Coordination Chemistry Reviews, 102 (1990) 111-145
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 2

ELEMENTS OF GROUP 2

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0010-8545/90/$12.25

2.1 INTRODUCTION

As for the previous annual reviews of this series,[1] the chemistry of the alkaline earth metals reported in the literature from January 1986-June 1987 is considered in sections reflecting topics of current interest and significance. For those subjects common to Group 1 and Group 2 elements (e.g. complexes of crowns, cryptands and related molecules), the published data are discussed in the appropriate section of Chapter 1; those topics unique to the Group 2 elements are covered in this Chapter.

Sensitive spectrophotometric methods for the determination of beryllium[2] and calcium[3] have been reported. Whereas that for beryllium[2] is based on the formation of the beryllium(II)alizarine fluorine blue complex and its subsequent extraction into toluene with adogen, that for calcium[3] involves the formation of the calcium(II) salt of arsenazo[2-(2-arsenaphenyl)azo-7-(4-antipyril)azo-1,8-dihydroxy-3,6-naphthalenedisulphonic acid in aqueous solution at pH = 10.0.

Growth rates for Mg, Mg_2, Mg_3, Mg_4, Mg_n and for Ca, Ca_2, Ca_n have been monitored[4] in argon matrices at 9K in the presence of CH_3X (X = F-I) to establish the following trends:

(i) clusters are more reactive than atoms
(ii) the reactivity of the cluster increases with size
(iii) magnesium species are less reactive than the corresponding calcium species
(iv) the reactivity of the methyl halide increases from chloride through bromide and fluoride to iodide

2.2 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

A limited resurgence of interest in intermetallic compounds containing alkaline earth metals can be perceived. Consequently this section has been divided in subsections covering not only the traditional binary and ternary derivatives but also intermetallic compounds.

2.2.1 Intermetallic Compounds

Hoffmann et al. have undertaken detailed analyses of the structural chemistry of $BaAl_4$,[5] $CeMg_2Si_2$,[5] $CaAl_2Zn_2$,[5] $CaAl_2Si_2$,[6] $CaBe_2Ge_2$[7] and $BaPdSn_3$;[8] donor-acceptor layer formation, lattice site preferences and interatomic distances are considered in particular detail.

Xrd analyses of the structures of Mg_5Gd,[9] $Ca_{28}Ga_{11}$,[10] Ca_3Ga_5[11] and Ca_8In_3[12] have been completed; pertinent crystallographic parameters are collated in Table 1. For the latter two phases the stuctural studies have resulted in the refinement of their stoichiometries; previously, they were known as Ca_2Ga_3 and Ca_3In, respectively.

Table 1. Crystallographic parameters for a number of intermetallic phases containing an alkaline earth metal.

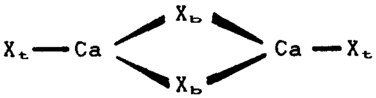
Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Ref
Mg_5Gd	cubic	$F\bar{4}3m$	2234.4	-	-	9
$Ca_{28}Ga_{11}$	orthorhombic	Imm2	532.4	6144.5	748.8	10
Ca_3Ga_5	orthorhombic	Cmcm	446.3	1079.9	1502.5	11
Ca_8In_3	triclinic	P1	960.6	971.7	978.2	12
			(69.65)	(78.85)	(60.34)	

2.2.2 Binary Derivatives

As for previous reviews, those papers in which the catalytic activity of alkaline earth metal oxides is described, although numerous, are not considered here since their content is of but peripheral interest to the inorganic chemist.

The topics covered in the papers abstracted for this subsection are diverse. A significant proportion, however, involve structural studies of hydrides,[13-14] halides[15-20] and hydroxides;[20,21] where appropriate, pertinent crystallographic parameters are collected in Table 2. A reinvestigation[13] of the structure of $BaH_2(BaD_2)$ employing X-ray and neutron powder diffraction techniques (Table 2) has shown that the hydrogen positions correspond with those in CaD_2;[14] the classification of $BaH_2(BaD_2)$ in the $PbCl_2$-structure type is discussed.[13]

The molecular parameters of gas phase CaX_2 ($X = Cl-I$) as determined in an electron diffration investigation[15] are summarised in Table 3. For accurate determination of these data, it was necessary to include dimers (1) in the refinement. The Ca...X_t contacts were assumed to be equal to the corresponding monomer interatomic distances; the Ca...X_b distances were found to be 269.9 and 278.1pm for Ca_2Cl_4 and Ca_2Br_4, respectively; and the Ca...I_b distance was assumed to be 20pm longer than the Ca...I_t contact.



(1)

The hydrates $CaCl_2.6H_2O$,[16] $SrCl_2.6H_2O$[16] and $SrI_2.2H_2O$[17] have been structurally characterised (Table 2) using neutron[16] and X-ray[17] diffraction methods. In the highly symmetrical isostructural hexahydrates,[16] the metal atoms are coordinated by nine water molecules (Ca...O = 245.3, 259.4; Sr...O = 257.0,

Table 2. Crystallographic parameters for diverse hydrides, halides and their derivatives, and hydroxides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
BaH_2	orthorhombic	Pnma	680.3	417.0	786.0	-	13
BaD_2	orthorhombic	Pnma	678.9	417.1	785.2	-	13
$CaCl_2,6H_2O$	tetragonal	P321	787.6	-	395.4	-	16
$SrCl_2,6H_2O$	tetragonal	P321	796.0	-	412.4	-	16
$SrI_2,2H_2O$	orthorhombic		1558.1	434.0	988.1	-	17
$Ba_3Br_4Cl_2$	orthorhombic	Pnma	820.3	486.1	963.6	-	18
Ca_2NCl	trigonal	$R\bar{3}m$	366.6	-	1971.1	-	19
Ca_2NBr	trigonal	$R\bar{3}m$	371.7	-	2055.8	-	19
Ca(OD)Cl	hexagonal	$P6_3mc$	386.8	-	990.1	-	20
$Sr(OH)_2,H_2O$	orthorhombic	$Pmc2_1$	364.8	619.8	671.3	-	21
β-$Ba(OH)_2.H_2O$	orthorhombic	$Pmc2_1$	389.5	636.6	695.2	-	21
γ-$Ba(OH)_2.H_2O$	monoclinic	$P2_1/m$	704.9	418.4	633.3	111.45	21
$Ba(OH)_2.3H_2O$	orthorhombic	Pnma	764.0	1140.3	596.5	-	21

271.5pm); three adjoin one atom and six are shared between two such atoms giving an $[(H_2O)_3M(H_2O)_6M(H_2O)_3]^{4+}$ cationic arrangement. The Sr atom in the dihydrate,[17] is also located

Table 3. Molecular parameters for CaX_2 (X = Cl-I) in the gas phase.[15]

Parameter	$CaCl_2$	$CaBr_2$	CaI_2
r_g(Ca...X)	248.3	261.6	284.0
l(Ca...X)	11.3	11.0	12.9
r_g(X...X)	474.6	508.2	545.8
l(X...X)	23.8	24.1	26.2
Relative monomer concentration(%)	98.1	94.7	97.6

in a nine coordinate environment; in this case, however, the structure consists of distorted face-shared $SrI_5(H_2O)_4$ tricapped trigonal prisms (Sr...I = 337.2-347.6, 384.2; Sr...O = 268.2-273.1pm) forming columns and channels along (010).

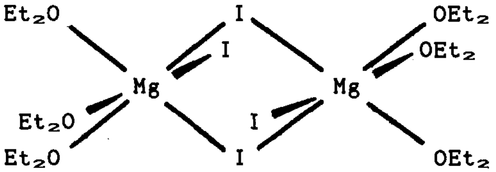
A neutron diffraction (Table 2) and electron microscopic study[18] of halogen ordering in $Ba_3Br_4Cl_2$ has revealed two crystallographically independent sites for the halogens. The larger square pyramidal site is filled by bromines (Ba...Br = 338.5-359.7pm); the smaller tetrahedral site is occupied randomly by both bromine and chlorine atoms (Ba...Br/Cl = 312.6-319.4pm).

