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Invited Review

Magnesium compounds: classification and analysis of crystallographic and structural data

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Contents

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1. Introduction

Systematic studies of the stereochemistry of both coordination and organometallic compounds have expanded rapidly over the last three decades. The stereoselective behaviour in such derivatives can often be related to well known stereochemical specificity of biological systems, catalysts and related phenomena. Such systems are also of considerable commercial value for stereoselective industrial processes.

Magnesium is widely distributed in minerals and in the oceans, and is an important metal centre in living systems. It is found in substantial deposits such as dolomite ($CaCO_3 \cdot Mg(CO)_3$) and carnalite ($MgCl_2 \cdot KCl \cdot 6H_2O$).

The metal itself is a greyish white substance with a surface oxide film which protects it to some extent from the environment. Thus it is not easily attacked by water, but it does dissolve readily in dilute acids to give

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the corresponding magnesium salts. It reacts with most alkyl and aryl halides in ether solution to give the well-known Grignard reagents [1]. These are probably the most widely used of all organometallic compounds in both organic and organometallic syntheses.

About 30 elements are recognised as essential to life [2]. Some are required in bulk, or at least macroscopic amounts, in essentially all forms of life, and one of these elements is magnesium [3]. For example, the key pigments for the conversion of solar energy into biologically useful forms are the chlorophylls [4], which contain a magnesium(II) atom bound to the four nitrogen atoms of a porphyrin ring in a square planar array.

Magnesium chemistry has been an active field of study for a considerable time, and the relationships between the structure, reactivity and catalytic activity (particularly the Grignard reagents) have proved of major importance. Some aspects of the coordination chemistry of alkali and alkali-earth cations, together with some crystallographic data on Grignard reagents and other magnesium compounds, have been briefly reviewed earlier [5]. Many structures of magnesium compounds have been summarised in annual reports [6], but to date no overall review and classification of the data has been carried out. The aim of this review is to provide such a survey, and to draw together the basic crystal and structural data for magnesium compounds up to the end of 1991.

The structures have been classified according to the coordination number of the magnesium, and subdivided into monomers, oligomers and polymers. The compounds have been listed and referenced in order of increasing coordination number, increasing complexity of the coordination sphere, and increasing van-der-Waals's radii of the principal coordinated atom. Under varying conditions, magnesium has been isolated with coordination numbers from two to ten, with six being the most frequent.

2. Magnesium mononuclear compounds

2.1. Coordination number two

The lowest coordination number found for magnesium is two, and the few examples for this class of compounds are listed in Table 1. Only the linear arrangement of ligating atoms is found, the example of $Mg\{C(SiMe_3)_3\}_2$ [7] is shown in Fig. 1. This is the first, and to date the only, example of a two coordinate magnesium compound in the solid state analysed by X-ray diffraction. The Mg–C distance of 211.6(2) pm is somewhat shorter than that found for $Mg(neopentyl)_2$, at 212.6(6) pm, as found by electron diffraction [8]. Not surprisingly, the limitation to coordination number two is the requirement for very bulky ligands.

2.2. Coordination number four

From the three principal geometries, only the tetrahedral environment is expected and found for magnesium with coordination number four. This is typical for non-transition metals. The tetrahedral magnesium compounds are usually colourless, but there are several coloured examples, such as pale pink and yellow, and even one red compound. The crystallographic and structural data for tetrahedral magnesium compounds are given in Table 2, where it can be seen that none of the examples has the ideal symmetry of T_d. The structure of $Mg\{N(SiMe_3)_2\}_2(thf)_2$ is shown in Fig. 2 as a typical example in which there is substantial deviation from the ideal tetrahedral geometry. The dihedral angle between the planes of the O–Mg–O and N–Mg–N atoms is 100.8°, which is well below the ideal value.

The data show the occurrence of mono-, bi- and even tridentate ligands, but there is no example of a tetradentate ligand. There is also no example of four monodentate ligands all with the same donor atom. The mean values of the Mg–L(monodentate) bond distances, in parenthesis, increases in the order of

TABLE 1. Crystallographic and structural data for mononuclear magnesium compounds. Coordination number two [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)	L'–Mg–L (°)	Ref.
$Mg\{C(SiMe_3)_3\}_2$	tr	909.3(7)	68.52(2)	MgC_2	C [b] 211.6(2, 0)	C,C [b] 180	7
(colourless)	$P\bar{1}$	930.8(2)	74.26(5)				
	1	1190.7(4)	59.98(4)				
$Mg(np)_2$ [c] (white)				MgC_2	C 212.6(6, 0)	C,C 180	8

[a] Where more than one chemically equivalent distance or angle is present the mean value is specified. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean. [b] The coordinated atom or ligand is specified in these columns. [c] By gas phase electron diffraction at 113 K.

TABLE 2. Crystallographic and structural data for mononuclear magnesium compounds. Coordination number four [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$Mg\{PO_2(OEt)_2\}_2$	m	2214(2)		MgO_4	O [b]	189.7(5, 0)	O,O [b]	109.5(2, 1.8)	9
(colourless)	$C2/c$	799.8(4)	96.72(5)			190.5(5, 0)			
	4	930.0(3)							
$Mg\{\eta^3$-HB(3[t]Bupz)(Me)	or	1636.2(4)		MgN_3C	N	213.5(8, 5)	N,N	91.1(3, 5)	10
(colourless)	*Pnma*	1592.0(5)			C(Me)	211.8(11)	N,C	124.5(3, 1.8)	11
	4	982.4(4)							
$Mg\{\eta^3$-HB(3-[t]Bupz)$_3$}(CHMe$_2$}	or	1717.1(2)		MgN_3C	N	216.6(5, 9)	N,N	91.3(2, 3.5)	11
(colourless)	*Pnma*	1589.3(7)			C	218.2(8)	N,C	124.3(2, 5)	
	4	1003.4(3)							
$Mg\{\eta^3$-HB(3,5-[t]Bupz)$_3$}(CH_2SiMe_2)	m	2389.7(8)	not given	MgN_3C	N	207.6(6, 64)	N,N	90.0(2, 1.9)	11
(colourless)	$C2/c$	801.0(2)			C	209.6(9)	N,C	125.2(3, 8.3)	
	8	3007.2(8)							
$Mg\{N(SiMe_3)_2\}_2(thf)_2$	m	1404.3(3)		MgO_2N_2	O	209.4(5, 8)	O,O	89.8(2)	12
(colourless)	$P2_1/c$	1209.9(2)	97.46(1)		N	202.1(5, 6)	N,N	127.9(2)	
	4	1857.4(2)					O,N	113.6(2, 2.9)	
$Mg(Mecb)_2(dox)_2$	m	1989.0(4)		MgO_2C_2	O	203.8(8, 0)	O,O	99.5(5)	13
(not given)	$C2/c$	930.4(2)	118.29(2)		C	215.6(5, 0)	C,C	123.5(4)	
	4	2199.7(5)					O,C	107.9(3, 2.7)	
$Mg(C_{16}H_{14})(thf)$	m	1833.6(1)		MgO_2C_2	not given		not given		14
(pale yellow)	$P2_1/a$	1079.1(1)	105.99(1)						
	8	2277.6(1)							
$Mg(C_{17}H_{18})(thf)_2$	or	816.5(1)		MgO_2C_2	O	not given	not given		14
(pale yellow)	$P2_12_12_1$	1375.7(3)			C	211.3(9, 0)			
	4	1960.8(3)							
$Mg(thf)_2(C_{20}H_{26}Si_2)$	or	3396.7(8)		MgO_2C_2	O	200.9(6, 12)	O,O	99.6(2)	15
(yellow)	*Fdd*2	3545.5(6)			C	233.4(7, 1)	O,C	120.1(2, 3.6)	
	16	978.3(2)					C,C	78.2(3)	
$Mg(C_5H_{11}O)_2$	or	1842.4(3)		MgO_2C_2	O	207.1(3, 0)	O,O	96.4(1)	16
(not given)	*Fdd*2	2220.9(3)			C	214.4(4, 0)	O,C	103.3(1, 7.6)	
	8	639.6(1)					C,C	140.2(2)	
$Mg(C_{14}H_{19}O_4(Ph)$	m	1128.4(1)		MgO_2C_2	O	219.6(3, 10)	O,O	71.4(1)	17
(colourless)	$P2_1/m$	1827.7(2)	101.50(1)		C	212.7(4)	O,C	110.7(1, 14.8)	
	8	1868.2(2)			C(Ph)	215.4(4)	C,C	127.8(1)	
$Mg(Et_2O)_2Br_2$ [c]	tr	1130(2)	117.06(20)	MgO_2Br_2	O	212(–, 3)	O,O	121.7	18
@ 223 K	$P\bar{1}$	1120(2)	111.48(20)		Br	288(–, 14)	Br,Br	89.8	
(not given)	4	1545(20)	91.36(20)				O,Br	81.8, 120.9	
				MgO_2Br_2	O	215(–, 2)	O,O	113.9	
					Br	325(–, 7)	Br,Br	62.9	
							O,Br	112.5, 113.0	
$Mg(Me_3Si)_2(dme)$	or	1646.1(2)		MgO_2Si_2	O	212.4(4, 0)	O,O	76.3(2)	19
(pale pink)	*Pbcn*	934.8(1)			Si	263.0(2, 0)	Si,Si	125.2(1)	
	4	1195.0(2)					O,Si	111.0(1)	
$Mg(Me)_2(C_7H_{13}N)_2$	m	1214.7(2)		MgN_2C_2	N	223.9(6, 8)	N,N	108.2(2)	20
(not given)	$P2_1/c$	1266.1(4)	108.94(18)		C	219.4(9, 31)	C,C	129.0(3)	
	4	1201.6(5)					N,C	104.6(3, 1.8)	
$Mg(Me)_2(Me_4en)$	or	1190.2(4)		MgN_2C_2	N	224.2(6, 15)	N,N	81.5(2)	21
(colourless)	*Cmca*	1120.1(3)			C(Me)	216.6(6, 0)	C,C	130.0(4)	
	8	1836.7(6)					N,C	108.7(2,6)	

TABLE 2 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$Mg(Ph)_2(Me_4en)$ (colourless)	m $P2_1/a$ 4	1198.4(2) 997.6(1) 1577.1(2)	92.44(1)	MgN_2C_2	N C	220.2(3, 3) 216.7(3, 0)	N,N N,C C,C	82.5(1) 112.4(1, 3.6) 119.2(1)	22
$Mg(C_7H_{11})_2(Me_4en)$ (not given)	or $Pbcn$ 4	1014.5(2) 1248.6(2) 1758.7(2)		MgN_2C_2	N C	220.2(12, 0) 217.9(15, 0)	N,N N,C C,C	84.2(5) 114.2(6, 3.8) 113.1(6)	23
$Mg\{2\text{-}C(SiMe_3)_2py\}_2$ (not given)	m $P2_1/c$ 8	2402(2) 1678(3) 1641(2)	107.15(7)	MgN_2C_2	N C	213.1 221.9	N,N C,C N,C	117.4(9) 157.0(7) 67.3(2), 126.3	24
$Mg(C_{15}H_{26}N_2)Cl_2$ (not given)	or $P2_12_12_1$ 4	1118.0(4) 1195.7(4) 1257.3(5)		MgN_2Cl_2	N Cl	215.5(9, 5) 227.4(6, 5)	N,N N,Cl Cl,Cl	85.0(4) 112.4(3, 10.9) 117.6(2)	25
$Mg(PHPh)_2(Me_4en)$ (white)	tr $P\bar{1}$ 2	1191.6(6) 1161.2(7) 908.0(6)	68.42(4) 85.11(5) 62.39(4)	MgN_2P_2	N P	226.6(8, 40) 259.0(5, 3)	N,N P,P N,P	79.9(3) 122.5(1) 109.3(3, 16.7)	26
$Mg(C_{22}H_{32}N_2)Br_2$ (not given)	or $P2_12_12_1$ 4	1665.4(3) 1972.3(4) 863.7(2)		MgN_2Br_2	N Br	213(3, 5) 246.4(1, 10)	N,N N,Br Br,Br	85.8(9) 114.1(8, 17.0) 112.1(5)	27
$Mg(SiMe_3)_2(Me_4en)$ (colourless)	m $P2_1/c$ 4	1435.9(19) 930.9(10) 1706.0(20)	110.85(9)	MgN_2Si_2	N Si	219.2(8, 1) 262.8(4, 4)	N,N Si,Si N,Si	82.8(4) 115.3(1) 113.5(3, 2.9)	28
$Mg(SiMe_3)_2(Me_4pn)$ (colourless)	m $P2_1/c$ 4	912.6(10) 2663.9(28) 997.7(9)	120.30(7)	MgN_2Si_2	N Si	219.1(3, 7) 266.0(2, 9)	N,N Si,Si N,Si	93.1(1) 119.7(1) 110.2(1, 3.2)	29
$Mg(Et_2O)_2(Et)Br$ (not given)	m $P2_1/c$ 4	1318(3) 1027(3) 1142(3)	103.3(3)	MgO_2CBr	O C Br	204(2, 1) 215(2) 248(1)	O,O O,C O,Br C,Br	101.2(6) 110.7(8, 1.1) 103.4(5, 4) 125.0(5)	30
$Mg(Et_2O)_2(Ph)Br$ (not given)	or $P2_12_12_1$ 4	1225 1281 1102		MgO_2CBr	O C Br	204(–, 3) 220 244	O,O O,C O,Br	not given not given 107(–, 4)	31
$Mg(Et_2O)_2(CPh_3)Br$ (red)	or $Pna2_1$ 4	1632(1) 1595.4(9) 1025.3(6)		MgO_2CBr	O C Br	203(1, 1) 225(1) 246.5(5)	O,O O,C O,Br C,Br	101.5(4) 114.5(5, 1.4) 104.1(3, 1.6) 116.4(3)	32
$Mg(thf)_2(Ph)Br$ (not given)	m $P2_1/c$ 4	810(2) 1003.8(12) 2075.4(9)	96.1(2)	MgO_2CBr	not given				33
$Mg(^tBu)(C_{15}H_{26}N_2)Cl$ (not given)	or $P2_12_12_1$ 4	2568.9(6) 1003.0(2) 794.2(2)		MgN_2CCl	N C Cl	217.3(12, 2) 219(2) 233.2(7)	N,N N,C N,Cl C,Cl	83.9(5) 117.9(6, 1.7) 109.1(4, 8.3) 114.7(5)	25
$Mg(Et)(C_{15}H_{26}N_2)Br$ (not given)	or $P2_12_12_1$ 4	1127.8(2) 1411.2(3) 1174.6(2)		MgN_2CBr	N C Br	215(3, 1) 224(3) 248.2(9)	N,N N,C N,Br C,Br	84.0(8) 120.5(9, 9.1) 105.9(7, 2.5) 115.1(8)	34
$Mg(Et)(i\text{-}C_{15}H_{26}N_2)Br$ (not given)	or $P2_12_12_1$ 4	1064.6(4) 1449.1(4) 1185.7(3)		MgN_2CBr	N C Br	218.0(3, 15) 222.4(15) 250.6(6)	N,N N,C N,Br C,Br	83.9(5) 117.9(6, 11.8) 112.2(4, 10.8) 112.1(5)	35

TABLE 2 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L′–Mg–L (°)		Ref.
$Mg(Et)(C_{22}H_{32}N_2)Br$ (not given)	or $P2_12_12_1$ 4	1102.0(4) 2366.0(10) 866.6(6)		MgN_2CBr	N 216(4, 3) C 235(5) Br 250.6(16)		N,N N,C N,Br C,Br	83.1(1) 114.6(1, 6.6) 115.8(1, 10.9) 111.4(1)	27

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] There are two crystallographically independent molecules.

increasing covalent radii of the ligand atoms: O, 73 pm (206.4 pm) < C, 77 pm (218.1 pm) < Cl, 99 pm (229.3 pm) < P, 106 pm (259.0 pm) < Br, 114 pm (267.2 pm). It is well known that the hard magnesium(II) atom prefers to bond to a relatively hard group, but Table 2 clearly shows bonding to borderline and even soft ligands. In these cases, the Mg–L bond distances are found to be relatively larger than in the hard ligand cases.

One of the important characteristics for describing tetrahedral geometry is the L–Mg–L angle. In the ideal geometry the value of these angles should be 109.5°, but angles from 62.9 to 157.0° are found experimentally (Table 2), confirming a significant deviation from ideal. There are at least two factors responsible for this, both associated with the ligands. Differences in the steric requirements of the ligands is a major factor, and accommodation to bi- or tridentate behaviour is another.

Two independent molecules, differing by degree of distortion, have been found in $Mg(Et_2O)_2Br_2$ [18]. The coexistence of two species of differing degree of distortion within the same crystal is typical of the general class of distortion isomerism [36].

2.3. Coordination number five

Pentacoordinated magnesium compounds show a range of colours from colourless, violet through green to orange and red. Crystallographic and structural data for five-coordinate magnesium compounds are listed in Table 3. Two types of geometry are observed, square pyramidal and trigonal bipyramidal, of which the first predominates. The structure of red $[Mg(tpp)(H_2O)](2\text{-pic})_2$ [41] is shown in Fig. 3 as an example. The coordination geometry about the magnesium(II) atom is square pyramidal, with the Mg atom 41.4 pm above the plane of the four chelating nitrogen atoms. The apical position is occupied by water. An interesting structural feature is the hydrogen bonding of the coordinated water molecule to two picoline molecules. The O–H · N distances for these interactions are 185.0 and 173.3 pm. Overall, the porphyrin core is non-planar with large displacements at the C_b atoms. Individually, the pyrrole rings are planar within 2 pm, and they are inclined at 7.0, 0.9, 7.2 and 5.3° to the mean plane of the core [41].

In the series of square pyramidal magnesium compounds [37–46] there is only one example where the Mg^{II} atom is occupied by five equal unidentate ligands, $[Mg(Me_3AsO)_5](ClO_4)_2$ [37]. In the remaining examples, basal planes contain four nitrogen atoms of tetradentate macrocycles. In all examples, the apical position is occupied by an oxygen donor (Me_3AsO, H_2O or ClO_4).

The displacement of the Mg^{II} atom from the basal plane towards the apical O ligand is in the range from 27.3 to 49.6 pm (Table 3). It would seem that there is a correlation between this displacement and the differences between the Mg–L(eq) and Mg–L(ap) bond distances. The bigger the difference, the less the displacement of the magnesium. For example, the displacement of 49.6 pm [38] occurs with the difference between Mg–N(eq) and Mg–OH_2(ap) of 1.8 pm. In another example [39] the displacement is 45 pm and the difference is 2.9 pm, and another of 41.4 pm and 8.0 pm respectively [41]. In the example where the magnesium is closest to the basal plane (27.3 pm) [46], the mean Mg–N(eq) distance (207.2 pm) is shorter than

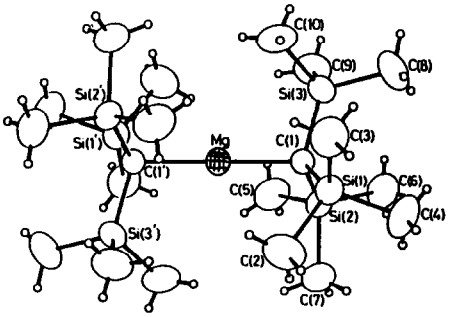


Fig. 1. Structure of $Mg[C(SiMe_3)_3]_2$ [7].

TABLE 3. Crystallographic and structural data for mononuclear magnesium compounds. Coordination number five [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	Mg–L (pm)		Mg-out-of-plane (pm)	L'–Mg–L (°)		Ref.
$[Mg(Me_3AsO)_5](ClO_4)_2$	m	1133.0(5)		MgO_5	O_{eq} [b]	203.0(9, 20)	45.4(3)	O,O [b]	87.0(4, 1.3)	37
(colourless)	$P2_1/n$	2756.2(6)	90.58(5)						152.6(5, 7.9)	
	4	1132.8(6)			O_{ap}	192(1)		O,O_{ap}	103.7(5, 5.2)	
$[Mg(pc)(H_2O)](py)_2$	m	1709.8(3)		MgN_4O	N_{eq}	204.0(2, 3)	49.6(4)	N,N	86.6(1, 2)	38
(deep violet)	$P2_1/n$	1695.1(3)	105.88(3)						151.9(1, 1)	
	4	1244.9(3)			H_2O_{ap}	202.2(3)		N,O	104.1(1, 2.9)	
$[Mg(tpp)H_2O]2Me_3CO$	tr	1069.4(6)	105.18(5)	MgN_4O	N_{eq}	208.3(6, 20)	45	N,N	88.0(2, 7)	39
@ 133 K	$P\bar{1}$	1292.5(7)	90.27(5)						158.2(3, 1.3)	
(not given)	2	1563.1(11)	102.27(4)		O_{ap}	205.4(6)		N,O	100.9(2, 5.2)	
$[Mg(tpp)ClO_4]$	m	1382.5(1)		MgN_4O	N_{eq}	209.6(5, 16)	43	N,N	87.6(2, 8)	40
(not given)	$P2_1/c$	1307.6(1)	107.64(1)					N,O	102.0(2, 2.2)	
	4	2063.9(1)			O_{ap}	201.2(5)				
$[Mg(tpp)(H_2O)](2\text{-pic})_2$	tr	1024.7(2)	87.23(2)	MgN_4O	N_{eq}	209.2(7, 22)	41.4	N,N	90.0(2, 3.2)	41
(red)	$P\bar{1}$	1332.5(3)	88.69(2)					N,O	101.4(2, 2.1)	
	2	1770.0(3)	86.88(2)		H_2O_{ap}	201.2(6)				
$[Mg(Mechl\text{-}a)(H_2O)]Et_2O$	or	2301(3)		MgN_4O	N_{eq}	not given	40	not given		42
(green)	$P2_12_12_1$	1908(3)			H_2O_{ap}	203(1)				
	4	842(1)								
$[Mg(Etchl\text{-}a)(H_2O)]H_2O$	trg	885.9(1)		MgN_4O	N_{eq}	not given	39	not given		43
(green)	$P3_1$	–								44
	3	3811.9(5)			H_2O_{ap}	not given				
$[Mg(Etchl\text{-}b)(H_2O)]H_2O$ [c]	trg	885.5(2)		MgN_4O	N_{eq}	208.1(9, 83)	not given	N,N	90.0(4, 5.1)	44
(green)	$P3_1$	–							159.3(4, 1.7)	
	3	3805.9(7)			O_{ap}	201.2(7)		N,O	100.3(4, 7.9)	
$[Mg(Mechl\text{-}a)(H_2O)]H_2O$	m	876(1)		MgN_4O	N_{eq}	not given	34	not given		45
(green)	$P2_1$	2586(3)	119.20(5)		O_{ap}	203(1)				
	2	847(1)								
$Mg(tpp)(H_2O)$	tg	1346(2)		MgN_4O	N_{eq}	207.2(10, 0)	27.3	N,N	89.0(5)	46
(red)	$I4/m$	–						N,O	97.6(5)	
	2	968(2)			O_{ap}	209.9(10)				
$[Mg(thf)_3(dphb)$	m	1452.9(2)		MgO_3C_2	O_{eq}	209(1, 3)		O_{eq},O_{eq}	112.3(3)	47
(not given)	$P2_1/c$	1592.9(2)	102.03(1)		C_{eq}	226(2)		O_{eq},C_{eq}	123.8(3, 4.1)	
	4	1144.0(2)			O_{ap}	218(1)		O_{ap},O_{ap} [d]	174.4(3)	
					C_{ap}	232(2)				
$[Mg(thf)_3(an)$ [e]	m	803.9(5)		MgO_3C_2	O	205.9(8, 3.2)		O,O	92.7(3, 12.0)	32
(orange)	Cc	3748(2)	101.94(4)		C	229(1, 4)		C,C	70.9(4)	
	8	1594.1(6)						O,C	110.7(4, 19.3)	
									169.0(4)	
				MgO_3C_2	O	205.0(9, 21)		O,O	91.5(4, 9.5)	
					C	230(1, 1)		C,C	71.9(5)	
								O,C	103.9(5, 12.3)	
									153.0(5, 2.6)	
$Mg(thf)_3(an)$	tr	1919.3(29)	97.14(11)	MgO_3C_2						48
(orange)	unknown	812.7(9)	98.54(13)							
	8	3050.3(409)	89.92(11)							

TABLE 3 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)	Mg-out-of-plane (pm)	L'–Mg–L (°)	Ref.
$Mg(thf)_3(Me_2an)$ [e] (orange red)	m $P2_1/c$ 8	809.0(1) 2130.1(4) 2999.2(5)	92.2(1)	MgO_3C_2	O not given C 232(1, 1)		O,O not given C,C 72.6	49
$Mg(thf)_3(Me)Br$ (not given)	m Cc 4	1250 1230 1340	122.30	MgO_3CBr	O_{eq} 213(–, 15) C_{ap} 241 Br_{ap} 253		not given	50
[Mg(*p*-^{t}BuPh)(1,3-xyl-18-crown-5)] (colourless)	tr $P\bar{1}$ 2	498.6(3) 657.9(3) 1878.0(17)	98.84(8) 91.34(7) 81.56(8)	MgO_3C_2	O_{eq} 214.6(4) C_{eq} 214.1(4, 13) O_{ap} 232.7(4, 10)		O_{eq},O_{eq} 109.2(2, 6) C_{eq},C_{eq} 139.3(2) O_{ap},O_{ap} 156.8(1)	51

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] At 120 K, $a = 876.0(2)$ pm and $c = 3767.3(8)$ pm. [d] $O_{eq}–Mg–O_{ap} = 83.7(3, 1.7)°$; $C_{eq}–Mg–O_{ap} = 98.5(3)°$; $O_{eq}–Mg–C_{ap} = 98.2(3, 2.2)°$; $C_{eq}–Mg–C_{ap} = 77.9(3)°$. [e] There are two crystallographically independent molecules. [f] $O_{eq}–Mg–O_{ap} = 78.4(1, 7.4)°$; and $C_{eq}–Mg–O_{ap} = 93.7(2, 19.7)°$.

the $Mg–OH_2$(ap) (209.9 pm), the comparative distance being – 1.7 pm, consistent with the above suggestion.

In the remaining examples [47–51] of Table 3, the coordination geometry of the magnesium is a distorted trigonal bipyramid. From a general consideration of the chemistry of magnesium, one would expect the square pyramidal arrangement to be preferred geometry of five coordinated magnesium. The examples of trigonal bipyramidal geometry are all with a soft ligating atom, carbon, and in fact they are all organometallic derivatives. It is well known that the energy difference between these two geometries is small, but all the factors governing the actual choice of geometry are not very clear. However, it can be generalised that trigonal bipyramidal structures are favoured by non-metallic central atoms, and the square pyramidal arrangements tend to be favoured by incomplete inner d-subshells. Clearly the ligands must also play a role, and it appears to be a rather important one in the case of magnesium stereochemistry.

The data in Table 3 show mono-, bi- and tetradentate ligands. In the series of square pyramidal compounds, with the exception of one example [46], the Mg–L(ap) bond distances are shorter than the Mg–L(eq) ones, and the apical sites are less crowded of course. On the other hand, in most cases of trigonal bipyramidal geometry, where equatorial sites are not so crowded, the mean value of Mg–L(eq) bond distances are shorter than the corresponding apical distances.

In general, the mean value of the Mg–L bond distance increases as the covalent radius of the donor atom increases. For example, 204.8 pm (O) < 207.7 pm (N) < 229 pm (C) < 253 pm (Br).

The L(eq)–Mg–L(eq) angles in the square plane are in the range 84.4 to 90.0° (average 88.4°), and 144.7 to 160.4° (average 155.5°), which indicate a considerable deviation from an idealized geometry which requires 86.6° and 151.9° respectively. The L(eq)–Mg–L(ap) angle in the ideal square pyramid is 104.1°, and this is contrasted by the range of 92.4 to 108.9° (average 101°) found experimentally, also indicating a deviation from ideal.

The experimental values found in the trigonal bipyramidal cases are in the range 67.7 to 139.3° (average 112.3°) for L(eq)–Mg–L(eq); 62.9 to 135.9° (average 90.9°) for L(eq)–Mg–L(ap); and 156.8 to 174.4° (average 165.6°) for L(ap)–Mg–L(ap). By contrast, the idealised angles are 120°, 90° and 180° respectively. Thus these derivatives also show a considerable degree of distortion from ideal. The ring carbon or oxygen atoms occupying different positions (apical and equatorial) are primarily responsible for these distortions.

Two crystallographically independent molecules, differing only by degree of distortion, have been found in orange $Mg(thf)_3$(an) [32] and orange-red $Mg(thf)_3(Me_2$-an) [49].

2.4. Coordination number six

The overwhelming majority of magnesium coordination chemistry is six-coordinate, most of these are colourless or white with just a few red examples. Crystallographic and structural data for mononuclear magnesium compounds of coordination number six are given in Table 4. The three principle types of distortion for the octahedron are, trigonal, rhombic and tetragonal, all of which are found in magnesium complex

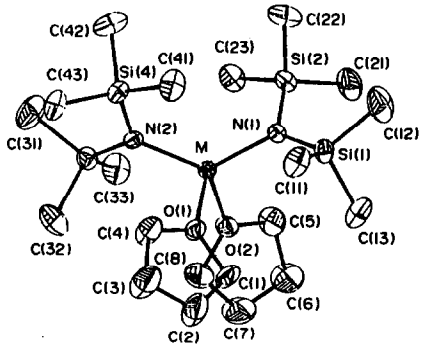


Fig. 2. Structure of $Mg\{N(SiMe_3)_2\}_2(thf)$ [12].

chemistry. An example of a six-coordinated complex, Mg(1,3-xylyl-18-crown-5)(phenyl)$_2$ [157], is shown in Fig. 4. Here the magnesium exhibits an unusual type of hexacoordination. Two apical carbons are essentially sp hybridized giving a Ph–Mg–Ph unit (angle C(17)–Mg–C(23)) is 163.8(2)° and the dihedral angle between the two phenyl rings is 66.2(2)°. Magnesium is rather tightly bound to O(2) (220.4(3) pm) and O(3) (222.2(4) pm), and less so to O(1) (251.6(4) pm) and O(4) (252.0(4) pm) [157].

The data in Table 4 shows mono-, bi-, tri-, tetra-, penta- and even hexadentate ligands. The most common coordination sphere of the magnesium(II) atom is the MgO_6 chromophore with six water molecules. The Mg–OH_2 bond distances are in the range from 196.1 to 214.9 pm (average 207.1 pm) which is a wider range than those found amongst the rest of the monodentate O donor ligands (201.2 to 223.6 pm, average 207.7 pm).

There are several examples [60,72–74,86,102,117, 127,129,130,162,166] in which two crystallographically independent molecules, differing by degree of distortion, occur. There are also two examples, $[Mg(H_2O)_6]_3(PO_4)_2 \cdot 4H_2O$ [74] and $[Mg(H_2O_6)(genH)_2 \cdot 2H_2O$ [108] which exist in two isomeric forms, again differing mostly by degree of distortion. There is also an example, $Mg(thf)_4(PhC{\equiv}C)$ [156] in which *cis* and *trans* isomers have been proposed.

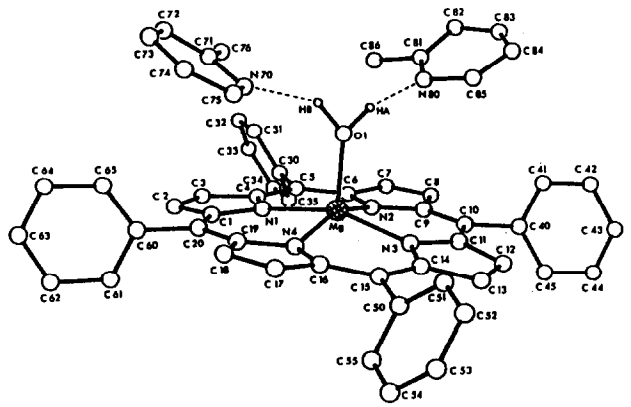


Fig. 3. Structure of [Mg(tpp)(H$_2$O)](2-pic)$_2$ [41].

