

Monoaquapentakis(trimethylphosphine oxide)magnesium(II) Perchlorate

BY Y. S. NG, G. A. RODLEY AND WARD T. ROBINSON*

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

(Received 7 January 1978; accepted 27 January 1978)

Abstract. $[\text{Mg}(\text{Me}_3\text{PO})_5\text{H}_2\text{O}](\text{ClO}_4)_2$, orthorhombic, $Pna2_1$, $a = 21.903$ (6), $b = 13.999$ (3), $c = 11.545$ (3) Å, $D_m = 1.34$, $D_x = 1.32$ g cm⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 4.80$ cm⁻¹. The structure consists of an assemblage of octahedral $[\text{Mg}(\text{Me}_3\text{PO})_5\text{H}_2\text{O}]^{2+}$ cations each hydrogen-bonded to two perchlorate anions *via* the coordinated water molecule. Comparisons between the binding properties of phosphine and arsine oxides to Mg centres are made.

Introduction. Recrystallization of $[\text{Mg}(\text{Me}_3\text{PO})_5\text{H}_2\text{O}](\text{ClO}_4)_2$ was carried out by dissolving powder samples (Jameson & Rodley, 1975) in an acetonitrile–triethyl orthoformate solution. Colourless, plate-shaped crystals appeared overnight. Systematic absences ($0kl$: $k+l$ odd; $h0l$: h odd) indicate that the space group is either $Pnma$ or $Pna2_1$. The latter was chosen and subsequently confirmed by the successful solution of the structure.

Intensities were obtained from a plate-shaped crystal with a maximum dimension of 0.35 mm. 3514 data

were collected in the range $0 < \theta \leq 20^\circ$ on a Hilger & Watts diffractometer with Zr-filtered Mo $K\alpha$ radiation. Lorentz and polarization effects were corrected for but no absorption corrections were made. Although the crystals appeared to be well formed under the microscope, they diffracted X-rays poorly and their mosaicities were high.

The structure was solved with *MULTAN* (Main, Woolfson & Germain, 1971). In the final full-matrix least-squares refinements, the Mg, five P and two Cl atoms were given anisotropic thermal parameters. The calculations converged with a final R of 0.115 for 1596 reflections with $|F_o|^2 \geq 2\sigma(|F_o|^2)$. The absolute configuration was established by carrying out structure factor calculations for the two enantiomorphous structures and the model adopted was that favoured by the Hamilton R -factor ratio test (Hamilton, 1965).†

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33371 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* To whom correspondence should be addressed.

Table 1. Positional parameters for $[\text{Mg}(\text{Me}_3\text{PO})_5\text{H}_2\text{O}](\text{ClO}_4)_2$

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Mg	0.3399 (4)	0.2306 (7)	0.1000*	C(23)	0.240 (2)	0.072 (3)	-0.134 (5)
P(1)	0.4528 (5)	0.3137 (8)	-0.066 (2)	C(31)	0.219 (2)	0.281 (3)	0.348 (4)
P(2)	0.2591 (4)	0.1905 (8)	-0.150 (1)	C(32)	0.141 (2)	0.153 (3)	0.224 (4)
P(3)	0.2190 (4)	0.1731 (8)	0.258 (2)	C(33)	0.250 (2)	0.092 (4)	0.342 (6)
P(4)	0.4168 (5)	0.2842 (8)	0.336 (1)	C(41)	0.437 (2)	0.402 (4)	0.306 (5)
P(5)	0.3912 (4)	-0.0025 (7)	0.095 (2)	C(42)	0.411 (2)	0.255 (4)	0.474 (5)
Cl(1)	0.4121 (5)	0.6284 (7)	0.093 (2)	C(43)	0.484 (2)	0.212 (3)	0.295 (4)
Cl(2)	0.1213 (6)	0.459 (1)	0.098 (2)	C(51)	0.444 (3)	-0.041 (4)	0.218 (6)
O(1)	0.418 (1)	0.298 (2)	0.038 (2)	C(52)	0.330 (2)	-0.067 (3)	0.106 (5)
O(2)	0.313 (1)	0.216 (1)	-0.074 (2)	C(53)	0.423 (2)	-0.046 (3)	-0.031 (4)
O(3)	0.256 (1)	0.183 (2)	0.154 (2)	O(11)	0.365 (1)	0.566 (2)	0.067 (3)
O(4)	0.367 (1)	0.253 (2)	0.271 (3)	O(12)	0.402 (2)	0.703 (3)	0.031 (5)
O(5)	0.381 (1)	0.099 (2)	0.107 (3)	O(13)	0.409 (2)	0.662 (3)	0.198 (5)
O(6)	0.3004 (9)	0.374 (2)	0.096 (3)	O(14)	0.463 (2)	0.596 (3)	0.040 (4)
C(11)	0.417 (1)	0.396 (2)	-0.158 (4)	O(21)	0.181 (2)	0.450 (3)	0.082 (5)
C(12)	0.526 (2)	0.371 (3)	-0.026 (4)	O(22)	0.096 (3)	0.526 (4)	0.161 (6)
C(13)	0.470 (1)	0.206 (3)	-0.142 (4)	O(23)	0.110 (3)	0.490 (5)	-0.007 (7)
C(21)	0.195 (2)	0.264 (3)	-0.118 (4)	O(24)	0.100 (2)	0.386 (4)	0.139 (5)
C(22)	0.274 (2)	0.205 (3)	-0.294 (3)				

