Inorganica Chimica Acta, 151 (1988) 233–236

The Crystal and Molecular Structures of Magnesium Tetraphenylporphyrin Complexes Involving Water and Methanol Coordination

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(Received November 3, 1987)

We report the X-ray structures of three Mg tetraphenylporphyrin (TPP) complexes, MgTPP$(CH_3OH)_2$, MgTPP$(CH_3OH)_2[(CH_3)_2CO]_2$ and MgTPP$(H_2O)[(CH_3)_2CO]_2$. Hydrogen bonding of acetone molecules to axially coordinated methanol and water molecules is a prominent feature of the latter two complexes. The availability of the non-hydrogen bonded system, MgTPP$(CH_3OH)_2$ provides a means by which the effect of the hydrogen bonding (on axial binding of oxygen to Mg) may be assessed. Both of the acetone complexes apparently involve weak π interaction of the C=O bond with the porphyrin ring.

The molecular structure of the aquo complex, MgTPP$(H_2O)[(CH_3)_2CO]_2$ is closely similar to those reported for other related complexes, MgPc$(H_2O)(py)_2$ [1] (Pc = phthalocyanin, py = pyridine), MgTPP(H_2O)(2-picoline)$_2$ [2] and the ethyl chlorophylide hydrate derivatives of chlorophyll a and b [3, 4]. This is a further indication that this particular five-coordinate configuration involving solvate hydrogen bonding to coordinated water is an electronic and bonding arrangement which could be adopted in chlorophyll systems.

Experimental

The complexes were prepared using as a starting material MgTPP obtained from the Adler *et al.* [5] method of reacting Mg(II) with (TPP)H_2. Recrystallisation of the product from a mixture of methanol and acetone (with heating) yielded the complex MgTPP$(CH_3OH)_2[(CH_3)_2CO]_2$. The aquo complex, MgTPP$(H_2O)[(CH_3)_2CO]_2$, was obtained by recrystallisation of MgTPP$(CH_3OH)_2[(CH_3)_2CO]_2$ from a mixture of water and acetone. The complex, MgTPP$(CH_3OH)_2$, may be obtained by recrystallising the methanol/acetone product from methanol.

X-ray intensity data were collected at −140 °C on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo Kα radiation. Crystal data and data collection parameters are summarised in Table I. Crystal stability was monitored by record-

TABLE I. Summary of Crystallographic Data

Complex	MgTPP$(CH_3OH)_2$	MgTPP$(CH_3OH)_2[(CH_3)_2CO]_2$	MgTPP$(H_2O)[(CH_3)_2CO]_2$
Formula	$C_{46}H_{36}N_4O_2Mg$	$C_{52}H_{48}N_4O_4Mg$	$C_{50}H_{42}N_4O_3Mg$
a (Å)	11.041(6)	10.01(1)	10.694(6)
b (Å)	12.870(8)	17.75(2)	12.925(7)
c (Å)	13.303(8)	12.74(2)	15.631(11)
α (deg)	90	90	105.18(5)
β (deg)	113.29(4)	110.7(1)	90.27(5)
γ (deg)	90	90	102.27(4)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
V (Å^3)	1736(2)	2115(4)	2033(2)
Z	2	2	2
Crystal dimensions (mm)	0.5 × 0.5 × 0.25	0.8 × 0.6 × 0.47	0.5 × 0.3 × 0.2
Absorbance coefficient (cm^{-1})	0.93	0.89	0.88
Scan type	$\theta-2\theta$	ω	$\theta-2\theta$
Scan range (deg)	2.1	2.1	2.3
Scan speed (deg min^{-1})	3.9–29.3	5–29.3	4.9–59
2θ range (deg)	3–45	3.50	4–40
Unique reflections	3650	3718	3812
Observed reflections $I > 3\sigma(I)$	2150	2244	2274
Least-squares parameters	241	277	403
R	0.049	0.070	0.077
R_w	0.057	0.101	0.099
Max. L. S. shift/error	0.02	0.03	0.06
Final difference Fourier max. (e Å^{-3})	±0.3	±0.5	±0.5
Weighting factor, g	0.0005	0.0056	0.0037

0020-1693/88/$3.50

ing three check reflections every 100 reflections and no significant variations were observed. Intensities were corrected for Lorentz and polarisation effects but only the data for $MgTPP(CH_3OH)_2[(CH_3)_2CO]_2$ were corrected for absorption.