There are several examples which have been studied by two or three groups of investigators: $NH_4[Mg(H_2O)_6]Cl_3$ [57–59]; $Rb[Mg(H_2O)_6]Cl$ [59,60]; $[Mg(H_2O)_6](ClO_4)_2$ [61,62]; $NH_4[Mg(H_2O)_6]AsO_4$ [69,70]; $NH_4[Mg(H_2O)_6]PO_4$ [76,77]; $[Mg(H_2O)_6]SO_3$ [83–85]; $[Mg(H_2O)_6]SO_4 \cdot H_2O$ [87–89]; $[Mg(H_2O)_6]_2S_2O_3$ [91–93] and $Mg(thf)_4Br_2$ [156,159,160]. As can be seen in Table 4, not all of the duplicate data agree, and in some instances this review is the first time that duplicates have been cross referenced.

2.5. Coordination number seven

There is no indication of other than colourless materials for the heptacoordinated magnesium compounds. The crystallographic and structural data for these systems are given in Table 5. Of the three idealized geometries for seven-coordination, pentagonal bipyramidal, capped octahedral and capped trigonal prismatic, only two are found in magnesium chemistry. Pentagonal bipyramid geometry is the most common, with only two examples of the capped trigonal prism. As an example of the former, the structure of Mg(18-crown-6)(ClHCl)$_2$ [175] is shown in Fig. 5. The geometry of the crystal is a distorted pentagonal bipyramid with the two chlorine atoms in axial positions, and the five oxygen atoms of the crown forming the pentagonal plane. There are another ten examples [171–179] in which the magnesium atoms are in a distorted pentagonal bipyramidal environment.

It might be expected that the M–L(ax) bond distances should be smaller than the M–L(eq) distances since the apical sites are less sterically hindered than the five in plane equatorial sites. From the data in Table 5 it can be seen that the mean Mg–OH_2(ax) bond distance is 205.9 pm which is 7 pm longer than the mean Mg–OH_2(eq) bond distances. The mean Mg–L(ax) bond distances increase in the order: 205.9 pm (OH_2) < 207.9 pm (NCS) < 243.4 pm (Cl), which is also the order of increasing covalent radii of the coordinated atoms. The mean Mg–L(eq) bond distances increase in the given order: 204.5 pm (H) < 205.2 pm (O) < 220.3 pm (where L has five O donor atoms) < 226.7 pm (where L has four O donor atoms) < 227.0 pm (where L has five N donor atoms).

One of the important characteristics for describing pentagonal bipyramidal geometry is the ratio of M–L(ax) to M–L(eq) distances. However, distortions from ideality will be more definitively revealed in the bond

(*continued on page 19*)

TABLE 4. Crystallographic and structural data for mononuclear magnesium compounds. Coordination number six [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$[Mg(H_2O)_6]Cl_2$ [c] (colourless)	m $C2/m$ 2	986.07(2) 710.71(2) 607.37(2)	93.758(2)	MgO_6	O [b]	206.0(1, 3)	O,O [b]	90.00(5, 1.33)	52
$[Mg(H_2O)_6]Cl_26H_2O$ (colourless)	m $P2_1/c$ 2	859(2) 1440(3) 875(5)	129.6(2)	MgO_6	O	206.2(7, 3)	O,O	90.0(3, 1.5)	53
$[Mg(H_2O)_6]Cl_2$(dox) (colourless)	m $P2_1/n$ 2	1215(3) 796(2) 686(2)	91.23(15)	MgO_6	O	206.3(4, 10)	O,O	90.0(2, 4.1)	54
$[Mg(H_2O)_6]Cl_2(C_8H_{16}O_4)$ (colourless)	m $C2/c$ 4	1640.6(5) 844.3(3) 1272.9(5)	93.18(2)	MgO_6	O	206.6(2, 16)	O,O	90.00(5, 1.77)	55
$[Mg(H_2O)_6]Cl_2(CH_2)_6N_4]_24H_2O$ (not given)	tr $P\bar{1}$ 1	954 951 932	93.48 101.23 120.07	MgO_6	O	210(–, 0)	O,O	90.0(–, 6.5)	56
$NH_4[Mg(H_2O)_6]Cl_3$ (colourless)	m $C2/c$ 4	932.0(3) 958.2(3) 1332.7(4)	90.12(4)	MgO_6	O	205.3(2, 6)	O,O	89.7(1, 4)	57
$NH_4[Mg(H_2O)_6]Cl_3$ (colourless)	tr $P1$ 4			MgO_6	O	196–214(1)			58
$NH_4[Mg(H_2O)_6]Cl_3$ (colourless)	m $C2/c$ 4	930.0 955.0 1330.1	89.96 90.06 90.00	MgO_6	O	205.3(3, 0)	not given		59
$Rb[Mg(H_2O)_6]Cl_3$ [e] (colourless)	tr $P1$ 2	667.2(2) 1328.2(15) 663.9(5)	89.83(8) 91.72(6) 90.41(8)	MgO_6	O	204.3(13, 36)	O,O	90.0(6, 2.1) 177.5(6, 2.1)	60
				MgO_6	O	204.9(13, 67)	O,O	90.0(6, 5.6) 174.0(6, 2.5)	
$Rb[Mg(H_2O)_6]Cl_3$ (colourless)	m $C2/c$ 4	927.0 955.3 1328.2	90.40 90.17 89.72	MgO_6	O	204.3(4, 4)	O,O	90.00(14, 28) 180.0	59
$[Mg(H_2O)_4](ClO_2)_2$ (yellow)	tg $P4_2mc$ 2	747.1(8) – 998.0(2)		MgO_6	O	196.1(11, 0) 207.1(7, 0) 212.1(12, 0)	O,O	90.0(4, 2.3) 180.0(6)	61
$[Mg(H_2O)_6](ClO_2)_2$ (yellow)	tg $P4_2/nmc$ 2			MgO_6	O	204.6(2, 0) 206.1(5, 0)	O,O	90.0(–) 180.0(–)	62
$[Mg(H_2O)_6](ClO_4)_219H_2O$ [d]				MgO_6	O	217			63
$[Mg(H_2O)_6](ClO_4)_234H_2O$ [d]				MgO_6	O	222			63
$[Mg(H_2O)_6](ClO_4)_294H_2O$ [d]				MgO_6	O	221			63
$[Mg(H_2O)_6]I_8$ [c] (not given)	tr $P\bar{1}$ 1	890.9(3) 971.9(3) 772.5(2)	114.46(2) 102.78(2) 105.09(1)	MgO_6	O	205.0(12, 18)	O,O	90.0(6, 2.0)	64

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)	L'–Mg–L (°)	Ref.
$[Mg(H_2O)_6](B_2O_3)_2H_2O$ (not given)	m $P2_1/c$ 4	1266.4(1) 1009.1(2) 1132.2(1)	109.6(1)	MgO_6	O 205.8(3, 14) 214.2(3, 12)	not given	65
$[Mg(H_2O)_6]SiF_6$ (not given)	m $P2_1/c$ 2	646.0(5) 952.4(5) 846.0(5)	99.24(3)	MgO_6	O not given		66
$[Mg(H_2O)_6](N_3)_2$ (colourless)	or $Fmmm$ 4	644.3(1) 1134.4(1) 1333.5(3)		MgO_6	O 204.4(2)	not given	67
$[Mg(H_2O)_6](NO_3)_2$ (not given)	m $P2_1/c$ 2	619.4(2) 1270.7(3) 660.0(2)	92.99(2)	MgO_6	O 205.8(6, 5)	O,O 90.0(3, 1.3)	68
$NH_4[Mg(H_2O)_6](AsO_4)$ (not given)	or $Pm2_1n$ 2	700 1114 614		MgO_6			69
$NH[Mg(H_2O)_6](AsO_4)$ (not given)	or $Pmn2$ 2	705.4(4) 620.5(3) 1136.8(6)		MgO_6	O 208.0(5, 23)	not given	70
$K[Mg(H_2O)_6](AsO_4)$ (not given)	or $Pm2_1n$ 2	703 1126 623		MgO_6			71
$[Mg(H_2O)_6](HAsO_4)H_2O$ [e] (colourless)	m $C2/c$ 8	669.18(5) 2574.4(2) 1153.8(1)	95.15(1)	MgO_6	O 205.2(2, 3) 209.2(2, 0)	O,O 176.7(1, 3.1)	72
				MgO_6	O 206.4(2, 14) 210.8(2, 0)	O,O 177.2(1, 2.7)	
$KH[Mg(H_2O)_6]_2(PO_4)_23H_2O$ [e] (not given)	tr $P\bar{1}$ 1	628.8(1) 1222.8(3) 655.4(1)	93.64(1) 89.18(1) 94.69(1)	MgO_6	O 206.9(1, 21)	O,O 90.00(6, 1.78)	73
				MgO_6	O 205.5(1, 21)	O,O 90.00(5, 2.41)	
$KH[Mg(H_2O)_6]_2(AsO_4)_23H_2O$ [e] (not given)	tr $P\bar{1}$ 1	639.0(2) 1247.7(3) 665.9(2)	93.54(2) 88.71(2) 94.51(2)	MgO_6	O 207(1, 3)	O,O 90.0(5, 2.2)	73
				MgO_6	O 207(1, 1)	O,O 90.0(4, 2.6)	
α-$[Mg(H_2O)_6]_3(PO_4)_24H_2O$ [e] (not given)	tr $P\bar{1}$ 1	690.2(2) 696.1(2) 1598.2(4)	87.66(2) 85.22(2) 60.81(2)	MgO_6	O 206.8(5, 18)	O,O 90.0(2, 3.5)	74
				MgO_6	O 207.6(5, 27)	O,O 90.0(2, 10.8) 169.5(2, 1.4)	
β-$[Mg(H_2O)_6]_3(PO_4)_24H_2O$ [e] (not given)	tr $P\bar{1}$ 1	693.7(3) 693.2(3) 1613.2(5)	82.15(3) 89.72(3) 119.49(3)	MgO_6	O 206.3(4, 26)	O,O 90.0(2, 2.5)	75
				MgO_6	O 207.7(3, 38)	O,O 90.2(1, 9.9)	
$NH_4[Mg(H_2O)_6]PO_4$ (colourless)	or $Pmn2_1$ 2	694.1(2) 613.7(2) 1119.9(4)		MgO_6	O 207.1(2, 37)	O,O 90.00(8, 4.00)	76
$NH_4[Mg(H_2O)_6]PO_4$ (colourless)	or $Pmn2_1$ 2	695.5(1) 691.4(1) 1121.8(2)		MgO_6	O 208.7(2, 33)	O,O 90.3(1, 3.5)	77

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	Mg–L (pm)		L′–Mg–L (°)	Ref.
$Na[Mg(H_2O)_6]PO_4H_2O$ (not given)	tg $P4_2/mmc$ 2	673.1(2) 1098.2(4)		MgO_6	O	208.7(2, 36)	O,O 90.00(4, 62)	78
$K[Mg(H_2O)_6]PO_4$ (not given)	or $Pmn2_1$ 2	687.3(2) 616.0(2) 1108.7(3)		MgO_6	O	207.1(9, 32)	not given	79
$Tl[Mg(H_2O)_6]PO_4$ (not given)	or $Pm2_1n$ 2	686.1 1135 613.5						80
$Rb[Mg(H_2O)_6]PO_4$ (not given)	or $Pm2_1n$ 2	685.2 1127 617.7						80
$Cs[Mg(H_2O)_6]PO_4$ (not given)	hx $P6_3mc$ 2	689.9 – 1199						80
$[Mg(H_2O)_6](PO_2H_2)_2$ (not given)	tg $I4_1/acd$ 8	1033(1) – 2038(2)		MgO_6	O_{eq} O_{ap}	204.4(3) 206.6(5)	O,O 90.00(25, 1.95)	81
$[Mg(H_2O)_6](HPO_3)$ (not given)	rh $R3$ 3	596	96.24	MgO_6	O	210	not given	82
$[Mg(H_2O)_6]SO_3$ [c] (not given)	rh $R3$ 1	593.3(2)	96.28(2)	MgO_6	O	205.9(2) 211.2(2)	O,O 90.0 (1, 3.8) 174.9(1)	83
$[Mg(H_2O)_6]SO_3$ (not given)	rh $R3$ 3	589.5(2)	96.0(1)	MgO_6	O	206.0(5) 208.3(5)	not given	84
$[Mg(H_2O)_6]SO_3$ @ 120 K (not given)	rh $R3$ 1	591.1(1)	96.25(2)	MgO_6	O	205.2(7) 210.63(7)	O,O 90.00(3, 4.04) 174.72(3)	85
$[Mg(H_2O)_6]SO_4$ [e] (not given)	m $C2/c$ 8	1011.0(5) 721.2(4) 24.41(1)′	98.30(5)	MgO_6 MgO_6	O O	205.7(2, 23) 206.5(2, 18)	not given	86
$[Mg(H_2O)_6]SO_4H_2O$ (white)	or $P2_12_12_1$ 4	1186.8(10) 1199.6(10) 685.7(7)		MgO_6	O	206.5(2, 34)	O,O 90.0(2, 4.2) 176.7(2, 1.9)	87
$[Mg(H_2O)_6]SO_4H_2O$ (white)	or $P2_12_12_1$ 4	1187.6(2) 1200.2(2) 685.9(1)		MgO_6	O	207.0(1.33)	not given	88
$[Mg(H_2O)_6]SO_4H_2O$ [e] (white)	or $P2_12_12_1$ 4	1186.8(10) 1199.6(10) 685.7(7)		MgO_6	O	207.2(6, 37)	O,O 176.77(4, 1.4)	89
$K_2[Mg(H_2O)_6](SO_4)_2$ (not given)	m $P2_1/a$ 2	907.2 1221.2 611.3	104.50	MgO_6	O	205.6 210.3 211.8	O,O 90.00(–, 66)	90

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)	L'–Mg–L (°)	Ref.
$[Mg(H_2O)_6]S_2O_3$ (colourless)	or *Pnma* 4	932(1) 1436(4) 687(1)		MgO_6	O 208.4(13, 31)	O,O 90.0(6, 9)	91
$[Mg(H_2O)_6]S_2O_3$ [c] (colourless)	or *Pnma* 4	940.5(4) 1444.9(4) 686.6(4)		MgO_6	O 205.2(5, 1) 212.5(5, 0)	O,O 90.0(2, 8)	92
$[Mg(H_2O)_6]S_2O_3$ [c] @ 120 K		930.4(3) 1444.7(3) 684.7(3)		MgO_6	O 203.6(3, 1) 211.4(3, 0)	O,O 90.0(1, 9)	92
$[Mg(H_2O)_6]SeO_3$ (colourless)	rh *R*3 1	596.5(2)	97.28(2)	MgO_6	O 208.3(3, 22)	O,O 90.0(1, 2.9) 176.3(1)	93
$[Mg(H_2O)_6TeO_3$ (colourless)	rh *R*3 1	601.1(3)	97.36(4)	MgO_6	O 209.1(3, 11)	O,O 90.0(2, 2.4) 177.6(2)	93
$Cs_2[Mg(H_2O)_6](CrO_4)_2$ (not given)	m $P2_1/a$ 2	962.1(5) 1296.8(5) 637.5(3)	106.17(4)	MgO_6	O 208.3(3, 26)	O,O 90.0(1, 8)	94
$[Mg(H_2O)_6]Cr_2O_7$-$2(CH_2)_6N_4$	tr *P*1 2	1002(5) 1368(8) 981(5)	96.1(5) 87.9(5) 101.0(8)	MgO_6	O 210.1(6, 33)	O,O 90.0(2, 4.2)	95
$[Mg(H_2O)_6](C_4H_3O_4)_2$ (not given)	m $P2_1/a$ 2	674.2(2) 1020.1(1) 1181.6(2)	104.06(2)	MgO_6	O 204.9(1, 13)	O,O 90.0(1, 1.1)	96
$[Mg(H_2O)_6](C_4H_3O_4)_2$ [e] (not given)	m $P2_1/c$ 2	1020.7(5) 1182.9(5) 674.5(3)	104.2(1)	MgO_6	O 207.7(4, 7)	O,O 90.0(2, 1.7)	97
$[Mg(H_2O)_6](C_6H_4O_2N)_2$ @ 108 K (reddish green)	m $P2_1/c$ 2	1057.9(1) 624.2(1) 1319.8(3)	106.97(1)	MgO_6	O 202.18 207.70 208.01	not given	98
$[Mg(H_2O)_6](nic)_24H_2O$ (colourless)	m $P2_1/a$ 4	1379.7(5) 2322.8(10) 690.4(3)	93.35(3)	MgO_6	O 206.4(7, 55)	O,O 90.0(3, 2.3) 177.3(4, 2.5)	99
$[Mg(H_2O)_6](dnpo)2H_2O$ (yellow)	m $P2_1/c$ 2	1347.3(4) 1296.9(4) 667.0(2)	104.98(2)	MgO_6	O 206.6(5, 16)	O,O 90.0(2, 1.9)	100
$[Mg(H_2O)_6](PhSO_3)_2$ (not given)	m $P2_1/n$ 2	2260 632 694	93.36	MgO_6	O 204	O,O 90	101
$[Mg(H_2O)_6](C_8H_5O_4)_2$ [e] (not given)	m $P2_1/c$ 4	656.5(1) 3084.0(4) 1005.5(1)	89.22	MgO_6	O 205.3(9, 21) 212.5(9, 0)	O,O 90.0(4, 1.6)	102
				MgO_6	O 206.4(9, 3) 212.4(9, 0)	O,O 90.0(4, 2.2)	

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	Mg–L (pm)	L′–Mg–L (°)	Ref.
$[Mg(H_2O)_6](C_8H_5O_4)_2 2H_2O$	tr	704.18(8)	84.31(1)	MgO_6	O 206.4(8, 3)	O,O 90.0(3, 1.71)	102
(not given)	$P\bar{1}$	928.59(13)	109.34(1)		211.7(10)		
	1	954.92(14)	108.99(1)				
$[Mg(H_2O)_6](4\text{-OHbenz})_2 2H_2O$	or	768.0(9)		MgO_6	O 207.1(4, 1)	O,O 90.0(3, 1.1)	103
(white)	*Pcab*	1120(1)			212.9(4, 0)		
	4	2406(3)					
$[Mg(H_2O)_6](C_8H_5O_5)_2$	m	1305.3(3)		MgO_6	O 207.4(5, 31)	O,O 90.0(2, 2.4)	104
(colourless)	$P2_1/a$	537.5(1)	90.44(2)				
	2	1493.1(2)					
$[Mg(H_2O)_6](amcp)_2 4H_2O$	tr	682.0(2)	90.65(1)	MgO_6	O 206.7(5, 0)	O,O 90.0(3, 2.6)	105
(not given)	$P\bar{1}$	2253.0(5)	86.97(2)		208.6(5, 0)		
	2	857.2(2)	88.46(2)				
$[Mg(H_2O)_6](C_{16}H_{12}SO_3)_2 6H_2O$	tr	1113.03(5)	102.071(5)	MgO_6	O 205.8(60, 7)	O,O 90.0(3.0, 2.4)	106
(not given)	$P\bar{1}$	1353.83(6)	97.224(6)				
	2	697.03(3)	91.009(4)				
$[Mg(H_2O)_6](ort) 2H_2O$	m	1098.4(1)		MgO_6	O 206.7(2, 42)	O,O 90.0(1, 3.5)	107
(colourless)	$P2_1/c$	1290.1(1)	98.51(1)			180.0(1)	
	2	694.4(1)					
$[Mg(H_2O)_6](Hgen)_2 2H_2O$	m	957.3(2)		MgO_6	O 205.5(4, 12)	O,O 90.0(2, 1.3)	108
(colourless needles)	$P2_1/c$	1462.7(3)	101.91(1)				
	2	717.0(1)					
$[Mg(H_2O)_6](Hgen)_2 2H_2O$	m	1039.7(2)		MgO_6	O 205.7(2, 49)	O,O 90.0(1, 2.9)	108
(colourless plates)	$P2_1/c$	1430.6(3)	104.64(2)				
	2	673.2(1)					
$[Mg(H_2O)_6](2\text{-aepH})_2 2H_2O$	tr	802.7(1)	92.72(1)	MgO_6	O 206.0(1, 19)	O,O 90.0(1, 2.2)	109
@ 223 K	$P\bar{1}$	765.3(1)	106.85(1)				
(colourless)	1	758.0(1)	93.14(1)				
$[Mg(H_2O)_6]H_2edta$	m	778.1(1)		MgO_6	O 207.6(1, 23)	O,O 90.00(5, 3.18)	110
(colourless)	$P2_1/c$	1347.8(2)	91.55				
	2	838.5(1)					
$[Mg(H_2O)_6](caf)_2 Br_2$	tr	962.0(7)	107.03(7)	MgO_6	O 207.7(5, 12)	O,O 90.0(2, 3.0)	111
(colourless)	$P\bar{1}$	1077.9(8)	108.88(7)				
	1	764.5(6)	72.71(8)				
$[Mg(EtOH)_6]Cl_2$	trg	793.0(1)		MgO_6	O 206.9(3, 0)	not given	112
(colourless)	$P\bar{3}$	–					
	1	996.4(1)					
$[Mg(MeOH)_6]Cl_2$	trg	776(1)		MgO_6	O not given		113
(colourless)	$R\bar{3}$	–					
	3	2240(3)					
$[Mg(MeOH)_6]Br_2$	trg	795(1)		MgO_6	O 207(1, 0)	O,O 92.4(2)	113
(colourless)	$R\bar{3}$	–					
	3	2231(3)					114
$[Mg(MeOH)_6]I_2$	trg	828(1)		MgO_6	O not given		113
(not given)	$P\bar{3}$	–					
	1	723(1)					

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)	Ref.
$[Mg(N\text{-}Mea)_6]Cl_2$ (not given)	tr $P\bar{1}$ 1	816.2(2) 981.3(2) 995.2(2)	107.85(2) 98.60(2) 81.28(2)	MgO_6	O	206.4(2, 21)	O,O 90.00(10, 3.87)	115
$[Mg(urea)_6]Br_2(urea)_4$ (not given)	m $P2_1/c$?	972.3(4) 722.8(3) 2375.1(9)	95.79(4)	MgO_6	O	206.8(3, 16)	O,O 90.0(1, 3.1)	116
$[Mg(dmf)_6](ClO_4)_2$ [e] (not given)	m $P2_1/a$ 4	2068.6(11) 1096.2(18) 1488.5(9)	91.45(5)	MgO_6 MgO_6	O O	205.4(15, 10) 204.3(17, 37)	O,O 90.0(–, 2.1) O,O 90.0(–, 2.0)	117
$[Mg(apy)_6](ClO_4)_2$ (colourless)	hx $P\bar{3}$ 1	1406 – 976		MgO_6	O	205.9(6, 0)	O,O 90.0	118
$[Mg(H_2O)_5(sach)]$-(sach)$2H_2O$ (not given)	tr $P\bar{1}$ 2	1430.5(13) 1128.8(10) 701.7(7)	97.02(2) 78.11(3) 100.13(3)	MgO_6	O H_2O	201.2(2) 204.3(2, 13) 210.9(2, 5)	O,O not given	119
$Mg(H_2O)_4(ac)_2$ (not given)	m $P2_1/c$ 2	480.7(2) 1197.3(5) 855.4(4)	95.36(3)	MgO_6	H_2O_{eq} $O_{ap}(ac)$	208.2(4, 27) 207.4(4, 0)	not given	120
$[Mg(H_2O)_4(N\text{-}Mea)_2]$-$(NO_3)_2$ (not given)	or $Pbca$ 4	660.3(1) 1293.4(2) 1939.7(3)		MgO_6	O H_2O	204.7(1, 0) 207.2(1, 18)	O,O 90.0(1, 4.0)	121
$Mg(H_2O)_4(sal)_2$ (colourless)	m $P2_1/m$ 4	2308.8(10) 520.2(1) 684.0(1)	90.27(3)	MgO_6	O H_2O	202.2(4, 0) 205.8(13, 0) 212.0(13, 0)	O,O 90.0(5, 2.9)	122
$Mg(H_2O)_4(p\text{-}NH_2sal)_2$ (colourless)	m $P2_1/a$ 4	959.5(6) 1325.7(4) 676.6(2)	97.12(4)	MgO_6	O H_2O	209.8(3, 0) 199.8(4, 0) 214.9(4, 0)	O,O 90.0(2, 1.8)	122
$[Mg(H_2O)_4(peah)_2]$-$2H_2O$ (colourless)	tr $P\bar{1}$ 1	661.4(1) 691.8(1) 951.7(1)	89.35(1) 72.65(1) 81.34(1)	MgO_6	O_{eq} H_2O_{eq} H_2O_{ap}	206.2(1, 0) 204.9(1, 0) 212.4(1, 0)	O,O 90.0(1, 2.0) 180.0(1)	123
$Mg(H_2O)_4(mcpac)_2$ (not given)	tr $P\bar{1}$ 1	1571.5(3) 814.0(2) 515.9(1)	81.23(2) 90.06(2) 73.01(2)	MgO_6	O H_2O	203.8(13, 0) 207.8(11, 0) 211.8(12, 0)	O,O 90.0(5, 3.4)	124
$[Mg(H_2O)_4(L\text{-}aspH)(D\text{-}aspH)]$ (not given)	m $P2_1/c$ 2	572.5(2) 1428.3(3) 912.5(2)	102.58(2)	MgO_6	H_2O_{eq} O_{ap}	206.7(1, 3) 205.7(2, 0)	O,O 90.0(1, 1.7)	125
$Mg(H_2O)_4(DL\text{-}asp)$ (colourless)	m $P2_1/c$ 2	571.0(2) 1429.1(7) 911.7(4)	102.57(3)	MgO_6	O H_2O	205.5(2, 0) 206.5(3, 1)	O,O 90.0(1, 1.5)	126

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$Mg(H_2O)_4(meO_4S)_2$ [e]	m	1065.8(2)		MgO_6	O	204.1(2, 0)	O,O	not given	127
(not given)	$P2_1/c$	771.7(1)	92.02(2)		H_2O	206.3(2, 43)			
	6	2144.9(3)		MgO_6	O	205.1(2, 4)	O,O	not given	
					H_2O	207.3(2, 25)			
$[Mg(H_2O)_4SO_4]$ [c]	m	592.2(6)		MgO_6	O	208.3(5, 1)	not given		128
(not given)	$P2_1/m$	1360.4(4)	90.51(10)		H_2O	207.1(5, 19)			
	?	790.5(5)							
$[Mg(H_2O)_4SO_4]H_2O$ [e]	tr	631.4(5)	81.7(1)	MgO_6	O	209.1(5, 0)	not given		129
(not given)	$P\bar{1}$	1050.5(18)	109.49(12)		H_2O	205.4(5,5)			
	2	603.0(6)	105.5(3)	MgO_6	O	209.7(5, 0)			
					H_2O	204.3(5, 5)			
$[Mg(H_2O)_4(CrO_4)]H_2O$ [e]	tr	638.4	81.33	MgO_6	O	208(2, 0)	O,O	90.0(–, 1.4)	130
(not given)	$P\bar{1}$	1070.2	108.45		H_2O	206(2, 3)			
	2	611.5	104.20	MgO_6	O	208(2, 0)	O,O	90.0(–, 1.4)	
					H_2O	206(2, 2)			
$[Mg(H_2O)_4(Memal)]$	or	745.5(2)		MgO_6	O	206.3(1, 0)	O,O	90.0(6, 2.23)	131
(colourless)	*Pnma*	798.5(2)						177.38(7, 35)	
	4	1427.9(2)			H_2O	205.9(2, 10)			
$[Mg(H_2O)_4((S)\text{-}C_4H_4O_5)]\text{-}H_2O$	or	1140.3(9)		MgO_6	OH	212.5(5)	O,O	75.6(2)	132
	$P2_12_12_1$	1548.6(10)			OOC	207.0(5)	O,H_2O	92.7(2, 6.8)	
(colourless)	4	595.4(4)			H_2O	206.7(5, 22)	H_2O,H_2O	90.1(2, 7.4)	
$[Mg(H_2O)_4(C_4H_4O_5)]\text{-}H_2O$	or	592.3(3)		MgO_6	OH	211.2(2)	O,O	75.3(1)	133
	$P2_12_12_1$	1134.0(2)			OOC	205.9(1)	O,H_2O	92.8(1, 7.0)	
(colourless)	4	1539.7(3)			H_2O	204.4(2, 24)	H_2O,H_2O	88.1(1, 2.8)	
$[Mg(H_2O)_4(C_8H_{12}O_6)]\text{-}Cl_2$	m	1217.5(5)		MgO_6	O	211.9(3, 25)	O,O	90.0(2, 15.9)	134
	$P2_1/c$	764.3(1)	96.68(1)					171.2(2, 3.3)	
(not given)	4	1606.2(6)			H_2O	205.0(4, 29)			
$[Mg(H_2O)_4(fl\text{-}3\text{-}mp)]\text{-}H_2O$	m	4087.7(3)		MgO_6	O	205.0(2, 19)	O,O	90.0(1, 5.4)	135
	$C2/c$	629.6(1)	101.72(1)		H_2O	207.7(2, 21)			
(bright yellow)	8	1413.9(1)							
$[Mg(thf)_4(H_2O)_2]Br_2$	tr	777(1)	84.9(3)	MgO_6	O(thf)	211.7(7)	O,O	90.00(40, 97)	136
(not given)	$P\bar{1}$	926(1)	71.2(3)			216.4(7)			
	1	927(1)	69.1(3)		H_2O	204.2(10)			
$[Mg(urea)_4(H_2O)_2]Br_2$	m	845.5(1)		MgO_6	O	206.4(1.14)	O,O	90.0(1, 3.8)	137
(not given)	$P2_1/c$	1120.6(1)	103.52(2)		H_2O	210.8(2)			
	2	912.7(1)							
$Mg(acac)_2(H_2O)_2$	m	1098.36(16)		MgO_6	O_{eq}	203.4(4, 7)	O,O	90.00(20, 1.53)	138
(colourless)	$P2_1/c$	535.37(2)	106.356(14)		H_2O_{ax}	214.8(4)			
	2	1117.61(10)							
$Mg(C_2H_3O_4)_2(H_2O)_2$	m	4939.1(5)		MgO_6	O	204.6(1, 1)	not given		139
(not given)	$P2_1/c$	1131.00(13)	90.312(7)		H_2O	206.3(1, 0)			
	2	964.97(9)							

