The average Mg—O length with the four equatorial Me_3PO ligands is 2·08 Å and only slightly longer than that found for the Me_3AsO complex (Ng, Rodley & Robinson, 1976). Compared with the anhydrous five-coordinate square-pyramidal $[Mg(Me_3PO)_5]^{2+}$ 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 $[Mg(Me_3AsO)_5]^{2+}$ [0·454 (3) Å] and $[Mg(Me_3PO)_5]^{2+}$ [0·463 (7) Å]. It appears that the effect of a sixth ligand (H_2O) is to weaken and lengthen the otherwise strong Mg—O(5) bond {from 1·92 (1) Å in $[Mg(Me_3AsO)_5]^{2+}$ and 1·94 (2) Å in $[Mg(Me_3PO)_5]^{2+}$ to 2·05 (3) Å in $[Mg(Me_3PO)_5H_2O]^{2+}$}. 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 $M \leftarrow O \leftarrow P$ π delocalization for the phosphine oxide complexes.

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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

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Abstract. $[Mg(Me_3PO)_5](ClO_4)_2$, monoclinic, $P2_1/n$, $a = 11{\cdot}27\,(1)$, $b = 27{\cdot}27\,(2)$, $c = 11{\cdot}27\,(1)$ Å, $\beta = 90{\cdot}3\,(2)°$, $D_x = 1{\cdot}31$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo } K\alpha) = 4{\cdot}85$ cm^{-1}. The Mg atom is coordinated by O atoms of five Me_3PO ligands in a square-pyramidal $[Mg(Me_3PO)_5]^{2+}$ 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 $[Mg(Me_3PO)_5](ClO_4)_2$ are extremely sensitive to moisture and care was taken to exclude moisture during the preparation. The complex was prepared inside a dry box containing P_2O_5 as a desiccant. Since the $[Mg(Me_3PO)_5](ClO_4)_2$ crystals are more moisture-sensitive than $[Ni(Me_3AsO)_5](ClO_4)_2$ (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).

$[Mg(Me_3PO)_5](ClO_4)_2$ is isomorphous with $[Mg(Me_3AsO)_5](ClO_4)_2$ and it therefore crystallizes in space group $P2_1/n$ (Ng, Rodley & Robinson, 1976). Good crystals of $[Mg(Me_3PO)_5](ClO_4)_2$ 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 ($\theta \leq 22{\cdot}5°$) was obtained and used for structure refinement.

The refined coordinates of $[Mg(Me_3AsO)_5](ClO_4)_2$ were used as starting parameters for $[Mg(Me_3PO)_5]$-

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* To whom correspondence should be addressed.

Table 1. *Positional parameters for* $[\mathrm{Mg(Me_3PO)_5}](\mathrm{ClO_4})_2$

	x	y	z
Non-group atoms			
Mg	0·0808 (7)	0·1151 (2)	0·1447 (6)
P(1)	0·2468 (7)	0·1036 (3)	−0·0946 (6)
P(2)	0·3167 (7)	0·0927 (3)	0·3091 (6)
P(3)	−0·0861 (7)	0·1008 (3)	0·3807 (5)
P(4)	−0·1514 (6)	0·0953 (3)	−0·0240 (6)
P(5)	0·0753 (9)	0·2399 (3)	0·1509 (8)
O(1)	0·136 (2)	0·1003 (7)	−0·026 (2)
O(2)	0·242 (2)	0·0935 (7)	0·198 (2)
O(3)	0·026 (2)	0·1043 (7)	0·313 (2)
O(4)	−0·085 (1)	0·0950 (6)	0·090 (1)
O(5)	0·083 (2)	0·1862 (7)	0·142 (2)
C(11)	0·342 (3)	0·051 (1)	−0·064 (3)
C(12)	0·217 (3)	0·110 (1)	−0·246 (3)
C(13)	0·336 (3)	0·157 (1)	−0·059 (3)
C(21)	0·266 (3)	0·047 (1)	0·417 (3)
C(22)	0·463 (3)	0·078 (1)	0·278 (3)
C(23)	0·315 (3)	0·150 (1)	0·384 (3)
C(31)	−0·165 (4)	0·047 (2)	0·347 (4)
C(32)	−0·047 (3)	0·104 (1)	0·541 (3)
C(33)	−0·192 (4)	0·149 (1)	0·341 (3)
C(41)	−0·120 (3)	0·043 (1)	−0·115 (3)
C(42)	−0·308 (3)	0·092 (1)	0·002 (3)
C(43)	−0·122 (3)	0·150 (1)	−0·114 (3)
C(51)	0·128 (4)	0·262 (2)	0·298 (4)
C(52)	−0·043 (7)	0·263 (3)	0·102 (6)
C(53)	0·193 (5)	0·270 (2)	0·065 (4)
Group atoms			
Cl(1)	0·075 (2)	0·4161 (5)	0·152 (1)
O(11)	−0·017 (7)	0·453 (3)	0·152 (8)
O(12)	0·098 (8)	0·407 (3)	0·031 (3)
O(13)	0·170 (6)	0·438 (4)	0·213 (7)
O(14)	0·025 (7)	0·376 (2)	0·211 (7)
Cl(2)	0·071 (2)	0·2552 (8)	−0·341 (2)
O(21)	0·05 (2)	0·222 (4)	−0·440 (6)
O(22)	−0·044 (6)	0·264 (6)	−0·30 (1)
O(23)	0·143 (8)	0·229 (5)	−0·261 (8)
O(24)	0·13 (1)	0·297 (3)	−0·390 (9)

