# Magnesium Ion Binding to *myo*-Inositol: The Crystal Structure of *myo*-Inositol–Magnesium Chloride–Hydrate (1:1:4)

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The crystal structure of the complex *myo*-inositol-magnesium chloride-water (1:1:4) was studied as a model system for the carbohydrate-cation association. The complex crystallizes in the monoclinic space group  $P_{2_1/c}$ ,  $a = 12 \cdot 175$  (5),  $b = 7 \cdot 643$  (1),  $c = 16 \cdot 062$  (6) Å,  $\beta = 96 \cdot 68^{\circ}$  (1) with Z = 4. The magnesium is coordinated to two *cis*-vicinal hydroxyl groups of inositol and four water molecules in an octahedral geometry. As a consequence of the cation binding, the cyclohexane ring geometry in the vicinity of the coordination site is distorted. Deviations of nearly 15° from the normal occur in some torsion angles. Structural features of the complex are discussed with regard to metal ion binding to phosphoinositides.

#### Introduction

The transmission of nerve messages and changes in vesicular membrane structure can be depicted as processes based on stereospecific structural events accompanying the alternate binding of calcium and magnesium ions at anionic sites of membranes (Williams, 1970). Both mono- and polyphosphoinositides are constituents of the nerve myelin sheath (Dawson & Eichberg, 1965) and membrane systems of various tissues (Hawthorne & Michell, 1966). Phosphoinositides play a role in mitochondrial swelling (Vignais, Vignais & Lehninger, 1963) and the polyphosphoinositides may participate in ion transport across membranes (Galliard & Hawthorne, 1963; Hendrickson & Reinertsen, 1969). It has been suggested that the hydroxyl groups of the inositol moiety might act as secondary ligating sites for alkaline-earth metal ions (Hendrickson & Reinertsen, 1969).

Complexes between cyclitols and alkaline-earth metal ions are known to exist in solution (Angyal & Davies, 1971), (reviewed by Rendleman, 1966), and crystalline complexes have been prepared with myoinositol (Bugg, & Cook 1972; Windaus, 1907). The ability of myo-inositol to form such complexes is particularly relevant to its presence in phospholipids in view of the report that complexing of calcium with inositol is accompanied by conformational changes in the polyhydroxy moiety (Bugg & Cook, 1972). Precise data on the stereochemical features of complexes with other ions is pertinent to the understanding of the suspected role of this cyclitol as a lipid constituent active in ion transport and binding. A study of a complex between the magnesium ion and myo-inositol was therefore undertaken.

# Experimental

Equimolar amounts (2 mmoles) of *myo*-inositol and magnesium chloride hexahydrate were dissolved in

2 ml of an aqueous solution (saturated at 25°C with respect to both components) by heating. The cooled solution yielded large prismatic crystals, m.p. 140– 142°C. Crystallographic examination determined the composition to be a 1:1 complex with four molecules of hydration. Elemental analysis exhibited error attributable to the hygroscopic nature of the crystals (C<sub>6</sub>H<sub>20</sub>O<sub>10</sub>. MgCl<sub>2</sub> requires: Cl, 20·40%, found: Cl, 20·00%). Crystal data for the monoclinic crystals are: space group  $P2_1/c$ ,  $a=12\cdot175$  (5),  $b=7\cdot643$  (1), c= $16\cdot062$  (6) Å,  $\beta=96\cdot68^{\circ}$  (1),  $D_m=1\cdot55$  g cm<sup>-3</sup> (by flotation in dibromomethane: chloroform)  $D_c=1\cdot56$  g cm<sup>-3</sup> for Z=4,  $V=1484\cdot4$  Å<sup>3</sup>; Cu K $\alpha$ ,  $\lambda=1\cdot5418$  Å,  $\mu=$  $47\cdot5$  cm<sup>-1</sup>.

A crystal was sealed in a glass capillary and the intensities were collected on a Picker FACS-1 automatic diffractometer by  $\theta/2\theta$  scans at 2°/min using monochromatic Cu  $K\alpha$  radiation (graphite monochromator). Background counts of 20 sec with both crystal and counter stationary were taken at the beginning and end of each scan. For the 2433 independent reflections measured for  $2\theta \le 127^\circ$ , 193 had intensities less than the average intensity of those reflections absent due to space-group extinction and were designated unobserved. Three standard reflections monitored periodically indicated that the complex had undergone negligible degradation during the data collection (0.4%)change). Following corrections for background and Lorentz-polarization, the intensities were reduced to structure amplitudes (FACS-1, 1972). No corrections were applied for absorption or extinction. An approximate absolute scale was obtained from a Wilson plot (Shiono, 1969).