Single crystal xrd analysis[19] of Ca_2NX (X = Cl,Br), prepared by reaction of 1:1 molar mixtures of Ca_3N_2 and CaX_2 in steel ampoules under argon (50h, 1013K; 15h, 1273K; 40h, 1223K; 25d, 1398K), has shown that they crystallise with the anti-α-$NaFeO_2$ structure type (Table 2). The anions are cubic close packed with a rhombohedral distortion, the sequence of the layers being $X^-...N^{3-}...X^-...N^{3-}$. The Ca atoms are shifted towards the nitrogens giving a structure in which Ca_2N^+ layers are held together by halide anions.[19]

The position of the deuterium atom in Ca(OD)Cl has been located from a neutron powder diffraction profile refinement (Table 2);[20] it lies on a 2(a) site at (0,0,0.1733) attached to the oxygen on a similar 2(a) site at (0,0,0.0737). The standard deviations in the interatomic distances (Ca...O = 235(5), Ca...Cl = 295(5), O...H = 98(5)pm) are disappointing owing to the high R value (0.195) caused by the presence of an impurity.[20]

A detailed single crystal xrd study[21] of $Sr(OH)_2.H_2O$, $Ba(OH)_2.H_2O$ and $Ba(OH)_2.3H_2O$ has revealed the existence of β- and γ-polymorphs for $Ba(OH)_2.H_2O$ (Table 2). The Sr atom polyhedron in $Sr(OH)_2.H_2O$, which is isostructural with β-$Ba(OH)_2.H_2O$, is 8-coordinate (Sr...O = 260.9-269.4pm). An 8-fold Ba atom coordination geometry is found for $Ba(OH)_2.3H_2O$ (Ba...O = 270.3-291.8pm) as well as for β-$Ba(OH)_2.H_2O$ (Ba...O = 279.6-288.6pm); the Ba atom in γ-$Ba(OH)_2.H_2O$ is surrounded by nine oxygens, seven relatively close (Ba...O = 268.8-291.6pm) and two somewhat more remote (Ba...O = 313.7pm).[21]

Large angle X-ray scattering data have been used to determine the structure of solutions of MgI_2 in Et_2O (2.8M) and thf (1.7M).[22] In Et_2O, a dimeric structure (2), based on a Mg_2I_2 core, is found; three solvent molecules are probably coordinated to each Mg atom to complete an octahedral arrangement (Mg...I = 265; Mg...O =210pm).[22] In thf, dissociation occurs giving the MgI^+ ion as the predominant species; the undissociated complex is thought to be a $MgI_2(thf)_2$ moiety with approximately tetrahedral geometry (Mg...I = 256; Mg...O = 210pm).[22]



(2)

The stability constants of the MCl^+ ion (M = Ca-Ba) in methanol have been determined both conductometrically ($278 \leqslant T/K \leqslant 318$) and potentiometrically (T = 298K).[23] At 298K, the value of K_{MCl^+} increased from 403(12) for $SrCl^+$ through 408(7) for $CaCl^+$ to 464(11) for $BaCl^+$. The formation of MCl_2 was extremely limited; while it was taken into account in the potentiometric study it was neglected in the conductometric study.

2.2.3 Ternary Derivatives

To avoid duplication with other Chapters in this review, the ternary compounds covered here do not include those which contain a metal from the p-block of the Periodic Table.

A significant proportion of commitment in this field lies in the synthesis, preferably as single crystals, of ternary phases for structural elucidation using X-ray or neutron diffraction methods; compounds thus studied include hydrides, borides, pnictides, oxides and halides. The low temperature structure of Mg_2NiD_4 (monoclinic, space group C2/c, a = 1434.3, b = 640.4, c = 648.3pm, β = 113.52°) has been assessed using powder neutron diffration data collected at 298K;[24] the Ni atoms are coordinated by four deuteriums in a near regular tetrahedral coordination polyhedron (Ni...D = 154pm; DNiD = 109.4°). The ternary borides, Mg_2IrB_{2-x} ($0.20<x<0.35$),[25] prepared by heat treatment of the elements under argon in a tantalum crucible (15h, 923K; 40h, 1273K), adopt the W_2CoBr_2 structure-type (monoclinic, space group C2/m, a = 858.0, b = 484.6, c = 683.6pm, β = 115.72° for x = 0.35).

2.2.3.1 Ternary Pnictides

Mewis et al.[26-32] have reported the preparation and structural characterisation of 29 novel pnictides. A listing of these phases is given in Table 4 together with crystallographic parameters. The phases of 1:1:1 stoichiometry are AlB_2-, Ni_2In- or $SiSi_2$-variants.[29,30] The AlB_2-type structure has either a statistical (P6/mmm) or ordered (P$\bar{6}$m2) distribution of Pt and P(As,Sb) atoms among the B sites; the Ni_2In-type structure ($P6_3/mmc$) can be described as an ordered superstructure of the AlB_2-type.[30] The phases of 1:2:2 stoichiometry adopt either $ThCr_2Si_2$- (I4/mmm), $CaBe_2Ge_2$- (P4/nmm) or $CeMg_2Si_2$-type (P4/mmm) structures,[26-28] while those of 1:2:3 or 1:4:6 stoichiometry are all pyrites-type variants.[31]

2.2.3.2 Ternary Oxides

Crystallographic parameters have been quoted for a number of ternary oxides; they are summarised in Table 5. The majority of the oxides were prepared by traditional solid state methods starting from the appropriate binary oxides. $BaFe_2O_4$ was prepared similarly, but from 1:1:1 mixtures of $Ba(OH)_2.2H_2O$: $Fe(COO)_2$:$BaCl_2.2H_2O$.[35] $BaOsO_4$, however, was obtained by

Table 4. Crystallographic parameters for diverse ternary pnictides synthesised by Mewis et al.

Ternary pnictide	Structure Type	Space Group	a/pm	b/pm	c/pm	β/°	Ref
$CaRu_2P_2$	$ThCr_2Si_2$	I4/mmm	404.6	-	977.1	-	26
$SrRu_2P_2$	$ThCr_2Si_2$	I4/mmm	403.3	-	1113.5	-	26
$BaRu_2P_2$	$ThCr_2Si_2$	I4/mmm	402.9	-	1206.4	-	26
$CaRu_2As_2$	$ThCr_2Si_2$	I4/mmm	417.4	-	1030.3	-	26
$SrRu_2As_2$	$ThCr_2Si_2$	I4/mmm	416.9	-	1118.7	-	26
$BaRu_2As_2$	$ThCr_2Si_2$	I4/mmm	415.2	-	1223.5	-	26
L.T.-$SrPd_2Sb_2$	$CaBe_2Ge_2$	P4/nmm	464.9	-	1062.5	-	27
H.T.-$SrPd_2Sb_2$	$ThCr_2Si_2$	I4/mmm	458.8	-	1073.7	-	27
L.T.-$BaPd_2As_2$	$CeMg_2Si_2$	P4/mmm	434.6	-	575.8	-	28
H.T.-$BaPd_2As_2$	$ThCr_2Si_2$	I4/mmm	448.6	-	1031.5	-	27
$BaPd_2Sb_2$	$ThCr_2Si_2$	I4/mmm	472.5	-	1077.2	-	27
CaPtP	AlB_2-variant	$Pmc2_1$	434.4	831.1	651.9	-	29
$CaPt_xP_{2-x}$ (x = 0.65)	AlB_2	P6/mmm	401.6	-	416.3	-	29
CaPtAs	AlB_2-variant	$I4_1md$	418.3	-	4371.1	-	29
CaPtSb	Ni_2In-variant	Pnma	731.7	457.4	786.9	-	29
$SrPt_xP_{2-x}$ (x = 0.75)	AlB_2	P6/mmm	408.7	-	443.2	-	30
SrPtAs	Ni_2I	$P6_3/mmc$	424.6	-	896.7	-	30
$SrPt_{0.7}As_{0.9}$	AlB_2	$P\bar{6}m2$	426.2	-	442.8	-	30
SrPtSb	AlB_2	$P\bar{6}m2$	450.4	-	450.7	-	30
BaPtSb	AlB_2	$P\bar{6}m2$	453.5	-	488.4	-	30
BaPtP	$SrSi_2$	$P2_13$	653.3	-	-	-	30
BaPtAs	$SrSi_2$	$P2_13$	671.6	-	-	-	30
$BaPt_{0.85}As_{0.90}$	AlB_2	$P\bar{6}m2$	432.5	-	476.3	-	30
$CaPt_2P_{2-x}$ (x = 1.43)	$CaBe_2Ge_2$	I4/mmm	409.9	-	1895.1	-	26
$BaPt_2P_3$	FeS-variant	$P2_1/c$	835.2	577.6	1157.4	106.7	31
$SrPt_4P_6$	Fes-variant	C2/c	825.2	798.4	1142.8	90.7	31
$SrPt_4As_6$		C2/c	858.2	832.1	1194.5	91.0	31
$BaPt_4As_6$	FeS-variant	C2/c	868.8	833.3	1197.1	90.8	31
$CaCu_4P_2$		$P4_2/mnm$	729.0	-	383.1	-	32