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$[Mg(daa)_2(H_2O)_2](daa)_2$-$(ClO_4)_2$ (colourless)	tr $P\bar{1}$ 1	1061.4(2) 1005.0(2) 765.5(2)	75.69(7) 70.49(8) 83.04(8)	MgO_6	O_{eq}	204.5(7, 4)	O,O	83.3(2)	140
					H_2O_{ap}	202.6(7, 0)	O,H_2O	89.9(2, 1)	
$[Mg(F_6acac)_3](C_{14}H_{19}N_2)$ (colourless)	m $P2_1/n$ 4	1277.5(5) 2126.8(8) 1359.4(6)	99.10(2)	MgO_6	O	205.8(9, 30)	O,O	90.0(3, 4.1) 173.9(5, 3.6)	141
$[Mg(ompa)_3](ClO_4)_2$ (colourless)	trg $P\bar{3}c1$ 2	1284.9(1) – 1828.5(2)		MgO_6	O	206.1(2)	O,O	90.0(1, 3.9)	142
$[Mg(C_4H_3O_3)_3](NMe_4)$ (not given)	m $C2/c$ 8	931.0(9) 2527.6(7) 1683.1(5)	101.97(4)	MgO_6	O	205.8(4, 28)	not given		143
$[Mg((gpp)_2)_2]4MeCN$ (colourless)	tg $P3_1$ 3	1574.4(4) – 2400.2(6)		MgO_6	O	205.5(8, 59)	O,O	90.0(–, 3.3)	144
$Mg(oep)(py)_2$ (not given)	tr $P\bar{1}$ 1	1060.7(3) 1042.3(4) 956.7(4)	114.69(4) 90.56(3) 99.27(3)	MgN_6	N_{eq}	207.0(2, 6)	N,N	90.0(1, 1.8)	145
					N_{ap}(py)	238.9(2, 0)			
$Mg(tpp)(1\text{-Meim})_2$ (red purple)	tg $P4_1/n$ 4	2076.4(5) – 965.9(3)		MgN_6	N_{eq}	207.8(6, 4)	N,N	89.8(2)	146
					N_{ap}(Meim)	229.7(8)	N,N_{ap}	90.7(3, 8)	
$Mg(tpp)(4\text{-pic})_2$ (red purple)	tr $P\bar{1}$ 1	1014.6(2) 1121.0(2) 1164.3(3)	65.63(2) 76.32(2) 67.42(1)	MgN_6	N_{eq}	207.1(3, 2)	N,N	90.9(1)	146
					N_{ap}(pic)	238.6(2)	N,N_{ap}	86.5(1, 2)	
$Mg(tpp)(pip)_2$ (red purple)	tr $P\bar{1}$ 1	994.4(3) 1143.6(3) 1191.4(3)	101.78(2) 104.59(2) 115.60(2)	MgN_6	N_{eq}	207.3(3, 2)	N,N	90.1(1)	146
					N_{ap}(pip)	241.9(4)	N,N_{ap}	89.6(1, 3)	
$[Mg(H_2O)_3(2,6\text{-pydc})]$-$2H_2O$ (colourless)	m $P2_1/n$ 4	892.0(3) 998.0(5) 1324.9(9)	96.89(4)	MgO_5N	O	216.4(4, 15)	O,O	93.8(1, 7.2)	122
					N	217.8(3)		148.3(1)	
					H_2O	202.9(4, 30)	O,N	83.0(1, 11.1)	
$[Mg(H_2O)_4(\text{i-nicO})$-(i-nicN)] (colourless)	m $P2_1/n$ 4	638(1) 3669(3) 711(1)	113.5(1)	MgO_5N	O	201.2(5)	O,N	176.7(1)	147
					N	227.1(5)	O,H_2O	91.9(2, 3.8)	
					H_2O	207.5(5, 28)	N,H_2O	88.1(2, 4.7)	
							H_2O,H_2O	90.1(2, 1.4)	
$[Mg(H_2O)_4(ort)]H_2O$ (not given)	tr $P\bar{1}$ 1	721.2(4) 835.9(3) 1005.6(6)	80.54(4) 70.80(5) 67.72(5)	MgO_5N	O	203.8(–) 213.0(1)	not given		148
					N	216.1(1)			
$Mg(H_2O)_4$(L-glu) @ 233 K (not given)	or $P2_12_12_1$ 4	7838(1) 1011.3(1) 1315.6(1)		MgO_5N	O	209.0(1)	O,N	76.3(1)	149
					N	221.1(2)	O,H_2O	94.1(1, 2.5)	
					H_2O	206.5(1, 60)		160.6(1)	
							N,H_2O	90.6(1, 5.1)	
								169.0(1)	
							H_2O,H_2O	90.6(1, 4.8)	
								170.4(1)	

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)	Ref.
$Mg(H_2O)_4(NCS)_2$	m	748.8(2)		MgO_4N_2	O	204.7(2, 0)	O,O 89.6(1)	150
(colourless)	$P2_1/a1$	903.0(2)	113.63(1)		O	212.6(2, 0)	N,N *ca* 180	
	2	786.9(2)			N	210.2(2, 0)	O,N 89.5(1, 2)	
$[Mg(H_2O)_4(NCS)_2]$-	or	922.5(2)		MgO_4N_2	O	205.5(6, 9)	not given	151
$(C_{12}H_{24}O_6)$	$Pna2_1$	1925.6(7)			O	212.6(3, 7)		
(colourless)	4	1326.7(4)			N	212.9(4, 16)		
$[Mg(H_2O)_4(pyr)_2]Cl_2$	tg	1505(1)		MgO_4N_2	O	205.7(7, 20)	O,O 85.7(4)	152
(colourless)	$I4_1/a$	–			N	222.9(5, 0)	O,N 91.3(4, 3.4)	
	8	1441(1)						
$Mg(2\text{-picCOO})_2(H_2O)_2$	m	1168(5)		MgO_4N_2	O	205(1, 0)	O,O 92.9(3, 6.4)	153
(colourless)	$P2_1/c$	885(1)	115.46(27)		N	222(1, 3)	N,N 92.7(3)	
	4	1600(5)			H_2O	205(1, 1)	O,N 76.0(3, 7)	
							93.6(3, 5.4)	
$Mg(dnphO)_2(Meim)_2$	m	834.0(4)		MgO_4N_2	O	196.3(5, 1)	O,O 85.3(5, 5.9)	154
(not given)	$P2_1/c$	1173.3(4)	104.65(4)		O	213.9(5, 13)	O,N 92.8(5, 4.2)	
	4	2569.0(6)			N(Meim)	211.5(5, 4)	N,N 96.0(5)	
$Mg(dnphO)_2(py)_2$	tr	829.7(4)	115.23(4)	MgO_4N_2	O	196.3(5, 1)	O,O 85.1(5, 6.7)	154
(not given)	$P\bar{1}$	1196.3(3)	109.10(4)		O	213.9(5, 13)	O,N 92.9(5, 5.4)	
	2	1434.5(8)	81.73(4)		N(py)	216.6(5, 4)	N,N 96.4(5)	
$Mg(cam)_2$	m	1115.2(2)		MgO_4N_2	O	199.3(8, 3)	O,O 90.0(3, 1.8),	155
							178.8(3)	
(colourless)	$P2_1$	2768.4(2)	107.02(2)		O	206.2(8, 2)	O,N 88.9(3, 7.7),	
							171.5(3, 1.0)	
	2	1016.8(2)			N	223.2(9, 4)	N,N 95.4(3)	
trans-$Mg(thf)_4(PhC{\equiv}C)_2$	tr	963(5)	98.10	MgO_4C_2	not given			156
(not given)	$P\bar{1}$	1105(5)	94.40					
	2	1700(5)	117					
cis-$Mg(thf)_4(PhC{\equiv}C)_2$	tr	857(5)	124.15	MgO_4C_2	not given			156
(not given)	$P\bar{1}$	1553(5)	80.15					
	1	1102(5)	136.30					
$Mg(C_{16}H_{24}O_5)(Ph)_2$	m	1027.7(2)		MgO_4C_2	O_{eq}	221.3(4, 9)	O,O 74.6(1)	157
(white)	$P2_1/n$	1383.7(1)	93.89(1)			251.8(4, 2)	O,C 96.5(2, 6)	
	4	1824.2(3)			$C_{ap}(Ph)$	219.0(5, 1)		
$Mg(acEt)_2(H_2O)_2Cl_2$	m	2236.3(5)		MgO_4Cl_2	Cl	253.1	O,Cl *ca* 90	158
(not given)	$C2/c$	811.3(3)	102.81(1)		O	206.4		
	4	863.1(1)			H_2O	205.4		
$Mg(thf)_4Br_2$	tg	784(2)		MgO_4Br_2	not given			156
(colourless)	$P4_12_12$	–						
	2	1730(5)						
$Mg(thf)_4Br_2$	tg	779(3)		MgO_4Br_2	not given			159
(colourless)	$P4_12_12$	–						
	2	1732(7)						
$Mg(thf)_4Br_2$	tg	784(2)		MgO_4Br_2	O	216.5(15)	not given	160
(colourless)	$P4_12_12$	–			Br	262.5(25)		
	2	1730(4)						

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)	L'–Mg–L (°)	Ref.
$[Mg(dhdbO)_4Br_2]0.5(tol)$ (yellow)	m $C2/c$ 4	1645.4(6) 1948.9(7) 1781.2(6)	96.01(3)	MgO_4Br_2	O 214.7(7, 36) Br 262.3(1)	O,O 90.0(2, 3) O,Br 90.0(1, 3) Br,Br 179.3(1)	161
$Mg(GeMe_3)_2(dme)_2$ [e] (red)	tr $P\bar{1}$ 4	937.5(1) 1680.9(5) 1776.9(3)	116.47(1) 99.85(1) 98.25(1)	MgO_4Ge_2	O 222(2, 10) Ge 272.2(7, 5)	O,O 79.0(6, 6.7) O,Ge 96.5(5, 6.0) Ge,Ge 99.2(2)	162
				MgO_4Ge_2	O 222(1, 4) Ge 271.5(6, 3)	O,O 80.3(5, 8.6) O,Ge 95.8(4, 6.6) Ge,Ge 99.4(2)	
$[Mg(py)_4(H_2O)]I_2(py)_2$ (colourless)	m $P2_1/c$ 4	1049(1) 1006(1) 3286(3)	92.4(2)	MgN_4O_2	N 224(7, 4) O 206(6, 6)	N,N 90.0(2, 7.1) N,O 90.0(2, 3.5) O,O not given	163
[Mg(tpp)(MeOH)$_2$] (@ 133 K (not given)	m $P2_1/n$ 2	1104.1(6) 1287.0(8) 1330.3(8)	113.29(4)	MgN_4O_2	N_{eq} 206.9(2, 1) O_{ap} 222.0(2)	N,N 90.0(1, 4) N,O 90.0(1, 4)	39
[Mg(tpp)(MeOH)$_2$]2Me$_2$CO @ 133 K (not given)	m $P2_1/c$ 2	1001(1) 1775(2) 1274(2)	110.7(1)	MgN_4O_2	N_{eq} 207.5(4, 7) O_{ap} 218.8(4)	N,N 90.0(1, 8) N,O 90.0(1, 2.1)	39
$Mg(C{\equiv}CBu)_2(Me_4en)_2$ (colourless)	tr $P\bar{1}$ 1	896.4(3) 950.6(3) 991.3(4)	73.02(3) 71.13(3) 69.58(2)	MgN_4C_2	N_{eq} 237.8(4, 4) C_{ap} 217.5(4, 0)	N,N 90.0(2, 1.8) N,C 90.0(2, 2) C,C not given	164
$Mg(C{\equiv}CPh)_2(Me_4en)_2$ (colourless)	or $Cmcm$ 4	1009.5(7) 2249.7(12) 1243.3(6)		MgN_4C_2	N_{eq} 237.5(3, 0) C_{ap} 218.8(6, 12)	N,N 80.4(2) N,C 90.0(2, 4) C,C 180.0	165
$Mg(py)_4Cl_2$ [e] (colourless)	tr $P\bar{1}$ 2	918.2(6) 1349(1) 1439(1)	106.74(6) 141.01(6) 73.19(6)	MgN_4Cl_2	N_{eq} 227(1, 1) Cl_{ap} 246.3(5)	N,N 90.9(6, 3) Cl,Cl not given N,Cl 90.0(4, 1.0)	166
				MgN_4Cl_2	N_{eq} 227(1, 1) Cl_{ap} 248.3(5)	N,N 88.1(6, 1.6) Cl,Cl not given N,Cl 90.0(4, 5)	
$[Mg(py)_4Br_2](py)_2$ (colourless)	or $Ccca$ 4	1156(1) 1500(1) 1721(2)		MgN_4Br_2	N_{eq} 223(5.6) Br_{ap} 276.7(8, 0)	not given	167
$Mg(thf)_2(B_6H_9)_2$ (not given)	tg $P4_12_12$ 4	1138(1) – 1642(2)		MgB_4O_2	O 201.9(5, 0) B 238.2(11) B 247.8(11)	O,O 94.0(2) B,B 40.4–141.8(4) O,B 101.7(3, 2.5) 142.4(3)	168
$[Mg(H_2O)_3(py)_3]Br_2$2py (colourless)	m $P2_1/c$ 4	1492(2) 1008(2) 1981(2)	96.5	MgO_3N_3	O 207(2, 3) N 221(3, 4)	O,O 94.1(1.5) N,N 88.2 (1.5, 1.5) O,N 90.7(1.5, 4.0)	152

TABLE 4 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)	Ref.
$Mg(thf)_3(thiq)Br$	or	1396.2(6)		MgO_4CBr	O	204.9(8)	O,O 86.5(3, 4.4)	169
@ 188 K	$Pna2_1$	1061.4(3)			C	224.5(11)	O,C 88.3(4, 11.5)	
(not given)	4	1797.9(11)			O(thf)	217.3(8, 63)	O,Br 92.3(2, 3.7)	
					Br	262.2(4)	C,Br 104.3(3)	
$Mg(C_{14}H_{19}O_4)Br$	m	1109.9(5)		MgO_4CBr	O_{eq}	213(1, 1)	O,O 73.9(4)	170
(colourless)	$P2_1/n$	1413.2(7)	100.80(5)			241(1, 8)	O,C 122.1(4, 2.4)	
	4	1011.3(6)			C_{eq}	210(1)	O,Br 98.1(3, 7)	
							C,Br 128.2(4)	
					Br_{ap}	251.7(4)		

[a] Where more than one chemically equivalent is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] By neutron diffraction. [d] By X-ray diffraction on aqueous solutions of magnesium perchlorate. [e] There are two crystallographically independent molecules present.

angles, L_{ax}–M–L_{ax}, L_{ax}–Mg–L_{eq} and L_{eq}–M–L_{eq} (*cis*, *trans*). In the ideal geometry, the values of these angles are 180, 90, 72 and 142°, respectively [181,182]. The first of these range from 169.1 to 180°, with an average value of 174.4°. The second of these differs from ideal by about 8° (range 82.0 to 98.1° with a mean of 89.7°). The third of these, within the pentagonal base, differ from ideal by about 22° (*cis*) and 29° (*trans*), confirming a significant deviation from the idealized geometry. An extreme example of this is $Mg(thf)_3(BH_4)_2$, where the bidentate (H-bonded) BH_4 anions are primarily responsible for the observed distortions (Table 5).

For the remaining two examples of the capped trigonal prismatic structure [179,180], the structure of the dinegative $[Mg(edta)(H_2O)]$ is shown in Fig. 6. Here the coordination sphere is built up by an oxygen atom of water in the unique capping position (Mg–O(c) = 206.0(3) pm), with the quadrilateral face containing two oxygen and two nitrogen atoms of hexadentate edta (Mg–O(qf) = 227.0(2) pm and Mg–N(qf) = 237.8(2) pm) and another two atoms of edta (Mg–O(e) = 207.8(2) pm) making the remaining edge.

This group also exhibits an example of distortion isomerism, $Mg(C_{10}H_{20}O_5)(NCS)_2$ [173], in which two crystallographically independent molecules, differing by degree of distortion, occur in the same crystal.

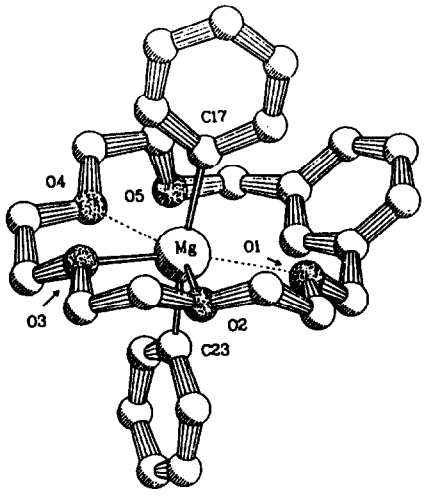


Fig. 4. Structure of Mg(1,3-xylyl-18-crown-5)$(Ph)_2$ [157].

2.6. *Coordination numbers eight and ten*

The crystallographic and structural data for these less common coordination numbers of magnesium are given in Table 6. All of the example to date are colourless. The structure of $Mg\{(Me_3Si)_3cp\}(Me_4en)Br$ is shown in Fig. 7 as an example of eight coordination, for which there are three examples all together [184–186]. In two of these examples [184,185] there are two independent molecules differing by degree of distortion in the same crystal. The examples include mono-, bi-, penta- and heptadentate ligands.

It might be expected that an increase in M–L bond distance would occur with increasing coordination number, but the experimentally observed trend is not so simple, as can be seen on comparing the mean Mg–O(H_2O) values: 203.7 pm (five coordinate Mg^{II}) < 205.7 pm (eight coordinate) < 205.9 pm (seven coordinate) < 207.1 pm (six coordinate). A similar effect is observed with Mg–N(Me_4en): 218.6 pm (four coordinate) < 225.5 pm (eight coordinate) < 237.7 pm (six coordinate).

For the ten coordinated examples there are two "sandwich" type organometallic derivatives, one with

TABLE 5. Crystallographic and structural data for mononuclear magnesium compounds. Coordination number seven [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$[Mg(C_{10}H_8O_6)(H_2O)_3]\cdot 4H_2O$ (colourless)	m $C2/c$ 8	2917(1) 675.8(2) 1734.7(8)	108.99(3)	MgO_7	H_2O_{eq} [b]	205.2(6)	O_{eq},O_{eq} [b]	72.1(2, 9.5) 143.8(2, 16.7)	171
					O_{eq}	212.6 (5, 18) (carboxy)	O_{eq},O_{ap}	89.6(2, 8.5)	
					O_{eq}	241.7(5, 19) (ether)	O_{ap},O_{ap}	169.1(2)	
					H_2O_{ap}	204.7(5, 16)			
$[Mg(C_{10}H_{20}O_5(H_2O)_2]\cdot Cl_2H_2O$ (colourless)	or $Fddd$ 8	983.0(2) 1743.5(3) 2406.5(4)		MgO_7	O_{eq}	208.6(6)	not given		172
					O_{eq}	221.8(9, 8)			
					H_2O_{ap}	204.5(4, 0)			
$[Mg(C_{10}H_{20}O_6)(H_2O)Cl]\cdot MeCN$ (colourless)	m $I2/m$ 4	743.0(3) 2230.1(9) 1154.4(6)	93.97(2)	MgO_6Cl	O_{eq}	217(1, 6)	O,O	72(2)	172
							O,H_2O	88(2)	
					H_2O_{ap}	206(1)	O,Cl	92(2)	
							H_2O,Cl	180.0	
					Cl_{ap}	244(1)			
$[Mg(C_{10}H_{20}O_5)(H_2O)Cl]\cdot CHCl_3$ (colourless)	tr $P\bar{1}$ 2	737.9(2) 1206.0(4) 1251.7(4)	112.93(2) 101.52(2) 92.35(2)	MgO_6Cl	O_{eq}	219(1, 4)	O,O	72(1)	172
							O,H_2O	90(3)	
					H_2O_{ap}	205.3(8)	O,Cl	90(3)	
					Cl_{ap}	242.5(5)	H_2O,Cl	177.5	
$MgC_{10}H_{20}O_5)(NCS)_2$ [c] (colourless)	tr $P1$ 2	1603.7(8) 716.1(4) 841.5(6)	105.26(5) 74.67(5) 103.61(4)	MgO_5N_2	O_{eq}	218.8(7, 51)	not given		173
					N_{ap}	208.1(6, 27)			
				MgO_5N_2	O_{eq}	218.5(7, 23)			
					N_{ap}	209.4(6, 23)			
$[Mg(C_{14}H_{20}O_5(NCS)_2$ (colourless)	or $Pbca$ 8	1639.9(3) 2578.4(5) 923.0(3)		MgO_5N_2	O_{eq}	218.5(7, 20)	O,O	72.3(3, 3.4)	174
							O,N	90.0(3, 5.2)	
					N_{ap}	206.1(7, 2)	N,N	177.9(3)	
$Mg(18\text{-crown-}6)(ClHCl)_2$ (not given)	orm $Pbca$ 8	1831.0(7) 751.2(6) 2908.5(8)		MgO_5Cl_2	O_{eq}	224–233(1)	not given		175
					Cl_{ap}	244.1(5, 13)			
$Mg(18\text{-crown-}6)Cl_2$ (pale yellow)	m $P2_1/n$ 4	1560.5(5) 1459.9(4) 740.2(2)	96.95(2)	MgO_5Cl_2	O_{eq}	225.6(4, 75)	not given		176
					Cl_{ap}	242.9(2, 0)			
$[Mg(C_{15}H_{23}N_5)(H_2O)_2]\cdot Cl_24H_2O$ (not given)	m $P2_1/a$ 4	2639.1(15) 856.2(8) 1109.1(9)	110.0(1)	MgN_5O_2	N_{eq}	224–231(1)	not given		177
					H_2O_{ap}	210(1, 0)			
$Mg(thf)_3(BH_4)_2$ (colourless)	m $C2/c$ 4	1212.0(8) 1264.6(8) 1242.4(7)	110.90(5)	MgH_4O_3	H_{eq}	203(4, 6)	H,H	66(–, 10); 152(–, 19)	178
					O_{eq}	207.7(2)			
					O_{ap}	210.1(2,0)	H,O	85(1); 142(1)	
							O,O_{ap}	85.23(7)	
							H,O_{ap}	92(1, 6)	
							O_{ap},O_{ap}	170.46	
$Mg(thf)_3(BH_4)_2$ (colourless)	m $C2/c$ 4	1218.1(4) 1264.2(5) 1246.0(5)	111.53(3)	MgH_4O_3	H_{eq}	205.5(17, 34)	H,H	50.6(13)	179
					O_{eq}	206.7(4)	O,O_{ap}	85.6(1)	
					O_{ap}	220.5(, 0)	O_{ap},O_{ap}	171.1(2)	
$Na_2[Mg(edta)(H_2O)]\cdot 5H_2O$ (colourless)	m C_2 2	1150.4(3) 980.1(3) 881.6(3)	110.88	MgO_5N_2	O_{qf} [d]	227.0(2, 0)	O_{qf},O_{qf}	163.52(13)	180
					N_{qf}	237.8(2, 0)	N_{qf},N_{qf}	75.35(10)	
					O_e	207.8(2, 0)	O_{qf},N_{qf} [e]	70.22(8)	
					H_2O_c	206.0(3)			

TABLE 5 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)	Ref.
$Na_2[Mg(edta)H_2O)]3H_2O$ (colourless)	or $P2_12_12_1$ 4	1336(3) 1652(3) 771(3)		MgO_5N_2	O_{qf} N_{qf} O_e H_2O_c	220(–, 4) 238(–, 3) 213(–, 2) 202(1)	not given	181

[a] Where more than one chemically distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] There are two crystallographically independent molecules. [d] The atom coordinated in a capped quadrilateral face (O_{qf}); in a capped edge (O_e); and in a unique capped position (O_c). [e] O_e–Mg–O_e = 175.27(25)°; O_e–Mg–O_{qf} = 78.12(9) and 101.19(9)°; O_e–Mg–N_{qf} = 74.16(8)°; O_{qf}–Mg–O_c = 81.76(6)°; N_{qf}–Mg–O_c = 142.32(5)°; O_e–Mg–O_c = 87.64(7)°.

two η^5-cp ligands [187], and one with two η^5-{$(Me_3Si)_3$cp} ligands [185]. In the latter case, there are two crystallographically independent molecules which are distortion isomers. The mean Mg–C(centroid) bond distance of 198(1) pm found in the former case [187] is shorter than the 203(1) pm found for the latter [185], presumably because of the steric effect of the trimethylsilyl groups.

TABLE 6. Crystallographic and structural data for mononuclear magnesium compounds. Coordination number eight and ten [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$[Mg(C_{22}H_{38}O_7)(H_2O)]$-$(ClO_4)_2$ [c] (colourless)	m $P2_1/c$ 8	1714.5(4) 2084.8(4) 1662.8(5)	92.31(2)	MgO_8	O [b] O H_2O	221.7(9, 94) 249(9) 205.6(9)	O,O [b]	not given	184
				MgO_8	O O H_2O	221.1(9, 86) 258.3(10) 204.5(10)	not given		
Mg{$(Me_3Si)_3$cp}$(Me_4$en)-(Br) [c] (colourless)	tr $P\bar{1}$ 4	954.6(1) 1085.2(1) 3072.7(2)	97.10(1) 93.01(1) 110.41(1)	MgC_5N_2Br	C [d] N Br	216.5 225.0(5, 20) 252.3(2)	N,N N,Br N,C [d] Br,C [d]	82.6(2) 96.5(1, 2.5) 123.0(–, 3) 124.9	185
				MgC_5N_2Br	C [d] N Br	216.9 223.9(5, 21) 251.0(2)	N,N N,Br N,C [d] Br,C [d]	83.0(2) 96.6(1, 1.2) 121.9(–, 3) 126.3	
Mg(cp)$(Et_4$en)Br (not given)	or $Pn2_1a$ 8	2396(5) 1263(4) 1156(5)		MgC_5N_2Br	N C Br	226(–, 9) 255(5) 263(1)	N,N N,Br	82.5(5) 94.9(–, 3.5)	186
$Mg(cp)_2$ (colourless)	m $P2_1/c$ 2	596.8(3) 807.3(3) 1092.3(4)	121.37(9)	MgC_{10}	C C [d]	230.4(8, 21) 198(1)	not given		187
$Mg(cp_2)$ [e] (colourless)				MgC_{10}	C C [d]	233.9(4, 0) 200.8(4)	not given		188
Mg{$(Me_3Si)_2$cp}$_2$ [c] (colourless)	m $P2_1/a$ 8	1879.4(3) 2272.0(4) 1980.3(1)	108.82(1)	MgC_{10}	C [d]	203(1, 1)	C [d]	171.8(2)	185
				MgC_{10}	C [d]	203(1, 1)	C [d]	170.4(2)	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] There are two crystallographically independent molecules. [d] The ring centroid of the cyclopentadienyl ligand. [e] By gas phase electron diffraction.

3. Double salts of magnesium

The data for these derivatives are given in Table 7, and are listed and referenced in order of increasing coordination number. In the double salt $[Mg(np)_3] \cdot [Mg(np)(crt)]$ [189], the magnesium of the $[Mg(np)_3]^-$ anion is three coordinate with a trigonal planar geometry. The seven coordinate geometry of the $[Mg(np)(crt)]^+$ cation is pentagonal bipyramidal, utilizing all six heteroatoms of the cryptand plus one bond to the neopentyl moiety. The closest approach of a cationic magnesium and an anionic magnesium is 718 pm.

In the yellow derivative $[Mg\{an(SiMe_3)_2\}(thf)_2] \cdot [Mg\{an(SiMe_3)_2\}(Me_4en)] \cdot 0.5(thf)$ [190], the magnesium atoms in both neutral complex species have distorted tetrahedral environments with chromophores of MgO_2C_2 and MgN_2C_2 respectively (Table 7).

The interesting compound $[Mg_2Me_5][Mg(C_{10}H_{20}O_5)(Me)]$ was shown [191] to have $[Mg(C_{10}H_{20}O_5)(Me)]^+$ cation units and $[Mg_2Me_5]^-$ anionic chains, as shown in Fig. 8. In the anionic unit the geometry is a distorted tetrahedron in which pairs of magnesium atoms are bridged by two carbon atoms (C3 and C4) and come within 281.1(2) pm of each other. These units are then linked by another carbon bridge (C5) to form polymeric chains. The six coordinate magnesium of the complex cation is bonded equatorially to all the crown ether oxygen atoms, and lies about 42 pm out of their mean plane. This Mg^{II} atom is also bonded to an apical methyl group (Mg–C = 214.0(7) pm).

In crystalline $[Mg(crt)(Et)]_2 \cdot [Mg_2Et_6]$ [189], the magnesium(II) atoms of the $[Mg_2Et_6]^{2-}$ anion are identical and share two bridging ethyl groups. The distorted tetrahedral environment is completed by two terminal ethyl groups. The magnesium atom of the

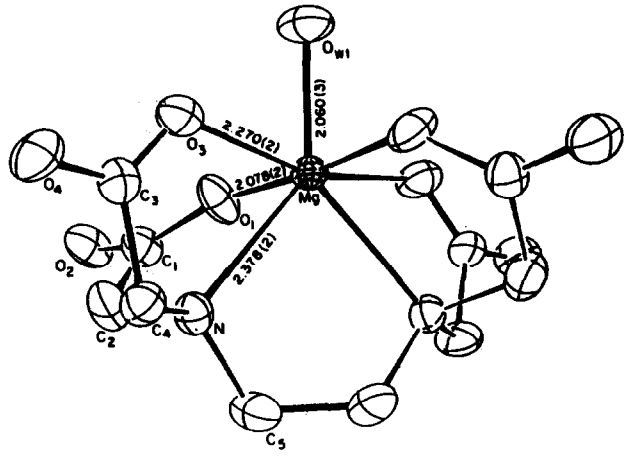


Fig. 6. Structure of $[Mg(edta)(H_2O)]^{2-}$ [180].

$[Mg(crt)(Et)]^+$ cation is six coordinated. The Mg–Mg distance of 281.6(5) pm and Mg–C–Mg angle of 73.2(3)° found in [189] are comparable with those found in the $[Mg_2Me_5]^{2-}$ anion [191].The effects of both electronic and steric factors can be seen in comparing the Mg–L bond distances: 217.0 pm (Me) < 222.4 pm (Et). The mean Mg–C(bridge) distances also follow the same trend, and are larger than the corresponding Mg–C(terminal) distances: 230.8 pm (Me) < 236.2 pm (Et).

Orange $[Mg_2(C_{12}H_8N_2)(thf)_6Br_2] \cdot [Mg(thf)_6Br_6]$ [192] has a neutral dimeric unit complexed to phenazine in which the magnesium atoms are five coordinate, each bound to an N-centre 48 pm out of the phenazine plane. The other four sites are occupied by three molecules of tetrahydrofuran and one bromine atom (Table 7). In the $Mg(thf)_6Br_2$ unit the magnesium is six coordinated.

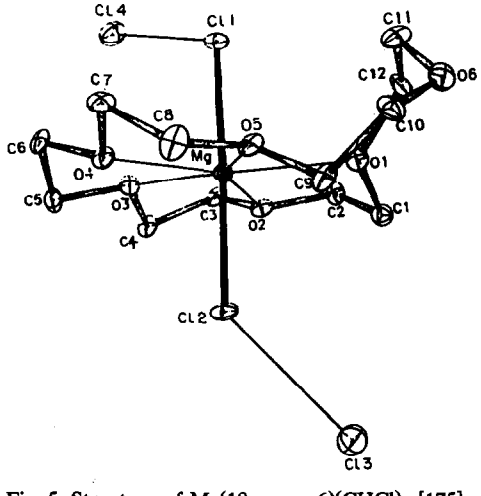


Fig. 5. Structure of $Mg(18\text{-crown-}6)(CHCl)_2$ [175].

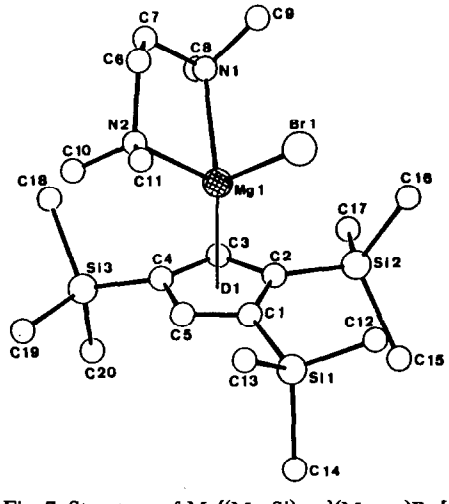


Fig. 7. Structure of $Mg[(Me_3Si)_3cp](Me_4en)Br$ [185].

