → 20
Total reflections	6566
Unique reflections	6319
Observed reflections $I > [\sigma(I)]$	2507
Number of parameters	433
R	0.074
R_w	0.065
Max. L.S. shift/error	0.15
Final difference Fourier max. (e$^-$ Å^{-3})	0.4

Data reduction gave 6319 unique reflections of which 2506, having $I > 3[\sigma(I)]$, were used in the subsequent structural analysis. Intensities were corrected for Lorentz-polarisation effects and an empirical absorption correction based on ψ-scan data was applied. Scattering factors for Mg were obtained from Cromer and Mann [7], and anomalous dispersion corrections were from Cromer and Liberman [8].

The Mg atom and 48 non-hydrogen atoms of the porphyrin ring were located by direct methods using the program RANT*. The remaining non-hydrogen atoms were located by difference Fourier techniques and the structure was refined using blocked cascade least squares methods. Hydrogen atoms were then fixed in theoretically idealized

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*All of the programs used for data reduction and structure solution are included in the SHELXTL (version 3.0) package [9].

0020-1693/86/$3.50

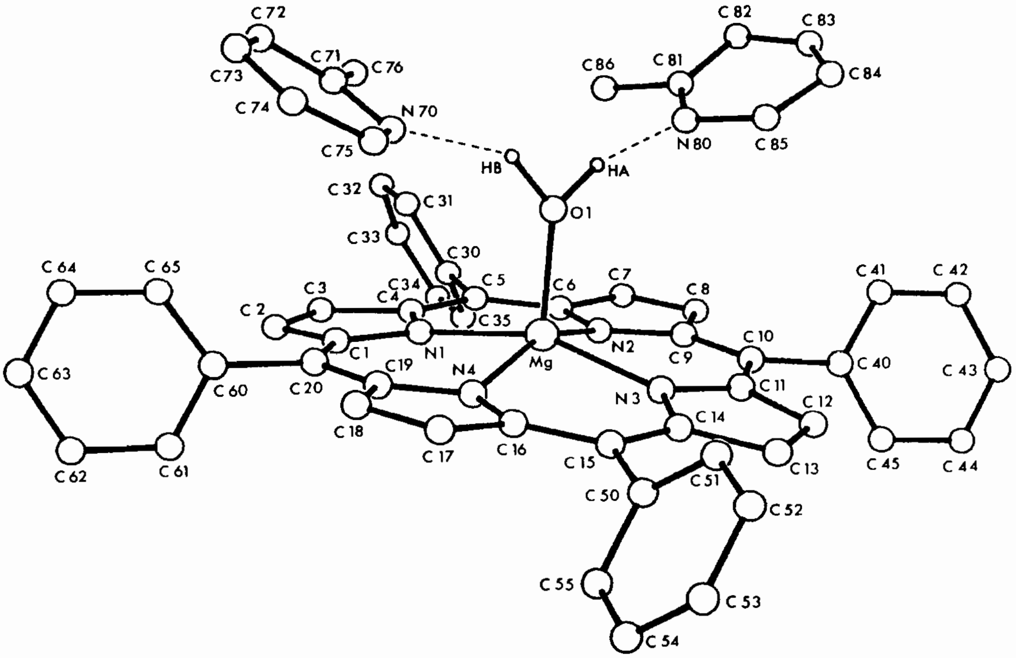

Fig. 1. Computer drawn perspective view of Mg(TPP)(H_2O)(2-pic)$_2$ showing the numbering system.

positions (C–H = 0.96 Å) (except HA and HB which were refined) and considered as fixed contributors in all refinements. The difference map showed an additional, disordered 2-picoline molecule which was taken into account during further refinements. In all refinements, the function minimized was $\Sigma w(F_o - F_c)^2$ where $w = [\sigma^2(F_o) + 0.0022(F_o)^2]^{-1}$. For the final refinement cycle, 598 variables were used which gave $R = 0.074$, $R_w = 0.0652$ and goodness of fit = 2.046. The ratio of final mean shift to standard deviation was 0.040 with a maximum shift value of 0.146. The final difference Fourier map showed no peaks larger than 0.4 e$^-$ Å^{-3}.