Table 5. Crystallographic parameters for diverse ternary oxides.

Ternary oxide	Structure Type	Space Group	a/pm	b/pm	c/pm	β/°	Ref
$Mg_3Nb_6O_{11}$	Trigonal	$P\bar{3}m1$	604.1	-	746.6	-	33
$SrNb_2O_6$	$CaTa_2O_6$	$P2_1/c$	772.2	559.4	1098.6	90.4	34
$SrNb_6O_{16}$	$NaNb_6O_{15}F$	Pmm2	395.6	1018.9	1479.4	-	34
$BaFe_2O_4$	orthorhombic	Pmcn	1734.7	933.6	1088.2	-	35
$BaOsO_4$	$CaWO_4$	-	566	-	1274	-	36
Ca_3UO_6	$GdFeO_3$	$P2_1/n$	572.9	595.6	830.0	90.6	37
Sr_2CaUO_6	$GdFeO_3$	$P2_1/n$	593.8	607.3	845.6	90.1	38
Ba_2SrUO_6	$GdFeO_3$	$P2_1/n$	625.0	627.0	883.6	89.8	38

thermal decomposition of $BaOsO_3$ in air at 1108-1163K.[36] The structures of the uranates(VI) were determined by Ijdo et al.[37,38] by Rietveld refinement of neutron powder diffraction data; they are based on the monoclinic $GdFeO_3$-type structure. In the mixed alkaline earth metal complexes,[38] the larger of the two atoms is located in the bicapped trigonal prismatic (Gd) sites while the other, together with the uranium atom, occupies the octahedral (Fe) sites. This results in SrO_8 (Sr...O = 248.9-305.4pm), CaO_6 (Ca...O = 233.1-234.4pm) and UO_6 (U...O = 206.6,208.7pm) coordination polyhedra in Sr_2CaUO_6 and BaO_8 (Ba...O = 264-322pm), SrO_6 (Sr...O = 245.7-247.1pm) and UO_6 (U...O = 208.1,210.5pm) coordination polyhedra in Ba_2SrUO_6.[38]

Phase relationships of the non-stoichiometric phases $BaFeO_{3-x}$ ($0.22<x<0.40$)[39] and $SrCoO_{3-x}$ ($0.20<x<0.71$)[40,41] have been studied as a function of composition using xrd,[39-41] electrical conductivity[39,40] and, for $SrCoO_{3-x}$, Mossbauer spectroscopy (using ^{57}Fe as an impurity probe).[41] In the $BaFeO_{3-x}$ system,[39] replacement of Fe^{4+} by Fe^{3+} (i.e. decrease in x) results in conversion of the orthorhombic $BaFeO_{2.60}$ phase into the hexagonal $BaFeO_{2.78}$ phase; crystallographic parameters are summarised in Table 6. Two independent studies[40,41] of the $SrCoO_{3-x}$ system have been completed by groups in Japan and Britain; their results are in good agreement. The Japanese authors[40] reported that samples prepared at high temperatures

Table 6. Crystallographic parameters for non-stoichiometric phases of the $BaFeO_{3-x}$ and $SrCoO_{3-x}$ systems.

Phase	Symmetry	a/pm	b/pm	c/pm	Ref
$BaFeO_{2.78}$	hexagonal	568.6	-	1392.2	39
$BaFeO_{2.60}$	orthorhombic	591.0	1646.2	1101.1	39
$SrCoO_{2.80}$	tetragonal	1086	-	765.7	40
$SrCoO_{2.50}$	orthorhombic	$\sqrt{2}(394.0)$	4(393.5)	$\sqrt{2}(387.0)$	40
$SrCoO_{2.29}$	cubic	391.2	-	-	40
$SrCo_{1-y}O_{3-x}$	hexagonal	548.5	-	413.7	40

(T/K>1073) crystallised with either (1073<T/K<1273) the brownmillerite solid solution $SrCoO_{3-x}$ (0.48<x<0.58) or (T/K>1473) oxygen dificient perovskite phase, $SrCoO_{2.29}$ and that samples annealed at low temperatures (T/K<1073K) crystallised as a mixture of Co_3O_4 and an oxygen/cobalt deficient phase $SrCo_{1-y}O_{3-x}$ ($y \sim 0.1$) with the 2H-$BaNiO_3$-type structure. They also noted[40] that the high oxygen content perovskite $SrCoO_{3-x}$ (0.20<x<0.33) was obtained by annealing the brownmillerite phase under high oxygen pressures at 573K. Representative crystallographic parameters for these non-stoichiometric phases[40] are included in Table 6. The British authors[41] concluded from Mossbauer data that the fully reduced phase $SrCoO_{2.5}$ contains cobalt atoms in both octahedral and tetrahedral sites and that it has the same magnetic spin arrangement as the analogous iron compound. They also reported[41] that oxidation of this phase yields a poorly defined non-magnetic hexagonal phase which may be related to that of the brownmillerite lattice with the retention of layers of tetrahedrally coordinated cobalt atoms but with a high to low spin transition occuring at the octahedral site.

The thermodynamics of the equilibria

$$SrMoO_3(s) + {}^1/_2O_2(g) \rightleftharpoons SrMoO_4(s)$$

$$\Delta G/J.mol^{-1} = -269732 - 62.749(T/K) + 16.978(T/K)\ln(T/K)$$

$$2SrO(s) + Mo(s) + O_2(g) \rightleftharpoons Sr_2MoO_4(s)$$

$$\Delta G/J.mol^{-1} = -593713 - 257.90(T/K) + 50.148(T/K)\ln(T/K)$$

have been determined[42] from measurements of oxygen partial pressures at equilibrium using galvanic cells based on calcia stabilised zirconia and yttria doped thoria electrolytes.