All three structures were solved by direct methods using the programme SOLV[8] and refined by blocked-cascade least-squares methods. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters set to 1.2 times the equivalent isotropic U of their carrier atoms. In all refinements the function minimised was $\Sigma w(|F_0|-|F_c|)^2$ where $w = [\sigma^2(F_0) + g(F_0)^2]^{-1}$. All programmes used in data collection and structure solution are contained in the SHELXTL (Version 4.0) package[8].

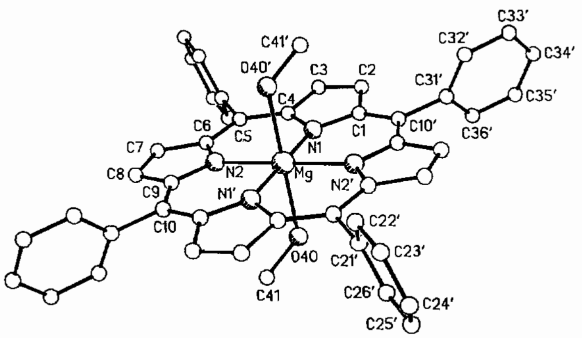

Fig. 1. Perspective view of $MgTPP(CH_3OH)_2$.

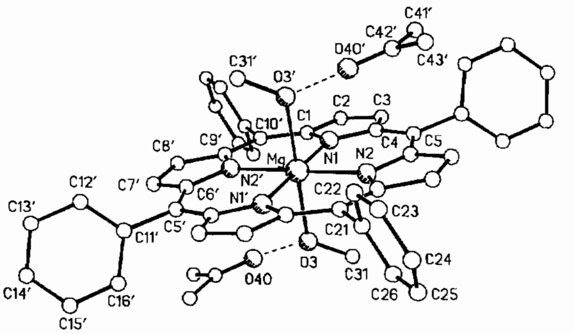

Fig. 2. Perspective view of $MgTPP(CH_3OH)_2[(CH_3)_2CO]_2$.

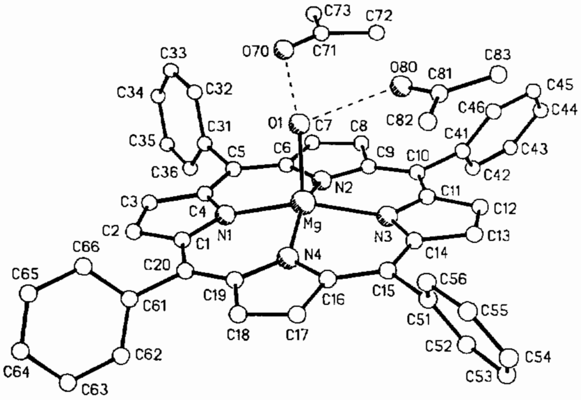

Fig. 3. Perspective view of $MgTPP(H_2O)[(CH_3)_2CO]_2$.

Results and Discussion

Perspective views of the complexes are shown in Figs. 1–3 where dashed lines indicate hydrogen bonds; the figures also define the numbering system used throughout the paper. The atomic coordinates are given in Table II. Important interatomic distances (Å) and bond angles (°) are given in Table III.

