Acta Cryst. (1988). C**44**, 365–367

Structure of $[Mg\{HO_3PCH(C_6H_5)_2\}_2].8H_2O$, a Layered Phosphonate Salt

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(*Received* 14 *July* 1987; *accepted* 7 *October* 1987)

Abstract. Bis(hydrogen diphenylmethylphosphonato)-magnesium octahydrate, $[Mg(C_{13}H_{12}O_3P)_2].8H_2O$, $M_r = 662.85$, triclinic, $P\bar{1}$, $a = 6.1051\,(15)$, $b = 8.8308\,(14)$, $c = 15.312\,(3)$ Å, $\alpha = 78.514\,(13)$, $\beta = 83.993\,(11)$, $\gamma = 75.772\,(15)°$, $V = 782.8\,(3)$ Å^3, $Z = 1$, $D_x = 1.41$ g cm^{-3} (163 K), Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.171$ cm^{-1}, $F(000) = 350$, $T = 163$ K, $R = 0.0351$ for 3749 reflections $[F_o \geq 4\sigma(F_o)]$. The structure consists of alternating polar and nonpolar layers stacked along the crystallographic c axis. The polar layers contain $Mg(H_2O)_6^{2+}$ ions, water of hydration and the phosphonate O atoms, and the nonpolar layers contain the benzhydryl groups. Two-dimensional hydrogen-bonding networks link $Mg(H_2O)_6^{2+}$ and the water of hydration to the phosphonate O atoms. The shortest hydrogen bonds in the structure, 1.68 (2) Å, connect the P—OH H atom and the water of hydration. Slightly longer contacts [1.79 (2), 1.85 (2), 1.91 (2), 1.92 (2) Å] connect the phosphonate O atoms (O1 and O3) to the H atoms of the $Mg(H_2O)_6^{2+}$ group. The coordination environment of the Mg atom is a very nearly regular octahedron of water O atoms.

Experimental. The compound was made by the reaction of $MgSO_4$ and $(C_6H_5)_2CHPO(OH)_2$ in 50% aqueous ethanol at 330 K. The pH was adjusted to 4.0 with NaOH to give a white crystalline precipitate. Data crystal was a clear, colorless plate of approximate dimensions $0.12 \times 0.25 \times 0.39$ mm, grown hydrothermally from 50% aqueous ethanol. Syntex $P2_1$ diffractometer, graphite monochromator, Syntex LT-1 low-temperature delivery system (163 K). Lattice parameters from least-squares refinement of 60 reflections with $19.9 < 2\theta < 36.9°$. ω-scan technique (4969 reflections, 4571 unique, $R_{\rm int} = 0.0156$; h 0→8, k −12→12, l −21→21), 2θ range 4.0–60.0°, 1° ω scan at 3–6° min^{-1}. Four reflections (121, 00$\bar{5}$, 211, $\bar{1}\bar{1}$2) were remeasured every 96 reflections to monitor instrument and crystal stability (maximum correction on $I < 0.5\%$; Henslee & Davis, 1975). Data also corrected for Lp effects and absorption (based on crystal shape; transmission-factor range 0.8791–0.9476). Data reduction described in Riley & Davis (1976). 822 reflections having $F_o < 4\sigma(F_o)$ considered unobserved. Structure solved by the heavy-atom method and refined by full-matrix least-squares procedures (Sheldrick, 1976) with anisotropic thermal parameters for the non-H atoms. By symmetry, Mg forced to lie on an inversion center. H-atom positions from a ΔF map and refined with isotropic thermal parameters. 276 parameters refined. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$. Intensity, I, given by $(I_{\rm peak} - I_{\rm background})$(scan rate), 0.02 is a factor to downweight intense reflections and to account for instru-

Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2) *for atoms of* $[Mg\{HO_3PCH(C_6H_5)_2\}_2].8H_2O$