The structure was solved by the direct method using the program *MULTAN* (Germain, Main & Woolfson, 1971). The successful set of starting phases which led to the correct structure was as follows:  $65\overline{2}$ , |E| = 3.73,  $\varphi = 0$ ;  $42\overline{5}$ , |E| = 3.31,  $\varphi = 0$ ; 339, |E| = 3.26,  $\varphi = 0$ ;  $25\overline{2}$ , |E| = 2.72,  $\varphi = 0$ ; 212, |E| = 2.67,  $\varphi = 0$ ;  $8.0,\overline{10}$ , |E| =2.31,  $\varphi = \pi$ ; 127, |E| = 2.30,  $\varphi = 0$ . Phases for the 190 Table 1. Atomic positional and thermal parameters for the complex myo-inositol-magnesium chloride-hydrate

All x, y and z parameters have been multiplied by  $10^4$  for the non-hydrogen atoms and  $10^3$  for hydrogens. The standard deviation of the least significant figure is in parentheses.

	x	у	Z
<b>Cl</b> (1)	251 (1)	6463 (1)	6764 (1)
Cl(2)	4920 (1)	6341 (1)	6119 (1)
Mg	2564 (1)	1588 (2)	6363 (1)
O(W1)	4069 (2)	1875 (5)	7041 (2)
O(W2)	2277 (3)	-705(5)	6965 (2)
O(W3)	2764 (3)	4033 (5)	5834 (2)
O(W4)	1526 (3)	2808 (5)	7086 (2)
$\tilde{O}(1)$	1314 (2)	857 (4)	5420 (2)
O(2)	3389 (2)	430 (4)	5391 (2)
O(3)	4461 (2)	-108 (4)	3978 (2)
O(4)	3617 (2)	- 3264 (4)	3341 (2)
O(5)	1964 (2)	- 4825 (4)	4232 (2)
O(6)	502 (2)	-2581(4)	4937 (2)
C(1)	1621 (3)	-30(5)	4701 (2)
<b>C</b> (2)	2779 (3)	580 (5)	4578 (2)
C(3)	3303 (3)	- 495 (5)	3932 (2)
C(4)	3206 (3)	-2462 (5)	4045 (2)
C(5)	2015 (3)	- 2965 (5)	4112 (2)
C(6)	1600 (3)	- 2008 (5)	4845 (3)
H(1)	110 (4)	24 (6)	416 (3)
H(2)	276 (4)	175 (7)	444 (3)
H(3)	296 (4)	-15 (6)	335 (3)
H(4)	368 (4)	- 283 (6)	466 (3)
H(5)	161 (4)	- 259 (6)	354 (3)
H(6)	212 (4)	-239 (6)	541 (3)
H(O1)	140 (4)	74 (6)	585 (3)
H( <i>O</i> 2)	337 (4)	41 (6)	582 (3)
H(O3)	454 (4)	113 (6)	391 (3)
H( <i>O</i> 4)	340 (4)	- 349 (7)	280 (3)
H(05)	194 (3)	- 481 (6)	495 (3)
H( <b>0</b> 6)	53 (4)	- 289 (6)	551 (3)
H(1W1)	428 (4)	183 (6)	762 (3)
H(1W2)	214 (5)	- 77 (8)	666 (3)
H(2W2)	269 (4)	-105(6)	746 (3)
H(1W3)	264 (4)	425 (6)	536 (3)
H(2W3)	280 (5)	371 (7)	621 (3)
H(1W4)	134 (4)	348 (7)	698 (3)

The form of the temperature factor expression was

 $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$ 

All  $\beta_{ij}$  have been multiplied by 10<sup>4</sup>. The isotropic parameters of the hydrogen atoms was 1.500.