For the octahedral complexes, $MgTPP(CH_3OH)_2$ and $MgTPP(CH_3OH)_2[(CH_3)_2CO]_2$, the Mg–ligand distances reflect the influence of hydrogen bonding in the latter case. The average Mg–N distance for the non-hydrogen bonded complex (2.069 Å) is marginally shorter than that for the hydrogen-bonded one (2.074 Å). The Mg–O (CH_3OH) distances are different in the opposite sense at 2.220 and 2.188 Å, respectively. This illustrates that slightly stronger Mg–O axial bonding is associated with the hydrogen-bonded, coordinated methanol group. This is analogous to that observed for the five-coordinated systems $MgTPP(H_2O)$ [7] and $MgTPP(H_2O)$(2-picoline)$_2$ [2], where the Mg–O bond distance decreases from 2.099 to 2.012 Å. The smaller decrease for the six-coordinate system is probably related to the effect of one hydrogen-bond on the binding of each axial ligand (CH_3OH) compared with two for the single H_2O ligand in the five-coordinate case.

TABLE II. Atom Coordinates × 10^4 (Å)

Atom	x	y	z
$MgTPP(CH_3OH)_2$			
Mg	5000	0	0
N(1)	5356(2)	−527(2)	1562(2)
N(2)	5610(2)	1475(2)	604(2)
C(1)	5062(3)	−1495(2)	1841(2)
C(2)	5249(3)	−1497(2)	2978(2)
C(3)	5639(3)	−533(2)	3374(2)
C(4)	5699(2)	81(2)	2479(2)
C(5)	6008(3)	1148(2)	2545(2)
C(6)	6005(3)	1786(2)	1677(2)
C(7)	6396(3)	2863(2)	1772(2)
C(8)	6239(3)	3192(2)	764(2)
C(9)	5739(3)	2323(2)	28(2)
C(10)	5436(3)	2334(2)	−1110(2)
C(21)	6316(3)	1675(2)	3622(2)
C(22)	7545(3)	1580(2)	4483(2)
C(23)	7798(3)	2054(2)	5483(2)
C(24)	6818(3)	2621(2)	5639(2)
C(25)	5590(3)	2724(2)	4785(2)
C(26)	5346(3)	2254(2)	3788(2)
C(31)	5740(3)	3317(2)	−1566(2)
C(32)	7048(3)	3605(2)	−1292(2)

(continued)