* Parameter fixed in all least-squares refinements.

Atom coordinates are given in Table 1, interatomic distances and bond angles in Tables 2 and 3. Programs used have been described elsewhere (Ng, Rodley & Robinson, 1977).

Discussion. A wide range of five-coordinate square-pyramidal complexes of compositions $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^+$ have been isolated, where $M = Mn, Fe, Co, Ni$ or Cu^{II} , and $L = Me_3PO$ or Me_3AsO (Brodie, Hunter, Rodley & Wilkins, 1968a). More recently, in the course of an investigation of Ca and Mg perchlorate complexes with Me_3PO and Me_3AsO (Jameson & Rodley, 1975), it was found that five-coordinate complexes can be prepared without difficulty with Me_3AsO , whereas complexes with Me_3PO were usually six-coordinate. Comparisons between complexes containing Me_3PO and Me_3AsO would help in understanding the coordinating properties of these ligands.

While the final R for the present structure is rather high and some of the parameters are less accurate than one would normally expect, the structure is nevertheless of sufficient accuracy for some important features to be delineated. In conjunction with the anhydrous $[Mg(Me_3PO)_5](ClO_4)_2$ structure, described in the following paper, the relative lengths of $Mg-O$ axial and basal bonds and the planarity of the ligands around the Mg atom have been established with sufficient precision to permit a quantitative discussion of the different binding abilities of Me_3PO and Me_3AsO .

Fig. 1 represents a perspective view of the octahedral $[Mg(Me_3PO)_5H_2O]^{2+}$ cation hydrogen-bonded to two $(ClO_4)^-$ anions. A stereoscopic packing diagram illustrating the arrangement of the ions in the unit cell is shown in Fig. 2. The distances between the O atom of the coordinated water molecule and the two hydrogen-bonded perchlorate atoms O(11) and O(21) are 3.06 (4) and 2.82 (5) Å respectively.

Table 2. Selected bond lengths (Å) in $[Mg(Me_3PO)_5H_2O](ClO_4)_2$

Mg—O(1)	2.07 (3)	P(1)—O(1)	1.44 (2)
Mg—O(2)	2.11 (3)	P(2)—O(2)	1.51 (3)
Mg—O(3)	2.06 (3)	P(3)—O(3)	1.46 (3)
Mg—O(4)	2.08 (3)	P(4)—O(4)	1.39 (3)
Average	2.08 (3)	Average	1.45 (5)
Mg—O(5)	2.05 (3)	P(5)—O(5)	1.45 (3)
Mg—O(6)	2.19 (2)		
P(1)—C(11)	1.76 (4)	P(2)—C(21)	1.78 (4)
P(1)—C(12)	1.85 (4)	P(2)—C(22)	1.71 (4)
P(1)—C(13)	1.78 (4)	P(2)—C(23)	1.73 (5)
P(3)—C(31)	1.83 (4)	P(4)—C(41)	1.74 (5)
P(3)—C(32)	1.78 (4)	P(4)—C(42)	1.65 (6)
P(3)—C(33)	1.64 (6)	P(4)—C(43)	1.85 (4)
P(5)—C(51)	1.91 (4)	P(5)—C(53)	1.72 (6)
P(5)—C(52)	1.63 (5)		
Cl(1)—O(11)	1.38 (3)	Cl(2)—O(21)	1.33 (4)
Cl(1)—O(12)	1.28 (5)	Cl(2)—O(22)	1.32 (6)
Cl(1)—O(13)	1.30 (6)	Cl(2)—O(23)	1.31 (8)
Cl(1)—O(14)	1.35 (4)	Cl(2)—O(24)	1.22 (5)