	$\beta_{11}$	β22	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl(1)	42 (1)	124 (2)	26 (0)	-9(1)	11 (0)	-4(1)
Cl(2)	60 (1)	97 (2)	29 (0)	-6(1)	-13(0)	4 (1)
Mg	29 (1)	91 (3)	13 (0)	1 (1)	4 (1)	0 (1)
O(W1)	38 (2)	205 (7)	19 (1)	-10(3)	0(1)	4 (2)
O(W2)	55 (3)	152 (7)	23 (1)	-17 (3)	-5(2)	22 (3)
O(W3)	60 (3)	115 (6)	22 (1)	-10(3)	1 (2)	14 (2)
O(W4)	70 (3)	122 (7)	39 (2)	24 (3)	25 (2)	8 (3)
O(1)	33 (2)	130 (6)	15(1)	13 (3)	2 (1)	-7(2)
O(2)	30 (2)	140 (6)	13 (1)	4 (2)	2 (1)	-4 (2)
O(3)	29 (2)	104 (6)	28 (1)	-1 (2)	9 (1)	2 (2)
O(4)	46 (2)	117 (5)	19 (1)	8 (3)	10 (1)	-8 (2)
O(5)	43 (2)	82 (5)	27 (1)	-4 (3)	2 (1)	0 (2)
O(6)	25 (2)	129 (6)	27 (1)	1 (3)	6 (1)	6 (2)
C(1)	21 (2)	91 (7)	15 (1)	12 (3)	-2(1)	0 (2)
C(2)	31 (3)	71 (7)	15(1)	2 (3)	2 (1)	2 (2)
C(3)	26 (2)	90 (7)	13 (1)	-1(3)	2 (1)	2 (2)
C(4)	26 (3)	73 (6)	13 (1)	2 (3)	2 (1)	0 (2)
C(5)	27 (2)	81 (7)	17 (1)	0 (3)	2 (1)	0 (2)
C(6)	18 (2)	103 (7)	17 (1)	-1(3)	2 (1)	1 (2)

reflections with  $|E| \ge 1.77$  were generated from this starting set. These phased E factors were used as coefficients in the calculation of an E map (Karle, Hauptman, Karle & Wing, 1958), and all non-hydrogen atoms were identified. The non-hydrogen atom structure was refined by the full-matrix least-squares procedure (Shiono, 1966) to an R ( $R = \sum ||F_{meas}| - |F_{calc}||/$  $\sum |F_{meas}|$ ) of 0.10. Hydrogen atoms were located from a difference Fourier map, and assigned a thermal parameter comparable to that of the atom to which they were bonded. Positions for one of the pair of hydrogen atoms for water molecules O(W1) and O(W4) could not be determined. Thirteen reflections affected by extinction were removed from the refinement;

#### Table 2. Structure factors

Listed are l,  $10|F_o|$ ,  $10A_c$ . Unobserved reflections or reflections affected by extinction as noted in the text are marked (\*).

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all had  $|F_0| > 30:002,004,011,012,013,021,022,023,025,026,031,104, and 402. In the final refinement the data were weighted according to the function suggested by Cruickshank$ *et al.* $(1961), <math>w = [a+b(F_o) + c(F_o)^2]^{-1}$ , a = 0.7, b = 0.14, c = 0.005, and all parameters but the thermal parameters for hydrogen atoms were refined to an *R* of 0.073. Positional and thermal parameters are presented in Table 1. The final structure factors are listed in Table 2.

The weighted mean value of bond lengths and angles were calculated using formulae described by Hamilton (1964).

#### **Results and discussion**

The complex was found to be composed of *myo*-inositol, magnesium chloride and water in the molar ratio (1:1:4). *myo*-Inositol, calcium bromide and water have been crystallized in a 2:1:5 ratio (Bugg & Cook, 1972). While this difference in the ratio of cyclitol to alkalineearth metal is a reflection of differences in metal ion properties and bonding modes in the solid state, both 2:1 and 1:1 carbohydrate-alkaline-earth metal complexes may exist in solution (Kamaiah & Vishnu, 1959). Therefore, the crystallized form probably does not represent the only bonding mode or stoichiometry for a particular cation.

The structure of one molecular unit is shown in Fig. 1. Prominent features of the complex include: the coordination of the magnesium ion to the *cis* vicinal hydroxyl oxygens at positions (1) and (2) and four water molecules in an octahedral geometry, the absence of bonds between the halide ions and the metal ion, and hydrogen bonding of the halide ions to the cyclitol.