Multinuclear (^{137}Ba, ^{47,49}Ti) n.m.r. studies[43] of polycrystalline $BaTiO_3$ have been successful at temperatures above the Curie point (T/K = 408) which correlates with a cubic-tetragonal phase transition; below the Curie point there is no observable n.m.r. intensity. These data suggest that the lowering of symmetry in going to the tetragonal phase induces electric field gradients which cause the central transition to broaden into the base-line by second order quadrupole interactions.[43]

Vibrational (i.r.) spectroscopic data have been measured[44] for $MgCu_3O_4$, $SrCuO_2$ and $BaCuO_2$ and a complete group theoretical analysis has been completed for $SrCuO_2$.[44]

2.2.3.3 Ternary Halides

A small number of papers[45-49] have been published in which aspects of the chemistry of mixed alkali and alkaline earth metal halides are described. Two independent groups of authors[45,46] have reported the combination of calcium fluoride with alkali metal fluorides as excellent reagents for nucleophilic fluorine transfer reactions. Clark et al.[45] recommend the use of the supported reagents $KF-CaF_2$ and $CsF-CaF_2$ for the fluorination of substrates such as $PhCH_2Br$, PhCOCl, MeCOCl and $1-C_{12}H_{25}Br$ in sulpholane or acetonitrile. Ichihara et al.[46] have employed the $KF-CaF_2$ reagent for low temperature fluorination of an extended series of substrates including variants of those considered by Clark et al. and RSO_2Cl (R = Me,Ph), $4-XC_6H_4SO_2Cl$ (X = Me,Br), EtOCOCl, Me_2NCOCl, $4-ClC_6H_4CH_2Br$, either in solution or in the liquid phase; for those species containing two halogens, the aryl halogen was not replaced.

Dunitz et al.[47] have shown, from a low temperature (T/K = 81) X-ray analysis of Li_2BeF_4, that the charge density can be described either as a superposition of spherical neutral atom densities or as a superposition of free-ion densities. Difference maps based on the two pro-crystal models are hard to tell apart. However, the two models are clearly differentiated by analysis of the weak low order reflections; the measured intensities are reproduced better by calculations based on neutral atom scattering curves. Dunitz et al.[47] comment that although this result appears to run counter to the current conventional wisdom concerning ionic solids, it is unlikely to have any important practical consequences.

In a dta study of the $CsCl-BeCl_2$ system, Russian authors have found evidence for the existence of three compounds; Cs_2BeCl_4 which melts congruently at 883K, $CsBeCl_3$ which decomposes in a peritectic reaction at 578K and $CsBe_2Cl_5$, which melts congruently at 568K.

Thermal treatment of 1:2 molar mixtures of KBr and $SrBr_2$ (943K, 3d; 793K,30d; cooling rate 20K/d) and of KI and SrI_2 (923K,3d; 673K,20d; cooling rate 20K/d) yielded KSr_2X_5 (X = Br,I);[49] pertinent crystallographic data are given in Table 7.

Table 7. Crystallographic parameters for diverse ternary halides

Ternary Halide	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
KSr_2Br_5	monoclinic	-	932.0	830.0	1329.2	90.06	49
KSr_2I_5	monoclinic	-	998.2	900.4	1430.0	89.94	49
$MgTcCl_6$	orthorhombic	-	985	695	698	-	51
$CaTcCl_6$	orthorhombic	-	993	699	703	-	52
$SrTcCl_6$	orthorhombic	-	996	701	704	-	53
$BaTcCl_6$	orthorhombic	-	1007	703	706	-	54
$BaTcBr_6$	orthorhombic	-	1042	741	748	-	55
$Ba_2Fe_3F_{10}$	monoclinic	$P2_1/c$	788.3	623.0	1868.0	111.8	50
$SrCoF_4$	orthorhombic	-	1445	392	566		59

With the exception of a single paper by Hoppe and Averdunk[50] in which the synthesis and structural characterisation of the novel ternary fluoride, $Ba_2Fe_3F_{10}$ is reported, the remaining papers abstracted for this subsection are by Russian authors.[51-59] Approximately half describe the chemistry of a series of isostructural ternary chlorides and bromides containing alkaline earth metals and technetium, $MTcX_6$;[51-55] the remainder describe phase equilibria in a number of fluoride systems.[56-59]

Hoppe and Averdunk obtained $Ba_2Fe_3F_{10}$ by reduction of a 3:7 molar mixture of BaF_2 and FeF_3 in an iron vessel (i.e. by reaction with the vessel wall) at 1023K for 60 days; relevant unit cell parameters are included in Table 7. Zaitseva, Kruglov et al.[51-55] have prepared $MTcCl_6$ (M = Ca-Ba) and $BaTcBr_6$ by reduction of the appropriate technetate(VII) by aqueous HCl (or HBr) in the presence of the corresponding alkaline earth metal halide. For example:

$$Mg(TcO_4)_2 + 16HCl + MgCl_2 \rightleftharpoons 2MgTcCl_6 + 8H_2O + 3Cl_2$$

All five compounds are isostructural;[51-55] their unit cell parameters are included in Table 7. Their i.r. spectra have been measured ($4000\text{-}200cm^{-1}$)[53-55] and found to be very similar. The compounds decompose in similar reactions to give the alkaline earth metal halide, technetium metal and halogen. For example:

$$MgTcCl_6(s) \longrightarrow MgCl_2(s) + Tc(s) + 2Cl_2(g)$$

The ternary chlorides decompose at $T{\sim}703K$,[51-54] while the ternary bromide breaks down at ~718K.[55]

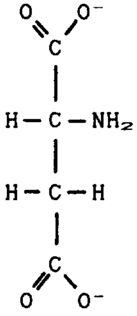
Dta and xrd studies of the BeF_2-ZnF_2,[56] BeF_2-NdF_3[57] and MgF_2-CdF_2[58] systems have shown them to be simple eutectics with no intermediate compound formation. Similar investigations of the MF_2-CoF_2 (M = Mg,Ca,Sr) systems[59] have shown that the phase equilibria become more complex with increasing atomic number of the alkaline earth metal. Thus, the MgF_2-CoF_2 system exhibits a continuous series of solid solutions, the CaF_2-CoF_2 system is a simple eutectic with restricted mutual solid solubility of the components and the SrF_2-CoF_2 system is a simple eutectic with very restricted mutual solid solubility of the components and intermediate compound formation. The 1:1 ternary fluoride, $SrCoF_4$, is formed in a eutectoid reaction at 1023K and decomposes in a peritectic reaction at 1057K.[59] The metastable phase has been characterised under ambient conditions;[59] its unit cell parameters are included in Table 7.

2.3 COMPOUNDS OF THE ALKALINE EARTH METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS

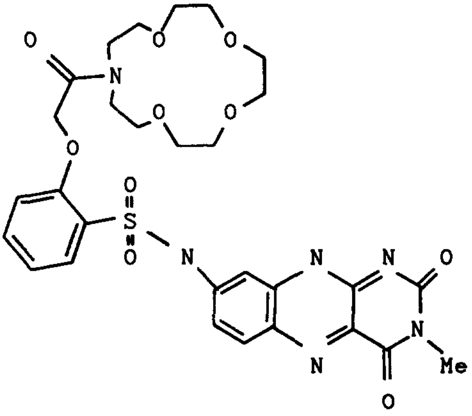
Consideration of the papers abstracted for this section indicated that a significant proportion belong to one of four subject groups (viz., complexes of significance in bioinorganic chemistry, complex formation in solution, cyclopentadienyl containing complexes and heterobimetallic complexes) which are common to several alkaline earth metals; these papers are considered in the appropriate subsection. The topics covered in the other papers are somewhat fragmented; these papers are discussed in subsections devoted to the individual alkaline earth metals.