TABLE 7. Crystallographic and structural data for double salts of magnesiums [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)	Ref.
$[Mg(np)_3][Mg(np)(crt)]$ (colourless)	m $P2_1/c$ 4	1321.9(4) 1474.0(6) 2131.5(9)	104.41(3)	MgC_3 [c]	C [b]	212.5(12) 224.0(12) 229.6(16)	C,C [b] 119.8(5, 5.0)	189
				MgO_4N_2 [d]	C	not given		
$[Mg\{an(SiMe_3)_2\}(thf)_2]$- $[Mg\{an(SiMe_3)_2\}$- $(Me_4en)] \cdot 0.5(thf)$ (yellow)	m $C2/c$ 8	4239(2) 1036.9(3) 3242(3)	114.85(3)	MgO_2C_2 [e]	O C	201.4(7, 1) 221.9(9, 4)	O,O 97.8(3) C,C 78.1(3) O,C 120.7(3, 8)	190
				MgN_2C_2 [e]	N C	212.6(10, 10) 222.3(10, 1)	N,N 85.1(4) C,C 78.9(3) N,C 124.7(3, 1.5)	
$[Mg_2Me_5][Mg(C_{10}H_{20}O_5)(Me)]$ (not given)	or $Pna2_1$ 4	1073.6(2) 1845.4(3) 1192.3(3)		MgC_4 [c]	C μ-C μ-C	217.0(6, 0) 229.1(9, 40) 232.7(6, 69)	not given	191
				MgO_5C [d]	O_{eq} C_{ap}	not given 214.0(7)	[f]	
$[Mg_2(Et)_6][Mg(crt)(Et)]_2$ (not given)	m $P2_1/n$ 2	1051.4(2) 856.0(4) 3225.0(10)	90.34(2)	MgC_4 [c]	C μ-C	222.4(9, 15) 236.2(9, 3)	C,C 114.4(4) [g]	189
				MgO_3N_2C [d]	not given			
$[Mg_2(C_{12}H_8N_2)(thf)_6Br_2]$- $[Mg(thf)_4Br_2]$ (orange)	m $C2/c$ 4	2842(3) 1257.1(6) 2112.9(3)	125.24(6)	MgO_3NBr [e]	O N Br	211.6(5, 50) 205.2(7) 251.3(3)	O,O 89.1(2, 1.6) O,N 100.3(2, 19.3) O,Br 94.8(2, 9.7) N,Br 135.9(1)	192
				MgO_4Br_2 [e]	O Br	210.6(6, 11) 265.6(1, 0)	O,O 90.0(2, 1) O,Br 90.0(1, 3) Br,Br 180	
$[Mg(atp)_2][Mg(H_2O)_6]_2$- $(dpa)_8 x H_2O$ (not given)	or $C222_1$?	1023.3(3) 2273.4(3) 3099.7(4)		MgO_6 [c]	O	206(2, 0)	O,O 85.4(7)	193
				MgO_6 [d]	H_2O	212(4, 0)	not given	
$[MgH_2O)_6][Mg(cit)(H_2O)]_2$- $2H_2O$ (not given)	m $P2_1/n$?	2022.2 668.6 913.5	96.86(3)	MgO_6 [d] MgO_6 [c]	H_2O H_2O cit.HO cit.COO	207.4(1, 13) 203.1(1) 211.8(1) 206.2(1, 43)	O,O 90.00(5, 1.88) O,O 76.32(5) 100.30(5)	194
$[Mg(H_2O)_4(H\text{-bipam})_2$- $[Mg(H\text{-atp})_2]12H_2O$ (colourless)	or $C222_1$ 4	2273.4(3) 1023.3(3) 3099.7(4)		MgO_6 [d]	H_2O	203(5, 0) 212(5, 0) 220(4, 0)	O,O 90(2, 29) 160(2, 6)	195
				MgO_6 [c]	O	201(2, 0) 209(2, 1)	O,O 90(1,8) 175(1, 3)	
$[Mg(H_2O)_4(thf)_2]$ [h] $[Mg(H_2O)_3(thf)_3]Br_4$ (yellow)	m $A/2a_1$ 8	2641.5(5) 1245.4(5) 1294.9(2)	116.81(1)	MgO_6 [d]	O H_2O	209.8(24, 0) 207.1(17, 4)	O,O 90.0(9, 3.6) 180.0	196
				MgO_6 [d]	O H_2O	210.6(31, 8) 206.9(18, 18)	O,O 90.0(8, 2.6) 178.9(9, 1.6)	
				MgO_6 [d]	O H_2O	209.3(18, 22) 205.5(20, 11)	O,O 90.0(8, 2.4) 178.2 (8, 1.4)	
$[Mg(H_2O)_6][Mg(edta)(H_2O)]$- $2H_2O$ (colourless)	or $Pbcn$ 4	1162.2(5) 949(1) 1926(2)		MgO_6 [d]	H_2O	207(1, 1) 215(1)	O,O 90.0(–, 3.2)	197
				MgO_5N_2 [c]	O_{eq} N_{eq} H_2O_{eq} O_{ap}	235(1, 0) 239(1, 0) 204(1) 201(1, 0)	not given	

TABLE 7 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$[Mg(H_2O)_6][Mg(edta)(H_2O)]$-$2H_2O$	o	1161.7(1)		MgO_6 [d]	H_2O	204.9(1, 2)	O,O	90.00(5, 2.57)	198
	Pbcn	949.5(1)				208.7(1, 0)			
(colourless)	4	1923.8(2)		MgO_5N_2 [c]	O_{eq}	233.6(1, 0)	O_{eq},H_2O_{eq}	75.13(4)	
					N_{eq}	239.6(1, 0)	O_{eq},N_{eq}	69.18	
					H_2O_{eq}	205.8(2)	N_{eq},N_{eq}	74.10(5)	
					O_{ap}	202.7(1, 0)	O_{eq},O_{eq}	96.65(5, 84)	
							O_{ap},N_{eq}	76.92(5)	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] the complex anion species. [d] The complex cation species. [e] The neutral complex species. [f] C–Mg–μ-C = 111.9(4, 4.5)°; μ-C–Mg–μ-C = 104.5(3, 1.2)°; Mg–C–Mg = 75.4(3, 9)°; Mg–Mg = 281.1(2) pm. [g] μ-C–Mg–μ-C = 106.8(3)°; Mg–C–Mg = 73.2(3)°; Mg–Mg = 281.6(5) pm. [h] There are two crystallographically independent complex cation species.

There are four examples [193–196] in which magnesium atoms are hexacoordinated with six O-donor ligands. It is interesting to note that in one case, two crystallographically independent $[Mg(OH_2)_4(thf)_2]^{2+}$ cations have been found with the $[Mg(OH_2)_3(thf)_3]^{2+}$ cation and four bromide anions [196], as another example of distortion isomerism.

In $[Mg(OH_2)_6][Mg(edta)(OH_2)] \cdot 2H_2O$ [197,198] the first magnesium(II) atom is octahedrally coordinated to six water molecules. The second magnesium (II) atom is close to pentagonal bipyramidal, with a coordination sphere consisting of hexadentate edta and one water molecule. The initial determination [197] was based only on visual intensity estimates of film X-ray data, and the precision was quite low (R value 11.3%) and hydrogen atoms were not located. The subsequent determination [198] was based on counter diffractometer data and refined to completion.

4. Binuclear magnesium compounds

The essentially colourless or white compounds of this class are listed in Table 8 together with their crystallographic and structural data. Five distinct types of bridging are seen to occur, with two bridging ligands per unit being the most common. The molecular structure of $[Mg\{\mu\text{-}C_3H_6N(Me)(c\text{-}hx)\}(Et)]_2$ [199] is shown in Fig. 9 as a representative example of this type. The bridging carbon atoms bring the magnesium atoms within 274.5(1) pm of each other with Mg–C–Mg angles of 74.1(1)°. This is the shortest Mg–Mg distance found in a magnesium complex. Both magnesium atoms are identically coordinated, the tetrahedral environment containing three carbon atoms and one nitrogen atom. A similar structure has been found for $[Mg(\mu\text{-}C_3H_6NMe_2)(Et)]_2$ [199] with almost identical Mg–C–Mg angles (74.0(1)°), and Mg–Mg distance (274.9(1) pm). In several cases two organic nitrogen atoms serve as bridges, for example $[Mg\{\mu\text{-}(NBu)_2SiMe_2\}(thf)]_2$ [200], $[Mg\{\mu\text{-}N(SiMe_3)C_6H_4N(SiMe_3)\text{-}O\}(Et_2O)]_2$ [201], $[Mg\{\mu\text{-}N(SiMe_3)_2\}(Bu)]_2$ [202], and $[Mg(\mu\text{-}C_5H_{13}N_2)(Me)]_2$ [203]. In five cases [204–207], two oxygen ligands are used for bridging. Bridging chlorine atoms are used in $[Mg(\mu\text{-}Cl)al(Me_4en)]_2$ [208], and in another two examples [209,210] bridging bromine atoms are employed.

A second type of bridging involves three atoms, as in $[\{Mg(\mu\text{-}N{=}CPh_2)(thf)Br\}_2(\mu\text{-}thf)]$ [211], where two nitrogen atoms and one oxygen atom are involved in a face shared environment. In another example [49] (Table 8) three bridging chlorine atoms are found between the two magnesium(II) atoms.

In a third type, "magnesiacyclohexane" [212] occurs exclusively as a dimer with a twelve membered ring structure, 1,7-dimagnesiacyclododecane. Each of the

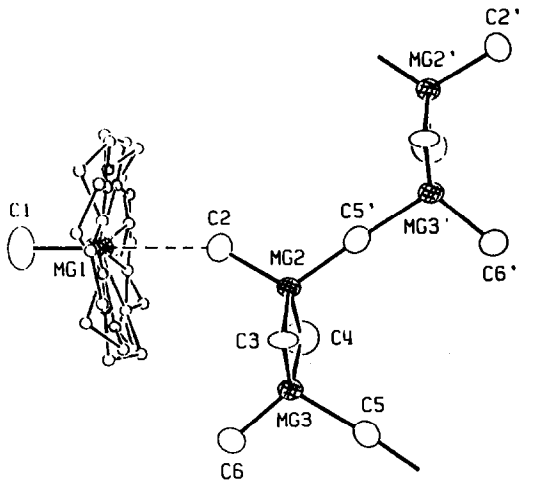


Fig. 8. Crystal packing of $[Mg_2Me_5][Mg(C_{10}H_{20}O_5)(Me)]$ [191].

TABLE 8. Crystallographic and structural data for binuclear magnesium compounds [a]

Compound (colour)	Cryst. cl Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		Mg–Mg (pm) Mg–L–Mg (°) μ-L–Mg–μ-L (°)	L'–Mg–L (°)		Ref.
[Mg(μ-C_3H_6N)(Me)-(c-hx)(Et)]$_2$ (white)	m $P2_1/c$ 2	1332.8(2) 800.73(9) 1350.4(2)	111.44(1)	MgC_3N [b]	C(Et) N μ-C	212.9(4) 219.5(2) 227.7(3, 10)	274.5(1) 74.1(1) 105.9(1)	C,N [b] C,μ-C	117.0(1) 117.4(1, 7)	199
[Mg(μ-$C_3H_6NMe_2$)-(Et)]$_2$ (white)	m $P2_1/n$ 2	895.9(1) 751.54(7) 1358.82(9)	94.640(6)	MgC_3N	C(Et) N μ-C	214.2(3) 218.1(2) 228.4(2, 11)	274.9(1) 74.0(1) 106.0(1)	C,N C,μ-C N,μ-C	116.3(1) 118.4(1, 3.0) 96.8(1, 13.5)	199
[Mg(μ-$(NBu)_2SiMe_2$)-(thf)]$_2$ (not given)	tr $P\bar{1}$ 2	1000.5(3) 998.0(3) 1120.9(3)	104.25(2) 112.76(2) 107.7(1)	MgN_3O	N O μ-N	199.3(4) 204.9(6) 215.0(4, 38)	288 84.1(1) 95.1(3)	N,μ-N N,O O,μ-N	102.2(2, 25.5) 107.2(2) 122.2(2, 6.4)	200
[Mg(μ-N($SiMe_3$)C_6H_4-N($SiMe_3$)-*o*)(Et_2O)]$_2$ (colourless)	or *Pbca* 4	1299.6(3) 1616.5(5) 1997.5(1)		MgN_3O	N O μ-N	199.7(7) 204.1(7) 208.4(7, 2)	not given 86.1(3) 93.9(3)	N,O N,μ-N O,μ-N	112.1(3) 103.2(3, 15.4) 119.6(3,2)	201
[Mg(μ-N($SiMe_3$)$_2$)-(Bu)]$_2$ (colourless)	tg $P\bar{4}n2$ 2	952.4(6) – 1738.5(9)		MgN_2C	C μ-N	208(1) 211.8(4, 0)	291.9(4) 87.1(2) 92.9(2)	N,C	133.6(1)	202
[Mg(μ-$C_5H_{13}N_2$)-(Me)]$_2$ [c] (white)	tr $P\bar{1}$ 2	724.4(2) 1038.7(3) 1245.4(4)	82.10(6) 88.61(17) 80.37(9)	MgN_3C	N μ-N C	219.0(3) 210.4(3, 3) 210.0(4)	293.2(2) 88.3(1) 91.7(1)	N,μ-N N,C μ-N,C	83.4(1) 115.2(1) 123.8(1, 2.9)	203
				MgN_3C	N μ-N C	218.2(3) 210.8(3, 11) 210.4(4)	294.5(2) 88.6(1) 91.4(1)	N,μ-N N,C μ-N,C	84.0(1) 117.4(1) 124.1(1, 6.3)	
[Mg(μ-$C_7H_{13}O$)-(Et_2O)Br]$_2$ (not given)	m $P2_1/c$ 4	1021.7(5) 1694.5(10) 1728.2(11)	98.26(5)	MgO_3Br	O μ-O Br	204.9(9) 195.3(7, 2) 241.7(4)	not given 95.0(3, 2) 84.8(3, 1)	O,Br	105.4(3)	204
[Mg(μ-OBu)(Et_2O)-Br]$_2$ (colourless)	m $P2_1/c$ 2	968(2) 1110(2) 1510(2)	129.1(2)	MgO_3Br	O μ-O Br	201(1) 191(1, 0) 243.5(7)	not given 96.7(6) 83.3(7)	O,μ-O O,Br Br,μ-O	110.6(7, 1.3) 107.0(5) 121.9(5, 7)	205
[Mg(bht)$_2$]$_2$ (white)	or $Pc2_1b$?	1066.0(2) 1978.2(5) 2921.1(8)		MgO_3	not given		not given	not given		206
[Mg(bhb)$_2$]$_2$1.5(tol) (white)	m $C2/c$ 4	4462.9(4) 1392.2(2) 2036.7(5)	97.43(1)	MgO_3	O μ-O	182.1(3, 2) 196.4(3, 13)	296.4(2) 98.0(1, 2) 82.1(1, 3)	O,μ-O	139.0(1, 7)	206
[Mg(μ-$C_{12}H_{27}N_2O_4$)-(np)]$_2$ (colourless)	m $P2_1/n$ 2	1020.3(2) 957.9(4) 2312.1(7)	95.93(2)	MgO_3NC	O μ-O C(np) N	214.2(5) 199.5(4, 16) 218.1(6) 237.7(5)	303.7(4) 99.2(2) 80.8(2)	O,μ-O O,C O,N [d]	100.3(2, 11.3) 116.6(2) 74.3(2)	207
[Mg(μ-Cl)(al)-(Me_4en)]$_2$ @ 150 K (colourless)	m $P2_1/n$ 4	844.5(1) 1102.0(1) 1350.4(1)	92.58(1)	MgN_2Cl_2C	N C(al) μ-Cl μ-Cl	224.8(2, 37) 217.9(3) 240.0(1) 269.4(1)	not given 95.32(3) 84.69(3)	N,N N,C N,Cl C,Cl	80.20(7) 99.26(8) 97.51(5, 9.67) 125.29(7)	208
[Mg(μ-Br)(Et)-(Et_3N)]$_2$ (not given)	m $P2_1/n$ 2	1046.8(2) 1267.3(3) 941.4(2)	90.26(4)	$MgBr_2NC$	N C μ-Br	215 218 256.7(–, 1)	not given	N,Br C,Br N,C	105.3 117 116.2	209
[Mg(μ-Br)(Et)-{O(^{i}Pr)$_2$}]$_2$ (not given)	m $P2_1/n$ 2	785(1) 1443(2) 1131(2)	100.3(1)	$MgBr_2OC$	O C μ-Br	201.9(6) 209.4(11) 257.9(3, 3)	not given 86.8(1) 93.2(1)	O,C O,Br C,Br	120.7(3) 117.0(3, 3) 102.2(2, 3)	210

TABLE 8 (continued)

Compound (colour)	Cryst. cl Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		Mg–Mg (pm) Mg–L–Mg (°) μ-L–Mg–μ-L (°)	L'–Mg–L (°)		Ref.
[{Mg(μ-N=CPh$_2$)-(thf)Br}$_2$(μ-thf)] (pale yellow)	m $C2/c$ 4	1781.9 1064.7 2205.1	112.86	MgO_2N_2Br	O μ-O μ-N Br	206.6(5) 245.3(5) 207.8(4) 247.4(2)	288.6(3) [e]	O,μ-O O,Br μ-O,Br N,N	173.1(2) 96.6(2) 87.4(1) 89.0(2)	211
[Mg$_2$(μ-Cl)$_3$(thf)$_6$]-($C_{14}H_{10}$) @ 100 K (blue)	m $C2/c$ 4	2821.2(3) 994.7(1) 1452.0(3)	100.043(9)	MgO_3Cl_3	not given		not given	not given		49
[Mg(CH$_2$)$_5$(thf)$_2$]$_2$ (colourless)	tr $P\bar{1}$?	885(2) 960(2) 963(2)	92.2(3) 93.2(3) 112.7(3)	MgO_2C_2	O C	210.0(8, 11) 214(1, 1)	not given	O,O C,C O,C	90.8(3) 141.5(3) 103.3(4, 3.5)	212
[Mg$_2$(egta)(H$_2$O)$_6$]-5H$_2$O (colourless)	or $Pna2_1$ 4	1409.8(2) 1239.6(3) 1592.5(3)		MgO_5N	O N H_2O	206.8(3, 24) 230.0(4, 19) 205.0(4, 45)	not given	O,O O,N [f]	95.8(1, 2) 77.1(1, 1.5)	213
[Mg$_2$(pdta)(H$_2$O)$_6$] (colourless)	tr $P\bar{1}$ 2	977.4(2) 1146.6(1) 976.0(2)	97.25(1) 105.10(1) 98.49(1)	MgO_6 MgO_5N_2 [g]	O H_2O O_{qf} N_e H_2O_c	205.1(2) 208.1(2, 48) 211.7(2, 64) 243.1(2, 4) 213.9(2)	not given	O,O O_{qf},O_{qf} [h]	90.0(1, 4.4) 176.0(1, 1.1) 91.2(1, 20.9)	214

[a] Where more than one chemically equivalent or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] There are two crystallographically independent molecules. [d] μ-O–Mg–C = 120.2(2, 10.5)°; μ-C–Mg–N = 78.3(2) and 146.0(2)°; C–Mg–N = 104.3(2)°. [e] Mg–O–Mg = 72.1(1)°; Mg–N–Mg = 88.0(2)°. [f] O–Mg–OH_2 = 90.6(2, 4.6) and 169.8(2, 2.9)°; N–Mg–OH_2 = 94.9(2, 1.3) and 165.0(2, 6)°; H_2O–Mg–OH_2 = 96.1(2, 1.8)°. [g] The Mg is in a monocapped trigonal prismatic environment; O_{qf} is in a quadrilateral face; N_e is in remaining edge, and H_2O_c is in a unique position. [h] O_{qf}–Mg–N_e = 73.0(1, 5.9) and 114.8(1, 25.9)°; N_e–Mg–N_e = 70.2(1)°; N_e–Mg–O_c = 142.7(1, 11.7)°; O_{qf}–Mg–O_c = 88.2(1, 18.5)°.

magnesium atoms attains tetracoordination by the ligation of two molecules of tetrahydrofuran.

The fourth type of bridging uses both functional ends of the egta molecule to act as a tridentate ligand to each magnesium atom [213]. The octahedral coordination sphere is made up of the amino nitrogen atom and the two carboxylate oxygen atoms occupying one face, while three water molecules occupy each of the other three sites (Table 8).

The fifth type is shown by the chelated, seven coordinate, magnesium moiety MgO_5N_2 of Mg$_2$(pdta)-(OH$_2$)$_6$ linked through acetate oxygen atoms to a pentahydrated magnesium(II) unit [214]. The MgO_6 chromophore has an almost octahedral O_h environment, as shown in Fig. 10, and Table 8.

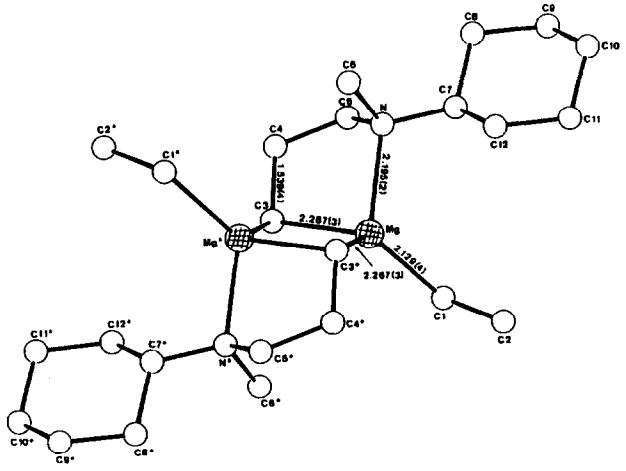


Fig. 9. Molecular structure of [Mg{μ-C_3H_6N(Me)(c-hx)}(Et)]$_2$ [191].

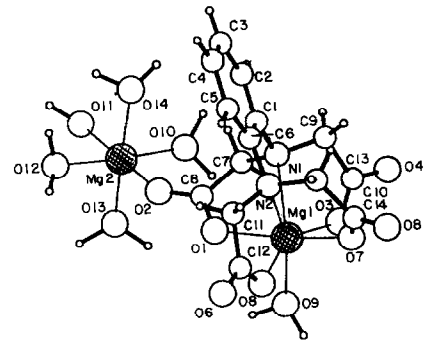


Fig. 10. Molecular sructure of [Mg$_2$(pdta)(H$_2$O)$_6$] [214].

The data in Table 8 indicate that the magnesium atom is only found in an oxidation state of two. It is interesting to observe that the mean Mg–L(terminal) bond distance is shorter than the Mg–L(bridge) value if L is a halogen donor, but that the opposite is true if L is an oxygen donor. The bridge distances and bond angles are all interdependent. For example, as the bridge angle opens the Mg–L distance decreases: 74.0° and 228.4 pm [199]; 84.1° and 215.0 pm [200]; 88.6° and 210.8 pm [203]; 98.0° and 196.4 pm [206], respectively. As the bridge angle opens, the Mg–Mg distance increases, for example: 74.1(1)° and 274.5(1) pm [199]; 84.1(1)° and 288 pm [200]; 87.1(2)° and 291.9(4) pm [202]; 88.3(1)° and 293.2(2) pm, 88.6(1)° and 294.5(2) pm [203]; 98.0(1)° and 296.4(2) pm [206]; 99.2(2)° and 303.7(4) pm [207], respectively.

From a stereochemical point of view, tetrahedral symmetry predominates [199–201,203–205,209,210, 212]. There are two examples of magnesium in a trigonal planar environment [202,206], three examples of pentacoordination [207,208,211], and two examples of hexacoordination [49,213]. There is only one example [214] in which two non-equivalent magnesium chromophores are found bridged together (Fig. 10). There

TABLE 9. Crystallographic and structural data for tri-, tetra-, and hexanuclear magnesium compounds [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$[Mg(acac)_2]_3$	tr	874.9(6)	111.84(6)	MgO_6	μ-O [b]	208.3(3, 8)	O,O [b]	not given	215
(colourless) trimer	$P\bar{1}$	1095.8(6)	101.64(6)	MgO_6 (2×)	O	202.4(3, 5)			
	1	1117.3(9)	108.35(5)		μ-O	213.8(3, 16)			
$[Mg(depa)_2]_3$	m	1117.9(8)		MgO_6	μ-O	209.3(5, 17)	not given		215
(colourless) trimer	$P2_1/n$	1281.2(9)	93.04(3)	MgO_6	O	201.3(5, 52)			
	2	2183.6(12)		(2×)	μ-O	211.6(5, 27)			
$[Mg(C_8H_8)(thf)_2]_3$	or	2470.6(8)		MgO_2C_2	O	207.2(6, 11)	O,O	94.1(2, 1)	216
(colourless) trimer	$F2dd$	894.8(3)			C	216.2(8, 8)	C,C	128.7(3, 1.9)	
	8	4431.5(9)							
$[Mg_4(\mu_4\text{-}O)(\mu\text{-}Br)_6(Et_2O)_4]$	tg	1068(3)		$MgBr_3O_2$	O	211(2)	Br,Br	119.34(30, 1.81)	217
	$P\bar{4}2_1c$	–			μ_4-O	192.5(8)	O,μ_4-O	179.80(70)	
(colourless) tetramer	?	1534(3)			μ-Br	261.5(8, 2)	Br,μ_4O	87.48(30, 1.00) [c]	
$[Mg_2(\mu_3\text{-}Cl)(\mu\text{-}Cl)_2(Et)(thf)_3]_2$	m	1212.8(3)		$MgCl_3OC$	C_{eq}	219(3)	C,μ-Cl	125.9(12)	218
	$P2_1/c$	1675.0(4)	104.02(2)	(2×)	μ-Cl_{eq}	240.1(11, 6)	C,O	95.4(16)	
(not given) tetramer	2	1097.2(3)			O_{ap}	214(2)	C,μ_3-Cl	95.4(10)	
					μ_3-Cl_{ap}	279.2(9)	[d1]		
				$MgCl_4O_2$	O	208(2, 4)	O,O	89.6(8)	
				(2×)	μ-Cl	248.9(9, 17)	O,μ-Cl	89.1(6, 6)	
					μ_3-Cl	250.2(10, 17)	[d2]		
$[Mg_4(MeO)_6(MeOH)_{10}]Cl_2$	tg	1137		MgO_6	O	206(–, 4)	not given		219
	$P42_1c$	–				219(–, 2)			
(not given) tetramer	2	1375							
$(NH_4)_4[Mg_4(C_{16}H_{20}O_{16})_6]$	tr	1875.6(2)	103.93(3)	MgO_6	not given		not given		220
	$P\bar{1}$	2007.2(7)	93.50(5)						
(colourless) tetramer	2	1777.1(9)	90.45(4)						
$[Mg(\eta^5\text{-cp})(\mu\text{-OEt})]_4$	or	1012.29(8)		MgC_5O_3	μ-O	207.0(1, 13)	O,O	83.9(1, 2.5)	221
	$Pbcn$	1753.3(1)					cp,cp	133.1(–, 2.5)	
(colourless) tetramer	4	1690.6(1)			C(cp) [e]	210.5(–, 2)	[e]		
$Mg_6(\mu_6\text{-}N)(\mu\text{-}NH^tBu)_9$	or	2660.3(5)		MgN_4	μ-N	209.3(2, 50)	not given		222
	$Pbca$	2040.5(3)			μ_6-N	214.8(3, 26)			
(colourless) hexamer	8	1990.2(2)							

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] Mg–Br–Mg = 75.63(4, 30)°. [d1] Mg–Cl–Mg = 94.2(3, 5.7)°; μ-Cl–Mg–μ_3-Cl = 83.3(3, 3) and 127.6(2)°; μ-Cl–Mg–μ-Cl = 106.1(4)°; μ_3-Cl–Mg–O = 169.2(7)°; μ-Cl–Mg–O = 90.3(7, 4)°. [d2] Mg–Cl–Mg = 96.4(3)°; μ_3-Cl–Mg–O = 93.6(6, 7)°; μ-Cl–Mg–μ_3-Cl = 89.5(3, 5.9)°; μ-Cl–Mg–μ-Cl = 177.5(5)°. [e] The mean value of Mg–centroid bond distance of cyclopentadienyl ring; Mg–O–Mg = 95.7(1, 2.9)°.

is one example of distortion isomerism, where two dimers are found in one crystal, differing only by degree of distortion [203].

5. Tri-, tetra-, and hexanuclear magnesium compounds

The crystallographic and structural data for these compounds are given in Table 9. There are three examples of tri-nuclear derivatives. In colourless $[Mg(acac)_2]_3$ and $[Mg(depa)_2]_3$ [215], each magnesium(II) atom is coordinated by six O atoms in a distorted octahedral array. The bridging of the central Mg atom with the terminal ones is achieved through common O atoms of the carbonyl groups. The mean Mg–O(bridge) bond distance of 210.8 pm is longer than that of the terminal Mg–O bonds (202.0 pm). The structure of another colourless trimer, $[Mg(C_8H_8)(thf)_2]_3$, is shown in Fig. 11, where it can be seen that each magnesium is bridged to the other two by a cycloocta-1,5-diene ligand. The pseudo tetrahedral coordination about each metal atom is completed by a pair of tetrahydrofuran ligands (Table 9).

The tetramer $[Mg_4(u_4\text{-}O)(\mu\text{-}Br)_6(Et_2O)_4]$ [217] consists of a Mg_4Br_6O unit surrounded by four ether molecules. The four Mg^{II} atoms occupy the corners of a tetrahedron and the oxygen atom is tetrahedrally coordinated to four magnesium atoms lying on the alternate faces of the octahedron described by the bromine atoms. The mean Mg–Br(bridge) bond distance is 261.5(8) pm and the Mg–Br–Mg angle is 75.63(4)° (Table 9). In another tetramer, $[Mg_2Cl_3(Et)(thf)_3]_2$ [218], four Mg^{II} atoms are bridged as shown in Fig. 12. Five nearest neighbours to the Mg(2) atoms form an approximate trigonal bipyramid, with O(3) and Cl(1) at the apices and Cl(1), Cl(2) and Cl(3) in the equatorial positions. The Mg(1) atoms are in approximate octahedral coordination.

Another colourless tetramer, $(NH_4)_4[Mg_4(C_{16}H_{20}O_{10})_6]$ [220], has an adamantane-like structure. The core of the chelate complex anion forms a tetrahedron

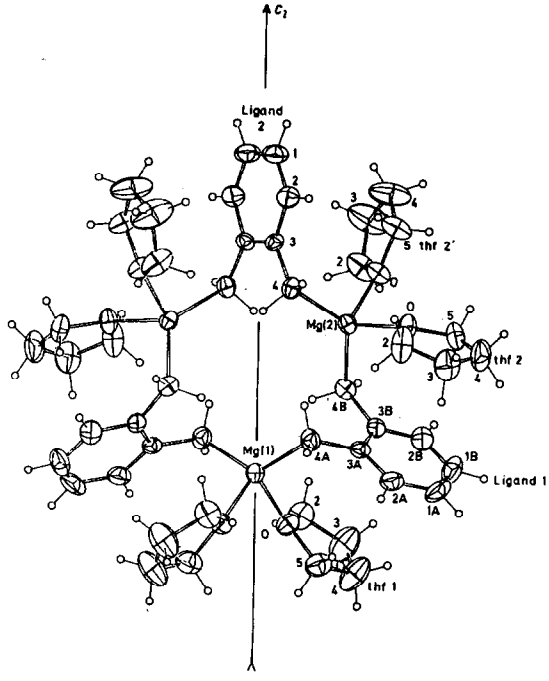


Fig. 11. Structure of $[Mg(C_8H_8)(thf)_2]_3$ [216].

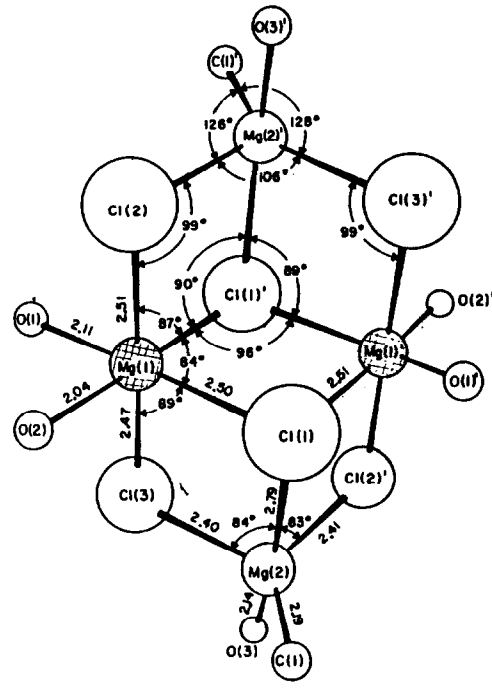


Fig. 12. Molecular structure of $[Mg_2Cl_3(Et)(thf)_3]_2$ [218].