The bond distances and angles for the *myo*-inositol molecule are given in Table 3. The C-C and C-O bond distances agree with those found by Rabinowitz & Kraut (1964) for *myo*-inositol. However, several bond angles are distorted from a tetrahedral arrangement and reflect strain introduced by the coordinated metal ion. As a consequence of magnesium bonding, the intramolecular  $O_{eq}(1)$  to  $O_{ax}(2)$  distance is shortened 0.334 Å and that for  $O_{eq}(3)$  to  $O_{ax}(2)$ , 0.109 Å, from a normal value of 2.887 (2) Å (Rabinowitz & Kraut, 1964). The decrease in the C-C-O angles for the C(1)-C(2) bond could be a manifestation of the magnesium ion attraction for the hydroxyls.

# Table 3. Distances and angles between bonded atoms of complexed myo-inositol

The standard deviations of the least significant figures are in parentheses.

<b>A</b> )		
1.430 (5)	O(6)-H(O6)	0.95 (5)
1.437 (5)	O(5)-H(O5)	1.15 (4)
1.426 (5)	O(4) - H(O4)	0.90 (5)
1.434 (5)	O(3) - H(O3)	0.96 (5)
1.430 (5)	O(2) - H(O2)	0.70 (5)
1.427 (5)	O(1)-H(O1)	0.69 (5)
1.521 (5)	C(6) - H(6)	1.08 (4)
1.530 (5)	C(5) - H(5)	1.03 (4)
1.517 (5)	C(4) - H(4)	1.13 (4)
1.521(5)	C(3)-H(3)	1.02 (4)
1.520 (5)	C(2) - H(2)	0.92 (5)
1.520 (5)	C(1) - H(1)	1.04 (4)
	1 · 430 (5) 1 · 437 (5) 1 · 426 (5) 1 · 430 (5) 1 · 430 (5) 1 · 427 (5) 1 · 521 (5) 1 · 530 (5) 1 · 517 (5) 1 · 520 (5) 1 · 520 (5)	$\begin{array}{c} 1.430 (5) \\ 1.437 (5) \\ 1.437 (5) \\ 0.(5)-H(O5) \\ 1.426 (5) \\ 0.(4)-H(O4) \\ 1.434 (5) \\ 0.(3)-H(O3) \\ 1.430 (5) \\ 0.(2)-H(O2) \\ 1.427 (5) \\ 0.(1)-H(O1) \\ 1.521 (5) \\ 0.(6)-H(6) \\ 1.530 (5) \\ 0.(5)-H(5) \\ 1.517 (5) \\ 0.(4)-H(4) \\ 1.521 (5) \\ 0.(3)-H(3) \\ 1.520 (5) \\ 0.(2)-H(2) \\ 1.520 (5) \\ 0.(1)-H(1) \end{array}$



Fig. 1. A stereoscopic view (Johnson, 1965) of the myo-inositol-magnesium chloride-hydrate complex with thermal ellipsoids scaled at 50% probability.

## Table 3 (cont.)

(U) Angles ()			
O(6) - C(6) - C(1)	110.5 (3)	C(6)-C(5)-H(5)	113 (3)
O(6) - C(6) - C(5)	109.4 (3)	C(4) - C(5) - H(5)	104 (2)
O(5)-C(5)-C(6)	110.4 (3)	O(5) - C(5) - H(5)	112 (3)
O(5) - C(5) - C(4)	108.5 (3)	C(5) - C(4) - H(4)	106 (2)
O(4) - C(4) - C(5)	112.0 (3)	C(3) - C(4) - H(4)	109 (2)
O(4) - C(4) - C(3)	107.0 (3)	O(4) - C(4) - H(4)	113 (2)
O(3) - C(3) - C(4)	106.7 (3)	C(4) - C(3) - H(3)	109 (3)
O(3)-C(3)-C(2)	110.0 (3)	C(2)-C(3)-H(3)	110 (3)
O(2)-C(2)-C(3)	111.4 (3)	O(3) - C(3) - H(3)	107 (3)
O(2)-C(2)-C(1)	104.3 (3)	C(3)-C(2)-H(2)	112 (3)
O(1)-C(1)-C(2)	107.1 (3)	C(1)-C(2)-H(2)	110 (3)
O(1)-C(1)-C(6)	109.7 (3)	O(2)-C(2)-H(2)	107 (3)
C(1)-C(6)-C(5)	110.2 (3)	C(2)-C(1)-H(1)	109 (2)
C(6) - C(5) - C(4)	109.9 (3)	C(6) - C(1) - H(1)	108 (2)
C(5)-C(4)-C(3)	110.3 (3)	O(1)-C(1)-H(1)	113 (2)
C(4)-C(3)-C(2)	114.2 (3)	C(6) - O(6) - H(O6)	104 (3)
C(3)-C(2)-C(1)	113.1 (3)	C(5) - O(5) - H(O5)	98 (2)
C(2)-C(1)-C(6)	110.9 (3)	C(4) - O(4) - H(O4)	139 (6)
C(1)-C(6)-H(6)	112 (2)	C(3) - O(3) - H(O3)	109 (3)
C(5)-C(6)-H(6)	108 (2)	C(2)-O(2)-H(O2)	147 (4)
O(6) - C(6) - H(6)	107 (2)	C(1) - O(1) - H(O1)	136 (4)