Table 3. Selected bond angles ($^\circ$) in $[Mg(Me_3PO)_5H_2O](ClO_4)_2$

Mg—O(1)—P(1)	143 (2)	O(5)—Mg—O(1)	93.6 (10)
Mg—O(2)—P(2)	143 (2)	O(5)—Mg—O(2)	94.1 (12)
Mg—O(3)—P(3)	141 (2)	O(5)—Mg—O(3)	94.9 (10)
Mg—O(4)—P(4)	141 (2)	O(5)—Mg—O(4)	88.6 (12)
Mg—O(5)—P(5)	161 (2)		
O(1)—Mg—O(2)	86.8 (10)	O(6)—Mg—O(1)	84.2 (9)
O(2)—Mg—O(3)	90.1 (9)	O(6)—Mg—O(2)	87.6 (11)
O(3)—Mg—O(4)	91.2 (12)	O(6)—Mg—O(3)	87.3 (10)
O(4)—Mg—O(1)	91.5 (11)	O(6)—Mg—O(4)	89.6 (12)
O(1)—Mg—O(3)	171.1 (11)	O(1)—P(1)—C(11)	111.4 (15)
O(2)—Mg—O(4)	176.9 (12)	O(1)—P(1)—C(12)	109.1 (17)
O(5)—Mg—O(6)	177.2 (11)	O(1)—P(1)—C(13)	113.0 (17)
O(2)—P(2)—C(21)	111.3 (16)	O(3)—P(3)—C(31)	113.2 (18)
O(2)—P(2)—C(22)	112.9 (17)	O(3)—P(3)—C(32)	111.0 (19)
O(2)—P(2)—C(33)	110.9 (19)	O(3)—P(3)—C(33)	108.6 (23)
O(4)—P(4)—C(41)	112.4 (22)	O(5)—P(5)—C(51)	107.0 (23)
O(4)—P(4)—C(42)	112.7 (24)	O(5)—P(5)—C(52)	114.1 (18)
O(4)—P(4)—C(43)	108.6 (18)	O(5)—P(5)—C(53)	119.8 (22)
C(11)—P(1)—C(12)	104.4 (18)	C(21)—P(2)—C(22)	106.6 (19)
C(12)—P(1)—C(13)	107.9 (17)	C(22)—P(2)—C(23)	105.0 (24)
C(13)—P(1)—C(11)	110.6 (18)	C(23)—P(2)—C(21)	109.8 (21)
C(31)—P(3)—C(32)	104.8 (19)	C(41)—P(4)—C(42)	116.8 (27)
C(32)—P(3)—C(33)	115.2 (23)	C(42)—P(4)—C(43)	99.7 (23)
C(33)—P(3)—C(31)	104.0 (25)	C(43)—P(4)—C(41)	105.3 (22)
C(51)—P(5)—C(52)	106.4 (26)		
C(52)—P(5)—C(53)	102.0 (24)		
C(53)—P(5)—C(51)	106.7 (21)		

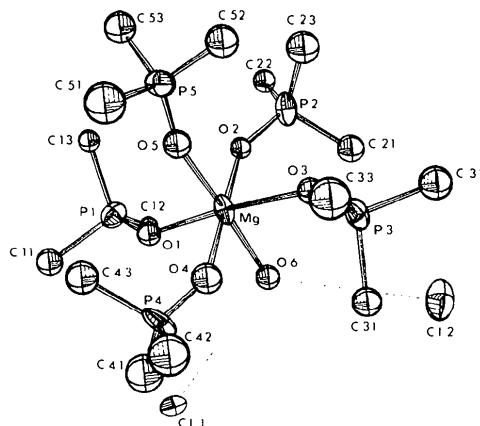


Fig. 1. Perspective view and numbering scheme of the cation in the compound $[Mg(Me_3PO)_5H_2O](ClO_4)_2$.

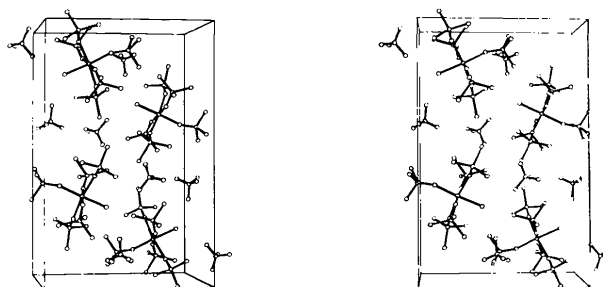


Fig. 2. A stereoscopic packing diagram showing the arrangement of the ions in the unit cell.