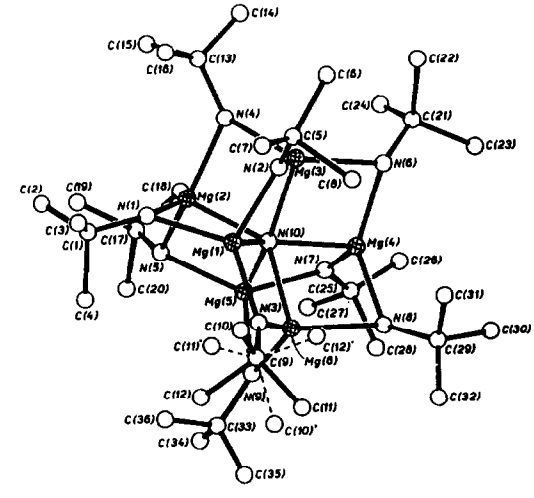


Fig. 13. Structure of $Mg_6(N)(NH^tBu)_9$ [222].

TABLE 10. Crystallographic and structural data for polynuclear magnesium compounds [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$Mg(Me)_2$ (colourless)	or *Ibam* 4	600(3) 1148(5) 545(3)		MgC_4	μ-C [b]	224.4(3)	C,C [c]	105(2)	224
$Mg(Et)_2$ (colourless)	tg $P4_2/m$ 2	729.4(20) – 533.8(20)		MgC_4	μ-C	226	C,C [d]	108	225
$[(np_2Mg)_2$-$(npMgBr_2]$ (not given)	tr $P1$ 2	965.4(1) 987.6(1) 1133.4(2)	85.35(1) 67.93(1) 74.59(1)	MgC_4	μ-C	234(2, 11)	C,C [e1]	108.7(7, 19.0)	226
				MgC_2Br_2	μ-C μ-Br	227(2, 7) 281.3(5, 5)	C,Br Br,Br [e2]	115.0(5, 14.4) 93.6(2)	
$Mg(\mu$-dox$)(np)_2$ (colourless)	m $C2/c$ 4	1704.0(4) 936.2(1) 1083.3(5)	98.64(2)	MgO_2C_2	μ-O C	213.2(1) 213.3(2)	O,O C,C O,C	89.47(6) 139.95(9) 104.13(7, 4.39)	227
MgF_2 (not given)	tg $P4_2/m2_1/n2/m$ 2	462.13(1) – 305.19(1)		MgF_6	μ-F_{eq} μ-F_{ap}	199.68(1, 0) 197.98(2, 0)	F,F [f]	80.33(1)	228
MgF_2 (not given)	tg $P4_2/mnm$ 2	462.8(5) – 304.5(3)		MgF_6	μ-F	198.4(1)	F,F	not given	229
MgF_2				MgF_6	μ-F_{eq} μ-F_{ap}	199.4(×2) 198.4(×4)			230
$Mg(CO_3)(H_2O)_3$ (colourless)	m $P2_1/n$ 4	770.53(11 536.73(6) 1212.12(11	90.451(13)	MgO_6	O H_2O	202.2(7) 213.1(8, 18) 206.6(7, 50)	O,O	60.5–117	231
$4MgCO_3$-$Mg(OH)_2$-$(H_2O)_4$ (colourless)	m $P2_1/c$ 2	1011(1) 897(1) 839(1)	114.6(9)	MgO_6	O OH H_2O	210(2, 5) 204(2) 216(2)	O,O	90.0(8, 13.0)	232
				MgO_6	O OH	202(3) 209(3)	O,O	90.0(9, 5.1)	
$KHCO_3MgCO_3$-$(H_2O)_4$ (colourless)	tr $P\bar{1}$ 1	671.3(3) 733.7(3) 636.4(1)	108.18(3) 108.92(3) 59.57(2)	MgO_6	O	205.6(4, 3) 209.8(3)	O,O	90.00(13, 1.64)	233
$MgSO_4$ $(1/3Mg(OH)_2$ $(1/3)H_2O$ (colourless)	tg $I4_1/amd$ 4	524.2(1) – 1299.5(3)		MgO_6	$O(SO_4)$ OH H_2O	208.1(2, 0) 208.7(1, 0) 208.7(1, 0)	O,O	90.0(1, 5.8) 127.3(1)	234
α-$Mg_2P_2O_7$	m $B2_1/c$ 8	1319.9(10) 829.5(5) 907.2(5)	104.9(1)	MgO_5 MgO_6	O O	204.4(–, 76) 207.2(–, 13) 213.8(–, 4)	not given		235
β-$Mg_2P_2O_7$	m $C2/m$ 2	649.4(7) 828(1) 452.2(5)	103.8(1)	MgO_6	O	204(–, 2) 215(–, 0)	not given		236
$Mg(PhPO_3)$-H_2O [h] (colourless)	or $Pmn2_1$ 2	561(1) 1428(2) 482(1)		MgO_6	O	not given			237

TABLE 10 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L′–Mg–L (°)	Ref.
MgP_4O_{11} (not given)	m $P2_1/c$ 4	534.3(2) 2222.8(5) 745.1(2)	110.888(5)	MgO_6	O	not given		238
$Mg_2P_4O_{12}$ (not given)	m $C2/c$ 4	1175.6(2) 828.5(1) 991.7(1)	118.96(2)	MgO_6	O	200.7(3) 209.5(3, 1)	not given	239
				MgO_6	O	199.0(3) 214.3(3, 18)		
$(NH_4)_3[Mg(H_2O)_4(HPO_4)_2]$ (yellow)	or *Pbca* 8	1149(2) 2366(6) 862(1)		MgO_6	O H_2O	207(3, 2) 210(3, 5)	O,O 90.0(–, 8.8) 174.0(–, 3.6)	240
$Mg(H_2O)_2(HPO_4)$ (colourless)	or *Pbca* 8	1020.3(3) 1067.9(4) 1001.5(3)		MgO_6	O H_2O	204.8(2, 33) 210.8(2, 2)	O,O 90.0(1, 5.6) 174.4(1, 1.6)	241
$Mg(H_2O)_3(HPO_4)$ (colourless)	or *Pbca* 8	1021.5(2) 1068.1(2) 1001.4(2)		MgO_6	O H_2O	204.9(5, 28) 211.8(5, 11)	not given	242
$[Mg(urea)_2(H_2PO_4)_2]$(urea) (not given)	m $P2_1/n$ 2	735.2(2) 2150.2(5) 537.0(1)	91.64(2)	MgO_6	O O(urea)	207.1(2, 5) 217.2(2, 0)	O,O 90.0(1, 9)	243
$[Mg_3(H_2O)_5\{(PhO)_2P(O)O\}_6$ (not given)	tr $P\bar{1}$ 2	1517.3(23) 2362.5(17) 1289.6(9)	104.85(6) 112.56(10) 86.23(10)	MgO_5	O H_2O	198.7(4, 25) 211.1(5)	O,O 98.9(2, 4.3) 158.2(2, 1.2)	244
				MgO_6	O H_2O	204.2(4, 33) 215.3(4, 24)	O,O 90.0(2, 12.3) 173.3(2, 3.9)	
$[Mg\{SO_3(OH)\}_2\{SO_2(OH)_2\}_2$ @ 183 K (not given)	m $P2_1/c$?	509.1(4) 1532.9(6) 788.2(6)	104.19(6)	MgO_6	O	202.9(4, 0) 206.5(4, 0) 208.9(4, 0)	not given	245
$Mg(pg)_3(H_2O)_3$ (not given)	m $P2_1$ 4	1267.7(2) 1234.0(5) 2150.2(2)	92.69(1)	MgO_6	O H_2O	203(–, 0) 211(–, 0)	not given	246
$Mg(pep)_2(H_2O)_2$ (colourless)	tr $P\bar{1}$ 1	517.2(3) 533.3(3) 1218.4(6)	85.30(4) 86.90(4) 86.56(4)	MgO_8	O_{eq} H_2O_{ap}	203.8(2, 22) 215.4(2)	O,O 90.0(1, 1.7)	247
$Mg(HCOO)_2(H_2O)_2$ @ 293 K (colourless)	m $P2_1/c$ 4	864.0(5) 714.9(3) 938.2(7)	98.05(1)	MgO_6	O	206.6(1, 10) 210.8(1, 0)	O,O 90.00(4, 1.99)	248
				MgO_6	O H_2O	211.8(1, 0) 206.6(1, 15)	O,O 90.00 (5, 11.17)	
$Mg(HCOO)_2(H_2O)_2$ @ 130 K (colourless)	m $P2_1/c$ 4	861.6(5) 710.7(3) 940.0(7)	98.46(1)	MgO_6	O	206.3(1, 6) 209.9(1, 0)	O,O 90.00(5, 1.72)	248
				MgO_6	O H_2O	211.8(1, 0) 206.6(2, 9)	O,O 90.00(6, 9.77)	
$Mg(HCOO)_2(H_2O)_2$ (colourless)	or *Pbca* 4	871.0(2) 842.7(2) 747.7(2)		MgO_6 MgO_6	O O H_2O	207.1(3, 23) 207.1(3, 23) 206.9(3, 0)	O,O 90.2(2) O,O 90.8(2, 1)	249

TABLE 10 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L′–Mg–L (°)		Ref.
$[Mg(icdh)(H_2O)_2]$-$3(H_2O)$ (not given)	tg $P4_12_12$?	10510 – 15030	105.1 – 150.3	MgO_6	O H_2O	215(–, 23) 197(–, 11)	not given		250
$[Mg(gal)]2H_2O$ (not given)	m Cc 8	760.5(1) 878.5(5) 1640.4(2)	92.56(1)	MgO_6	O	200.3(3) 205.0(2) 211.7(2)	O,O	74.8(1) 91.8(1, 2.0)	251
$MgCl_2$ (white)	tg	363.2(4) – 1779.5(16)		$MgCl_6$	Cl	not given			252
$MgCl_2$ (white)	tg $R\bar{3}m$?	363.63(1) – 1766.63(5)		$MgCl_6$	μ-Cl	248.73(8, 0)	Cl,Cl i	90.00(4, 3.14)	253
$KMgCl_3$ (white)	or $Pbnm$ 4	695.4(3) 697.1(3) 992.2(3)		$MgCl_6$	μ-Cl	250.0(4, 4)	Cl,Cl	90(2, 8)	254
$CsMgCl_3$ (not given)	tg $P6_3/mmc$ 2	726.9(6) – 618.7(5)		$MgCl_6$	μ-Cl	249.6	Cl,Cl	85.64	255
MgP_4 (black)	m $P2_1/c$ 2	514.4(2) 508.5(2) 752.6(3)	98.66(3)	MgP_6	P	260.8(3) 263.5(3) 286.2(3)	P,P	90.0(1, 3.1) 180.0	256
$[Mg(H_2O)_3(C_{24}H_{31}N_5O_5)$-$(NCS)](HSO_4)3H_2O$ (colourless)	or $P2_12_12_1$ 4	844.4(1) 1073.5(2) 3972.6(6)		MgO_5N	O H_2O SCN	208.8(–, 11) 207.2(–, 19) 210.1(–)	O,O O,N	88.9(–, 6.6) 92.5(–, 5.8)	257
$Mg(H_2O)_3$(L-asp) (colourless)	or $P2_12_12_1$ 4	614.0(1) 943.0(1) 1501.5(1)		MgO_5N	O N H_2O	207.1(2, 5) 220.3(3) 205.4(2, 55)	O,O O,N	90.0(1) 174.1(1) 80.8(1, 3.6)	258
Mg_2PO_4Cl (not given)	or $Pna2_1$ 4	1094.0(1) 793.05(6) 480.08(4)		MgO_5Cl	μ-O μ_3-O μ_3-Cl	205.7(2, 61) 242.2(2) 262.3(1)	O,O O,Cl	65.1–153.4(1) 91.3(1, 12.9) 173.8(2)	259
				MgO_4Cl_2	μ-O μ_3-O μ_3-Cl	204.4(2, 54) 238.2(3) 254.1(1, 119)	O,O O,Cl Cl,Cl	66.4–152.0(1) 95.8(1, 18.8) 162.5(1, 7.7) 83.0(1)	
$Mg(acEt)_2Cl_2$ (colourless)	or $P2_12_12_1$ 8	735.3(3) 2511.1(10) 863.1(2)		$MgCl_4O_2$	O μ-Cl	211.5(3, 5) 250.8(1, 19)	Cl,Cl O,O	91.2(1, 5.7) 177.5(1, 2) 177.5(1) [k]	260
$Mg(thf)_2Br_2$	or $P2nn$ 2	401(1) 752(1) 1820(1)		$MgBr_4O_2$	O μ-Br μ-Br	212.6(13) 263.3(13) 279.9(14)	O,O Br,Br O,Br	165.46(95) 88.09(50) 95.22(72, 2)	136
$Mg(C_9H_7)_2$ (white)	or $P2_12_12_1$ 8	2149.7(8) 1237.8(5) 1039.6(5)		MgC_7	η^1-C η^5-C	226(1) 232(1) 242(1, 12)	not given		261
				MgC_9	η^2-C η^5-C	238(1, 5) 242(1, 2) 244(1, 18)			

of four Mg^{II} atoms, coupled via each of the six edges by a tetradentate tetraethyl-2,3-dioxobutane-1,1,4,4-tetracarboxylato(2 −) bracket, making each of the four Mg^{II} atoms octahedrally surrounded by six oxygen atoms. Another colourless tetramer, the orthorhombic $[Mg(\eta^5\text{-cp})(\mu\text{-OEt})]_4$ [221] contains a four oxygen bridged cubane-like cluster of a Mg_4O_4 core with a mean Mg–O bond distance of 206.6(1) pm. Each Mg^{II} atom at the corner is ligated by the cyclopentadienyl ring, with a mean Mg–cp(centroid) bond distance of 210.5 pm (Table 9).

The hexamer $Mg_6(N)(NH^tBu)_9$ [222] is shown in Fig. 13. This structure is unique from at least two points of view. It is the first, and to date only, example of a hexanuclear magnesium cluster, and it is the only example of a hexacoordinated nitride. The structure consists of a nitride surrounded by six magnesium atoms (mean Mg–N = 214.8(3) pm) disposed in a nearly perfect trigonal-prismatic geometry. In addition to the nitride, each Mg atom is coordinated to three nitrogen atoms of the NH^tBu ligands to give a tetrahedrally arranged coordination sphere, each N donor bridging two Mg atoms along the edges of the trigonal prism. The mean Mg–Mg distances are 282 pm (triangular face edges) and 280 pm (rectangular face edges).

The crystal structure of fructose-1,6-biphosphatase complexed with fructose-6-phosphate, AMP and Mg^{II} has been solved [223], but because of the complexity has not been included in Table 9. The orthorhombic crystal has the $P2_12_12_1$, $Z = 2$, with unit cell dimensions of $a = 6160$ pm, $b = 16660$ pm, and $c = 8000$ pm. The structure revealed substantial quaternary and tertiary conformational changes relative to the unligated enzyme or its fructose 2,6-biphosphate complex. The divalent Mg^{2+} ions are located in negatively charged pockets, coordinated to two glutamic acid and two aspartic acid residues.

6. Polynuclear magnesium compounds

Crystallographic and structural data for polynuclear magnesium compounds are given in Table 10. The organometallic derivatives $Mg(Me)_2$ [224] and $Mg(Et)_2$ [225] consist of polynuclear chains with carbon atoms of the ligand acting as bridges between the magnesium atoms. The mean Mg–C distance is 224.4(3) pm for the

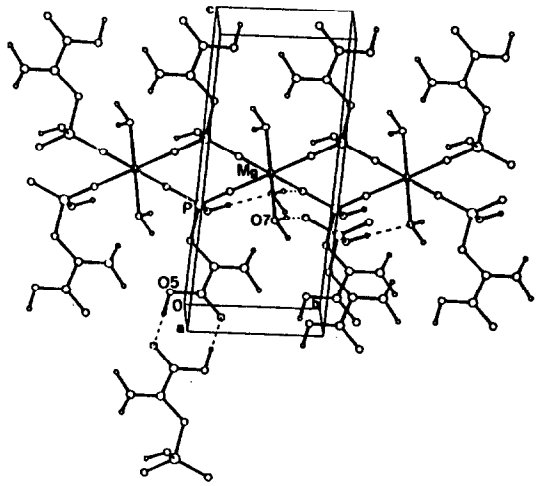


Fig. 14. Packing arrangement for $Mg(pep)_2(H_2O)_2$ [247].

methyl derivative, and 2 pm longer for the ethyl derivative, presumably because of greater steric interactions. An increase in the Mg–C–Mg bridge angle is reflected in an increased Mg–Mg distance (footnotes c and d of Table 10).

The structure of $[(np_2Mg)_2(npMgBr)_2]$ [226] involves an alternating pattern of two np_2Mg and npMgBr fragments, with tetracoordinated magnesium atoms, connected by doubly bridging neopentyl and bromides groups. The tetrahedral coordination in the former fragment utilizes four carbon atoms (mean Mg–C(bridge) = 234(2) pm). In the latter fragment it consists of two bromide atoms (mean Mg–Br(bridge) = 281.3(5) pm) and two carbon atoms (mean Mg–C(bridge) = 227(2) pm). The mean Mg–L–Mg angles follow the trend indicated above (footnotes e_1 and e_2), which also reflects the covalent radii of the bridging atoms.

Colourless $Mg(dox)(np)_2$ [227] has $Mg(np)_2$ units linked through dioxane units in the chair conformation to give polymeric chains. The magnesium atoms are in an approximately tetrahedral environment with two oxygen atoms (dioxane) and two carbon atoms (neopentyl).

As mentioned in Section 2.4, the overwhelming majority of mononuclear magnesium compounds are hexa coordinated, and the polynuclear derivatives are no exception, as can be seen in Table 10. The most

Notes to Table 10:

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] Mg–C–Mg = 75(2)°; Mg–Mg = 272.5(2) pm. [d] Mg–C–Mg = 72°; Mg–Mg = 267(1) pm. [e1] Mg–C–Mg = 74.5(6, 4)°. [e2] Mg–Br–Mg = 86.4(2)°. [f] Mg–Mg = 305.19(1) and 360.65(1) pm. [g] Mg–O–Mg = 77.8(1)°. [h] There are several other compounds of the composition $Mg(C_xH_yPO_3)\cdot H_2O$, $x = 5$ to 12 and $y = 11$ to 25), for which unit cell dimensions are available. [i] Mg–Cl–Mg = 93.94(4)°. [j] Mg–Cl–Mg = 76.59°. [k] O–Mg–Cl = 89.1(1, 3.8)°; Mg–Cl–Mg = 94.6(–, 3)°.

common ligating atom is a donor oxygen atom from an organic or inorganic moiety. As an example, the packing arrangement of $Mg(pep)_2(H_2O)_2$ [247] is shown in Fig. 14, where the Mg^{II} atoms occupy centres of symmetry. The six coordination sites are occupied by the oxygen atoms of two water molecules, and four oxygen atoms of two phosphoenolpyruvate anions. Two terminal oxygen atoms of each phosphate group bridge pairs of Mg^{II} atoms, forming linear chains along b.

The mean Mg–L(bridge) bond distance of the six coordinate polynuclear compounds increases with increasing covalent radius of the coordinated atom in the order 198.8 pm (F, range 197.9 to 199.7 pm) < 205.1 pm (O, range 199.0 to 209.6 pm) < 249.8 pm (Cl, 248.7 to 252.7 pm) < 270.2 pm (P, 260.8 to 286.2 pm) < 271.6 pm (Br, 263.3 to 279.1 pm). The mean Mg–μ_3-L(triple bridge) bond distances follow the same trend, but with longer distances than the single bridged units described above; 258.2 (μ_3-Cl, range 242.5 to 266.0 pm), 240.2 pm (μ_3-O, range 238.2 to 242.2 pm). The mean Mg–OH_2 bond distance of 208.6 pm found in hexa-coordinated polynuclear derivatives (Table 10) is about 1.5 pm longer than that found for the corresponding mononuclear derivatives (Table 4).

There are a few examples [232,239,248,249] in which two independent MgO_6 units occur. For example, in the basic carbonate, $4MgCO_3 \cdot Mg(OH)_2(H_2O)_4$ [232], one MgO_6 unit is made up of oxygen atoms from a hydroxyl group and a water molecule plus the carbonate groups, while the other has only hydroxyl and carbonate ligands. In $Mg_2P_4O_{12}$ [239] two MgO_6 octahedra differ by symmetry, one having 2 point symmetry and the other 1. In $Mg(HCOO)_{2z}(H_2O)_2$ [248,249] one MgO_6 unit consists entirely of formate groups while the other has four water molecules and one formate group.

Two non-equivalent magnesium chromophores (MgO_5 and MgO_6) have been found in two phosphate derivatives [235,244], and MgO_5Cl and MgO_4Cl_2 chromophores coexist in $MgPO_4Cl$ [259].

There are two derivatives which have isomeric forms, for example α- and β-$Mg_2P_2O_7$ [235,236], and monoclinic and orthorhombic $Mg(HCOO)_2(H_2O)_2$ [248,249]. These differ from each other mostly by degree of distortion.

The influence of temperature on degree of distortion of pseudo-octahedral structures has been reported for $Mg(HCOO)_2(H_2O)_2$ [248], where it was found that

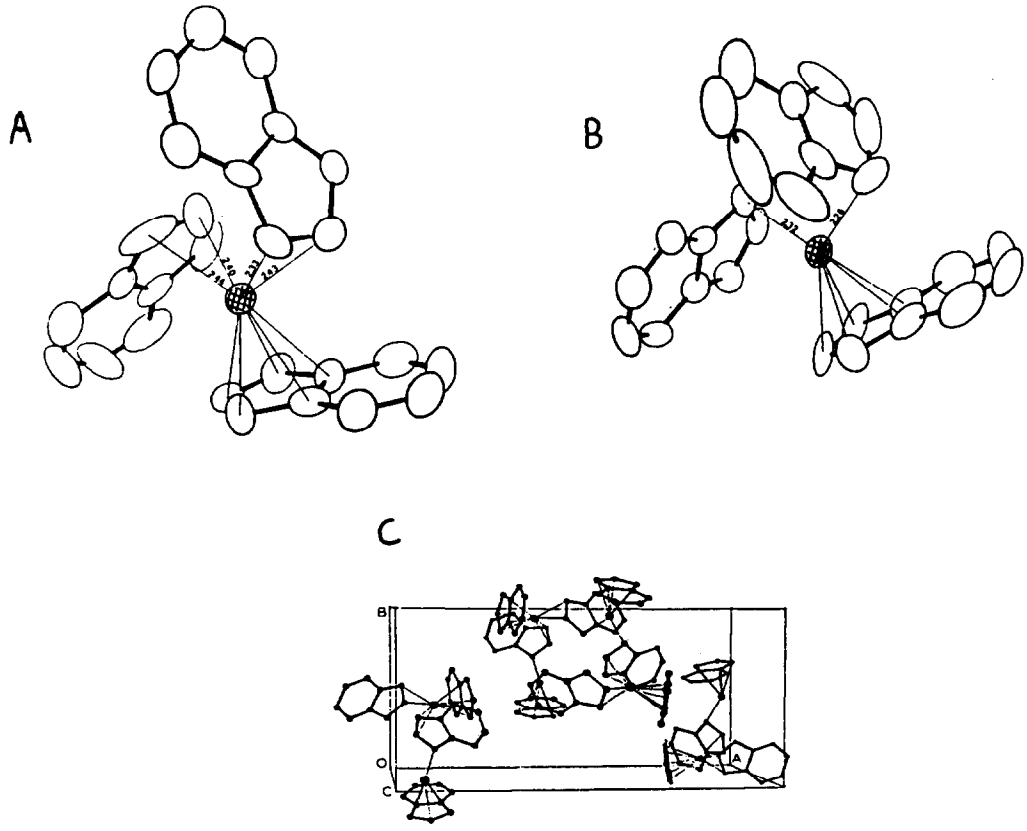


Fig. 15. Coordination environment of (a) Mg(1), (b) Mg(2), and (c) cell packing of $Mg(C_9H_7)_2$ units [261].

TABLE 11. Crystallographic and structural data for hetero-double salts of magnesium [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L′–Mg–L (°)		Ref.
$[Mg(H_2O)_4][UO_2(AsO_4)]_2$	m	1820.7(5)		MgO_4	O [b]	209(4, 0)	O,O	108	265
(not given)	$C2/m$	706.2(3)	99.65(5)			220(10, 0)			
	2	666.1(3)		UO_7	O_{eq}	235(2, 10)	O,O	70.3(4, 12.1)	
								147.4(5, 18.9)	
					O_{ap}	178(3, 1)	O,O_{ap}	90.0(8, 2.2)	
							$O_{ap}O_{ap}$	179.5(2)	
$[Mg(H_2O)_6]_{0.72}[Zn(H_2O)_6]_{0.28}$-	or	2266.6(3)		MgO_6	O	not given			266
$[Zn(hatp)_2]2hatp \cdot 12H_2O$	$C222_1$	1013.1(2)							
(not given)	4	3089.3(6)		ZnO_6	O	not given			
$[Mg(H_2O)_6][ZnCl_4]$ [c]	tr	656.2(1)	88.63(1)	MgO_6	O	203.8(3, 16)	O,O	90.00(12, 1.43)	267
(not given)	$P\bar{1}$	659.7(1)	89.43(1)						
	2	1410.1(1)	84.83(1)	MgO_6	O	206.7(2, 18)	O,O	90.00(9, 1.76)	
				$ZnCl_4$	Cl	226.67(8, 314)	Cl,Cl	109.35(3, 4.44)	
$[Mg(H_2O)_6][ZnBr_4]H_2O$ [c]	m	832.7(1)		MgO_6	O	205.6(11, 12)	O,O	90.0(5, 1.6)	268
(colourless)	$P2_1/n$	1259.6(3)	97.92(1)						
	4	1404.8(2)		MgO_6	O	204.4(11, 13)	O,O	90.0(5, 1.0)	
				$ZnBr_4$	Br	240.6(2, 24)	Br,Br	109.39(9, 2.76)	
$[Mg(H_2O)_6][ZnBr_3]_2$	or	1044.7(2)		MgO_6	O	203.9(11, 0)	O,O	90.0(4, 2.3)	269
(colourless)	$Immm$	1032.5(1)						179.85(4)	
	2	799.9(2)		$ZnBr_4$	Br	235.9(2, 0)	Br,Br	109.50(7, 13.84)	
					μ-Br	248.4(2, 0)			
$[Mg(H_2O)_6]_2$ [c][$CdCl_6$]	hx	998.09(9)		MgO_6	O	204.1(5)	O,O	90.0(21, 5.18)	270
(not given)	$P31c$	–				209.6(4)		173.52(20)	
	2	1155.60(9)							
				MgO_6	O	207.1(4, 0)	O,O	90.00(18, 2.74)	
								176.50(18)	
				$CdCl_6$	Cl	263.6(1, 5)	Cl,Cl	90.00(4, 3.16)	
								174.62(4)	
$[Mg(H_2O)_6][Cd_2(H_2O)Cl_5]Cl5H_2O$	or	2458.70(25)		MgO_6	O	205.2(5, 0)	O,O	90.0(2, 2.4)	271
(not given)	$Fdd2$	2242.29(42)				208.1(4, 0)		177.3(2, 1.4)	
	8	756.40(19)		$CdCl_5O$		236.4(4)	O,Cl	178.43(10)	
					Cl	253.9(1)	O,μ-Cl	87.25(9, 86)	
					μ-Cl	262.4(2, 5)	Cl,μ-Cl	92.76(4, 1.81)	
							μ-Cl,μ-Cl	89.87(4, 3.39)	

$[Mg(H_2O)_6][Ga(ehpg)]_2 3H_2O$	m	2094.6(4)		MgO_6	not given		not given		272
(pale orange)	$C2/c$	1301.0(1)	114.75(1)						
	4	1700.2(3)		GaO_4N_2	O	189.3(2, 7)	not given		
					O	200.6(2, 4)			
					N	209.0(2, 12)			
$K_2[Mg(H_2O)_6]_2V_{10}O_{20}$	tr	882.9(2)		MgO_6	O	207.2(2, 28)	not given		273
(not given)	$P\bar{1}$	1073.8(2)	114.23(3)						
	1	1109.1(6)		VO_6	O	192.1(2, 425)	not given		
$(NH_4)_2[Mg(H_2O)_6]_2V_{10}O_{28}$	tr	887.4(1)		MgO_6	O	207.5(2, 28)	not given		273
(not given)	$P\bar{1}$	1088.1(1)	114.46(1)						
	1	1108.1(1)		VO_6	O	192.1(2, 426)	not given		
$Rb_2[Mg(H_2O)_6]_2V_{10}O_{28}$	tr	887.9(2)		MgO_6	O	206.7(9, 37)	not given		273
(not given)	$P\bar{1}$	1090.4(3)	114.19(2)						
	1	1105.2(2)		VO_6	O	192.1(2, 417)	not given		
$[Mg(H_2O)_6][Fe(ehpg)]_2 3H_2O$	tr	1720(1)	92.433(5)	MgO_6	O	205.1(8, –)	not given		274
(red)	$P\bar{1}$	2152(1)	91.865(5)			215.8(8, –)			
	4	1238.8(9)	110.768(4)						
				FeO_4N_2	O	190.7(–, 7)	not given		
					O	204.1(–, 7)			
					N	217.2(–, 8)			
$[Mg(H_2O)_6][Fe(ehpg)]_2 3H_2O$	m	1707.4(15)		MgO_6	O	206.1(3, 7)	O,O	90.0(1, 4.6)	275
(dark red)	$C2/c$	1309.9(11)	113.57(5)			212.4(3, 26)		174.4(1, 5.6)	
	4	2086.8(11)							
				FeO_4N_2	O	191.1(3, 10)	not given		
					O	204.2(3, 7)			
					N	216.6(2, 13)			
$[Mg(H_2O)_6][FeCN)_6]$-	or	1386.3(4)		MgO_6	O	205.3(5, 4)	O,O	86.3(2)	276
$(C_6H_{13}N_4)_2$	$Pbca$	1386.3(4)							
(not given)	4	1385.6(4)		FeC_6	C	190.2(6, 7)	C,C	90.0(4, 2.3)	
$[Mg(H_2O)_6][Co(bdta)]_2 2H_2O$	m	3231.3(9)		MgO_6	O	202.4(2, 19)	O,O	90.0(4, 1.32)	277
(not given)	$C2/c$	773.4(1)	97.02(2)			208.0(2, 8)		177.98(9, 61)	
	4	1454.2(2)							
				CoO_4N_2	O	189.8(1, 22)	O,O	89.69(5, 3.55)	
					N	198.3(1, 24)	N,N	105.56(5)	
							O,N	87.74(5, 5.20)	
$[Mg(H_2O)_6][Mn(H_2O)_3Br_3]_2$	m	1347.7(15)		MgO_6	O	204.6(9, 3)	O,O	90.0(4, 3)	278
(not given)	$C2/m$	1003.1(8)	110.96(6)					180.0(4)	
	2	842.8(2)							
				MnO_3Br_3	O	221.6(7, 1)	O,O	88.0(3, 1)	
					Br	264.4(2, 7)	Br,Br	94.70(6, 1)	
							O,Br	88.6(2, 0)	
								175.1(2, 1)	
$[Mg_{0.82}(H_2O)_{5.3}][Pt(ox)_2]$	or	1656(1)		MgO_6	O	213(5, 0)	not given		279
(blue-violet)	$Cccm$	1427(1)				223(5, 0)			
	4	570(1)							
				PtO_4	O	200(3, 2) [d]	O,O	90(–, 8)	