To minimize individual bond-angle deviations, torsional alterations about C(1)-C(2) and adjacent bonds contribute to the spatial displacement of O(1)and O(2) necessary for their accommodation in the magnesium coordination geometry. The torsion angles for bond C(1)-C(2) are given in Table 4 and differ by as much as 14° from those of *myo*-inositol. While the primary effects of the molecular association are on the geometries of C(1) and C(2), the stereochemical arrangements of atoms bonded to C(3) and C(6) show differences from uncomplexed *myo*-inositol primarily in their respective torsion angles, see Table 4. The non-bonded distance between vicinal diequatorial oxygen atoms in *myo*-inositol is 2.841 (1) Å (Rabinowitz & Kraut, 1964). In this complex the  $O_{eq}(3) \cdots O_{eq}(4)$ distance is reduced to 2.770 (4) Å and  $O_{eq}(1) \cdots O_{eq}(6)$ lengthened to 2.882 (4) Å.

Bugg & Cook (1972) report that calcium binding to *cis* vicinal oxygen atoms results in a decrease of 0.2 Å in the O<sub>eq</sub> to O<sub>ax</sub> contact distance and 13–14° in the O<sub>eq</sub>-C-C-O<sub>ax</sub> torsion angle. The binding of magnesium to the *cis* hydroxyl groups of inositol induces conformational changes of equal or greater magnitude than found for calcium.

# Table 4. Torsion angles for bonds to C(1) and C(2) of myo-inositol

The standard deviations of the least significant figures are in parentheses.

Angle (°)			
Mg complex	Uncomplexed*		
49.8 (4)	57.3 (3)		
- 71.4 (4)	-63.8(3)		
169.4 (3)	176.4 (3)		
48.2 (4)	62.6 (3)		
63.5 (4)	59.3 (3)		
- 175.5 (3)	179.4 (3)		
-178.4 (3)	- 175.7 (3)		
- 57.4 (4)	- 55·0 (3)		
- 50.4 (4)	-63.5(3)		
69.4 (4)	61.2 (3)		
-167.5 (3)	-176.0 (3)		
-47.6 (4)	- 59·4 (3)		
	Ang Mg complex $49\cdot 8 (4)$ $-71\cdot 4 (4)$ $169\cdot 4 (3)$ $48\cdot 2 (4)$ $63\cdot 5 (4)$ $-175\cdot 5 (3)$ $-178\cdot 4 (3)$ $57\cdot 4 (4)$ $-50\cdot 4 (4)$ $69\cdot 4 (4)$ $-167\cdot 5 (3)$ $-47\cdot 6 (4)$		

\* Average angles for the two independent molecules in the structure of *myo*-inositol (Rabinowitz & Kraut, 1964) are listed.



Fig. 2. Hydrogen bonding and close contacts in the crystalline complex.

A = =1== (9)

		A	В	C
I	C(4)C(5)O(4)O(5)	-0.5248	0.2246	-0.8210
IIa*	C(4)C(5)O(4)O(5)	-0.3548	0.5995	-0.7174
IIb*	C(4)C(5)O(4)O(5)	-0.3942	-0.4098	-0.8225

# Table 5 (cont.)

	Deviation from the plane					
	I(Å)	J	II(Å)			
		а	b			
C(1)	0.334	-0.276	0.332			
C(2)	-0.152	0.350	-0.291			
C(3)	0.111	-0.119	0.127			
C(4)†	-0.302	0.300	-0.302			
C(5)†	0.292	-0.296	0.298			
C(6)	-0.166	0.112	-0.040			
O(1)	-0.189	0.064	0.012			
O(2)	-1.553	1.774	-1.720			
O(3)	-0.618	0.389	-0.360			
O(4)†	0.120	-0.148	<b>0</b> ∙148			
O(5)†	-0.140	0.145	-0.145			
O(6)	0.326	-0.542	0.684			

\* Calculations IIa, IIb are for the two independent molecules of myo-inositol in the crystal structure by Rabinowitz & Kraut, (1964).