The average Mg—O length with the four equatorial Me₃PO ligands is 2.08 Å and only slightly longer than that found for the Me₃AsO complex (Ng, Rodley & Robinson, 1976). Compared with the anhydrous five-coordinate square-pyramidal [Mg(Me₃PO)₅]²⁺ cation reported in the following article, an interesting feature is the lengthening of the axial Mg—O(5) distance on coordination of the water molecule in the sixth position. The Mg atom here is more coplanar [0.126 (9) Å] with the O and P atoms of its equatorial ligands than it is in [Mg(Me₃AsO)₅]²⁺ [0.454 (3) Å] and [Mg(Me₃PO)₅]²⁺ [0.463 (7) Å]. It appears that the effect of a sixth ligand (H₂O) is to weaken and lengthen the otherwise strong Mg—O(5) bond {from 1.92 (1) Å in [Mg(Me₃AsO)₅]²⁺ and 1.94 (2) Å in [Mg(Me₃PO)₅]²⁺ to 2.05 (3) Å in [Mg(Me₃PO)₅H₂O]²⁺}. This effect is also manifest in the marked reduction in the displacement of the Mg atom from the equatorial plane towards O(5). There is also a small change of the axial Mg—O(5)—P(5) angle to 161°, which is still considerably larger than the average value of the equatorial Mg—O—P angle of 142°.

It has been suggested that since the P atom is capable of accepting π -type back-donation from the O atom, then phosphine oxide would be a lower σ donor

to the metal ion than would the arsine oxide (Brodie, Hunter, Rodley & Wilkins, 1968*b*). M—O bond distances are similar in arsine oxide and phosphine oxide complexes. As phosphine oxide has a lower σ -donor power, it appears that the similar magnitudes of M—O bond lengths may indicate some M←O←P π delocalization for the phosphine oxide complexes.

References

- BRODIE, A. M., HUNTER, S. H., RODLEY, G. A. & WILKINS, C. J. (1968*a*). *Inorg. Chim. Acta*, **2**, 195–198.
 BRODIE, A. M., HUNTER, S. H., RODLEY, G. A. & WILKINS, C. J. (1968*b*). *J. Chem. Soc. A*, pp. 2039–2042.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
 JAMESON, G. B. & RODLEY, G. A. (1975). *Inorg. Nucl. Chem. Lett.* **11**, 547–551.
 MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures*. Univs. of York, England, and Louvain, Belgium.
 NG, Y. S., RODLEY, G. A. & ROBINSON, W. T. (1976). *Inorg. Chem.* **15**, 303–309.
 NG, Y. S., RODLEY, G. A. & ROBINSON, W. T. (1977). *Acta Cryst.* **B33**, 931–934.

Acta Cryst. (1978). **B34**, 2837–2839

Pentakis(trimethylphosphine oxide)magnesium(II) Perchlorate

BY Y. S. NG, G. A. RODLEY AND WARD T. ROBINSON*

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

(Received 7 January 1978; accepted 27 January 1978)

Abstract. [Mg(Me₃PO)₅](ClO₄)₂, monoclinic, $P2_1/n$, $a = 11.27$ (1), $b = 27.27$ (2), $c = 11.27$ (1) Å, $\beta = 90.3$ (2)°, $D_x = 1.31$ g cm⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 4.85$ cm⁻¹. The Mg atom is coordinated by O atoms of five Me₃PO ligands in a square-pyramidal [Mg(Me₃PO)₅]²⁺ environment. The perchlorate anions occupy isolated positions and the Mg...Cl distances are >6.4 Å. The axial Mg—O distance is significantly shorter than basal Mg—O distances due to π bonding in the axial direction.

Introduction. Crystals of [Mg(Me₃PO)₅](ClO₄)₂ are extremely sensitive to moisture and care was taken to exclude moisture during the preparation. The complex was prepared inside a dry box containing P₂O₅ as a desiccant. Since the [Mg(Me₃PO)₅](ClO₄)₂ crystals are

more moisture-sensitive than [Ni(Me₃AsO)₅](ClO₄)₂ (Ng, Rodley & Robinson, 1976), the technique of sealing the crystals in capillaries under a stream of dry nitrogen was unsuitable. To overcome this problem, a crystal-mounting apparatus was developed for selecting and mounting crystals in the absence of moisture (Rodley & Ng, 1977).

[Mg(Me₃PO)₅](ClO₄)₂ is isomorphous with [Mg(Me₃AsO)₅](ClO₄)₂ and it therefore crystallizes in space group $P2_1/n$ (Ng, Rodley & Robinson, 1976). Good crystals of [Mg(Me₃PO)₅](ClO₄)₂ were difficult to obtain. In excess of twenty crystals were photographically examined but found to be unsuitable for collecting intensities. Ultimately an adequate data set ($\theta \leq 22.5^\circ$) was obtained and used for structure refinement.

The refined coordinates of [Mg(Me₃AsO)₅](ClO₄)₂ were used as starting parameters for [Mg(Me₃PO)₅]-

* To whom correspondence should be addressed.