TABLE 11 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L′–Mg–L (°)	Ref.
$[Mg(H_2O)_6]_3[Ce(NO_3)_6]_2 6H_2O$	rh	1100.4(6)		MgO_6	O	205.7(5, 1)	not given	280
(not given)	$R\bar{3}$	–						
	3	3459.2(12)		CeO_{12}	O	263.5(5, 40)	not given	
$[Mg(H_2O)_6][Th_2(schb)_3]$	m	1248.8(6)		MgO_6	O	209(2, 2)	O,O 90.0(7, 8)	281
(orange)	$P2_1/c$	2204.4(5)	104.82(3)					
	2	2431.6(5)		ThO_6N_3	O	232(2, 7)	O,O not given	
					μ-O	247(1, 6)	N,N 119.5(5, 5.3)	
					N	274(2, 5)	[e]	
$[Mg(acEt)_6][AlCl_4]_2$	c	1661(1)		MgO_6	O	205.3(4, 0)	O,O 87.6(2)	282
(colourless)	$Pa\bar{3}$							
	4			$AlCl_4$	Cl	210.0(2, 5)	Cl,Cl 109.5(2, 1.1)	
$[Mg(thf)_6][MoOCl_4(thf)]_2$	m	1221(1)		MgO_6	O	209.2(6, 4)	O,O 90.0(3, 7)	283
(green)	$P2_1/c$	1069.7(9)	90.74(8)			215.6(6, 0)		
	2	1853(1)						
				$MoCl_4O_2$	Cl_{eq}	237.8(3, 9)	Cl,Cl 90.0(2, 2.1)	
							Cl,O 90.0(3, 8.2)	
					O_{ap}	163.4(6)	O,O 178.8(3)	
					O_{ap}(thf)	230.8(7)		
$[Mg(MeOH)_6]_2[Nb_2(MeO)_9]Cl_3$	m	1623.5(4)		MgO_6	O	not given	not given	284
(colourless)	$C2$	1445.3(4)	94.02(2)					
	2	1020.9(3)		NbO_6 [f]	O	196.6(5, 23)	not given	
					μ-O	206.9(2, 50)		
$[Mg(MeOH)_6]_2[Nb_2(MeO)_9]I$·2MeOH	or	1239.7(1)		MgO_6	O	not given		284
	$Cmcm$	1306.8(6)						
(colourless)	2	2434.7(3)		NbO_6 [f]				
$[Mg(MeCN)_6][Sb_2Cl_8]$	tr	896.8(8)	97.1(1)	MgN_6	N	213.5(8, 1)	N,N 90.0(3, 2.2)	285
(colourless)	$P\bar{1}$	1022.0(11)	79.8(1)			217.9(8, 0)		
	1	838.9(9)	78.1(1)					
				$SbCl_6$	Cl	239.9(3, 32)	Cl,Cl 90.0(1, 20.1)	
					μ-Cl	296.0(3, 600)	169.3(1, 8.8) [g]	
$[Mg(thf)_4Cl_{1.56}Br_{0.44}]$·$[V(Me_4taa)(mes)]$thf	tr	1267.1(4)	113.58(3)	MgO_4X_2	not given		not given	286
	$P\bar{1}$	1350.1(5)	93.80(3)					
(not given)	2	1461.3(4)	109.79(3)	VN_4C	N_{eq}	200.6(7, 4)	N,N not given	
					C_{ap}(mes)	208.5(8)	N,C 108.2(3, 3.4)	

$[Mg_2(\mu\text{-}Cl)_3(thf)_6][MoOCl_4(thf)]$	tr	982.7(7)	118.22(7)	MgO_2Cl_3	O	208.0(6, 25)	O,O	90.4(3, 1.7)	283
(green)	$P\bar{1}$	1406(1)	100.90(6)		μ-Cl	257.0(4, 24)	O,Cl	92.6(3, 4.1)	
	2	1823(2)	96.43(7)					174.6(3, 9) [h]	
				$MoCl_4O_2$	Cl_{eq}	235.9(3, 4)	Cl,Cl	90.0(2, 1.8)	
							Cl,O	90.0(3, 8.5)	
					O_{ap}	166.5(7)	O,O	179.3(3)	
					O_{ap}(thf)	237.6(6)			
$[Mg_2(\mu\text{-}Cl)_3(thf)_6][Ti(thf)Cl_5]$	m	1716(1)		MgO_3Cl_3	O	207.8(3, 37)	O,O	89.8(3, 2.7)	287
(yellow)	$P2_1/c$	1284.5(8)	112.80(7)		μ-Cl	250.7(4, 8)	O,Cl	93.0(2, 3.5)	
	4	2082(1)						174.2(3, 1.8) [i1]	
				$TiCl_5O$	O	215.8(5)	Cl,Cl	93.0(2, 3.3)	
					Cl	229.6(3, 24)		171.3(2, 3) [i2]	
$[Mg_2(\mu\text{-}Cl)_3(thf)_6][(C_4Ph_4)TiCl_3]$	m	1774(1)		MgO_3Cl_3	O	208(2, 4)	O,O	90.7(9, 2.6)	288
(blue)	$C2$	1445(1)	92.94(6)		μ-Cl	250(1, 3)	O,Cl	92.7(8, 3.5)	
	4	2203(1)						174.7(8, 1.2) [j]	
				TiC_4Cl_3	C	224(2, 3)	C,C	43.3(9, 12.7)	
					Cl	224(1, 1)	Cl,Cl	101.6(7, 3.3)	
							C,Cl	114.8(7, 27.3)	
$[Mg_2(\mu\text{-}Cl)_3(thf)_6]$-	tr	1031.0(2)	80.46(2)	MgO_3Cl_3	O	207.8(5, 16)	not given		289
$[Nb(PhCCPh)(thf)Cl_4]0.5(thf)$	$P\bar{1}$	1511.7(2)	89.79(2)		μ-Cl	250.2(3, 40)			
(greenish brown)	2	1714.8(4)	87.24(1)						
				$NbCl_4C_2O$	Cl	243.2(2, 11)	Cl,Cl	88.82(6, 2.17)	
					C	205.2(6, 2)		163.49(6, 36)	
					O	229.8(4)	[k]		
$[Mg_2(\mu\text{-}Cl)_3(thf)_6]_2[Nb_4OCl_8(PhC_4)_2]6(thf)$	tr	1520.0(3)	98.93(2)	MgO_3Cl_3	O	208.1(6, 23)	not given		290
(brown)	$P\bar{1}$	1551.5(4)	106.90(2)		μ-Cl	250.3(3, 30)			
	1	1630.6(3)	102.97(2)						
				NbC_4Cl_3O	C	224.8(7, 139)	C,C	36.9(3, 9)	
					μ-Cl	254.2(2, 122)		70.0(3, 3)	
					μ_4-O	211.77(7, 17)		98.1(2, 7.6) [l]	
$[Mg_4(\mu\text{-}ome)_6(dme)_2][Hg(Me_2PhSi)_3]_2$	m	1628.7(3)		MgO_6	μ_3-O	198.5(2)	O,O	90(–, 18)	291
(deep red)	$P2_1/n$	2415.8(5)	101.58(2)		μ_4-O	210(2)			
	2	1215.9(3)			O	220.7(2, 31)			
				$HgSi_3$	Si	251.6	Si,Si	119.8	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] There are two crystallographically independent molecules. [d] Pt–Pt = 285 pm. [e] Th–O–Th = 101.8(5, 1.3)°. [f] Averaged over the three crystal structures. Nb–Nb = 264.0(1, 12) pm, and Nb–O–Nb = 79.3(4, 7)°. [g] Sb–Cl–Sb = 101.4(1, 5.5)°. [h] Cl–Mg–Cl = 84.5(2, 8)°; Mg–Cl–Mg = 78.2(2, 5)° and Mg–Mg = 316.6(4) pm. [i1] Cl–Mg–Cl = 84.3(2, 1.2)°; Mg–Cl–Mg = 78.4(2, 2)° and Mg–Mg = 316.9 pm. [i2] Cl–Ti–O = 85.7(2, 7) and 178.5(2)°. [j] Cl–Mg–Cl = 83.9(4, 8)°; Mg–Cl–Mg = 78.9(4, 4)°; Mg–Mg = 318(1) pm. [k] Cl–Nb–C = 85.3(2, 2.3) and 110.8(2, 1.9)°; Cl–Nb–O = 81.82(2, 5)°; C–Nb–C = 36.9(2)°; C–Nb–O = 161.5(2, 1.1)°. [l] C–Nb–Cl = 95.0(2, 14.3), 125.0(2, 4.1) and 159.0(2, 5.1)°; C–Nb–O = 81.9(2, 5) and 105.7(2, 2)°; Cl–Nb–Cl = 74.00(6, 6) and 91.5(6, 2.14)°; Cl–Nb–O = 77.67(4, 2.05) and 165.72(5, 26)°; Nb–O–Nb = 76.03(2)°; Nb–C–Nb = 71.2(2, 4.5)°; Nb–Cl–Nb = 79.81(6, 7)°; Nb–Nb = 260.82(7) pm.

some of the Mg–O bond distances and also unit cell dimensions change on going from 293 K to 130 K (Table 10).

A white bis(indenyl) magnesium compound [261] exhibits magnesium atoms in two different environments, and indenyl groups of a fundamentally different nature. As shown in Fig. 15(a to c), each Mg atom is coordinated to three indenyl moieties, one in a pentahapto fashion and two in a less symmetric manner. The substance exists in an infinite polymer arrangement with both bridge and terminal indenyl groups (Table 10).

While most of the derivatives in Table 10 are colourless, white or slightly coloured (yellow), there is one example, the phosphide MgP_4, in which the electronic structure is such as to give a black material [256].

The crystal structure of yellow Mg_3BN_3 in the low pressure phase has been solved by ab initio calculations from X-ray powder data [262]. The unit cell is hexagonal, space group $P6_3/mmc$ with $a = 354.453(4)$ pm, $c = 1603.536(30)$ pm, with $Z = 2$. The structure was described as ABB'BACC'CA... layers perpendicular to the c axis, with linear N=B=N molecular anions at positions A, Mg^{II} at position B and C, and Mg^{II} with three coordinating N atoms at positions B' and C'. A report of an ab initio analysis of data for $Mg(BH_4)_2$ has also been made [263]. A magnesium complex structure of isocitrate dehydrogenase (*Escherichia coli*) [264] shows the Mg^{II} atom coordinated by isocitrate and two bound water molecules in a roughly octahedral manner. The above three derivatives are not included in Table 10.

7. Hetero-double salts of magnesium

Crystallographic and structural data for these derivatives are given in Table 11, where the compounds are listed and referenced in order of increasing coordination number of the magnesium atom and increasing complexity of the coordination sphere. The first example contains a $[Mg(H_2O)_4]^{2+}$ ion in a distorted tetrahedral environment of four water molecules [265]. Layers of these ions alternate with layers of uranyl arsenate, in which the coordination of the uranium atom is pentagonal bipyramidal. The remainder of the hetero-double salt examples contain six coordinated magnesium, with the most common ligand being the water molecule. The mean $Mg–O(H_2O)$ bond distance is 207.0 pm (range 200.5 to 220.0 pm), which is almost the same as that found for the corresponding hexa-aquo mononuclear Mg^{2+} cations (207.1 pm, range 196.1 to 214.9 pm; Table 4) but smaller than that found for the homo-double salts (208.2 pm, range 203.0 to 220.0 pm; Table 7).

In another four examples [282–284] the octahedral environment of the Mg^{II} atom consists of six acEt molecules [282], six thf molecules [283] and six methanol molecules (two examples) [284]. There is only one example where magnesium is coordinated to six nitrogen atoms [285] from MeCN ligands with Mg–N distances of 213.4(7) pm, 213.6(9) pm and 217.9(3) pm. The $[SbCl_4]^-$ counterion is polymeric.

There are five examples [283,287–290] which contain the identical dimeric blue coloured $[Mg_2Cl_3(thf)_6]^+$ cation. A structure of one of these examples

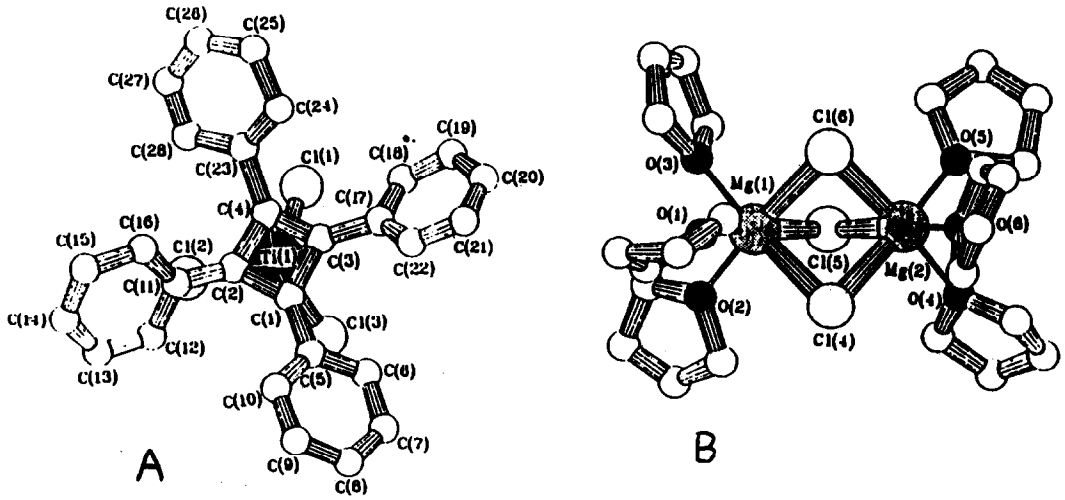


Fig. 16. Structure of (a) $[C_4Ph_4TiCl_3]^-$ and (b) $[Mg_2Cl_3(thf)_6]^+$ [288].

[288] is shown in Fig. 16 as a representative of this class. The $[(C_4Ph_4)TiCl_3]^-$ anion (Fig. 16(a)) contains the C_4Ph_4 group as a tetraphenylcyclobutadienyl ring, which, together with the three chlorine atoms complete the seven coordination of the titanium atom. The structure of the $[Mg_2Cl_3(thf)_6]^+$ cation (Fig. 16(b)) shows that each Mg^{II} atom is octahedrally surrounded by three chlorine atoms, which serve as bridges between pairs of Mg^{II} atoms, and three disordered thf molecules. As the Mg–Cl–Mg bridge angle opens, the Mg–Mg distances increases and the Cl–Mg–Cl angle closes. The values are, respectively: 78.2(2)°, 316.6(4) pm and 84.5°; 78.4(2)°, 316.9 pm and 84.3(2)°; 78.9(4)°, 318(1) pm and 83.9(4)° [288].

The mean Mg–O(thf) bond distance of 207.9 pm (range 204.0 to 211.0 pm) is about 0.7 pm longer than that found in binuclear magnesium compounds at 207.2 pm (range 204.9 to 210.0 pm). By contrast, the mean Mg–Cl(bridge) bond distance of 250.4 pm (range 247.0 to 254.2 pm) for these triple bridged derivatives is about 4.3 pm shorter than that of the double bridges in the binuclear series, 254.7 pm (range 240.0 to 269.4 pm) (Table 8).

There is an example [291] that has three discrete ionic groups, an $[Mg_4(ome)_6(dme)_2]^{2+}$ cation with two $[Hg(Me_2PhSi)_3]^-$ anions. The cation has four six coordinated Mg^{II} atoms tightly bound by two types of $CH_3OCH_2CH_2O^-$ (ome) bridging units. One of these consists of two pairs of symmetry related, three coordinated, O atoms in Mg–O–Mg bridges (Mg–O = 198.5(2) pm). The other consists of two four coordinated O atoms in symmetry related Mg_3O bridges (mean Mg–O = 210(2) pm). The remaining sites around the Mg^{II} atoms are occupied by two O atoms on dme and/or the methoxy group of the (ome) moiety. The anion has a three coordinated mercury atom with trigonal planar symmetry (Table 11).

Three examples [267,268,270] have two crystallographically independent hexa-aquo magnesium cations, differing mostly by degree of distortion. In another example there are two isomeric forms, triclinic [274] and monoclinic [275] in which the six coordinated magnesium and iron sites both differ by their degree of distortion.

In this series of hetero-double salts, the second metal atom can come from both the transition and non-transition regions of the Periodic Table. The following examples of symmetry for the second metal atom are found: trigonal planar Hg^{II} [291]; square planar Pt^{II} [279]; tetrahedral Al^{III} [282], Zn^{II} [267–269]; trigonal bipyramidal V^{III} [286]; octahedral Cd^{II} [270,271], Ga^{III} [273], Fe^{III} [274,275], Fe^{II} [276], Co^{III} [277], Mn^{II} [278], Mo^{V} [283], Nb^{IV} [284], Sb^{III} [285] and Ti^{IV} [287]; pentagonal bipyramidal V^{VI} [265]; 4 + 3 coordinated Ti [288]; capped trigonal prism Nb [289]; octa-coordinated Ce^{III} [280] and dodeca-coordinated Ce^{III} [280].

8. Heteronuclear magnesium compounds

8.1. Heterobinuclear

The data for these compounds are summarised in Table 12 and listed in order of increasing distance between magnesium and the other closest metal atom. There are three examples [292,293] in which the magnesium has a distorted tetrahedral environment with chromophores MgO_2BrCo (Mg–Co = 248.0(4) pm) [292], MgN_2BrCo (Mg–Co = 256.5(3) pm) [292], and MgO_2BrFe (Mg–Fe = 259.3(7) pm) [293]. The Mg–M distances indicate a bond with a strong covalent character. In this series of compounds the most common form of bridging is via two ligands. For example, in the $[(Me_4en)Li(\mu\text{-}Bz)_2MgBz_2]^-$ anion [294] the carbon atom of benzyl groups bridges the Li and Mg centres, bringing the metal atoms within 271.9(18) pm of each other with a bridge angle of 73.1(6)°. This is the shortest Mg–M distance found for such a case. In five other cases [295–297] two oxygen ligands form the bridges. In another four examples [298–301] chlorine atoms serve as bridges, and in one case [302] the bridges are bromine atoms. Except for two cases [299,302] in which the coordination around the Mg^{II} centre is tetrahedral, magnesium is found in a distorted octahedral environment in this series of derivatives.

Figure 17 shows an example of a hetero-binuclear complex with magnesium and titanium [303]. Both metals are octahedrally coordinated and share an edge via two chlorine bridges. The two metals are also joined by the carboxyl group of the $ClCH_2COO^-$ group. The large Mg–Ti distance of 360.9(4) pm rules out any metal–metal bond.

In the tetrahedrally coordinated magnesium examples, the mean Mg–L bond distances reflects the covalent radii of the donor atom, for example: 207.1 pm (L = O(thf)) < 218.1 pm (L = C(Bz). The Mg–L(bridge) distances are longer but follow the same trend: 231.8 pm (C) < 241 pm (Cl) < 252.9 (Br). A similar trend is also observed for the hexa-coordinated derivatives, but with longer bond distances: 211.5 pm (L = O(thf)), and 251.4 pm (Cl bridge). The ligands themselves span the range from monodentate through to hexadentate. The colours range from white to yellow, blue and red.

8.2. Heterotrinuclear

The relevant data for these compounds is given in Table 13. There are six distinct types of bridging, an example of the first type is shown in Fig. 18 for an orange-red magnesium-cerium complex [305]. The three

TABLE 12. Crystallographic and structural data for hetero-binuclear magnesium compounds [a]

Compound (colour)	Cryst. cl Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	M–L (pm)		Mg–M (pm) Mg–L–M (°) μ-L–M–μ-L (°)	L′–M–L (°)		Ref.
[(η^5-cp)(η^3-C_3H_5)CoMg(thf)$_2$Br]	tr	755.2(1)	80.20(1)	MgO_2Br	O [b]	not given	248.0(4)	(O,O) [b]	not given	292
(not given)	$P\bar{1}$	1100.3(2)	82.26(1)		Br	not given				
	2	1180.5(2)	76.46(1)	CoC_8	not given					
[(η^5-cp)(η^2-C_2H_4)(Ph)CoMg(Me_4en)Br]	m	1002.2(2)		MgN_2Br	not given		256.5(3)	not given		292
(not given)	$P2_1/n$	1214.2(2)	101.26(3)							
	4	1756.2(3)		CoC_8	not given					
[(η^5-cp)(diphos)FeMg(thf)$_2$Br](thf)	m	1225.8(4)		MgO_2Br	O	208.7(15, 12)	259.3(7)	O,O	91.7(9)	293
(red)	$P2_1/c$	1302.7(4)	102.48(2)		Br	252.2(7)		Fe,O	117.4(6, 1.6)	
	4	2657.7(11)		FeC_5P_2	not given			Fe,Br	129.2(2)	
[(Me_4en)Li(μ-Bz)$_2$MgBz$_2$][Li(Me_4en)$_2$]	m	1236.1(60)		MgC_4	C	224.4(12, 19)	271.9(18)	C,C	111.1(5)	294
(not given)	$P2_1/c$	1236.1(20)	109.62(8)		μ-C	231.8(10, 5)	73.1(6, 5)	C,μ-C	110.2(4, 3.5)	
	4	2366.8(70)					104.7(4)			
				LiN_2C_2	N	213.8(21, 29)		N,N	87.6(7)	
					μ-C	225.1(19, 22)	109.2(9)	N,C	114.9(9, 8.8)	
				LiN_4	N	208.4(20, 8)		N,N	88.0(8, 1.5)	
						218.8(22, 25)			121.1(11, 2.1)	
[CuMg(μ-fsaen)(H_2O)$_2$]H_2O	tg	1284(5)		MgO_6	O_{eq}	197.8(2, 0)	300.1(4)	O,O	98.1(1, 12.7)	295
(brick red)	$P3_121$	–			μ-O_{eq}	204.9(3, 0)	98.2(1)		163.4(1)	
	3	999(5)			H_2O_{ap}	211.5(3, 0)	78.2(1)			
				CuO_2N_2	N	191.7(3)		N,N	86.0(1)	
					μ-O	192.0(3)	85.0(1)	O,N	94.5(1)	
									179.1(1)	
[(hfac)$_2$Mg(μ-salen)Cu]	tr	950.1(7)	83.7(1)	MgO_6	O	{205.3–303.1(5)}		O,O	90.0(2, 13.8)	296
(not given)	$P\bar{1}$	1543(1)	112.8(1)		μ-O		210.9(5)		169.4(2, 5.0)	
	2	1204.2(8)	107.8(1)	CuO_2N_2	N	not given				
					μ-O	191.7(5, 4)				

$[Mg(thf)_2(\mu\text{-acac})_2FeCl_2]$	or	973.0(2)		MgO_6	O_{eq}	200.7(4, 5)	not given	O,O	106.9(2)	297
(not given)	$P2_12_12_1$	1456.9(3)			$\mu\text{-}O_{eq}$	205.7(4, 5)	101.6(2, 5)	O,μ-O	87.3(2, 2)	
	4	1717.3(4)			O_{ap}(thf)	213.8(4, 10)	78.6(2)		165.6(2, 1) [c]	
					O_{ap}	213.8(4, 10)				
				FeO_2Cl_2	μ-O	207.4(4, 11)		O,O	77.9(1)	
					Cl	223.2(2, 5)		O,Cl	110.9(1, 2.4)	
								Cl,Cl	125.43(9)	
$[Mg(thf)_2(\mu\text{-acac})_2CoBr_2]$				MgO_6	O_{eq}	201(1, 1)		not given		297
(blue)					$\mu\text{-}O_{eq}$	208(1, 3)				
					O(thf)	213(2, 0)				
				CoO_2Br_2	μ-O	200(1, 2)				
					Br	236.9(4, 14)				
$[Mg(thf)_2(\mu\text{-acac})_2NiBr_2]$				MgO_6	O_{eq}	200.6(6, 4)	–	O,O	108.5	297
(blue)					$\mu\text{-}O_{eq}$	205.7(5, 2)	77.6		177.0	
					O(thf)	212.3(6, 13)	–	O,μ-O	87.0(–, 3)	
				NiO_2Br_2	μ-O	199.1(5, 3)		O,O	80.7	
					Br	234.1(2, 4)		Br,Br	128.5	
$[FeCl_2(\mu\text{-Cl})_2Mg(thf)_4]$	or	918(1)		MgO_4Cl_2	O	209.2(5, 19)	345.5(3)	O,O	90.8(2, 3.1)	298
(yellow)	*Pbcn*	1630(2)			μ-Cl	250.1(2, 0)	90.2(1)		177.5(2)	
	4	1585(1)					86.9(1)	O,Cl	89.9(2, 2.7)	
									174.8(2)	
				$FeCl_4$	Cl	222.8(2, 0)		Cl,Cl	113.3(1, 7.3)	
					μ-Cl	237.7(2, 0)		μ-Cl,μ-Cl	92.8(1)	
$[(C_8H_8)(\eta^5\text{-cp}^*)Th(\mu\text{-Cl})_2Mg(CH_2CMe_3)$-	m	1972.6(4)		$MgCl_2OC$	O	205(2)	not given	not given		299
(thf)]0.5(tol)	$P2_1/m$	1323.2(4)	97.30(2)		C	210(3)	95.9(3, 2)			
(not given)	8	2532.8(5)			μ-Cl	241(1, 0)	92.8(4)			
				ThC_xCl_2	C(cp) [d]	254	–			
					$C(C_8H_8)$ [d]	202	–	not given		
					μ-Cl	289.0(7, 6)	74.4(2)			
$[(acEt)_4Mg(\mu\text{-Cl})_2Ti(OH)Cl_3]$	tr	962.3(3)	99.82(2)	MgO_4Cl_2	O	202.7(5, 13)	376.1(3)	O,O	91.4(2, 5.9)	300
(yellow)	$P\bar{1}$	978.3(3)	96.49(2)		μ-Cl	251.8(3, 14)	97.9(1, 6)		176.7(2)	
	2	1701.5(5)	111.15(2)				80.9(1)	O,Cl	90.6(2, 5.7)	
									173.1(2, 4)	
				$TiCl_5O$ [d]	HO	204.3(8, 11)	–	O,O	92.7(1)	
					Cl	233.6(6, 20)	–	O,Cl	93.2(1, 7.1)	
					μ-Cl	246.8(2, 10)	83.0(1)	[e]		
$[Mg(acEt)_4(\mu\text{-Cl})_2TiCl_4]$	tr	1712.2(7)	111.10(7)	MgO_4Cl_2	O	203.8(5, 16)	377	O,O	90.15(9, 5.39)	301
(yellow)	$P\bar{1}$	983.3(3)	107.22(6)		μ-Cl	252.8(2, 16)	97.80(3, 75)		176.2(2)	
	2	964.6(3)	103.11(6)				81.16(4)	O,Cl	91.43(8, 2.79)	
									172.3(9)	
				$TiCl_6$	Cl	229.3(2, 38)		Cl,Cl	90.00(3, 7.71)	
					μ-Cl	248.0(2, 14)			173.4(4, 1.5)	

TABLE 12 (continued)

Compound (colour)	Cryst. cl Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	M–L (pm)		Mg–M (pm) Mg–L–M (°) μ-L–M–μ-L (°)	L′–M–L (°)		Ref.
$[Li(thf)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(thf)]$	m	925.6(2)		$MgBr_2OC$	O	206.1(13)	not given	O,Br	98.2(4, 6)	302
(white)	$P2_1/n$	1428.4(2)	96.24(4)		C	219(2)	80.4(9, 1)	C,Br	119.4(5, 6)	
	4	2494.4(1)			μ-Br	253.3(6, 18)	98.0(2)	O,C	118.9(6)	
				LiO_2Br_2	O	195(5, 0)		O,O	107(2)	
					μ-Br	247(4, 2)		Br,Br	101(1)	
								O,Br	112(2, 6)	
$[(ClacEt)_3Mg(\mu\text{-}Cl)_2(\mu\text{-}Clac)TiCl_3]$	m	1048.0(4)		MgO_4Cl_2	O	201.3(10, 9)	360.9(4)	O,O	89.5(2, 2.6)	303
(yellow)	$P2_1/c$	1964.1(9)	120.21(5)		μ-O	204.9(7)	93.45(9, 1)	O,Cl	91.8(2, 4.1)	
	4	1659.7(6)			μ-Cl	250.8(7, 8)	80.71(12)		175(3, 3)	
				$TiCl_5O$	μ-O	196.6(8)		Cl,Cl	92.4(1, 5.2)	
					Cl	224.3(6, 3)			171.5(1, 4)	
					μ-Cl	244.9(5, 8)		Cl,O	87.7(1, 2.3)	
									174(2)	
$[(thf)_3Mg(\mu\text{-}OEt)Al(Et)_2(C_{14}H_{10})](thf)$	m	4039.9(3)		MgO_4C	O_{eq}	not given		O,O	154	304
(yellow)	$P2_1/a$	878.7(1)	96.781(6)		$\mu\text{-}O_{ap}$	not given		O,μ-O	140(–, 4)	
	4	1047.3(1)			C_{ap}	not given		μ-O,C	109	
				AlC_3O	C_3	not given				
					μ-O	not given				

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] $O\text{–}Mg\text{–}O_{ap} = 89.5(2, 2.3)°$; $\mu\text{-}O\text{–}Mg\text{–}O_{ap} = 90.7(2, 1.7)°$; $O_{ap}\text{–}Mg\text{–}O_{ap} = 177.9(2)°$. [d] The Th–C(centroid) bond distance. [e] The OH and Cl atoms are disordered: O–Ti–μ-Cl = 90.3(1) and 173.9(1, 3.1)°; Cl–Ti–Cl = 93.1(1, 6.2) and 175.1(1)°; Cl–Ti–μ-Cl = 89.2(1, 4.8) and 171.8(1, 4)°.

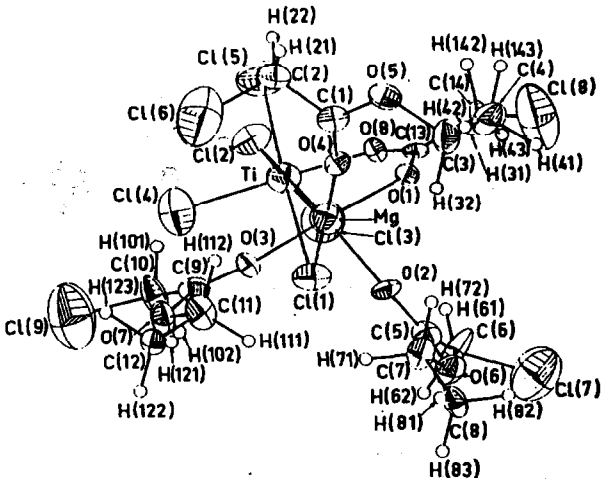


Fig. 17. Structure of $[(acacEt)_3Mg(\mu\text{-Clac})TiCl_3]$ [305].

metal atoms form a triangular skeleton bonded by three bridging and two capping chlorine atoms. The two magnesium(II) atoms are in octahedral environments of four chlorine atoms and the two nitrogen donors of a Me_4en molecule. The cerium(III) atom has four chlorine atoms and two η^3-allyl groups. A similar structure has been found for a magnesium-lanthanum derivative [305] with bromine bridges. As in other series, the mean Mg–Cl distances are shorter than the mean Mg–Br values. Mean values for the bridging ligands also show that triple bridge distances are larger than single bridge values, for example: 248.0 pm (μ-Cl) < 264.7 pm (μ-Br); and 259.6 pm (μ_3-Cl) < 276.9 pm (μ_3-Br).