Results and Discussion

A perspective view of MgTPP(H_2O)(2-pic)$_2$ (2-pic = 2-picoline) is shown in Fig. 1 which also defines the numbering system used throughout this paper. The atomic coordinates are given in Table II. Important interatomic distances (Å) and bond angles (°) are: Mg–N(1) (2.114(7)), Mg–N(4) (2.082(6)), Mg–N(3) (2.096(7)), Mg–N(2) (2.074(6)), Mg–O(1) (2.012(6)), O(1)–HA (1.094(5)), O(1)HB (1.058(5)), N(1)–Mg–N(4) (86.8(2)), N(4)–Mg–N(3) (87.8(3)), N(1)–Mg–N(2) (87.9(3)), N(1)–Mg–O(1) (99.3(2)), N(3)–Mg–N(2) (88.5(3)), N(3)–Mg–O(1) (103.0(2)), N(4)–Mg–O(1), (103.9(2)), N(2)–Mg–O(1) (99.3(2)), Mg–O(1)–Hb (138.3(4)), Mg–O(1)–HA (122.6(4)) and HA–O(1)–HB (93.8(4)). Other averaged bond distances are Ca–N = 1.388(8), Cb–Cb = 1.338(12), Ca–Cb = 1.449(11), Ca–Cm =

TABLE II. Atom Coordinates (×10^4)

Atom	x	y	z
Mg	8362(3)	2023(2)	7675(2)
N(1)	7733(6)	826(4)	7057(3)
C(9)	10163(7)	3310(6)	6659(4)
N(4)	8009(6)	1126(5)	8647(3)
N(3)	9621(6)	2818(4)	8313(4)
C(16)	8221(8)	1389(5)	9379(4)
C(19)	7151(7)	359(5)	8717(4)
C(6)	9175(7)	2236(6)	5971(4)
C(11)	10413(8)	3555(6)	8021(4)
N(2)	9369(6)	2511(4)	6708(3)
C(1)	7046(7)	31(5)	7340(4)
C(4)	7812(7)	785(5)	6286(4)
C(14)	9707(8)	2783(6)	9097(5)
C(10)	10654(7)	3810(5)	7254(4)
C(18)	6783(8)	185(5)	9498(4)
C(8)	10435(8)	3570(6)	5868(4)
C(5)	8427(7)	1442(6)	5780(4)
C(7)	9836(8)	2921(6)	5451(5)
C(15)	9065(7)	2123(6)	9589(4)
C(13)	10631(8)	3510(6)	9289(5)
C(41)	11117(8)	5514(5)	6686(4)
C(42)	11936(8)	6291(6)	6513(5)
C(43)	13234(9)	6173(7)	6719(5)
C(44)	13687(9)	5323(7)	7114(5)
C(45)	12864(8)	4532(6)	7276(5)
C(40)	11563(7)	4632(5)	7074(4)
C(12)	11007(8)	3988(6)	8654(4)
C(17)	7437(8)	803(6)	9901(4)
C(51)	9067(8)	3045(6)	10805(4)
C(52)	9319(9)	3071(7)	11571(4)

(continued on facing page)

TABLE II. *(continued)*

Atom	*x*	*y*	*z*
C(53)	9807(8)	2225(7)	11964(5)
C(54)	10072(8)	1359(7)	11597(5)
C(55)	9833(7)	1316(6)	10831(5)
C(50)	9316(8)	2188(6)	10423(4)
C(31)	7073(9)	1322(6)	4624(5)
C(32)	6945(10)	1118(7)	3878(5)
C(33)	8045(10)	865(6)	3448(5)
C(34)	9251(9)	825(6)	3742(4)
C(35)	9373(8)	1027(6)	4503(4)
C(30)	8280(8)	1271(6)	4957(4)
O(1)	6759(5)	2960(4)	7595(3)
N(80)	7058(9)	4764(7)	6746(6)
C(81)	6882(13)	4977(11)	6051(10)
C(82)	6902(19)	5877(16)	5607(14)
C(85)	7412(11)	5528(8)	7190(11)
C(83)	7354(23)	6507(18)	6053(17)
C(86)	6543(13)	4202(11)	5611(8)
C(84)	7480(15)	6434(14)	6892(13)
C(20)	6743(7)	−171(5)	8101(4)
C(2)	6713(7)	−558(6)	6730(4)
C(3)	7169(7)	−117(6)	6089(4)
C(61)	6460(9)	−1880(7)	8688(5)
C(62)	5705(12)	−2706(8)	8881(6)
C(63)	4459(11)	−2700(7)	8647(6)
C(64)	3903(8)	−1888(6)	8256(5)
C(65)	4662(8)	−1074(6)	8077(5)
C(60)	5933(8)	−1050(6)	8289(4)
N(70)	4425(9)	2013(6)	7746(7)
C(75)	4108(13)	1859(8)	8481(9)
C(71)	3570(10)	1763(7)	7238(7)
C(73)	2090(10)	1230(7)	8200(7)
C(72)	2405(15)	1399(8)	7442(10)
C(74)	2929(17)	1443(9)	8730(9)
C(76)	3954(13)	1923(9)	6443(7)
HA	6717	3637	7220
HB	5731	2917	7629
C(90)	4032(10)	4785(7)	9695(6)
C(91)	6290(16)	4202(11)	9235(9)
C(92)	5076(23)	4305(16)	9176(13)
C(93)	5376(26)	4681(17)	9759(14)
C(94)	6739(24)	4730(18)	9685(14)