TABLE II. *(continued)*

Atom	*x*	*y*	*z*
C(33)	7358(3)	4511(2)	-1710(2)
C(34)	6368(3)	5136(2)	-2399(2)
C(35)	5073(3)	4865(2)	-2671(2)
C(36)	4750(3)	3955(2)	-2272(2)
O(40)	7044(2)	-405(2)	221(2)
C(41)	7711(3)	188(3)	-320(3)
$MgTPP(CH_3OH)_2[(CH_3)_2CO]_2$			
Mg	5000	0	0
N(1)	3458(3)	-704(2)	219(3)
C(1)	2229(4)	-922(2)	-610(4)
C(2)	1365(4)	-1333(2)	-100(4)
C(3)	2070(4)	-1355(2)	996(4)
C(4)	3420(4)	-965(2)	1214(4)
C(5)	4478(4)	-854(2)	2275(4)
C(6)	5703(4)	-388(2)	2508(4)
C(7)	6808(4)	-303(2)	3586(4)
C(8)	7803(4)	163(2)	3440(4)
C(9)	7325(4)	354(2)	2261(4)
C(10)	8123(4)	779(2)	1751(4)
N(2)	6043(4)	16(2)	1721(3)
C(11)	4330(4)	-1283(2)	3235(4)
C(12)	4184(4)	-941(2)	4165(4)
C(13)	4060(4)	-1362(3)	5053(4)
C(14)	4077(5)	-2140(3)	4992(4)
C(15)	4221(5)	-2498(2)	4082(4)
C(16)	4348(4)	-2077(2)	3214(4)
C(21)	9492(4)	1098(2)	2532(4)
C(22)	10806(4)	776(2)	2631(4)
C(23)	12061(5)	1070(3)	3386(4)
C(24)	12038(5)	1679(3)	4069(4)
C(25)	10728(5)	2001(3)	3966(4)
C(26)	9486(5)	1714(2)	3218(4)
O(3)	3658(3)	959(2)	63(3)
C(31)	3095(6)	1069(3)	928(5)
O(40)	1205(4)	1164(2)	-1761(3)
C(41)	2119(6)	1989(3)	-2803(5)
C(42)	1006(5)	1503(3)	-2635(4)
C(43)	-382(6)	1448(4)	-3555(5)
$MgTPP(H_2O)[(CH_3)_2CO]_2$			
Mg	5154(2)	5148(2)	7345(2)
N(1)	5049(5)	3698(4)	6371(4)
N(2)	4114(5)	5664(4)	6464(4)
N(3)	5766(5)	6810(4)	8045(4)
N(4)	6767(5)	4860(4)	7914(4)
C(1)	5703(7)	2883(5)	6376(4)
C(2)	5191(7)	1916(6)	5646(5)
C(3)	4237(7)	2167(6)	5220(5)
C(4)	4166(7)	3275(6)	5655(5)
C(5)	3348(7)	3854(6)	5387(5)
C(6)	3364(7)	4968(5)	5742(4)
C(7)	2550(7)	5559(5)	5415(5)
C(8)	2807(7)	6596(5)	5952(4)
C(9)	3780(7)	6656(6)	6618(5)
C(10)	4260(7)	7587(6)	7329(5)
C(11)	5219(7)	7657(6)	7986(5)
C(12)	5770(7)	8629(6)	8661(4)
C(13)	6674(7)	8365(6)	9140(5)
C(14)	6674(7)	7230(5)	8746(4)
C(15)	7498(7)	6650(5)	9032(4)
C(16)	7539(7)	5559(6)	8638(4)
C(17)	8438(7)	4986(6)	8893(5)
C(18)	8220(7)	3959(6)	8327(5)
C(19)	7198(7)	3896(6)	7701(4)
C(20)	6707(6)	2977(5)	6993(4)
C(31)	2317(7)	3207(5)	4670(5)
C(32)	1089(7)	2805(6)	4925(5)
C(33)	119(7)	2241(6)	4286(5)
C(34)	320(8)	2080(6)	3388(5)
C(35)	1533(8)	2466(6)	3139(5)
C(36)	2518(7)	3028(5)	3787(5)
C(41)	3692(6)	8577(5)	7404(5)
C(42)	3740(7)	9087(6)	6729(6)
C(43)	3178(7)	9964(6)	6798(7)
C(44)	2563(8)	10354(7)	7538(6)
C(45)	2502(7)	9856(6)	8224(6)
C(46)	3060(7)	8968(6)	8156(5)
C(51)	8445(7)	7281(6)	9803(5)
C(52)	9411(7)	8159(6)	9725(5)
C(53)	10296(7)	8739(6)	10434(6)
C(54)	10206(8)	8433(7)	11223(6)
C(55)	9287(8)	7552(7)	11307(5)
C(56)	8402(7)	6974(6)	10590(5)
C(61)	7302(7)	1988(5)	6842(5)
C(62)	8482(7)	2014(6)	6489(6)
C(63)	9002(8)	1097(7)	6304(6)
C(64)	8354(7)	147(6)	6468(5)
C(65)	7200(7)	117(6)	6848(5)
C(66)	6665(7)	1029(6)	7042(5)
O(1)	3666(4)	4738(4)	8105(3)
O(70)	1252(5)	4374(4)	7218(4)
C(71)	737(7)	5141(7)	7238(5)
C(72)	1086(8)	6214(7)	7939(6)
C(73)	-271(7)	5052(6)	6538(6)
O(80)	3447(8)	6451(8)	9483(6)
C(81)	4011(10)	7037(8)	10193(7)
C(82)	4952(9)	6708(10)	10654(8)
C(83)	3697(13)	8106(11)	10557(8)

TABLE III. Selected Interatomic Distances (Å) and Angles (°)