† Atoms used in the least-squares plane calculation. The equation for the plane is Ax + By + Cz = D.

Since the common four-atom arrangements used for least-squares plane calculations for cyclohexane rings encompass sites perturbed by the magnesium coordination, an unconventional location was chosen in order to have an undistorted reference for comparison with the uncomplexed molecule. The atomic displacements for atoms C(4), C(5), O(4), and O(5), see Table 5, are unaffected by complexing. The hydroxyl positions are particularly sensitive indicators that all other atoms are affected by the coordination at O(1) and O(2). The difference in the displacement of C(2) in the complexed and uncomplexed molecules is indicative of a decrease in pucker of that portion of the ring.

In the inositol complexes with both calcium (Bugg & Cook, 1972) and magnesium the cations are bound to their characteristic number of ligands, [8] and [6] respectively (Phillips & Williams, 1966). While calcium binds an equal number of hydroxyl groups and water molecules, the coordination geometry around magnesium is composed of the two hydroxyl groups from inositol and four water molecules. The oxygen atoms are arranged in an octahedral geometry around the magnesium atom, see Fig. 1. The bond distances and angles descriptive of this geometrical arrangement are given in Table 6. The distances and angles are normal (Andress & Gundermann, 1964; Sasvari & Jeffrey, 1966), except for some involving the hydroxyl groups, where constraints are imposed by the cyclohexane ring. Oxygen atoms alone constitute the primary coordination sphere of magnesium, and the chlorine atoms are 4.673 (2) Å, Cl(2) and 4.759 (2) Å, Cl(1) from the cation. The magnesium geometry is not appreciably different from that found in MgCl<sub>2</sub>.6H<sub>2</sub>O (Andress & GunderE.s.d. (Å)

0.003

0.003

0.002

mann, 1964) or MgCl<sub>2</sub>.  $12H_2O$  (Sasvari & Jeffrey, 1966) where the cation is six-coordinated to oxygen at 2.06 Å. However, in the organic complex, as in MgCl<sub>2</sub>.  $12H_2O$ , hydration of the anions and subsequent steric considerations place the chlorine ions approximately 0.7 Å farther from the magnesium than in MgCl<sub>1</sub>.  $6H_2O$ .

D

-7.0708

-0.5526

- 4.9202

#### Table 6. Coordination distances and angles

The standard deviations of the least significant figures are in parentheses.

(a) Coordination distances between magnesium and oxygen atoms (Å).

Mg-O(W1)	2.032 (4)
Mg-O(W2)	2.051 (4)
Mg-O(W3)	2.079 (4)
Mg-O(W4)	2.038 (4)
Mg-O(1)	2.094 (3)
Mg-O(2)	2.143 (3)

(b) Angles between oxygen atoms coordinated to the magnesium atom (°).

O(W1)-Mg-O(W2)	91.8 (2)
O(W1)-Mg-O(W3)	88.9 (2)
O(W1) - Mg - O(W4)	103.0 (2)
O(W1)-Mg-O(1)	161.9 (2)
O(W1)-Mg-O(2)	88.0 (1)
O(W2)-Mg-O(W3)	174.4 (2)
O(W2)-Mg-O(W4)	88.4 (2)
O(W2)-Mg-O(1)	87.9 (1)
O(W2)-Mg-O(2)	96.3 (1)
O(W3)-Mg-O(W4)	86.0 (2)
O(W3)-Mg-O(1)	93.1 (1)
O(W3)-Mg-O(2)	89.2(1)
O(W4)-Mg-O(1)	95.0 (1)
O(W4)-Mg-O(2)	167.9 (2)
O(1)Mg-O(2)	74.1 (1)

Cl(1) is within van der Waals contact of five oxygen atoms and Cl(2) of four. The geometries of the hydration polyhedra are those of a distorted trigonal bipyramid and tetrahedron, respectively, see Table 7. Each anion is within hydrogen-bonding distance of two equatorial hydroxyl groups of different molecules. Thus, for a particular molecule of *myo*-inositol in the unit cell, any hydroxyl not coordinated to magnesium is hydrogen bonded to a chlorine anion. In the case of hydroxyl(5), the hydrogen-bond acceptor appears to be a water molecule.