For non-H atoms, the U value is $U_{\rm eq}$ calculated as $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	U
Mg	0.5	0.5	0.0	0.0144 (2)
P1	0.25316 (6)	0.04283 (4)	0.15064 (2)	0.01226 (10)
O1	0.1286 (2)	0.17319 (11)	0.08044 (6)	0.0159 (3)
O2	0.2333 (2)	0.12529 (11)	0.13593 (7)	0.0172 (3)
O3	0.4998 (2)	0.03775 (11)	0.15406 (6)	0.0163 (3)
O4	0.4354 (2)	0.38243 (13)	−0.09596 (7)	0.0203 (3)
O5	0.6716 (2)	0.28691 (12)	0.06753 (7)	0.0203 (3)
O6	0.2013 (2)	0.46924 (13)	0.07083 (7)	0.0187 (3)
O7	0.1400 (2)	0.16585 (12)	−0.09587 (8)	0.0184 (3)
C1	0.0980 (2)	0.0714 (2)	0.25682 (9)	0.0142 (4)
C2	0.0972 (2)	0.2356 (2)	0.27418 (9)	0.0147 (4)
C3	0.2890 (3)	0.2674 (2)	0.30229 (10)	0.0204 (5)
C4	0.2859 (3)	0.4193 (2)	0.31582 (11)	0.0259 (5)
C5	0.0933 (3)	0.5406 (2)	0.30169 (11)	0.0265 (5)
C6	0.0973 (3)	0.5097 (2)	0.27430 (10)	0.0238 (5)
C7	0.0956 (3)	0.3578 (2)	0.26028 (10)	0.0191 (4)
C8	0.1675 (3)	−0.0596 (2)	0.33685 (9)	0.0174 (4)
C9	0.0001 (3)	−0.0962 (2)	0.40083 (10)	0.0244 (5)
C10	0.0538 (4)	−0.2122 (2)	0.47634 (11)	0.0332 (6)
C11	0.2746 (4)	−0.2919 (2)	0.48889 (11)	0.0357 (7)
C12	0.4439 (4)	−0.2571 (2)	0.42652 (12)	0.0330 (6)
C13	0.3910 (3)	−0.1408 (2)	0.35031 (11)	0.0243 (5)
HO2	0.102 (4)	−0.133 (2)	0.1217 (14)	0.052 (7)
HO4*A*	0.323 (4)	0.359 (3)	0.101 (2)	0.056 (8)
HO4*B*	0.537 (4)	0.304 (3)	−0.107 (2)	0.059 (7)
HO5*A*	0.808 (4)	0.251 (2)	0.0747 (12)	0.032 (5)
HO5*B*	0.609 (4)	0.205 (2)	0.0964 (14)	0.047 (6)
HO6*B*	0.164 (4)	0.378 (3)	0.0768 (14)	0.052 (7)
HO6*A*	0.171 (4)	0.491 (2)	0.1187 (13)	0.040 (6)
HO7*A*	0.266 (4)	0.101 (2)	−0.1145 (14)	0.046 (6)
HO7*B*	0.136 (4)	0.159 (2)	−0.0459 (14)	0.040 (6)
H1	0.056 (3)	0.072 (2)	0.2453 (10)	0.010 (4)
H3	0.421 (3)	0.185 (2)	0.3110 (11)	0.025 (5)
H4	0.413 (3)	0.442 (2)	0.3368 (12)	0.033 (5)
H5	0.087 (3)	0.645 (2)	0.3120 (12)	0.036 (5)
H6	0.233 (3)	0.585 (2)	0.2672 (12)	0.029 (5)
H7	−0.230 (3)	0.340 (2)	0.2388 (10)	0.015 (4)
H9	−0.152 (3)	−0.044 (2)	0.3918 (11)	0.024 (5)
H10	−0.069 (3)	−0.233 (2)	0.5186 (12)	0.032 (5)
H11	0.315 (3)	−0.373 (2)	0.5427 (12)	0.036 (5)
H12	0.593 (3)	−0.311 (2)	0.4354 (12)	0.029 (5)
H13	0.514 (3)	−0.119 (2)	0.3075 (11)	0.028 (5)

0108-2701/88/020365-03$03.00

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Table 2. *Bond lengths* (Å) *and angles* (°) *for non*-H *atoms of* $[Mg\{HO_3PCH(C_6H_5)_2\}_2]_2.8H_2O$