$(\mathrm{ClO_4})_2$. The perchlorate O atoms appeared disordered or subject to large thermal motions. The perchlorate anions were subsequently treated as tetrahedral rigid groups (Mingos & Ibers, 1970). Refinement with anisotropic thermal parameters for the Mg, five P and three axial C atoms and isotropic thermal parameters for all other atoms yielded an R of 0·133 for 1596 reflections with $|F_o|^2 \geq 2\sigma(|F_o|^2)$. In the final cycle, no parameter underwent shifts $>0·4\sigma$. Table 1 lists the final atomic parameters with their e.s.d.'s. Selected interatomic distances and bond angles are given in Tables 2 and 3.*

Table 2. *Selected interatomic distances* (Å) *in* $[\mathrm{Mg(Me_3PO)_5}](\mathrm{ClO_4})_2$

Mg–O(1)	2·06 (2)	P(1)–O(1)	1·48 (2)
Mg–O(2)	2·00 (2)	P(2)–O(2)	1·51 (2)
Mg–O(3)	2·02 (2)	P(3)–O(3)	1·49 (2)
Mg–O(4)	2·04 (2)	P(4)–O(4)	1·49 (2)
Average	2·03 (3)	Average	1·49 (2)
Mg–O(3)	1·94 (2)	P(5)–O(5)	1·47 (2)
P(1)–C(11)	1·82 (4)	P(2)–C(21)	1·83 (3)
P(1)–C(12)	1·75 (3)	P(2)–C(22)	1·73 (4)
P(1)–C(13)	1·82 (4)	P(2)–C(23)	1·78 (4)
P(3)–C(31)	1·77 (4)	P(4)–C(41)	1·79 (3)
P(3)–C(32)	1·86 (4)	P(4)–C(42)	1·79 (3)
P(3)–C(33)	1·84 (4)	P(4)–C(43)	1·83 (4)
P(5)–C(51)	1·86 (5)		
P(5)–C(52)	1·57 (8)		
P(5)–C(53)	1·84 (5)		

Table 3. *Selected bond angles* (°) *in* $[\mathrm{Mg(Me_3PO)_5}](\mathrm{ClO_4})_2$

Mg–O(1)–P(1)	137·4 (12)	O(5)–Mg–O(1)	100·2 (9)
Mg–O(2)–P(2)	139·2 (12)	O(5)–Mg–O(2)	106·9 (9)
Mg–O(3)–P(3)	138·9 (12)	O(5)–Mg–O(3)	99·5 (9)
Mg–O(4)–P(4)	136·0 (11)	O(5)–Mg–O(4)	105·9 (9)
Mg–O(5)–P(5)	173·7 (16)		
O(1)–Mg–O(2)	86·9 (8)	O(1)–Mg–O(3)	160·3 (8)
O(2)–Mg–O(3)	87·3 (8)	O(2)–Mg–O(4)	147·2 (8)
O(3)–Mg–O(4)	87·9 (8)		
O(4)–Mg–O(1)	86·8 (8)		
O(1)–P(1)–C(11)	110·5 (15)	O(2)–P(2)–C(21)	113·0 (13)
O(1)–P(1)–C(12)	110·9 (13)	O(2)–P(2)–C(22)	111·3 (14)
O(1)–P(1)–C(13)	113·7 (14)	O(2)–P(2)–C(23)	111·9 (14)
O(3)–P(3)–C(31)	112·1 (16)	O(4)–P(4)–C(41)	113·0 (13)
O(3)–P(3)–C(32)	107·1 (14)	O(4)–P(4)–C(42)	110·6 (12)
O(3)–P(3)–C(33)	112·7 (15)	O(4)–P(4)–C(43)	113·2 (14)
O(5)–P(5)–C(51)	111·3 (18)	C(11)–P(1)–C(12)	111·9 (16)
O(5)–P(5)–C(52)	114·8 (28)	C(12)–P(1)–C(13)	104·0 (16)
O(5)–P(5)–C(53)	111·4 (20)	C(13)–P(1)–C(11)	105·6 (16)
C(21)–P(2)–C(22)	106·3 (16)	C(31)–P(3)–C(32)	111·4 (18)
C(22)–P(2)–C(23)	107·7 (17)	C(32)–P(3)–C(33)	110·8 (17)
C(23)–P(2)–C(21)	106·2 (15)	C(33)–P(3)–C(31)	102·8 (19)
C(41)–P(4)–C(42)	104·9 (14)	C(51)–P(5)–C(52)	117·1 (30)
C(42)–P(4)–C(43)	108·0 (16)	C(52)–P(5)–C(53)	104·4 (31)
C(43)–P(4)–C(41)	106·7 (15)	C(53)–P(5)–C(51)	95·9 (22)

Discussion. $[\mathrm{Mg(Me_3PO)_5}](\mathrm{ClO_4})_2$ is isomorphous with $[M(\mathrm{Me_3AsO})_5](\mathrm{ClO_4})_2$ (M = Ni, Mg) (Ng, Rodley & Robinson, 1976). A stereoscopic view of the packing of the ions in the unit cell is presented in Fig. 1. A perspective view of the five-coordinate square-pyramidal cation is given in Fig. 2 and defines the atom labelling.