The second type of bridge features an oxo-centred trimetal cluster in which the geometry about the magnesium atom is a distorted trigonal bipyramid [306]. The U_2OMg unit, two chlorine bridges and one oxygen bridge along the triangular edges, and the centroids of the uranium coordinated pentamethylcyclopentadienyl groups all lie in a plane. The magnesium atom is thus doubly bridged to each uranium, and the uranium atoms are quadruply bridged to each other.

In a third type [307], a central magnesium(II) atom, octahedrally coordinated, is linked to each of two zinc(II) atoms by three crotonate bridges. Of these, two are of the syn–syn bidentate type and the third is monodentate, bridging through only one oxygen atom.

The fourth, and most common type involves two bridging ligands. In four examples [308–310,164] two carbon atoms serve as bridges between metal atoms. In these examples the magnesium(II) atoms are in a tetrahedral environment of four carbon ligands. The mean Mg–C(μ-Me) bond distance of 223.4 pm (range 219.2 to 229.5 pm) is about 6 pm shorter than that of the Mg–C(μ-Ph) value of 229.5 pm (range 227.0 to 232.0 pm) as a result of the different steric requirements of these two groups. In two other cases with oxygen bridges [311] and chlorine bridges [312] the magnesium atoms are octahedrally coordinated.

In a fifth type, a single oxo-group is utilized as the bridge between metal atoms. In several cases the oxo-groups are located *trans* in the octahedral environment around the magnesium centre, and take the apical position a square-pyramidal tungsten [313–315] or rhenium [316]. The Mg–O–W(Re) angles are in the range from 180.0 to 164.2(4)°. In the rhenium derivative two crystallographically independent molecules with different degrees of distortion occur.

The sixth type of bridging involves two atom linkages between metal atoms. Examples of these include a M–N–O–Mg–O–N–M link (M = W or Mo) [317], a Co–N–N–Mg–N–N–Co link [318], and a Mo–C–O–Mg–O–C–Mo link [319]. In this series of compounds the dominant colour is red to orange, but there are several colourless examples along with a green and a grey.

8.3. Hetero-oligonuclear

Crystallographic and structural data for tetra-, penta- and hexa-nuclear derivatives of this class are gathered in Table 14. Three examples contain two magnesium(II) atoms plus another pair of metal atoms, Li^I [309], Al^{III} [200] and Ti^{III} [312], and these have similar structures. Two pseudo-tetrahedral LiN_2C_2 [309], AlN_2C_2 [200] and cp_2TiCl_2 [312] fragments are doubly bridged by two carbon ligands [309], two nitrogen ligands [200] or two chlorine atoms [312] to two magnesium(II) atoms. Two more carbon ligands [309], two iodine atoms [200] or two chlorine atoms [312] provide further bridging to the magnesium atoms. A tetrahedral magnesium environment with a MgC_4 chromophore is found in the first example [309]. The bridging carbon ligands bring the magnesium atoms within 288.2(2) pm, with Mg–C–Mg angles of 77.3(3)°. The magnesium and lithium atoms approach to 293.6 pm.

The penta-coordination about magnesium in the second example [200] includes the Mg–C interaction at 269(1) pm. The iodine bridged Mg–Mg distance is 410.1(8) pm, and the nitrogen bridged Mg–Al distance is 261.2(4) pm with Mg–Al–Mg angles of 77.1(2)°. This reflects the steric requirements of the ligands.In the third example the magnesium atoms are pseudo-octahedral.

Related structures have been found for three other derivatives in this series [294,164] (Table 14). A typical structure is shown in Fig. 19 [294]. All three examples contain magnesium units with trigonal bipyramidal coordination with three arynyl [294] or three allynyl [164] plus two amine nitrogen atoms. Two Li^I atoms [294] or

TABLE 13. Crystallographic and structural data for hetero-trinuclear magnesium compounds [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	M–L (pm)		M–M (pm) M–L–M (°) μ-L–M–μ-L (°)	L'–M–L (°)		Ref.
$[Mg_2(Me_4en)_2(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3Ce(\eta^3\text{-}C_3H_5)_2]$	or	1124.5(2)		$MgCl_4N_2$	N [b]	223.6(7, 9)	261.3(4)	N,N [b]	83.2(4, 1)	305
(orange red)	$P2_12_12_1$	1505.3(1)			μ-Cl	248.0(4, 28)	81.4(1, 1.4)	N,μ-Cl	97.0(2, 1.7)	
	4	1820.6(1)			μ_3-Cl	259.6(3, 10)	83.8(2, 1)	[c1]		
				CeC_6Cl_4	C	274(2, 5)	276.6(4, 6)	C,C	28.34(4, 1.3)	
					μ-Cl	287.9(2, 1)	85.84(8, 6)		52.9(4, 5)	
					μ_3-Cl	300.8(2, 15)	70.59(7, 82)		101.5(3, 29.2) [c2]	
$[Mg_2(Et_2O)_4(\mu_3\text{-}Br)_2(\mu\text{-}Br)_3Ce(\eta^3\text{-}C_3H_5)_2)]$	m	2022.3(3)		$MgBr_4O_2$	O	207.2(8, 6)	not given	O,O	93.2(3)	305
(orange red)	$C2/c$	1133.3(2)	122.58(2)		μ-Br	267.2(3, 59)	79.8(1)	O,μ-Br	95.1(2, 3.6)	
	4	1891.7(3)			μ_3-Br	276.4(4, 6)	84.47(9, 1.72)	[d1]		
				CeC_6Br_4	C	266(2, 1)	not given	C,C	28.8(5, 2.1)	
					μ-Br	310.9(1, 0)	86.32(7, 1.44)		55.1(6)	
					μ_3-Br	311.4(1, 0)	72.19(5, 1.05)		104.6(5, 20.3) [d2]	
$[Mg_2(Et_2O)_4(\mu_3\text{-}Br)_2(\mu\text{-}Br)_3Nd(\eta^3\text{-}C_3H_5)_2]$	m	2020.3(3)		$MgBr_4O_2$	O	207.3(7, 5)	not given	O,O	93.4(2)	305
(green)	$C2/c$	1128.6(3)	122.58(2)		μ-Br	262.1(3, 5)	81.4(1, 2.7)	O,μ-Br	93.0(2)	
	4	1892.5(4)			μ-Br	277.3(3, 11)	83.55(9, 1.44)	[e1]		
				NdC_6Br_4	C	266(2, 5)	not given	C,C	27.9(5, 4)	
					μ-Br	306.3(1, 0)	85.70(7, 1.64)		48.8(5)	
					μ_3-Br	307.4(1, 0)	73.12(3, 1.34)		101.7(7, 18.8) [e2]	
$[\{(cp^*)U(\mu\text{-}C_{12}H_{14}P)\}_2Mg(C_{12}H_{15}P)_2(\mu_3\text{-}O)\text{-}(\mu\text{-}O)(\mu\text{-}Cl)_2]$	hx	1757.8(5)		MgC_2Cl_2O	C_{eq}	223(4, 0)	not given	C,C	120(2)	306
(not given)	$P6_522$	–			$\mu_3\text{-}O_{eq}$	194(4)	128.0(6)	C,Cl	86(1)	
	6	4681.3(7)			$\mu\text{-}Cl_{ap}$	279(1, 0)	86(1)	C,O	128(1)	
								Cl,O	78.9(1)	
				UC_7O_2Cl	C(cp*)	285(2, 3)	343.7(3)	C,C	151(1)	
					μ-C	264(2, 4)	106(1, 2)	C,O	79.9(6, 12.9)	
					μ-O	213(2)		C,Cl	80.4(6, 7)	
					μ_3-O	218(2)		O,Cl	72.3(6)	
					μ-Cl	292.8(9)			146.4(8)	
$[(qu)Zn(\mu\text{-}crot)_3]_2Mg$	tr	1096.5(3)	104.85(1)	MgO_6	O	206.0(1, 2)	not given	O,O	90.0(1, 1.0)	307
(not given)	$P\bar{1}$	1097.7(3)	111.82(1)		μ-O	205.7(1)				
	1	1107.5(3)	101.86(1)							
				ZnO_4N	O	199.0(1, 91)		O,O	55.6–126.0(1)	
					μ-O	237.6(3)		O,N	97.1(1, 1.4)	
					N	208.1(3)			151.7(1)	

$[(Me_4en)Li(\mu\text{-}Me)_2]_2Mg$ (colourless)	m $P2_1/c$ 4	1372.6(2) 1547.6(4) 1205.8(5)	92.69(3)	MgC_4	μ-C	226.0(7, 35)	261.6(11, 1) 70.3(3, 5)	C,C	109.5(3, 1.4)	308
				LiN_2C_2	N μ-C	210.1(11, 14) 228.4(12, 23)		N,N N,C C,C	88.4(4, 1.0) 115.2(4, 2.6) 107.1(5, 4)	
$[(Me_4en)Li(\mu\text{-}Ph)_2]_2Mg$ (colourless)	m $P2_1/c$ 4	1808.5(29) 1379.5(6) 1652.6(8)	101.05(9)	MgC_4 LiN_2C_2	not given		not given	not given		309
$[(Me_2Al(\mu\text{-}Me_2]_2Mg$ (colourless)	tr $P\bar{1}$ 2	695.5(2) 1080.2(2) 1028.7(2)	102.35(2) 105.03(1) 92.49(1)	MgC_4 AlC_4	μ-C C μ-C	220.7(10, 15) 196.5(10, 8) 210.2(9, 21)	270.4(4, 2)	not given C,C	119.6(3, 4)	310
$[(Me_6dta)Na(\mu\text{-}Ph)_2]_2Mg$ (orange)	m $P2_1/n$ 4	1844.9(4) 1532.4(4) 1857.5(5)	118.71(2)	MgC_4	μ-C	229.5(7, 25)	330.1(4, 23) not given 109.5(2, 5.1)			164
				NaN_3C_2	N μ-C	257.9(11, 42) 279.0(6, 101)		N,N C,C	70.5(3, 1.0) 117.0(3, 3) 83.1(–, 9)	
$[(Me_2Al(\mu\text{-}OMe)_2]_2Mg(dox)]$ [f] (colourless)	or *Pnnm* 2	1342(2) 1074(2) 730(2)		MgO_6	μ-O O(dox)	206(1, 1) 224(2)	293(1) 98.05(39, 76) 76.11(26)			311
				AlO_2C_2	μ-O C(Me)	183(2, 3) 201(2, 0)		O,O C,C	87.80(30) 106.61(38)	
$[\{cp_2Ti(\mu\text{-}Cl)_2\}_2Mg(thf)_2]$ (green)	m $P2_1/c$ 2	810.4(2) 1137.1(4) 1628.2(9)	91.53(3)	$MgCl_4O_2$	O μ-Cl	210.5(4, 0) 250.7(2, 3)	not given 98.16(7, 10) 90.00(6, 6.90)	O,O O,Cl	not given 90.0 (1, 1.3)	312
				$TiC_{10}Cl_2$	C_{ap} μ-Cl	237.0(8, 33) 256.7(2, 2)		Cl,Cl	80.59(7)	
$[\{W(o\text{-}xyl)_2(\mu\text{-}O)\}_2Mg(thf)_4]CH_2Cl_2$ (red)	m $C2/c$ 4	2052.6(6) 2207.6(4) 1754.0(5)	122.50(2)	MgO_6	O(thf) μ-O	210.0(4, 2) 203.3(5, 4)	180.0	O,O	90.0(1, 2.1) 176.5(2, 7)	313
				WC_4O	C_{eq} μ-O_{ap}	217.7(5, 15) 173.5(5, 9)		C,C C,O	83.0(2, 1.9) 139.2(2, 14.4) 110.4(1, 7.2)	
$[\{W(o\text{-}xyl)_2O\}_2Mg(thf)_4]$ (red)	or *Pbca* 4	1806.1(5) 1675.9(5) 1563.7(5)		MgO_6	O(thf) μ-O	210(1, 1) 207(1, 0)	170.4(8)	O,O	90.0(6, 1.3)	314
				WC_4O	C_{eq} μ-O_{aq}	216(2, 2) 171(1)		C,C C,O	80.8(9, 5.5) 133.0(9, 2.9) 113.6(8, 4.0)	

TABLE 13 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	M–L (pm)		M–M (pm) M–L–M (°) μ-L–M–μ-L (°)	L′–M–L (°)		Ref.
$(Me_4WO)_2Mg(thf)_4$	tr	995.9(5)	63.95(2)	MgO_6	O(thf)	210.6(7, 4)		O,O	90.0(3, 3)	315
(orange-red)	$P\bar{1}$	995.9(3)	116.20(3)		μ-O	201.0(6, 0)	178.5(3)			
	1	1051.7(2)	104.09(3)							
				WC_4O	C_{eq}	219.2(16, 141)		C,C	53.9–130.8(5)	
					μ-O_{ap}	173.3(6)		C,O	111.0(5, 5.4)	
$(Me_4ReO)_2Mg(thf)_4$	tr	1043.7(3)	78.95(3)	MgO_6	O	208.8(9, 13)		O,O	90.0(4, 6)	316
(orange-red)	$P\bar{1}$	995.1(3)	63.50(2)		μ-O	202.9(8, 0)	175.0(4)			
	1	951.0(3)	69.50(2)							
				ReC_4O	C_{eq}	209.1(40, 38)		C,C	not given	
					μ-O_{ap}	169.4(8, 0)		C,O	113.7(9, 3.9)	
$[(Me_3SiCH_2)_4Re(\mu\text{-}O)]_2Mg(thf)_2]$ [g]	m	2483.0(2)		MgO_4	O(thf)	202.1(1, 0)		O,O	100.4(4)	316
(red-purple)	$P2/c$	1157.4(2)	113.59(2)		μ-O	192.3(7, 0)	171.4(4)			
	4	2426.2(3)								
				ReC_4O	C_{eq}	211.7(13, 17)		C,C	82.3(5, 2.4)	
					μ-O_{ap}	174.2(7)			136.5(4, 6.3)	
								C,O	111.8(5, 3.8)	
				MgO_4	O(thf)	201.5(10, 0)		O,O	103.6(4)	
					μ-O	191.6(10, 0)	164.2(4)			
				ReC_4O	C_{eq}	212.6(12, 19)		C,C	82.6(5, 1.1)	
					μ-O_{ap}	173.7(10)			136.9(5, 8.9)	
								C,O	111.6(5, 5.5)	

$[\{(cp)(CH_2SiMe_3)_2W(\mu\text{-}NO)\}_2MgI_2]$-	tg	1636.86(9)		MgO_2I_2	μ-NO	211	O,O	159.2	317
Et_2O	$P\bar{4}2_1m$	–			I	276	O,I	95.7	
(red)	2	909.27(6)					I,I	112.0	
				WC_7N	μ-ON	177			
					C	not given			
$[\{(cp)(CH_2SiMe_3)_2Mo(\mu\text{-}NO)\}_2MgI_2]$-	tg	1642.43(9)		MgO_2I_2	not given				317
Et_2O	$P\bar{4}2_1m$	–							
(red)	2	907.29(8)		MoC_7N	not given				
$[\{PMe_3)_3Co(\mu\text{-}N_2)\}_2Mg(thf)_4]$				MgO_4N_2	O_{eq}	208			318
(orange)					N_{ap}	204			
				CoP_3N	P	213			
					N	172			
$[\{(\eta^5\text{-}cp)Mo(CO)_2(\mu\text{-}CO)\}_2Mg(py)_4]$	tr	850.5(2)	117.88(1)	MgN_4O_2	N_{eq}	223.3(2, 0)	not given		319
(gray)	$P\bar{1}$	1107.3(2)	108.26(1)		μ-CO_{ap}	204.7(2, 0)			
	1	1103.4(2)	90.34(1)						
				MoC_8	OC	188.7(2)	not given		
					μ-OC	194.7(3, 0)			
					C(cp)	not given			

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c1] N–Mg–μ_3-Cl = 96.5(2, 3.1) and 177.1(2, 1.4)°; μ-Cl–Mg–μ-Cl = 161.2(2, 3)°; μ_3-Cl–Mg–μ-Cl = 83.0(2, 2.4)°. [c2] C–Ce–μ-Cl = 80.0(3, 2.3) and 116.5(4, 15.8)°; C–Ce–μ_3-Cl = 93.1(3, 9.5), 147.7(3, 6.1) and 170.2(3, 1.1)°; μ-Cl–Ce–μ-Cl = 133.15(5)°. [d1] O–Mg–μ_3-Br = 89.1(2) and 174.8(2)°; μ-Br–Mg–μ-Br = 165.3(1)°. [d2] C–Ce–μ-Br = 76.9(4, 6) and 116.9(4, 14.3)°; C–Ce–μ_3-Br = 91.1(4, 5.9), 147.0(5, 1.2) and 169.7(4)°; μ-Br–Ce–μ-Br = 132.24(4)°. [e1] O–Mg–μ_3-Br = 97.2(2, 1.2)°; O–Mg–μ-Br = 173.8(2, 1.2)°; μ-Br–Mg–μ-Br = 162.6(1)°. [e2] C–Nd–μ-Br = 92.1(4, 9.1), 149.7(4, 2) and 175.3(4)°; C–Nd–μ-Br = 79.1(4, 2.0) and 115.7(4, 12.7)°. [f] the complex is an infinite polymer of trimer units held together by dioxane molecules. [g] There are two crystallographically independent molecules present.

TABLE 14. Crystallographic and structural data for hetero-oligonuclear magnesium compounds [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	M–L (pm)		M–M (pm) M–L–M (°) μ-L–M–μ-L (°)	L′–M–L (°)		Ref.
$[Mg_2(\mu\text{-Ph})_6\text{-}Li_2(Me_4en)_2]$ (not given)	m $C2/c$ 4	1674.3(5) 1656.6(4) 1713.7(6)	 94.68(3) 	MgC_4	μ-C [b] μ-C	218.4(3, 2) 230.8(3, 22)	288.2(2) [c] 77.3(3) 102.7(1)	C,C [b]	110.91(1, 4.9)	309
				LiN_2C_2	N μ-C	214.0(6, 27) 244.6(–, 27)	293.6 [d] not given	N,N N,C	87.0(2) not given	
$[Me_2Si(N^tBu)_2(AlMe_2)\text{-}(MgI)_2]$ (not given)	m $P2_1/c$ 2	909.5(4) 2185(1) 1228.5(6)	 121.6(1) 	MgN_2I_2C	μ-N C μ-I	227.9(6, 20) 261(1) 283.0(3, 19)	410.1(8) [c] 92.9(1) 87.1(1)	N,I C,I	103.7(2, 1) 165.9(2, 4) 106.2(4, 1.1)	200
				AlN_2C_2	C μ-N	199(1, 3) 188.2(6, 5)	261.2(4) [d] 77.1(2, 4) 80.4(2)	C,C C,N	108.9(5) 116.1(5, 94)	
$[(\eta^5\text{-cp})_2Ti(\mu\text{-Cl})_2\text{-}Mg(thf)_2(\mu\text{-Cl})_2]_2$ (aquamarine)	tg $I4_1/a$ 8	2401.8(6) – 1492.7(7)	 	$MgCl_4O_2$	O μ-Cl	212(1, 1) 250.1(8, 28)	not given 96.0(3) 90.3(3, 8.7)	O,O O,Cl	86.1(5) 90.8(4, 5.8) 169.5(5, 1.5)	312
				$TiC_{10}Cl_2$	C μ-Cl	236(2, 3) 254.6(6, 11)	not given 98.8(2, 3)	Cl,Cl	80.2(2)	
$[Li(\mu\text{-C}{\equiv}\text{CPh})_3Mg\text{-}(Me_4en)]_2$ (not given)	m $C2/c$ 4	2329.4(20) 1103.0(4) 2238.8(10)	 105.05(5) 	MgC_3N_2	N_{eq} $\mu\text{-}C_{eq}$ N_{ap} $\mu\text{-}C_{ap}$	220.2(5) 218.6(5, 3) 235.0(4) 230.7(4)	not given not given not given	C_{eq},C_{eq} C_{eq},N_{eq} $C_{eq}C_{ap}$ [e1]	132.8(2) 113.6(2, 3.3) 91.0(2, 1.7)	294
				LiC_4	μ-C	230.4(9, 47)	[e2]	C,C	97.9(3, 12.1) 155.9(3)	
$[Na(\mu\text{-C}{\equiv}\text{CBu})_3Mg\text{-}(Me_4en)]_2$ (colourless)	tr $P\bar{1}$ 1	1081.7(4) 1163.5(2) 1281.2(3)	65.50(2) 77.98(2) 86.07(2)	MgC_3N_2	N_{eq} $\mu\text{-}C_{eq}$ N_{ap} $\mu\text{-}C_{ap}$	225.4(3) 216.9(3, 2) 252.0(3) 225.7(3)	not given 88.0(1, 5)	C_{eq},C_{eq} C_{eq},C_{ap} N_{eq},C_{ap} N_{ap},C_{ap}	134.7(1) 86.7(1, 2) 92.2(1) 167.9(1)	164
				NaC_4	μ-C	260.1(3, 30)		C,C	96.4(1) 168.3(1) [f]	
$[Na(\mu\text{-C}{\equiv}\text{CBu})_3Mg\text{-}(Me_5dta)]_2$ (colourless)	tr $P\bar{1}$ 1	1102.1(4) 1220.5(4) 1398.4(4)	103.03(3) 110.97(4) 102.62(3)	MgC_3N_2	N_{eq} $\nu\text{-}C_{eq}$ N_{ap} $\mu\text{-}C_{ap}$	229.9(4) 218.8(5, 4) 245.1(4) 224.7(5)	not given 88.0(2, 1.3)	C_{eq},C_{eq} C_{eq},C_{ap} N_{eq},C_{ap} N_{ap},C_{ap}	130.3(2) 96.8(2, 7) 90.1(2) 165.9(2)	164
				NaC_4	μ-C	260.1(4, 21)		C,C	97.9(2) 167.8(2) [g]	
$[Mg(\mu\text{-OH})_6Co_3(en)_6]\text{-}(ClO_4)Cl3H_2O$ (red)	m $P2_1/c$ 4 4	1248.5(3) 2292.2(6) 1584.0(4)	 108.75(3) 	MgO_6	μ-O	207	not given	not given		320
				CoN_4O_2	not given					

[(thf)Mg{(μ-N^{t}Bu)-Al(H)}$_3$] (colourless)	or *Pbca* 8	1710.7(2) 1730.5(4) 2022.0(5)		MgN_3O	O μ-N	200.2(2) 209.0(3, 8)	not given 88.3(1) 86.3(1)	O,N	128(2)	321
				AlN_3H	H μ-N	152(2, 2) 191.3(2, 20)	not given 89.5(1)	N,N N,H	90.9(1) 97.1(1)	
[Fe(μ-H)$_6$Mg$_4$(thf)$_8$Br$_{3.5}$Cl$_{0.5}$] (yellow)	m *C2/c* 4	2042.7(4) 1162.3(2) 2166.1(7)	109.39(2)	MgH_3O_2Br	O μ-H Br	207.7(9, 13) 211(9, 9) 253.1(4, 5)	not given 82(4, 8) 73(4, 5)	H,O [h1]	92(3, 8) 158 (3, 4)	322
				FeH_6	μ-H	174(11, 27)		H,H	90(4, 2) 176(4, 0)	
[Fe(μ-H)$_6$Mg$_4$(thf)$_8$Br$_{3.5}$Cl$_{0.5}$ (yellow) (@ 80 K) [h2]				MgH_3O_2Br	O μ-H Br	207.7(3, 27) 204.5(4, 57) 248.3(2, 4)	not given 85.3(2, 2.3) 67.6(1, 1.2)	H,O [h2]	93.5(1, 12.4) 155.3(1, 2.6)	322
				FeH_6	μ-H	160.9(5, 6)		H,H	90.0(1, 8) 178.9(1, 6)	
Cu_4(μ-Ph)$_6$MgEt$_2$O (yellow)	tr *P1* 1	1039.4(2) 1048.0(4) 990.9(4)	107.86(3) 96.56(2) 111.25(2)	MgC_3O	O μ-C	204.6(9) 235(1, 0)	275.4(4) [i1] 79.0(4) 117.1(4)	C,O	not given	323
				CuC_2	μ-C μ-C	195(1) 209(1)	242.7(2) [i2] 73.1(3)	C,C	119.7(4) 160.9(4)	
[Mg$_2$(μ-Br)$_2$(Et$_2$O)-(^{i}Pr)MoH(cp)$_2$]$_2$ (pale yellow)	m *P2$_1$/c* 2	856.6(8) 1295.5(12) 1861.7(15)	93.9(1)	$MgBr_2C$	C μ-Br	not given 255(3, 4)	276(3) [f1]	Br,Br Br,Mo	94(3) 119(2, 1)	324
				$MgBr_2O$	O μ-Br	not given 260(3, 1)	281(3) 87(1, 1)	Br,Br Br,Mo	91(3) 116(2, 3)	
[Mg$_2$(μ-Br)$_2$(Et$_2$O)-(C$_6$H$_{11}$)MoH(cp)$_2$]$_2$ (pale yellow)	m *C2/m* 2	1567.1(8) 1199.6(5) 1508.5(8)	109.55(8)	$MgBr_2C$	C μ-Br	222(2) 267.0(5, 0)	285.3(7) [f2]	Br,Br Br,C	89.4(2) 110.5(1)	324
				$MgBr_2O$	O μ-Br	208(2) 255.9(4)	273.7(6) 87.7(2)	Br,Br Br,O	94.4(6) 100.3(2)	
				$MoC_{10}H$	H C(cp)	not given 231(2, 4)				
[{Cu(mes)}$_4$(μ-SAr)$_2$-(MgSAr)$_2$] (red)	or $P2_12_12_1$ 2	2514.0(3) 1902.6(2) 855.4(1)		MgN_2S_2	N S μ-S	218.3(8, 3) 237.5(4) 242.7(4)		N,N S,S N,S	116.4(3) 132.5(2) 95.9(2, 1)	325
				Cu^1C_2	μ-C	200.3(8, 22)	270.0(1) [k]	C,C	142.8(3)	
				Cu^2C_2S	μ-C μ-S	205.4(8, 10) 238.9(2)	407.9(1) [k]	C,C C,S	168.1(3) 95.7(2, 5.7)	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] The Mg–Mg distance. [d] The Mg–Mg distance. [e1] C_{eq}–Mg–N_{ap} = 92.1(2, 1)°; N_{eq}–Mg–N_{ap} = 80.2(2)°; C_{ap}–Mg–N_{ap} = 172.1(2)°. [e2] Li–Li = 302.5 pm; Li–C–Li = 82.8°. [f] Na–C–Na = 83.6(1)°. [g] Na–C–Na = 82.1(2)°. [h1] H–Mg–Br = 101(3, 11) and 171(3, 3)°; O–Mg–Br = 97.0(3, 1.2)°; O–Mg–O = 92.1(3, 1.8)°; Mg–H–Fe = 166(6, 13)°. [h2] By neutron diffraction; H–Mg–Br = 103.4(1, 5.0) and 166.6(1, 6)°; O–Mg–Br = 97.7(1, 2.8)°; O–Mg–O = 92.5(1, 1)°; Mg–H–Mg = 170.7(3, 3.8)°. [i1] The value for Mg–Cu_{eq}; Mg–Cu_{ap} = 382.8(4) pm. [i2] The value for Cu_{eq}–Cu_{ax}; Cu_{eq}–Cu_{eq} = 301.9(3) pm. [j1] Mg–Mo–Mg = 104(2)°. [j2] Mg–Mg–Mg = 108.7(4)°. [k] Cu^1–Cu^2 = 244.8(1, 17) pm; Cu^1–C–Cu^2 = 74.2(3, 8)°; Cu^2–S–Mg = 136.4(1)°.

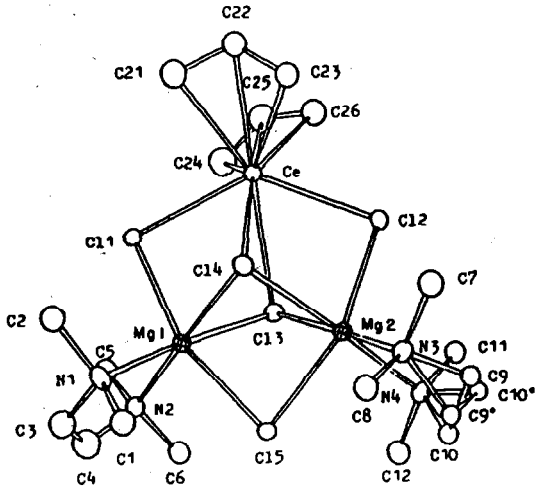


Fig. 18. Structure of $[Mg_2(Me_4en)(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_2Ce(\eta^3\text{-}C_3H_5)_2]$ [305].

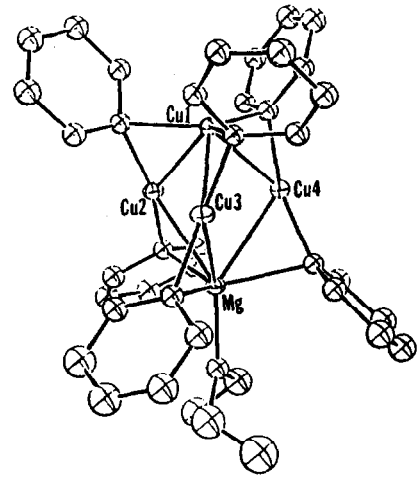


Fig. 20. Molecular plot of $Cu_4Ph_6Mg(Et_2O)$ [323].

Na^I atoms [164] link the magnesium atoms via the acetylidic carbon atoms.

A red mixed chloride-perchlorate salt has a complex cation consisting of a Mg^{II} atom octahedrally coordinated to three $[(en)_2Co(OH)_2]^+$ chelating groups via the OH groups [320].

A cubane like $(AlN)_4$ framework, with one Al replaced by Mg provides the skeleton for a colourless compound [321]. The fourth coordination position for magnesium is occupied by a thf molecule, and by an H atom for the aluminum.

There are two yellow coloured hetero-pentanuclear magnesium compounds. One consists of an octahedral $[FeH_6]^{4-}$ anion capped on four of the eight triangular faces by $[MgX(thf)_2]^+$ units [322]. A crystallographic C_2 axis passes through Fe_1, $H(1)_1$ and H(2). The magnesium atoms are octahedrally coordinated. The second derivative is shown in Fig. 20, where it can be seen that the metal atoms form a trigonal-bipramidal arrangement. The six phenyl groups bridge the M(apical)–M(equatorial) sites in a perpendicular fashion, while the M_{eq}–M_{eq} distances are clearly nonbonding (Table 14). Coordination is completed by an ether molecule on the Mg atom to form a pseudo tetrahedral environment.

There are three examples of hetero-hexanuclear magnesium derivatives, two of which are isostructural [324], differing only by the substitution of a cyclohexyl group for an isopropyl. The isopropyl derivative is shown in Fig. 21. The two magnesium atoms in this structure are both chemically and crystallographically

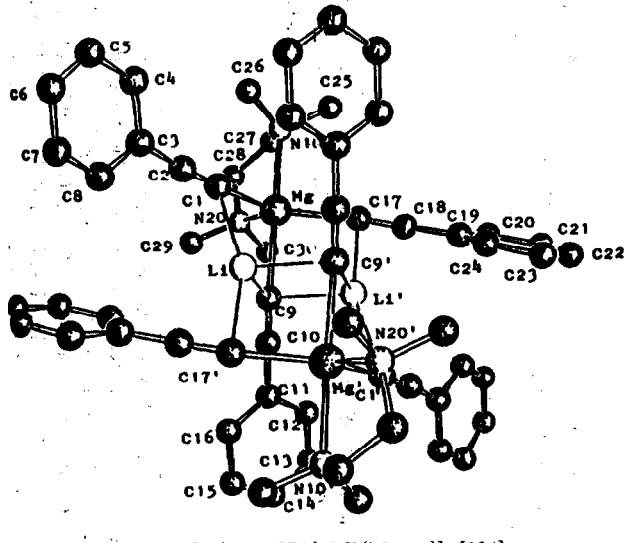
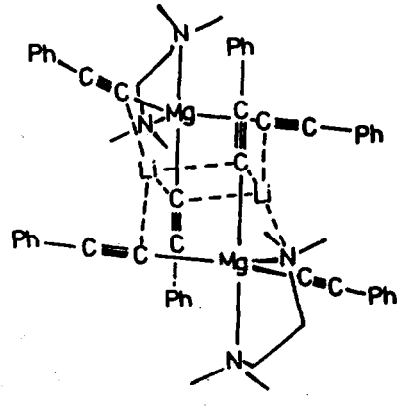


Fig. 19. Structure of $[Li(\mu\text{-}C{\equiv}CPh)_3Mg(Me_4en)]_2$ [294].