Hydrogen bonding in the crystal structure is illustrated in Fig. 2. The dashed lines represent all contacts to the oxygen atoms which are less than the sum of the van der Waals radii. The hydrogen atoms have been excluded from the drawing. The dimensions and angular arrangement of the hydrogen bonds are given in Table 8. Although hydroxyl groups O(3) and O(6)are at less than the van der Waals distance from  $O(2)_{xym}$ 

#### Table 7. Distances and angles involving the chlorine ions and oxygen atoms

The standard deviations of the least significant figures are in parentheses.

(a) Distances between chlorine ions and oxygen atoms (Å)\*

CI CI CI	(1) - O(W2) (1) - O(W4) (1) - O(W4)	3·268 (4) 3·209 (4) 3·175 (4)	Cl(2)— $O(W1)Cl(2)$ — $O(W3)Cl(2)$ — $O(4)$	3·093 (3) 3·152 (4) 3·015 (3)
Cl	(1) - O(5) (1) - O(6)	3·224 (3) 3·074 (3)	Cl(2)—O(3)	2.986 (3)
(b) Angles between of	xygen atoms bonded to	chlorine ions (°)		
0	$(W_2) - Cl(1) - O(W_4)$	102.4 (1)	O(W1)-Cl(2)-O(W3)	116.4 (1)

$= \langle - \rangle = \langle - \rangle \langle - \rangle \rangle$	
$O(W_2) - Cl(1) - O(W_4)$	106.6 (1)
$O(W_2)-Cl(1)-O(5)$	152.1 (1)
$O(W_2) - CI(1) - O(6)$	77·2 (1)
O(W4)-Cl(1)-O(W4)	122.6 (1)
O(W4) - Cl(1) - O(5)	95 <sup>.</sup> 9 (1)
O(W4)-Cl(1)-O(6)	105.1 (1)
O(W4)-Cl(1)-O(5)	80.1 (1)
O(W4)-Cl(1)-O(6)	129.0 (1)
O(5) - Cl(1) - O(6)	77.8 (1)

and  $O(1)_{sym}$  respectively, their preference to hydrogen bonc to chlorine ions precludes the donation of hydrogen atoms to these oxygen atoms. The latter hydroxyl groups are hydrogen bonded to water molecules within the magnesium hydration polyhedra.

## Table 8. IIydrogen bonds and close intermolecular contacts

The	standard	deviations	of	the	least	significant	figures	are	in
parentheses.									

Acceptor	Donor		Hydrogen	Hydrogen
$(\overline{A})$	(D)	<i>D–A</i> (Å)	$-A(\text{\AA})$	$-D-A(^{\circ})$
O(1)	O(6 <sup>i</sup> )	2.580 (4)		
O(W4)	O(1)	3.048 (5)	2.53 (5)	37 (4)
O(W1)	O(2)	2.902 (4)	2.33 (5)	30 (4)
O(W2)	O(2)	3.126 (5)	2.53 (5)	28 (4)
O(2)	O(3 <sup>11</sup> )	2.706 (4)		
$Cl(2^{iii})$	O(3)	2.986 (3)	2.05 (5)	9 (3)
Cl(2 <sup>ii</sup> )	O(4)	3.015 (3)		
$O(W2^i)$	O(4)	2.708(5)	1.90 (5)	21 (6)
$O(4^{iv})$	O(W2)	2.708(5)	1.78 (5)	5 (3)
$O(5^{viii})$	O(W3)	2.783 (5)	2.02(5)	11 (4)
$O(W3^{\circ})$	O(5)	2.783 (5)	1.86 (4)	
Cl(1 <sup>v</sup> )	O(6)	3.074 (3)	2.14 (5)	
$Cl(2^{vi})$	O(W1)	3.093 (3)	2.17 (5)	9 (3)
O(Ì)	O(W2)	2.877 (5)	2.46(6)	32 (6)
Cl(2)	O(W3)	3.152 (4)		
O(W4)	O(W3)	2.810 (5)	2.31 (6)	36 (5)
O(W1)	O(W3)	2.879 (5)	2.38 (6)	35 (5)
Cl(1)	O(W4)	3.209 (4)	2.64(5)	9 (5)
$Cl(1^{vii})$	O(W4)	3.175 (4)		