1	2	3	1–2	1–2–3
O4	Mg	O5	2·079 (1)	89·06 (5)
O5	Mg	O6	2·047 (1)	90·60 (4)
O6	Mg	O4	2·070 (1)	90·14 (5)
O4	Mg	O4*		180·0
O4	Mg	O5*		90·94 (5)
O4	Mg	O6*		89·86 (5)
O5	Mg	O5*		180·0
O5	Mg	O6*		89·40 (4)
O6	Mg	O6*		180·0
O1	P1	O2	1·519 (1)	110·33 (6)
O2	P1	O3	1·580 (1)	107·80 (6)
O3	P1	O1	1·502 (1)	115·19 (6)
C1	P1	O1	1·824 (1)	105·84 (6)
C1	P1	O2		105·66 (6)
C1	P1	O3		111·63 (7)
C2	C1	C8	1·525 (2)	112·7 (1)
C8	C1	P1	1·524 (2)	116·32 (9)
C2	C1	P1		109·32 (9)
C3	C2	C7	1·396 (2)	118·9 (1)
C3	C2	C1		121·2 (1)
C7	C2	C1	1·390 (2)	119·9 (1)
C4	C3	C2	1·393 (2)	120·2 (1)
C5	C4	C3	1·385 (2)	120·6 (2)
C6	C5	C4	1·381 (3)	119·4 (2)
C7	C6	C5	1·398 (2)	120·4 (1)
C2	C7	C6		120·5 (2)
C9	C8	C13	1·392 (2)	118·5 (1)
C9	C8	C1		118·3 (1)
C13	C8	C1	1·392 (2)	123·1 (1)
C10	C9	C8	1·392 (2)	120·9 (2)
C11	C10	C9	1·373 (3)	120·1 (2)
C12	C11	C10	1·381 (3)	120·0 (1)
C13	C12	C11	1·400 (2)	120·2 (2)
C8	C13	C12		120·2 (2)

* Atoms related by $1-x$, $1-y$, $-z$.

Table 3. H-*bonding interactions for* $[Mg\{HO_3PCH(C_6H_5)_2\}_2].8H_2O$

1	2	3	1–2	1–3	1–2–3
$O7^{i}$	HO2	O2	1·67 (2) Å	2·546 (2) Å	175 (2)°
O7	HO4*A*	O4	2·24 (2)	2·934 (2)	148 (2)
$O2^{ii}$	HO4*B*	O4	1·93 (2)	2·768 (2)	178 (2)
$O1^{iii}$	HO5*A*	O5	1·91 (2)	2·738 (2)	175 (2)
O3	HO5*B*	O5	1·80 (2)	2·717 (2)	177 (2)
O1	HO6*B*	O6	1·86 (2)	2·731 (2)	171 (2)
$O3^{iii}$	HO7*A*	O7	1·78 (2)	2·674 (2)	175 (2)
O1	HO7*B*	O7	1·96 (2)	2·707 (2)	172 (2)

Symmetry operations: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $1+x, y, z$.

ment instability, and k is the correction due to Lp effects, absorption and decay. $\sigma(I)$ estimated from counting statistics; $\sigma(I) = [(I_{\rm peak} + I_{\rm background})^{1/2}({\rm scan\ rate})]$. Final $R = 0{\cdot}0351$ for 3749 reflections, $wR = 0{\cdot}0357$ ($R = 0{\cdot}0484$, $wR = 0{\cdot}0366$ for all reflections) and a goodness of fit = 1·758. Maximum $|\Delta/\sigma| < 0{\cdot}1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were −0·31 and 0·51 e Å^{-3} (near P). Scattering factors for the non-H atoms from Cromer & Mann (1968), with anomalous-dispersion corrections from Cromer & Liberman (1970), and scattering factors for the H atoms from Stewart, Davidson & Simpson (1965); linear absorption coefficient from *International Tables for X-ray Crystallography* (1974).* Positional and thermal parameters for the non-H atoms are listed in Table 1, and the bond lengths and angles for the non-H atoms are listed in Table 2. Hydrogen-bonding details are in Table 3. The atom-labeling scheme is shown in Fig. 1. Fig. 2 is a packing diagram. The least-squares-planes program was supplied by Cordes (1983); other computer programs from reference 11 of Gadol & Davis (1982).

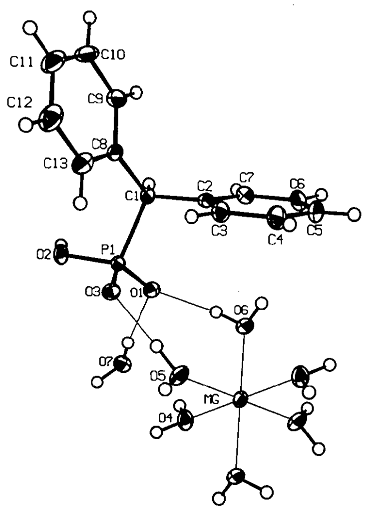

Fig. 1. *ORTEP* (Johnson, 1965) view of the asymmetric formula unit and atom-labeling scheme.