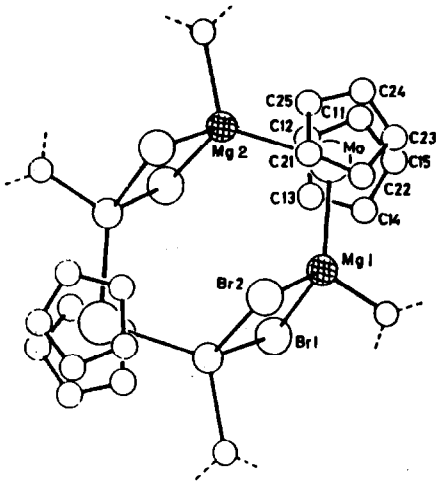


Fig. 21. Projection of $[Mg_2(\mu\text{-}Br)_2(Et_2O)(^iPr)Mo(H)(cp)_2]_2$ [324].

distinct. The third derivative consists of a tetranuclear mesitylcopper(1) unit bound to two bis(thiophenolato)-magnesium(II) units (Fig. 22) [325]. One thiophenolato unit is S, N chelated to the magnesium centre, and the other (N bound to Mg) uses its S atom to bridge to the copper atom. The four Cu^I atoms are almost coplanar with Cu–Cu distances of 243.1(1) pm and 246.4(1) pm with a shortest diagonal of 270.0(1) pm. The central mesityl copper unit contains a pair of two coordinated Cu^I atoms (CuC_2) and two trigonal planar Cu^I atoms (CuC_2S_2).

The magnesium atoms in this series of compounds are found in tetrahedral, trigonal-bipyramidal and pseudo-octahedral environments. There are two examples [324] in which one position of the tetrahedral environment around magnesium is occupied by a Mo atom.

The mean Mg–L(eq) bond distance is shorter than the Mg–L(ap) distance, for example: 225.2 *vs.* 238.6 pm (L = Me_4en); 217.7 *vs.* 227.0 pm (L = RC–C). The mean Mg–L(terminal) bond distance is shorter than that of the Mg–L(bridge): 205.9 *vs.* 207.0 pm (L = OL); 250.7 *vs.* 259.5 pm (br). The mean Mg–L bond distance increases with increasing covalent radius of the coordinated atom in the order: 207 pm (μ-OH) < 218.5 pm (μ-NL) < 229.3 pm (μ-CL) < 250.1 pm (μ-Cl) < 259.5 (μ-Br) < 283.0 pm (μ-I).

The other metal atoms present come from both transition and non-transition groups. The latter are two or three coordinate (Cu^I), and four coordinate (Li^I, Na^I, Al^{III}). The transition metals are six coordinate (Co^{III}, Fe^{III}), and higher ($(cp)_2MoH$ and $(cp)_2TiCl_2$).

8.4. Hetero-polynuclear

The crystallographic and structural data for these compounds are given in Table 15, and are listed and referenced in order of increasing coordination number of magnesium. The structure of $[MgSr(egta)(H_2O)_8]_n$ [213] is shown in Fig. 23 as an example. Two crystallographically unique Mg^{II} atoms appear in the asymmetric unit cell, Mg^1 occupying a special position of 1 symmetry, while Mg^2 resides on a site of 2 symmetry. The coordination sphere for each Mg^{II} atom is octahedral and consists of two water molecules plus the

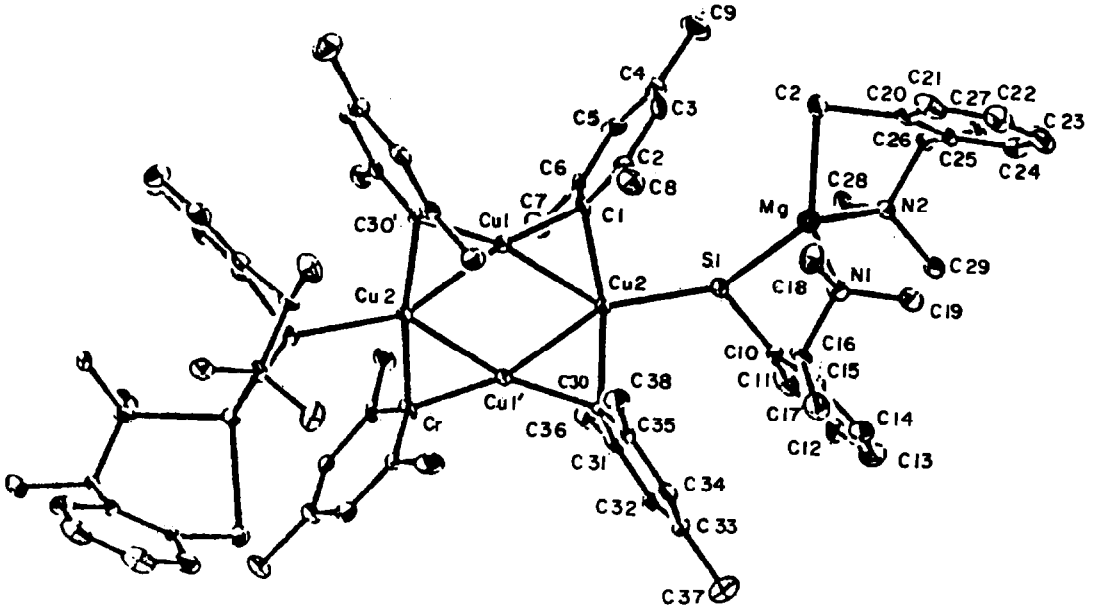


Fig. 22. View of $[(Cumes)_4(\mu\text{-}SAr)(MgSAr)_2]$ [325].

TABLE 15. Crystallographic and structural data for hetero-polynuclear magnesium compounds [a]

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromo-phore	Mg–L (pm)		L'–Mg–L (°)		Ref.
$(KCa)_{1.04}Mg_{0.95}Al_{5.2}Si_{12.6}O_{36}$	tg	1322.9(5)		MgO_3	O [b]	208(1, 0)	O,O [b]	not given	326
(not given)	$P\bar{6}m2$	–							
	?	733.8(4)		CaO_6	O	261.9(8, 0)			
$[Mg_{2.2}Al_{5.8}(PO_4)_8]$-$(Pr_2NH_2)_2$	m	1021.92(2)		MgO_4 [c]	O	153.9(3, 5)	O,O	109.5(1, 1.3)	327
(not given)	$I112/b$	1021.98(3)							
	1	1001.26(3)	90.987(2)	AlO_4	O	177.0(3, 5)	O,O	109.5(1, 1.5)	
$Mg_{0.54}Co_{0.46}P_2O_7$	m	697.7(1)		MO_5 [d]	O_{eq}	202.2(3, 65)	O,O	93.1(1, 21.4)	328
(violet)	$P2_1/c$	833.0(2)	113.74(1)		O_{ap}	211.9(3)	O,O_{ap}	160.4(1, 9.2)	
	4	903.2(9)							
				MO_6	O	207.1(3, 27)	O,O	90.4(1, 13.6)	
						214.1(3, 20)		163.7(1, 6.1)	
$MgCu(C_8H_4O_4)_2(H_2O)_4$	or	655.1(7)		MgO_6	O	203.1(5, 0)	O,O	90.0(2, 7.2)	329
(not given)	$P2_12_12_1$	2058.9(10)			H_2O	206.2(6, 8)		173.0(2, 1.4)	
	2	683.2(8)							
				CuO_6	O	194.0(4, 7)	O,O	50.8(2)	
					O	285.1(5)		173.9(2)	
$[(H_2O)_4Mg(edds)Cu]$-$3H_2O$	or	839.2(2)		MgO_8	O	207.5(5)	O,μ-O	89.6(2)	330
(blue)	$P2_12_12_1$	1085.5(2)			μ-O	210.9(5)	O,H_2O	91.2(2, 3.5)	
	4	2150.8(6)			H_2O	207.7(5, 8)		178.5(2) [e1]	
				CuO_4N_2	O_{eq}	198.4(4, 3)	O,O	91.1(2)	
					N_{eq}	200.7(1, 6)	N,N	85.6(2)	
					O_{ap}	230.4(4)	O,N	92.0(2, 1.9)	
					μ-O_{ap}	254.6(4)		[e2]	
$[Mg(H_2O_4MoO_4]H_2O$ [f]	tr	652.9(7)	76.44(9)	MgO_6	μ-O	202.6(4)	O,O	90.0(–, 2.1)	331
(not given)	$P\bar{1}$	1070.6(12)	109.03(9)		H_2O	208.4(5, 13)			
	2	634.1(7)	90.31(9)						
				MgO_6	μ-O	202.4(4)	O,O	90.0(–, 1.0)	
					H_2O	207.8(5, 18)			
				MoO_4	μ-O	175.6(4)	O,O	109.5(2, 1.5)	
(Zn)Mg($C_{32}H_{59}O_7$)	m	1262.9(4)		MO_6	not given				332
(not given)	$P2_1$	1225.9(4)	90.4(1)						
	2	2295.8(6)							
$[Zn(edta)Mg(H_2O)_4]$-$2H_2O$	or	1444(2)		MgO_6	O	208(5)	not given		333
(colourless)	$Pna2_1$	976(1)							
	4	1310(5)		ZnO_4N_2	O	210(4)			
					N	224(4)			
Mn(edta)Mg9H_2O	or	1180(5)							334
(not given)	Pbcn	950(1)							
	4	1939(2)							
Cd(edta)Mg9H_2O	tr	767(5)	90.0(5)						334
(not given)	$P\bar{1}$	784(2)	100.0(5)						
	2	2040(10)	104.0(5)						
$MgSr(egta)(H_2O)_8$	or	2133.1(4)		MgO_6	μ-O	205.2(4, 74)	O,O	90.0(2, 7.7)	213
(colourless)	Pccn	1679.9(4)			H_2O	210.2(5, 15)			
	8	1437.2(2)							
				SrO_7N_2	O	263.0(5, 25)	O,O	58.4–160.8(1)	
					μ-O	267.4(5, 86)	O,N	57.5–125.3(1)	
					N	284.6(5, 44)	N,N	170.8(1)	
					H_2O	255.4(5)			

TABLE 15 (continued)

Compound (colour)	Cryst. cl. Sp. group Z	a (pm) b (pm) c (pm)	α (°) β (°) γ (°)	Chromophore	Mg–L (pm)		L'–Mg–L (°)	Ref.
$MgBa(egta)(H_2O)_{8/3}$· $1/3Me_2CO$ (colourless)	or $Pca2_1$ 12	2180.5(5) 1544.4(2) 2011.5(4)		MgO_6	μ-O H_2O	210.0(3, 71) 208.1(3, 43)	O,O 90.0(1, 6.8) 172.4(1, 1.9)	213
				BaO_8N_2	O μ-O N	283.6(3, 127) 280.4(3, 48) 289.4(4, 41)	O,O 56.2–149.6(1) O,N 57.0–126.2(1) N,N 176.1(1, 1.9)	
$(H_3O)_2Mg(UO_2)$· $(SiO_4)_2(H_2O)_4$ (not given)	m $C2/m$?	1738.2(6) 704.7(1) 661.0(2)	105.9(2)	MgO_6	O	201.9(6, 0) 212.4(6, 0)	not given	335
				UO_7	O	181.0(6, 1) 235.2(4, 100)		
$NaMg_2CrSi_3O_{10}$ (not given)	tr $P\bar{1}$?	1023.8(4) 1064.2(4) 878.0(3)	105.15(3) 96.50(4) 125.15(3)	MgO_6	O	209.7(13, 90)	not given	336
				CrO_6	O	200.6(11, 94)		
				NaO_8	O	251.9(12, 446)		
$Cs_2MgFe(CN)_6$ (yellow)	c $Fm3m$?	1044.6(3)		MgN_6	N	218.2(7, 0)	not given	337
				FeC_6	C	190.0(7, 0)		
$MgAl_2Si_3O_{12}$ (not given)				MgO_8	O	219.8(4×) 234.3(4×)	O,O 69.2; 72.9 109.4 [g]	338
				AlO_6	O	188.6(6×)	O,O 90.0(–, 2.1)	
				SiO_4	O	163.5(4×)	O,O 99.6; 114.7	

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean. [b] The chemical identity of the coordinated atom or ligand is specified in these columns. [c] The crystallographic data are consistent with random incorporation of Mg in Al sites (Al, Mg = M). [d] The Mg and Co atoms are randomly distributed between $[MO_5]$ square pyramids and $[MO_6]$ octahedra. [e1] H_2O–Mg–OH_2 = 88.7(2, 2.6) and 173.9(2)°; H_2O–Mg–μ-O = 91.2(2, 8) and 177.4(2)°. [e2] O–Cu–O_{ap} = 94.2(2, 4.6)°; O–Cu–μ-O = 91.5(2, 9.2)°; N–Cu–O_{ap} = 87.9(2, 10.1)°; N–Cu–μ-O = 86.4(2, 14.7)°. [f] There are two crystallographically different MgO_6 octahedra. [g] Mg–O–Mg = 101°.

oxygen atoms of four carboxylate groups from the $[Sr(egta)(H_2O)]^{2-}$ complex anions. The water molecules coordinated to the magnesium occupy *trans* positions, as required by the crystallographic 1 symmetry. For Mg^2, the crystallographically required 2-fold symmetry is satisfied by a *cis* arrangement of the two water molecules. The Sr^{II} atom is nine coordinated via

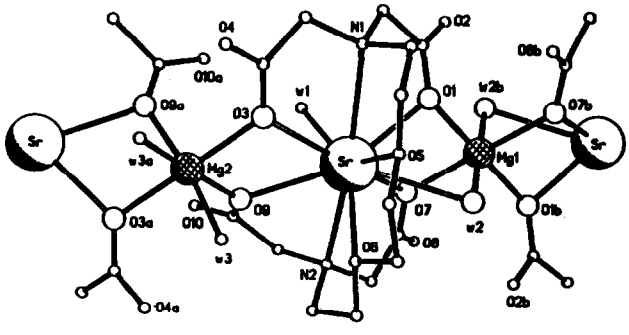


Fig. 23. View of $\{MgSr(egta)(H_2O)_8\}_n$ [213].

the eight donor atoms of the $egta^{4-}$ ligand and a water molecule, which occupy the vertices of a slightly distorted tricapped trigonal prism.

It is known that the hard magnesium(II) atom prefers to bond to a hard donor atom, and this is illustrated by $Cs_2MgFe(CN)_6$ [337] in which the CN group uses the harder N to bind Mg^{II} and the softer C to bind Fe^{II}. This is the only example in this series where the donor bonded to Mg^{II} is other than an oxygen atom.

Overall, magnesium is found in trigonal, tetrahedral, square pyramidal, pseudo octahedral and dodecahedral structures. The mean Mg–O bond distance increases with coordination number in the order: 204.2 pm (5-coord, range 195.7 to 211.9 pm) < 207.6 pm (6-coord, range 202.4 to 215.4 pm) < 227.1 pm (8-coord, 219.8 to 234.3 pm). However, the mean Mg–O bond distance for the trigonal planar environment [326] at 208 pm is about 0.4 pm longer than that of six-coordination. Also, the mean Mg–O(H_2O) bond distance of 208.0 pm (range 203.8 to 212.4 pm) found in this series is

TABLE 16. Summary of the magnesium–ligand(atom) bond distances (pm) [a]

Coord. atom	2-Coordination Range (Mean)	3-Coordination Range (Mean)	4-Coordination Range (Mean)	5-Coordination Range (Mean)	6-Coordination Range (Mean)	7-Coordination Range (Mean)	8-Coordination Range (Mean)
H(L)						197–209 [b] (204)	
μ-H					198.8–221.0 (207.8)		
μ-F					198.0–199.7 (198.9)		
μ-O					191.6–209.6 (202.4)		
μ_3-O				194	198.5–242.2 (219.4)		
μ_4-O				195.2	210		
OH_2			209.0–220.0 (214.5)	201.2–209.9 (203.7)	196.1–223.0 (207.5)	203.1–206.4 (205.7)	204.5–205.6 (205.1)
O(L)		181.9–209.8 (195.4)	181.9–221.9 (205.5) 189.7–212.4 [b] (201.3)	192.0–218.0 (205.2)	196.4–223.6 (209.0) 194.0–222.0 [b] (207.0) 201.0–209.0 [c] (205.5) 205.5 [f]	205.2 210.8–243.5 [d] (226.7) 208.6–233.0 [e] (220.3)	219.8–234.3 (227.1) 204.5–258.3 [g]
μ-O(L)		195.1–197.1 (196.4)	191.0–213.2 (197.9)	245.3	206–207 (206.5)		206.6
N_2					204		
μ_6-N			213.3–217.4 (214.8)				
N(L)		211.8	215 208.0–230.6 [b] (218.4) 201.2–217.0 [c] (212.4)	218.6–252.0 [b] (227.3) 200.9–216.4 [d] (207.7)	210.1–241.9 (222.0) 222.7–238.2 [b] (236.1) 206.4–208.2 [d] (207.3)	205.4–277.7 (207.9) 224–231[e] (227)	217–235 [b] (225.5)
μ-N(L)			204.3–212.5 (209.2)	207.8–229.9 (227.9)			
C(L)	211.6–212.6 (212.1)	208.0–229.6 (218.5)	209.4–230.4 (217.1) 201.4–223.4 [b] (215.3)	217.9–261.0 (227.7) 225–233 [b] (230)	214.0–220.0 (217.8)		208.2 [h]
μ-C(L)			215.0–245.0 (228.0)	217.0–218.8 (217.7)			
B(L)					238.2–247.8 [b] (243.0)		
Cl			226.9–233.2 (229.3)		246.3–253.1 (250.2)	242.5–245.4 (243.4)	
μ-Cl			241	240.0–279.0 (257.1)	245.2–254.3 (250.4)		
μ_3-Cl				279.2	242.2–266.0 (256.0)		
μ-S(L)			242.7				

TABLE 16 (continued)

Coord. atom	2-Coordination Range (Mean)	3-Coordination Range (Mean)	4-Coordination Range (Mean)	5-Coordination Range (Mean)	6-Coordination Range (Mean)	7-Coordination Range (Mean)	8-Coordination Range (Mean)
P			258.7–259.2 (259.0)				
μ-P					260.8–286.2 (270.2)		
Br		252.7	241.7–332.0 (263.7)	247.4–261.5 (254.0)	247.9–265.6 (258.7)		251.0–263.0 (255.4)
μ-Br			251.5–281.8 (264.0)		261.3–279.9 (268.2)		
μ_3-Br					275.8–278.2 (276.9)		
Si(L)			262.4–266.9 (264.1)				
Ge(L)					271.5–272.2 (271.9)		
I					276		
μ-I				281.1–284.9 (283.0)			

[a] The mean value is given in parentheses. [b] Bidentate ligand. [c] Tridentate ligand. [d] Tetradentate ligand. [e] Pentadentate ligand. [f] Hexadentate ligand. [g] Heptadentate ligand. [h] The Mg–cp(centroid) distance.

about 0.9 pm longer than that found in the hexacoordinated mononuclear Mg^{II} compounds (Table 4). There is one example of distortion isomerism, where two MgO_6 octahedra, differing by degree of distortion, are found.

9. Conclusions

Up to the end of 1991, almost four hundred magnesium compounds have been characterised by X-ray diffraction. The various geometries are found in increasing numbers in the order: 10-coord. < 2-coord. < 8-coord. < 7-coord. (mostly pentagonal bipyramidal) < 5-coord. (mostly square pyramidal) < 4-coord. (tetrahedral) < six coord. (trigonal, rhombic, tetragonal). The majority belong to the last group. The first two groups, which represent the highest and lowest coordination numbers respectively are built up of only organic C donor ligands. By far the most common ligands are water, organic C donor ligands and tetrahydrofuran. The ligands range from mono- through bi-, tri-, tetra-, penta-, hexa-, hepta- to octadentate in nature.

The nuclearity of the homonuclear (Mg) compounds range from mono-, bi-, tri-, tetra-, hexa- and polynuclear. The heteronuclear range from bi-, tri-, tetra-, penta-, hexa- and polynuclear.

Several compounds are found in two isomeric forms [32,74,108,235,236,248,249,274,275], the difference arising mostly in the degree of distortion. A *cis–trans* isomerism was proposed for $Mg(thf)_4(PhC{\equiv}C)$ [156]. Pairs of independent molecules differing by degree of distortion within the same crystal have been found for several structures [18,32,60,72–74,86,102,117,127,129, 130,162,166,173,183,184,196,203,267,268,270,316,331]. Such examples belong to the general class of distortion isomerism [36].

Most of the coloured Mg^{II} compounds are five coordinated, and this is essentially due to the N donor macrocyclic ligands.

In the square-pyramidal magnesium(II) compounds (section 2.3) a relationship between the displacement of the Mg atom from the basal plane and the difference between the Mg–L(eq) and Mg–L(ap) bond distances. When the difference increases and the apical ligand moves farther away, the magnesium atom comes close to being square planar.

The Mg–Mg bond distance of 267 pm [225] is the shortest reported in magnesium chemistry. The shortest heteronuclear metal–metal bond distance is 248.0(4) pm found for the Mg–Co bond [292]. In the binuclear compounds, as the Mg–Mg distance increases, the Mg–L–Mg angle opens and the Mg–L distances decrease.

A summary of the Mg–L bond distances for differ-

ent types of geometry is given in Table 16. The ligand atoms are listed in order of increasing covalent radii. The lowest coordination number (two) and the highest (ten) for magnesium is made up of only soft donors, the ten coordination resulting from cyclopentadienyl based ligands.

The rather unusual (for magnesium(II)) trigonal planar geometry does occur, except in the mononuclear series, and utilizes C, O, N and Br donor atoms, with the mean Mg–L bond distance increasing with the covalent radius of the donor atom. The shortest Mg–Mg bond distance found in the trigonal planar derivatives is 296.4 pm, and the shortest heteronuclear distance is for Mg–Mo at 274 pm.

Four coordinated magnesium has been found only in a tetrahedral environment with varying degrees of distortion. The mean Mg–L(terminal) bond distance is somewhat longer than that of the corresponding Mg–L(bridge) when L is a smaller donor atom such as O or N. The opposite is true when L is a larger donor such as C, Cl or Br). There is one unique example [222] which contains a single "hexadentate" nitrogen atom. Both the homonuclear and heteronuclear shortest metal–metal bond distances occur in tetrahedral magnesium derivatives.

The penta-coordinated magnesium compounds have examples where oxygen is tri-dentate [306] and tetradentate [217], and one example of chlorine as a tridentate ligand [218]. The shortest Mg–Mg distance for these derivatives is 288.6 pm.

Six coordination represents the most common environment for magnesium(II). Here also are found examples of multi-bridged donor atoms, tridentate chlorine [218,259,305], tridentate oxygen [259,291] and tridentate bromine [305]. There is also an example of tetradentate oxygen [291].

The hepta-coordinated magnesium derivatives are largely restricted to oxygen and nitrogen donor ligands (Table 16).

The octa-coordinated magnesium compounds utilize donor atoms similar to those found in the trigonal planar derivatives. The majority of mono- and polynuclear examples have the donor atoms in a dodecahedral arrangement about the magnesium. The mean Mg–L bond distance elongates with the covalent radius of L. There is an example in which two MgO_8 chromophores differ by degree of distortion [183].

This represents the first overview of structural data for magnesium chemistry. Despite the increasing availability of data retrieval systems, the tracing of relevant material is not always straightforward. One of the problems is associated with the choice of keywords for indexes, resulting in the effective invisibility of some material from a particular point of view. Some material is available only as supplemental material, which can obscure relevant structural features of comparative interest. There are several examples where two or even three groups have repeated the same work at different times with no cross referencing. There are also some published X-ray structures of magnesium compounds for which we could not obtain Journals or reprints during the course of collecting, collating and analyzing the presented data. These are: *cyclo*-(D-phenylalanyl-propyl-glycyl-D-alanyl-propyl)magnesium thiocyanate hydrogen sulphate heptahydrate [339]; Diaqua-dichloro-bis(aethylacetat)magnesium [340]; *cyclo*-tris(propyl-glycyl)magnesium perchlorate trihydrate [341]; hexakis(dimethylformamide)magnesium-bis(trichloro-iron) [342]; aqua(ethylenediamine tetra-acetato)magnesium (II) hexa-aqua-magnesium dihydrate [343].

Magnesium compounds are important from both a chemical and biological point of view, and structural information is important for understanding the role of magnesium in both of these areas. We hope that this review has brought together most of the structural information from both areas of endeavour in a systematic way, and to have highlighted similarities and differences that may prove of interest and use in further studies.

10. Abbreviations

ac	acetate
acac	acetylacetonate
acEt	ethyl acetate
2-aeph	2-aminoethyl(hydrogen)phosphonate
an	anthracene
an($SiMe_3$)$_2$	9,10-bis(trimethylsilyl)anthracene
apy	(1-phenyl-2,3-dimethyl-5-pyrazolone)antipyrine
asp	aspartate
aspH	hydrogen aspartate
atp	adenosine-5′-triphosphate
bdta	butane-1,4-diaminotetraacetate
Bu	butyl
bz	benzyl
caf	caffeine
cam	calcimycinate
$(CH_2)_6N_4$	hexamethylenetetramine
$C_3H_3O_4$	hydrogen malonate
$C_4H_3O_3$	triformylmethyl
$C_4H_3O_4$	hydrogen maleate
$C_4H_4O_5$	myo-inositol
$C_5H_{11}O$	4-methoxybutyl
$C_6H_7O_2N$	*para*-nitrosophenolate
C_6H_{11}	cyclohexyl
$C_6H_{13}N_4$	hexamethylene-diamin-1-ium

C_7H_{11}	2,4-dimethyl-2,4-pentadienyl
$C_7H_{13}N$	quiniclidine
$C_8H_5O_4$	*ortho*-phthalate
$C_8H_5O_5$	2-carboxylato-monoperoxybenzoate
C_8H_8	*ortho*-phenylenedimethylenate
$C_8H_{16}O_4$	1,4,7,10-tetraoxacyclodecane
C_9H_7	indenyl
$C_{10}H_8O_6$	(*ortho*-phenylenedioxy)diacetate
$C_{10}H_{20}O_5$	1,4,7,10,13-pentaoxacyclopentadecane
$C_{12}H_8N_2$	phenasine
$C_{12}H_{24}O_6$	1,4,7,10,13,16-hexaoxacyclooctadecane
$C_{14}H_{10}$	9,9-dihydro-9,10-anthrylene
$C_{14}H_{19}O_4$	[15] crown-4-ether
$C_{14}H_{20}O_5$	2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin
$C_{15}H_{19}N_2$	sparteine
$C_{16}H_{12}SO_3$	8-anilino-1-naphthalenesulphonic acid
$C_{16}H_{14}$	9,10-(propano)-9,10-dihydroanthracene
$C_{16}H_{20}O_{10}$	tetraethyl-2,3-dioxobutane-1,1,4,4-tetracarboxylate
$C_{16}H_{24}O_5$	1,3-xylyl-18-crown-5
$C_{17}H_{16}$	methyl derivative of $C_{16}H_{14}$ (see above)
$C_{20}H_{26}Si_2$	9,10-dihydro-9,10-bis(trimethylsilyl)-9,10-anthracene
$C_{22}H_{32}N_2$	6-benzylsparteine
$C_{22}H_{38}O_7$	6,7,8,9,10,11,17,18,19,20,21,22-dodecahydro-1,5,12,16,23,26,29-heptaoxa[$7^{3.14}$][5,5]-orthocyclohexane
$C_{24}H_{31}N_5O_5$	cyclic pentapeptide(D-phen-pro-gly-D-ala-pro)
$C_{33}H_{59}O_7$	phorinate antibiotic M144255
c-hx	cyclohexyl
cit	citrate
Clac	chloroacetate
cp	cyclopentadienyl
cp*	pentamethylcyclopentadienyl
CPh_3	triphenylmethyl
crot	crotonate
crt	2,1,1-cryptanol
$C(SiMe_3)_3$	tris(trimethylsilyl)methyl
2-$C(SiMe_3)_2$	2-bis(trimethylsilyl)pyridinemethyl
daa	diacetamide
depa	(diethoxyphosphinyl)acetonate
dhdbO	5,7-dihydrodibenz-[*c*,*e*]-oxyin
diphos	1,2-bis(diphenylphosphino)ethane
dme	1,2-dimethoxyethane
dmf	dimethylformamide
dnphO	2,4-dinitrophenoxidate, or phenoxide
dpa	2,2′-dipyridylamine
dphb	1,4-diphenyl-2-buten-1,4-diyl
dox	1,4-dioxane
edds	N,N′-ethylenediaminedisuccinate
edta	ethylenediaminetetraacetate
ehpy	ethylenebis(*ortho*-hydroxylphenyl)glycine
Et	ethyl
Et-chl-a	ethylchlorophylide
f-6-acac	hexafluoroacetylacetonate
f-6-p	fructose-6-phosphate
fl-3-mp	flavone-3-monophosphate
gal	galactase
genH	hydrogenurate
gpp	glycine-L-proline-L-proline-glycine-L-proline-L-proline
Hatp	adenosine-5′-triphosphate(3 −)
HB(3-^{t}Bupz)$_3$	tris(3-tert-butylpyrazolyl)hydroborate
HB(3,5-Me_2pz)$_3$	tris(3,5-dimethylpyrazolyl)hydroborate
Hbipam	hydrogen bis(2-pyridyl)amine
hfac	1,1,1,5,5,5-hexafluoropentane-2,4-dionate
icdh	isocitrate dehydrogenase
i-$C_{15}H_{19}N_2$	α-isosparteine
i-nic	isonicotinate
L-glu	glutamate
m	monoclinic
mcpac	4-chloro-2-methylphenoxyacetate
Me	methyl
Me_2an	1,4-dimethylanthracene
Me_3AsO	trimethylarsine oxide
Mecb	C-methyl-*ortho*-carboranyl
Mechl-a	methylpyrochlorophylide
Me_4en	N,N,N,N-tetramethylethylenediamine
Meim	methylimidazole
Memal	α-methylmalonate
MeO_4S	hydroxymethanesulphonate
Me_4pn	N,N,N′,N′-tetramethylpropanediamine
mes	mesityl
(Me_3Si)cp	tris(trimethylsilyl)cyclopentadienyl
Me_4taa	7,16-dihydro-6,8,16,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetra-aracyclotetradecinate
NH^{t}Bu	tert-butylamide
nic	nicotinate
N-Mea	N-methylacetamide
NMe_4	tetramethylammonium
np	neopentyl

$N(SiMe_3)_2$	bis(trimethylsilyl)amide
oep	octaethylporphyrinate
4-OHbenz	4-hydroxybenzoate
ome	1,2-dimethoxyethane
ompa	octamethylpyrophosphoramide
or	orthorhombic
ort	orotate
ox	oxalate
o-xyl	*ortho*-xylidene
qu	quinoline
rh	rhombohedral
sach	saccharinate
salen	N,N-ethylenebis(salicylideneaminate)
SAr	$SC_6H_4\{CH(Me)NMe_2\}$, dinegative anion
^{t}Bu	tert-butyl
thf	tetrahydrofuran
thig	N-pivaloyl-tetraphenylporphinate
tol	toluene
tpp	5,10,15,20-tetraphenylporphinate
tr	triclinic
trg	trigonal

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