2.3.1 Complexes of Significance in Bioinorganic Chemistry

There has been a marked reduction in the number of publications in this field. The six papers which have been abstracted cover interactions between Mg^{2+} and the membrane and blood brain barrier transport agent L-aspartate (2),[60] between Mg^{2+} and Ca^{2+} and the nucleoside, uridine,[61] and the nucleoside 5'-triphosphates, 5'-atp, 5'-ctp, 5'-utp and 5'-ttp,[62] and between Ca^{2+} and the sugars D-ribose and D-arabinose[63] and the enzyme and protein models, (3)[64] and (4).[65] Magnesium L-aspartate trihydrate (5)[60] which previously existed only in strongly basic aqueous medium has now been crystallised and structurally characterised. The L-aspartate dianion in (5) is facially bound to the octahedrally coordinated Mg as a tridentate ligand (Mg...O = 206.6,207.5; Mg...N = 220.3pm); the coordination geometry is



(2)



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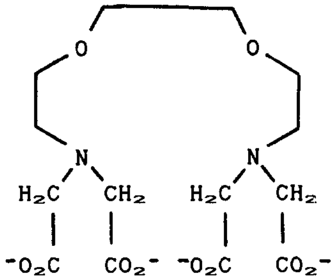


(4)

completed by an oxygen atom of a neighbouring complex (Mg...O = 199.0pm) and by two water molecules (Mg...O = 207.4,209.0pm).[60]

The stability constants of binary and ternary complexes of, inter alia, Mg^{2+} and Ca^{2+} with uridine as a primary ligand and glycine, histidine, histamine and oxalic acid as secondary ligands have been determined (I = 0.1M;308K)[61] in aqueous solution using potentiometric pH-titration methods. In the binary system, the uridine is thought to act as a bidentate ligand involving N(3) and O(4) in metal coordination; in the ternary systems, however, it behaves as a unidentate ligand binding through N(3) only.[61]

The stabilities of the monomeric metal ion complexes formed by, inter alia, Mg^{2+} and Ca^{2+} with the nucleoside 5'-triphosphates, 5'-atp, 5'-ctp, 5'-utp and 5'-ttp, have been determined (I = 0.1M;298K) under conditions where self association of the nucleoside 5'-triphosphate is negligible.[62] Whereas $Ca(5'\text{-atp})^{2-}$ exists solely as a phosphate-cordinated species, $Mg(5'\text{-atp})^{2-}$ is present, to the extent of 11(±6)% , in aqueous solution as an outer-sphere macrochelated isomer; the formation of this species is thought to be responsible for the marked increase in stability of $Mg(5'\text{-atp})^{2-}$ over the corresponding complexes involving the pyrimidine nucleoside 5'-triphosphates.[62]

Addition of Ca^{2+} to acetonitrile solutions of (3) effects both a spectral change in (3) and an enhancement of its photooxidising ability.[64] It is suggested that both changes are due to the lariat effect by which the dissociation of the 8-sulphonamide group of (3) is facilitated to serve as a cap for the Ca^{2+} ion complexed by the crown ether. It is further postulated that the crown ether in (3), by acting as an allosteric site induces an activity change in the flavin moiety serving as a catalytic site, thus mimicing "allosteric" enzymes.[64]

The thermodynamic parameters of the interaction between Ca^{2+} and the hydroxyl units of sugar molecules have been assessed by comparison of the properties of the isomers, D-ribose, which has a suitable sequence of hydroxyl groups for interaction with Ca^{2+}, and D-arabinose, which is an inactive complexant;[63] the Ca^{2+}-hydroxyls pair interaction parameters are ΔH° = 24 $kJ.mol^{-1}$, ΔS° = -83 $JK^{-1}mol^{-1}$, $\Delta V^\circ \sim 5cm^3mol^{-1}$ and ΔCp° = 40 $JK^{-1}mol^{-1}$.

The Ca^{2+}-binding selectivity of various proteins has been assessed using the octadentate ligand (4) as a model;[65] this ligand is an apt choice since its preference for the binding of Ca^{2+} over Mg^{2+} ($\sim 10^6$) is even greater than that typically exhibited by calcium-binding proteins. The molecular structure of $Ca^{2+}[Ca(\underline{4})]^{2-}.(22/3)H_2O$ (6), crystallised from aqueous solutions containing $Ca(OH)_2$ and the parent acid of (4) at pH = 9, has been determined using single crystal xrd methods.[65] The asymmetric unit of (6) contains three crystallographically independent $[Ca(\underline{4})]^{2-}$ anions, each of which comprises a Ca atom surrounded, in an approximately dodecahedral array, by the eight ligating atoms of the chelating ligand (Ca(1)...O = 236.5-250.2, Ca(1)...N = 260.3,261.7; Ca(2)...O = 234.7-255.0; Ca(2)...N = 260.2,261.3; Ca(3)...O = 236.5-248.3; Ca(3)...N = 256.7,257.5pm). The three crystallographically independent Ca^{2+} counterions, are surrounded by water molecules (Ca(4)...O = 238.6-243.7; Ca(5)...O = 239.3-248.5; Ca(6)...O = 240.8-246.9pm) and the oxygens of carboxylate groups that bridge between the $[Ca(\underline{4})]^{2-}$ anions and the partially aquated counterions (Ca(4)...O = 244.7-254.2; Ca(5)...O = 247.0-252.6; Ca(6)...O = 232.5-247.3pm); two of these counterions are 8-coordinate (four water molecules and four carboxylate oxygens - Ca(4), Ca(5)), while the third is 7-coordinate (three water molecules and four carboxylate oxygens - Ca(6)).[65] A similar study has been completed for the analogous compound, $Sr[Cd(\underline{4})].7H_2O$.[65] In this case, however, the asymmetric unit contains but one cation and one anion. The structure of the anion is similar to that of $[Ca(\underline{4})]^{2-}$ (Cd...O = 232.4-258.5; Cd...N = 242.1,243.7pm). The Sr^{2+} counterion is surrounded by nine oxygens, five of which come from bridging carboxylate groups one of which is quite remote (Sr...O = 255.9-261.4,299.5pm) and four of which come from water molecules (Sr...O = 255.4-273.4pm), in a slightly twisted tricapped trigonal prismatic array.[65]

2.3.2 Complex Formation in Solution

Potentiometric studies of aqueous solutions containing beryllium(II) and N-alkyliminobisacetic acids ($R-N(CH_2COOH)_2$; R = H, CH_3, C_2H_5, C_3H_7)[66] or nitrilotriscarboxylic acids {$N(CH_2COOH)_3$ (7); $N(CH(CH_3)COOH)_3$ (8); $N(C_2H_4COOH)_3$ (9); $N(CH_2COOH)_2(C_2H_4COOH)$ (10); $N(CH_2COOH)(C_2H_4COOH)_2$(11)}[67] have been undertaken (I = 0.5M;298K). For the N-alkyliminobisacetic acids[66] the only complexes formed have the stoichiometry $[Be(OH)L]^-$; the formation constants of the complexes are practically identical, the N-alkyl group having almost no effect on their stabilities. For the nitrilotriscarboxylic acids,[67] the complexes formed have the stoichiometries $[BeL]^-$ (7-11), [BeHL] (8,10,11) and $[BeH_2L]^+$ (10); the formation constants of the $[BeL]^-$ complex indicate the following order of coordination capacity:

lg K($[BeL]^-$) (7)(6.84)<(8)(7.37)<(10)(8.10)<(11)(9.25) $\sim$ (9)(9.23)

Complex formation equilibria of nitrilotris(methylenephosphonic acid) with M^{2+} (M = Mg-Ba) have also been studied potentiometrically (I = 0.1M;298K);[68] the formation constants K($[ML]^{4-}$) were determined together with the protonation constants K($[MHL]^{3-}$), K($[MH_2L]^{2-}$) and K($[MH_3L]^-$). The K($[MHL]^{3-}$) values are in the reverse order of the K($[ML]^{4-}$) values:

lg K($[ML]^{4-}$)   Ba(6.34) < Sr(6.52) < Mg(7.52) < Ca(7.86)

lg K($[MHL]^{3-}$)   Ba(9.72) > Sr(9.41) $\sim$ Mg(9.42) > Ca (8.80)

while the K($[MH_2L]^{2-}$) and K($[MH_3L]^-$) values are nearly equal, at 6.1 and 5.0 respectively, for the four group 2 cations.[68]

The thermodynamic characteristics of the formation of the complex $[Sr(edta)]^{2-}$ have been calculated[69] at T = 288.15, 298.15 and 308.15K and I = 0.3, 0.5 and 1.0M($NaClO_4$) from calorimetrically measured enthalpy changes.