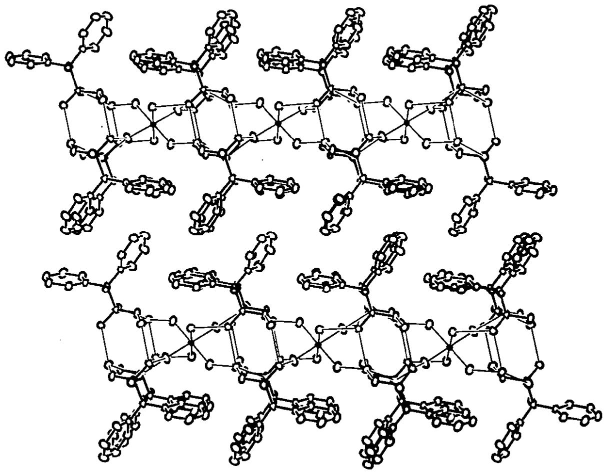

Fig. 2. Packing diagram of $[Mg\{HO_3PCH(C_6H_5)_2\}_2].8H_2O$. Hydrogen bonds are indicated as narrow lines. View down the a axis; c is the stacking axis.

Related literature. Many layered transition-metal phosphonate salts based on the $Zr(HPO_4)H_2O$ and $VO(HPO_4).0{\cdot}5H_2O$ parent structures are known (Alberti, Constantino, Alluli & Tomassini, 1978; Dines

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* Lists of anisotropic thermal parameters, bond lengths and angles involving H atoms, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44428 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& DiGiacomo, 1981; Dines, Cooksey, Griffith & Lane, 1983; Johnson, Jacobsen, Brody & Lewandowski, 1984), but no divalent metal phosphonates based on the layered $Mg(HPO_4).3H_2O$ (Abbona, Boistelle & Hauser, 1979) structure have been reported. Our finding that these compounds can be prepared on surfaces as thin multilayer films (Lee, Kepley, Hong, Cao & Mallouk, 1987) motivated a systematic study of the reactions of soluble Mg, Ca and Mn salts with alkyl- and arylphosphoric acids (Cao, Lee, Lynch & Mallouk, 1987) in which crystalline layered compounds of formula $M(O_3PR).H_2O$ and $M(HO_3PR)_2$ were found.

Funding for this project was provided by the Texas Advanced Technology Research Program, the Robert A. Welch Foundation, and the National Institutes of Health (GM 31077).

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Acta Cryst. (1988). C**44**, 367–369

Structure of a Complex of Palladium(II) Chloride and 5-Phenoxy-1-phenyltetrazole Co-crystallized with 1,2-Dichloroethane Solvent

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(*Received* 22 *July* 1987; *accepted* 9 *October* 1987)

Abstract. $[PdCl_2(C_{13}H_{10}N_4O)_2].C_2H_4Cl_2$, $M_r = 752\cdot75$, monoclinic, $P2_1/c$, $a = 10\cdot151$ (2), $b = 9\cdot695$ (3), $c = 17\cdot186$ (4) Å, $\beta = 104\cdot86$ (2)°, $V = 1703$ (1) Å^3, $Z = 2$, $D_m = 1\cdot55$, $D_x = 1\cdot57$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 41$ cm^{-1}, $F(000) = 780$, $T = 293$ K, $R = 0\cdot058$ for 2207 unique observed reflections with $F > 1\cdot5\sigma(F)$. The complex crystallizes with a molecule of 1,2-dichloroethane solvent. Each Pd atom is bound to two *trans* Cl atoms and, coordinatively, to the N(3) atom in each of the two tetrazolyl rings to form a square-planar structure. The Pd—N(3) bonds lie in the planes of the coordinated tetrazolyl rings.

Experimental. Compound obtained by addition of 5-phenoxy-1-phenyltetrazole to solution of bis(benzonitrile)palladium(II) chloride in dichloromethane. Crystals obtained by slow diffusion of pentane into a solution of this complex in 1,2-dichloroethane. Cuboid *ca* 0·30 mm in edge mounted in glass capillary. Density measured by flotation in a mixture of tetrachloromethane and hexane. Intensities measured by SERC service with an Enraf–Nonius CAD-4 diffractometer and ω–2θ scans. Unit cell determined from least-squares analysis of angle data for 25 reflections with $6 < \theta < 19°$. Data collected to $(\sin\theta)/\lambda$ of 0·59 Å^{-1},

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