$MgTPP(CH_3OH)_2$	
Mg–N(1)	2.070(2)
Mg–N(2)	2.068(2)
Mg–O(40)	2.220(2)
N(1)–Mg–N(2)	90.4(1)
N(1)–Mg–O(40)	90.6(1)
N(1)–Mg–N(2′)	89.6(1)
N(1)–Mg–O(40′)	89.4(1)
N(2)–Mg–O(40)	90.4(1)
N(2)–Mg–N(1′)	89.6(1)
N(2)–Mg–O(40′)	89.6(1)
$MgTPP(CH_3OH)_2[(CH_3)_2CO]_2$	
Mg–N(1)	2.081(4)
Mg–N(2)	2.068(4)

(continued)

TABLE III. *(continued)*

Mg–O(3)	2.188(4)
O(3)–O(40)	2.744(6)
N(1)–Mg–N(2)	89.3(1)
N(1)–Mg–O(3)	88.2(1)
N(1)–Mg–N(2′)	90.7(1)
N(1)–Mg–O(3′)	91.8(1)
N(2)–Mg–O(3)	92.1(1)
N(2)–Mg–N(1′)	90.8(1)
N(2)–Mg–O(3′)	87.9(1)
MgTPP(H_2O)[$(CH_3)_2CO$]$_2$	
Mg–N(1)	2.063(6)
Mg–N(2)	2.086(5)
Mg–N(3)	2.099(6)
Mg–N(4)	2.083(7)
Mg–O(1)	2.054(6)
O(1)–O(70)	2.81(1)
O(1)–O(80)	2.71(1)
N(1)–Mg–N(2)	88.4(2)
N(1)–Mg–N(3)	159.5(3)
N(1)–Mg–N(4)	88.3(2)
N(1)–Mg–O(1)	102.6(2)
N(2)–Mg–N(3)	87.3(2)
N(2)–Mg–N(4)	156.9(3)
N(2)–Mg–O(1)	97.0(2)
N(3)–Mg–N(4)	87.8(2)
N(3)–Mg–O(1)	97.9(2)
N(4)–Mg–O(1)	106.1(3)

For the aquo complex, MgTPP(H_2O)[$(CH_3)_2CO$]$_2$, the Mg–O (H_2O) distance is 2.054 Å. This is longer than the value observed for MgTPP(H_2O)(2-picoline)$_2$ (2.012 Å). Interatomic values suggest that the 2-picoline groups interact with the porphyrin ring system [2]. While non-bonded distances indicate the same kind of interaction for the C=O group of the acetone molecules (O70, C71, O80 and C81 are 3.33, 3.38, 3.41 and 3.55 Å, respectively, from the mean plane of the porphyrin ring) the electronic effect is likely to be smaller for the single π-bond interaction of acetone. This, in turn, may produce a smaller electron-withdrawing effect than that possible for the 2-picoline complex, thereby giving a longer Mg–O distance. (The distances of C=O to the mean plane of the porphyrin ring (3.15 and 3.42 Å for O40 and C42 respectively) indicate weak π interaction also exists for the six-coordinate complex, MgTPP-$(MeOH)_2$[$(CH_3)_2CO$]$_2$.

The displacement of the Mg atom from the porphyrin plane is 0.45 Å compared with the value of 0.414 Å for the 2-picoline complex [2]. The overall similarity of the structure of MgTPP(H_2O)[$(CH_3)_2$-CO]$_2$ with that of MgTPP(H_2O)(2-picoline)$_2$ [2] and other related complexes, having different equatorial ligands [1, 3, 4], further indicates the significance of axial binding of hydrogen-bonded H_2O in five-coordinate Mg complexes. The possibility of some π-interaction with the porphyrin ring appears to enhance the likelihood of this overall conformation being adopted.

Supplementary Material

Observed and calculated structure factors, bond lengths and angles, anisotropic temperature factors and H-atom coordinates are available from the authors on request.

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