Hydrolysis in aqueous $Ca(ClO_4)_2$ solutions at T = 373K and 413K and I = 3.0M($NaClO_4$) has been shown[70] to result in the formation of the complex $[Ca(OH)]^+$ [lg.β_{11} = -12.24(8) at 373K and -10.87(1) at 313K].

Several Russian groups have studied interactions in aqueous solutions containing both an alkaline earth metal salt and either urea,[71] formamide[72] or nicotinamide.[73] The complexes isolated from the $M(NO_3)_2(M = Mg,Ca)$-urea-H_2O[71] systems at 328K were $Mg(NO_3)_2.6CO(NH_2)_2$, $Mg(NO_3)_2.4CO(NH_2)_2.2H_2O$, $Mg(NO_3)_2.2CO(NH_2)_2.4H_2O$, and $Ca(NO_3)_2.4CO(NH_2)_2$, $Ca(NO_3)_2.CO(NH_2)_2$; those crystallised from the $MgCl_2$-formamide-H_2O[72] system were $MgCl_2.4HCONH_2.2H_2O$ and $MgCl_2.2HCONH_2.2H_2O$; and those obtained from the $MCl_2(M = Mg,Ca)$-nicotinamide-H_2O[73] systems at 298K were $MgCl_2.2(3\text{-}H_2NCO.C_6H_4N).6H_2O$ and $CaCl_2.2(3\text{-}H_2N.CO.C_6H_4N).6H_2O$.

2.3.3 Cyclopentadienyl Derivatives

This subsection has been introduced to cater for increased interest in alkaline earth metal salts of cyclopentadiene and its derivatives. A significant proportion of this activity can be attributed to Andersen et al.[74-77] who have studied the structural and reaction chemistry of $(\eta^5\text{-}C_5Me_5)_2M$ (M = Mg-Ba). Using gas phase electron diffraction methods they have shown that the thermal average gas phase structure of $(\eta^5\text{-}C_5Me_5)_2Mg$ differs considerably from those of $(\eta^5\text{-}C_5Me_5)_2M$ (M = Ca-Ba). Thus, $(\eta^5\text{-}C_5Me_5)_2Mg$ has a regular sandwich structure for which the predominant conformer is thought to be eclipsed (D_{5h} symmetry) although the staggered conformer (D_{5d} symmetry) cannot be ruled out, while $(\eta^5\text{-}C_5Me_5)_2M$ (M = Ca-Ba) are best described as bent sandwich structures in which the ring centroid-metal-ring centroid

Table 8. Interatomic distances and angles in the gas phase molecular structures of $(\eta^5\text{-}C_5Me_5)_2M$ (M = Mg-Ba)

$(\eta^5\text{-}C_5Me_5)_2M$	Mg[74]	Ca[74,75]	Sr[76]	Ba[76]
r(M...R.C.)/pm*	201.1	231.2	246.9	263.1
r(M...C)mean/pm	234.1	260.9	275.0	289.8
r(M...C)range/pm	-	255-267	270-280	284-295
l(M...C)mean/pm	11.9	9.9	10.5	14.8
R.C.-M-R.C. angle/°*	180	154	149	148

*R.C. = Ring centroid

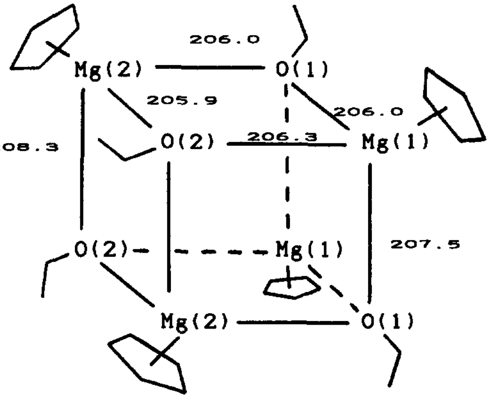
angle varies from 154° to 148°. Details of the structures are collected in Table 8.

Burns and Andersen[77] have also prepared a number of donor-acceptor complexes, $(C_5Me_5)_2M(bipy)$ (M = Mg-Ba), $(C_5Me_5)_2M(PEt_3)$ (M = Ca-Ba) and $(C_5Me_5)_2M(2,6\text{-xylylisocyanide})_2$ (M = Ca-Ba) by addition of the ligand to solutions of the appropriate base-free moieties, $(C_5Me_5)_2M$ (M = Mg-Ba), in hexane or toluene. The base-free species $(C_5Me_5)_2M$ (M = Sr,Ba) were isolated by the "toluene reflux" method from $(C_5Me_5)_2Sr(OEt_2)$ and $(C_5Me_5)_2Ba(thf)_2$ previously synthesised by reaction of $(C_5Me_5)_2Na$ with SrI_2 in ether or with BaI_2 in thf.[77]

Similar complexes of $(C_5H_5)_2Mg$ with O-, N- or P-donor Lewis bases have been identified in solution by ^{25}Mg n.m.r. spectroscopy;[78] whereas unidentate ligands invariably gave complexes of stoichiometry $(C_5H_5)_2MgL_2$, bidentate ligands formed complexes of stoichiometry $(C_5H_5)_2MgL$. Correlation of $\delta(^{25}Mg)$ with $\delta(^{13}C\{C_5H_5\})$ gives the following sequence of donor strength:

tmeda>thf>dme>1,4-dioxane>PMe_3>Et_2O>Et_3N~PhOMe~$(Me_2CH)_2O$

Some of the complexes, those containing tmeda, thf, dme, 1,4-dioxane and pyridine, have been isolated.[78] Reaction of $(C_5H_5)_2Mg$ with R_2Mg (R = OEt, Et, $\eta^1\text{-}CH_2CH{=}CH_2$ or $\eta^1\text{-}CH_2CH{=}CHCH_2Mg(C_5H_5)$) leads to mixed systems of the type $(C_5H_5)MgR$;[78] single crystal xrd studies of the ethoxide have shown it to be tetrameric, $\{(\eta^5\text{-}C_5H_5)MgOEt\}_4$ with a Mg_4O_4 cubic



r(Mg(1)...R.C.) = 219.6pm
r(Mg(2)...R.C.) = 210.3pm

[R.C. = Ring centroid]

(12)

core (12), the pseudo-tetrahedral coordination geometry of the magnesium atom being completed by the (η^5-C_5H_5) moiety.

The rate of molecular inversion of $(C_5H_5)_2Be$ in solution (cyclohexane and ether) has been estimated ($10^{10}s^{-1}$) from the observation of partially relaxed coupling to ^9Be in the ^{13}C n.m.r. spectrum.[79]

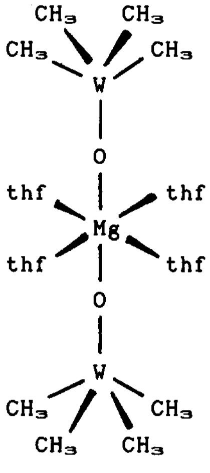
The free radicals, $(C_5H_5)M^{\cdot}$ (M = Ca,Sr) have been produced in a Broida oven by reaction of alkaline earth metal vapours with cyclopentadiene;[80] laser spectroscopic observation of these species suggest that they are "open-faced sandwich" complexes of C_{5v} symmetry.