The four basal Mg–O distances lie in the range 2·00 (2)–2·06 (2) Å. This variation probably reflects the poor quality of the data set. In view of the close similarity of the environment of each basal ligand, little significance should be attached to this variation. However, the presence of a considerably shorter axial

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33372 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

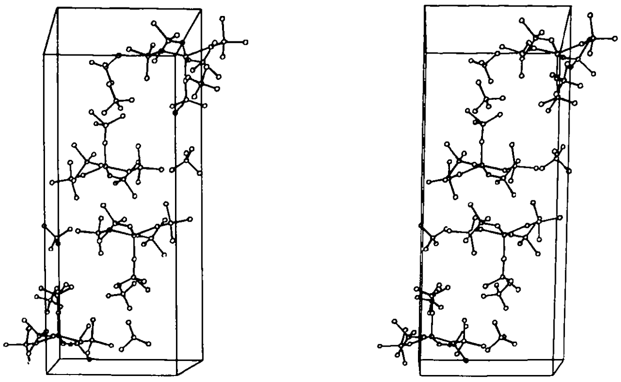

Fig. 1. Stereoscopic view of the packing of $[Mg(Me_3PO)_5](ClO_4)_2$ in the crystal looking down **b**.

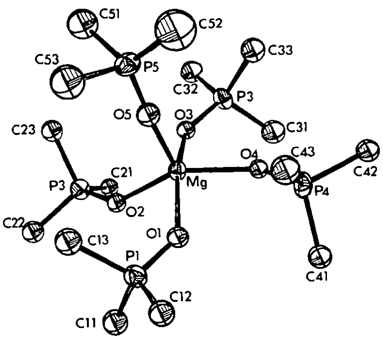

Fig. 2. Perspective view of the cation in the complex $[Mg(Me_3PO)_5](ClO_4)_2$.

Mg—O bond, 1·94 (2) Å, provides further evidence for the possibility of multiple bonding in the axial direction of five-coordinate Mg complexes. $[Mg(Me_3AsO)_5]^{2+}$ and $[Ni(Me_3AsO)_5]^{2+}$ reveal the same feature [M—O_{axial} = 1·92 (1) and 1·94 (2) Å, M—O_{basal} = 2·03 (2) and 2·00 (1) Å for M = Mg and M = Ni] (Ng, Rodley & Robinson, 1976).

The average basal Mg—O—P angle is 137·9°, of similar magnitude to that found for $[Mg(Me_3PO)_5H_2O]^{2+}$ (see previous paper), while that of the axial group is 173·7°. Deviations of O(5) and P(5) from the vector perpendicular to the basal plane are 0·01 and 0·04 Å respectively. The large axial angle provides further evidence for Mg—O axial π bonding, as a linear geometry would facilitate maximum overlap of $p\pi$ orbitals of Mg and O.

Although the geometry for $[Mg(Me_3PO)_5]^{2+}$ is not as well defined as for $[M(Me_3AsO)_5]^{2+}$ (M = Ni, Mg), all three structures are similar: a shorter M—O axial bond and the planarity of the basal ligands are retained on changing the central atom (Ni → Mg) and the penultimate ligand atom (As → P). In a previous discussion on steric effects it was suggested that the size of the As atom might be a factor in blocking the entry of a sixth ligand (Hunter, Emerson & Rodley, 1969). The present results on the formation of a five-coordinate square-pyramidal structure with phosphine oxide reveal that size [covalent radii: As = 1·21 and P = 1·1 Å (Cotton & Wilkinson, 1972)] is not the crucial factor in promoting five-coordination in these systems. If steric repulsion between the ligands were dominant, the larger As atom would produce greater interligand steric repulsion. A consequence of this might be, for example, a more linear Mg—O—As angle. However, the results show the reverse effect. The Mg—O—P angle is 173·7 whereas the Mg—O—As angle is 163·8°.

The structures of the five-coordinate complexes of the type reported here reveal a consistent and interpretable pattern. As reported earlier (Ng, Rodley & Robinson, 1976), the basic square-pyramidal geometry appears to be stabilized to a large extent by electrostatic interligand interactions amongst the basal groups. But another feature also appears to be important. Relatively strong axial coordination by one group, facilitated by the π-bonding properties of the ligands, appears to satisfy the axial binding requirements of the metal ion. This is indicated by the significant lengthening which occurs with the formation of a six-coordinate species where the axial binding potential of the metal is shared between two ligands {*e.g.* $[Mg(Me_3PO)_5H_2O]^{2+}$ in the previous paper}. Our investigation therefore shows that electronic and interligand electrostatic interactions are of prime importance in the formation of complexes of this type.

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