1.394(10) and Cm–Cphenyl = 1.497(1), where the numbers in parentheses are the estimated standard deviations and Ca = C1, C4, C9, C11, C14, C16, C19; Cb = C2, C3, C7, C8, C12, C13, C17, C18; Cm = C5, C10, C15, C20. The average bond angles are CaNCb = 207(1), NCaCb = 108.5(8), NCaCm = 125.5(8), CaCbCb = 107.9(6) and CaCmCa = 125.8(5). These values agree well with those reported for other metallo–TPP complexes [10].

An important structural feature is the hydrogen bonding of the coordinated water molecule to two 2-picoline groups. The O–H–––N distances for these interactions are 1.850 Å and 1.733 Å. A third group, presumably 2-picoline, is located in the lattice at a roughly equivalent position to that of the two hydrogen bonded 2-picoline groups, relative to the MgTPP(H_2O) entity. This third group shows two-fold disorder about a centre of symmetry. Because of disorder the nitrogen and methyl groups cannot be identified. However the distance from O1 (of the coordinated H_2O molecule) to the nearest atom of the disordered ring is 3.42 Å (to C91) indicating only a very weak hydrogen bonding interaction if the closest atom is indeed nitrogen.

Overall, the porphyrin core is non-planar with large displacements at the Cb atoms. Individually, the pyrrole rings are planar to 0.02 Å and they are inclined at 7.0°, 0.9°, 7.2° and 5.3° to the mean plane of the core. The smaller angle of inclination for one of the pyrrole rings, N2C6C7C8C9, is likely to be due to weak interaction with the aromatic ring of the one of the 2-picoline groups. Distances between atoms contained in the two groups are 4.127 Å (for C7 to C81 of 2-picoline) and 4.039 Å and 4.016 Å (for C8 to N80 and C81 of 2-picoline).

The greatest deviation from planarity is at the magnesium atom which is displaced by 0.414 Å out of the plane of the four chelating nitrogen atoms, compared with a corresponding value of 0.273 Å for MgTPP(H_2O) [1]. Although the latter value is probably underestimated [10] some increase in the displacement does appear to occur. Such an effect may be related to hydrogen bonding of the two 2-picoline groups to the coordinated water molecule in the solvated complex. This would effectively increase the electronegativity of the oxygen atom, producing a stronger interaction with Mg^{2+} and a greater tendency for the Mg atom to be displaced from the plane of the four chelating nitrogen atoms. Consistent with this interpretation is the observation that the Mg–OH_2 bond length is significantly shorter than that observed for MgTPP(H_2O) [1] (2.012 Å compared with 2.099 Å), even when the estimated error of 0.01 Å for the latter value is taken into account.

The particular feature of symmetrical hydrogen bonding to both hydrogen atoms of the coordinated water molecule closely resembles that found for the ethyl chlorophyllide a and b dihydrates [2, 3] and MgPc(H_2O)(py)$_2$ [4]. This special kind of hydrogen bonded water coordination appears to be a particular arrangement that can be readily adopted by magnesium porphyrin systems, and may, therefore, be a key feature of natural chlorophyll systems.

Supplementary Material

Tables S2-S5 listing observed and calculated structure factors, bond lengths, bond angles, anisotropic temperature factors and hydrogen atom coordinates (19 pages) are available from the authors on request.

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