2.3.4 Heterobimetallic complexes

Two different types of heterobimetallic complex containing Group 2 metals have been described during the period of this review; ionic species containing discrete cations and anions centered on different metals[81-84] and molecular species containing two metals connected either by bridging ligands[82,85-87] or by metal-metal bonds.[87] In the former category, the cation is invariably Group 2 metal based while the anion is transition metal based; cations include $[Mg(H_2O)_6]^{2+}$,[81] $[Mg(thf)_6]^{2+}$,[82,83] $[Mg_2Cl_3(thf)_6]^+$[82,83] and $[Ca(H_2O)_7]^{2+}$.[84] Structural studies of $[Mg(H_2O)_6]^{2+}[Co(Hedta)H_2O]^-_2.2H_2O$[81] and of $[Mg(thf)_6]^{2+}[MoOCl_4(thf)]^-_2$[83] have shown the cations to be tetragonally elongated octahedra. Similar studies of $[Mg_2Cl_3(thf)_6]^+[MoOCl_4(thf)]^-$[83] have revealed a $(\mu\text{-}Cl)_3$ bridged structure for the cation with three terminal thf molecules completing the distorted octahedral coordination geometry of the Mg atoms; viz., $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3]^+$ (Mg(1)...Cl = 249.4-252.1; Mg(2)...Cl = 249.8-252.5; Mg(1)...O = 208.1-210.5; Mg(2)...O = 206.3-207.2pm). A single crystal xrd analysis of $[Ca(H_2O)_7]^{2+}[Cd_2Br_6]^{2-}$[84] has confirmed the presence of a distorted 7-fold coordination sphere for the Ca atom (Ca...O = 236-247pm).

Treatment of a Grignard reagent or $[MgR_2(thf)_2]$ with $TiCl_4$ in thf gives TiR_4 together with $[MgCl_2(thf)_2]$ which reacts with further $TiCl_4$ to give the $(\mu\text{-}Cl)_2$ bridged Mg-Ti complex, $[(thf)_4Mg(\mu\text{-}Cl)_2TiCl_4]$,[82] as well as the ionic species $[Mg(thf)_6]^{2+}[TiCl_5(thf)]^-_2$ and $[Mg_2Cl_3(thf)_6]^+[TiCl_5(thf)]^-$ mentioned above.

Two groups have independently investigated the reaction of organomagnesium compounds with $MOCl_4$ (M = Mo,W) in thf,[85,86] the Mg-W complexes so formed are structurally similar, the only difference being in the organic residue. Treatment of $MOCl_4$ (M = Mo,W) in thf/ether mixtures leads to the paramagnetic (d^1) complexes, $[(Me_4MO)_2Mg(thf)_4]$ (M = Mo,W).[85] The centrosymmetric structure of the tungsten complex (13) consists of an Mg atom coordinated equatorially by four thf molecules (Mg...O = 210.2,211.0pm) and axially by two square pyramidal Me_4WO moieties (Mg...O = 201.0pm).[85] Reaction of the diGrignard reagent $[\{Mg(thf)_nCl\}_2\{(2\text{-}CH_2C_6H_4)_2\}]$, derived from $[Mg(anthracene)(thf)_3]$ and $(2\text{-}ClCH_2C_6H_4)_2$, with WCl_4O in thf yields $[\{(2\text{-}CH_2C_6H_4)_2WO\}_2Mg(thf)_4]$ (14).[86] The structure of (14) which has 2-fold symmetry, mirrors that of (13), the Mg atom being surrounded by the four thf molecules (Mg...O = 208.0,212.0pm) and the two $2\text{-}(CH_2C_6H_4)_2WO$ moieties (Mg...O = 202.9,203.6pm).[86]



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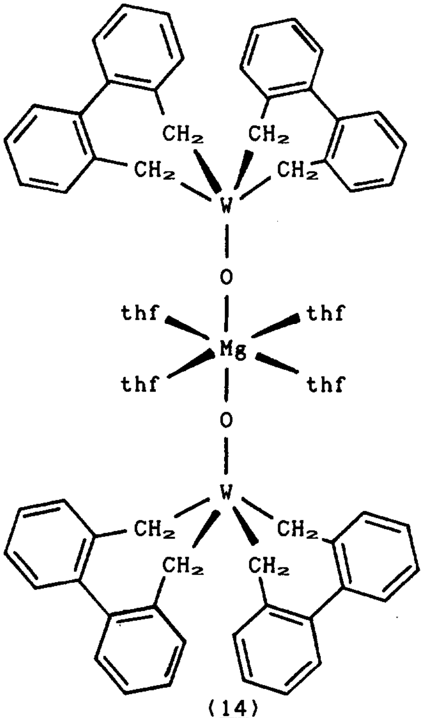


(14)

Treatment of $[(C_5H_5)Co(C_2H_4)_2]$ with PhMgBr in thf containing tmeda and with C_3H_5MgBr in thf yields the Mg-Co complexes $[(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}C_2H_4)PhMgBr(tmeda)]$ (14) and $[(\eta^5\text{-}C_5H_5)Co(\eta^3\text{-}(C_3H_5)MgBr(thf)_2]$ (15) respectively.[87] Their compositions have been confirmed by elemental analyses and they have been investigated by n.m.r. spectroscopy and by single crystal xrd methods. The structure of (15)(Figure 1a) is novel in that it contains a tmeda-modified complete Grignard reagent in the coordination sphere of a transition metal. Thus in addition to the presence of a Mg...Co bond (256.5pm), an ion pair interaction through a bridging phenyl group exists (Mg...C = 257.2pm). In the structure of (16) (Figure 1b), the terminal carbon atoms of the allyl group are significantly further from the magnesium atom (Mg...C = 289,306pm) than is the bridging carbon atom of the

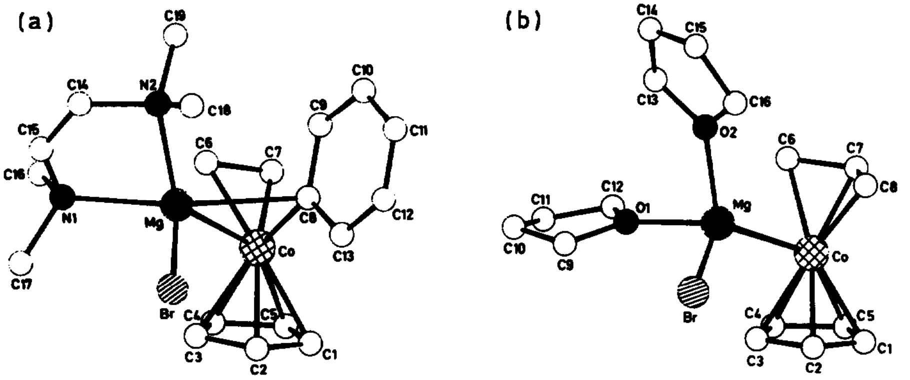
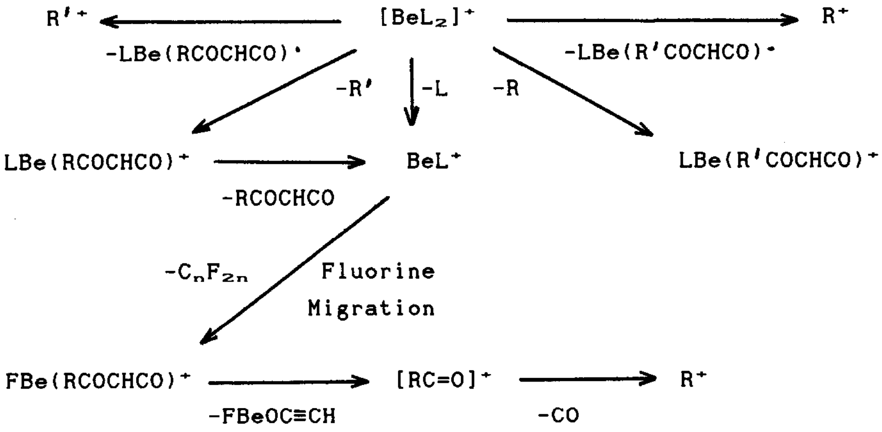


Figure 1. Molecular structures of (a) $[(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}C_2H_4)\text{-}PhMgBr(tmeda)]$ and of (b) $[(\eta^5\text{-}C_5H_5)Co(\eta^3\text{-}C_3H_5)\text{-}MgBr(thf)_2]$ (reproduced by permission from Angew. Chem. Int. Ed. Engl., 25(1986)923).

phenyl group of (15), leaving the Mg...Co bond (248.0pm) as the only contact between the two parts of the molecule. Both compounds can be regarded as dinuclear complexes formed by coupling of the singly negatively charged 18e anions $[(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}C_2H_4)C_6H_5]^-$ or $[(\eta^5\text{-}C_5H_5)Co(\eta^3\text{-}C_3H_5)]^-$ with the electrophilic cations $[MgBr(tmeda)]^+$ or $[MgBr(thf)_2]^+$ (Lewis acid/Lewis base adduct with $Mg \leftarrow Co$ bond).[87]

2.3.5 Beryllium Derivatives

A mass spectroscopic study[88] of diverse partially fluorinated β-diketonate complexes of beryllium ($Be(RCOCHCOR')_2$; R = Me, Ph, 2-C_4H_3S, 2-C_4H_3O, R' = CF_3; R = Ph, 2-C_4H_3S, R' = C_2F_5, C_3F_7) has yielded the fragmentation pathway outlined in Scheme 1.