Symmetry code

i	-x,	-y,	— z
ii	1 - x,	-y,	1 - z
iii	1 - x,	1 - y,	1 - z
iv	х,	-0.5-y,	0.5 + z
v	х,	-1+y,	Z
vi	1 - x,	-0.5+y,	1.5 - z
vii	-x,	-0.5+y,	1.5 - z
viii	х,	1 + y,	Z
ix	х,	-0.5-y,	0.5+z

01(2)	-(-)	
0(#1	$-C(2) - O(W_3)$	116.4 (1)
O(W1)	-Cl(2)-O(4)	70.9 (1)
O(W1) O(W3)	-Cl(2)-C(3) -Cl(2)-O(4)	$81 \cdot 2(1)$ $93 \cdot 4(1)$
O(W3	-Cl(2)-O(3)	138.0 (1)
O(4)	-CI(2) = O(3)	128.5 (1)

Presumably the forces between the magnesium ion and the oxygen atoms are ion-dipole interactions (Rendleman, 1966). Since the ratio of charge to atomic radius is greater for magnesium than calcium, and magnesium coordinates to fewer ligands than calcium, the magnesium-inositol complex may be a stronger association than that with calcium. The smaller stability constants found for magnesium than calcium carbohydrate complexes in aqueous solution (Angyal, 1972) may result from competitive ligation effects of the less sterically constraining water molecules.

Hydrogen bonding from the coordinated hydroxyl groups to water and from water to water within each polyhedron serves as a stabilizing influence for maintenance of the magnesium complex. No intrapolyhedral hydrogen bonding was found in the calcium-carbohydrate complexes examined (Bugg & Cook, 1972).

cis Vicinal hydroxyl groups possess more conformational flexibility than trans(eq/eq) groups. Coordination of an alkaline metal ion to vicinal hydroxyl groups causes a decrease in both the torsion angle O-C-C-O and intra-atomic oxygen to oxygen distance of the coordinated atoms. Angyal & MacDonald (1952) noted that such a deformation is energetically allowable for cis related groups, producing a decrease in pucker of the cyclohexane ring, and a lessening of 1,3-syn-diaxial steric interactions. In the case of trans-vicinal groups, the same motion increases ring pucker and produces unfavorable 1,3-syn-diaxial interactions. Although for the case in point such a structural alteration of the cis hydroxyl groups forces the coordinated oxygen atoms into steric opposition to one another, it serves to redirect the lone-pair electrons and minimize steric interference of the non-coordinated cyclitol atoms with components of the solvation polyhedron, e.g. H(6) with  $O(W^2)$ .

While the importance of cation binding to the hydroxyl groups of the *myo*-inositol moiety of phos-

phoinositides is uncertain, studies with synthetic bilayers have demonstrated that the negatively charged membrane components exhibit selective permeability for cations (Hopfer, Lehninger & Lennarz, 1970). Stability constants measured in aqueous solution cannot be realistically extended to membrane systems. Analysis of the structure of the inositol alkaline-earth metal complexes points up some interesting features.

Association of different alkaline-earth ions with *myo*inositol in a complex induces specific stereochemical changes in the cyclitol. It has been noted that greater conformational flexibility exists for *cis*-vicinal hydroxyl groups than *trans* disposed groups. Thus, in the case of monophosphoinositides it may be difficult to discriminate between simultaneous coordination between the phosphate and either the axial hydroxyl at C(2) or the equatorial hydroxyl at C(6) from steric considerations alone. Alkaline-earth metal binding to polyphosphoinositides does not seem to involve ligation to hydroxyl groups if two vicinal phosphates are present (Hendrickson & Reinertsen, 1969).

Quantitative differences in stereochemical parameters of the magnesium and calcium complexes with inositol do not appear to be great. However, examination of the hydration habits of these ions reveals that magnesium prefers to remain hydrated in salts whereas calcium forms salts of lower hydration (Peacocke & Richards, 1969). The structures of the calcium complexes examined (Bugg & Cook, 1972; Bugg, 1973; Craig, Stephenson & Stevens, 1972) show a higher ratio of carbohydrate to water than for this magnesium complex. The stoichiometric associations exhibited in the solid-state complexes may reflect the preferred levels of hydration for the respective ions. Williams (1970) has outlined a mechanism for altering membrane structure utilizing the differential bonding characteristics of calcium and magnesium.

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