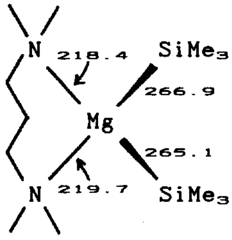
Scheme 1.

2.3.6 Magnesium Derivatives

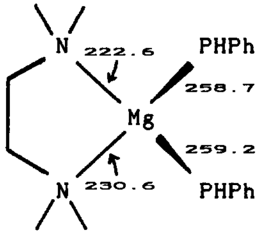
The synthesis and characterisation of a large number of diverse magnesium derivatives have been reported during the 18 months of this review. Many were ultimately characterised by single crystal xrd methods. Both monomeric and dimeric structures have been found; the monomers include the molecular species, $[(Me_3Si)_2Mg(tmpda)]$ (17),[89] $[(PhPH)_2Mg(tmeda)]$ (18),[90] $[(2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10})_2Mg(1,4\text{-}dioxane)_2].C_6H_5CH_3$ (19),[91] and $[(CH_3O(CH_2)_3CH_2)_2Mg]$ (20)[92] and the ionic species $[Mg(H_2O)_6](N_3)_2$ (21)[93] and $[Mg(CH_3NH.CO.CH_3)_2(H_2O)_4](NO_3)_2$, (22) [94] while the dimers include $[(CH_3)_2N(CH_2)_2CH_2MgCH_2CH_3]_2$ (23),[95] $[(CH_3)(C_6H_5)N(CH_2)_2CH_2MgCH_2CH_3]_2$ (24),[95] $[(Me_3Si)_2NMgCH(CH_3)CH_2CH_3]_2$ (25)[96] and $[CH_3CH{=}C(^tBu)OMgBr(Et_2O)]_2$ (26).[97] Schematic representations of the structures of these compounds are shown in Figure 2; where appropriate interatomic distances are included.

Addition of magnesium metal to a solution of $(Me_3Si)_2Hg$ in 1,3-bis(dimethylamino)propane/ether gave $[(Me_3Si)_2Mg(tmpda)]$ (17);[89] it has a monomeric structure (Figure 2) in which the

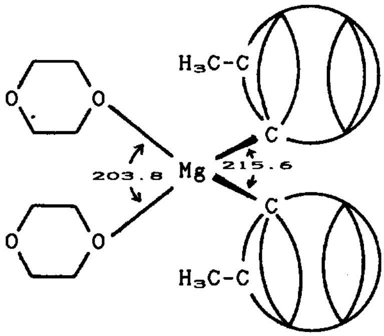
Figure 2. Schematic representations of the structures of diverse magnesium complexes (distances/pm).



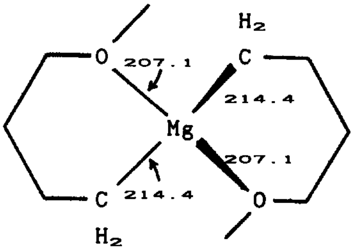
(17) [89]



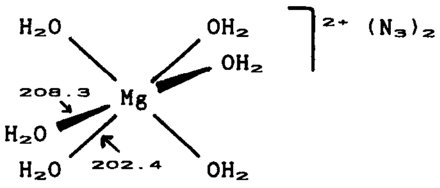
(18) [90]



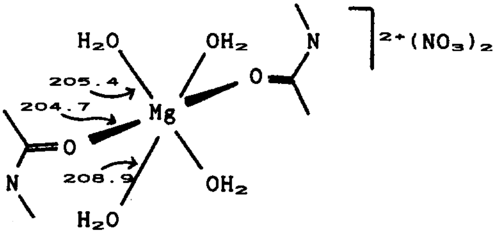
(19) [91]



(20) [92]

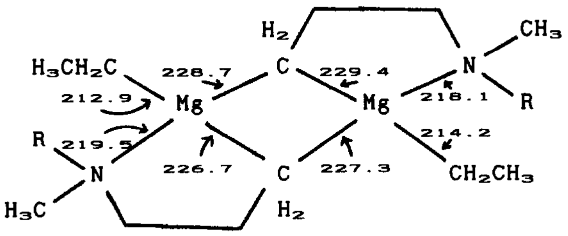


(21) [93]



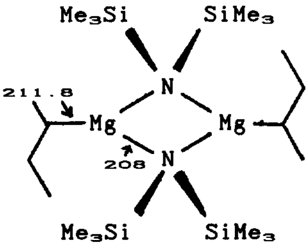
(22) [94]

Figure 2 continued

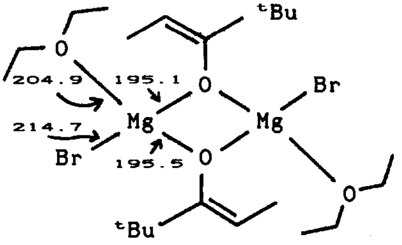


(23) R = CH_3 (data on RHS)[95]

(24) R = C_6H_{11} (data on LHS)



(25)[96]



(26)[97]

Mg atom is tetrahedrally coordinated by the silicons of the two anions and the two nitrogens of the chelating tmpda ligand. Selective monometalation of Ph_2PH by dialkylmagnesiums in heptane under mild conditions gives $[(PhPH)_2Mg]_\infty$, which is assumed to be a polymeric product containing bridging $[PhPH]^-$ groups. Treatment of the polymer with tmeda yields the hydrocarbon soluble $[(PhPH)_2Mg(tmeda)]$ (18),[90] which has a simple monomeric structure (Figure 2) in which the Mg atom is surrounded by the phosphorus atoms of two anions and the two nitrogens of the chelating tmeda ligand in a distorted tetrahedral array. Dioxane-induced disproportionation of the carboranyl Grignard reagent $(2\text{-Me-}1,2\text{-}C_2B_{10}H_{10})MgBr$ in toluene gave the toluene adduct, $[(2\text{-Me-}1,2\text{-}C_2B_{10}H_{10})_2Mg(1,4\text{-dioxane})_2].C_6H_5CH_3$ (19);[91] the Mg atom in the monomeric structure (Figure 2) of this complex is tetrahedrally coordinated by carbons from the two anions and oxygens from two solvate molecules; the toluene molecules are remote from the Mg atom. The reaction of MgH_2, prepared by homogeneous catalysis, with N,N-dialkylallyl- and N,N-dialkyl-3-butenyl-amines and alkyl-3-butenylethers in the presence of catalytic amounts of $ZrCl_4$ yields a series of bis(N,N-dialkylaminoalkyl)- and bis(alkoxylbutyl)magnesium compounds;[92] the analogous synthesis of bis(3-alkoxylpropyl)magnesium derivatives failed owing to cleavage of the alkyl ether with elimination of propene. In the structure (Figure 2) of bis(4-methoxybutyl)-magnesium (20),[92] the Mg atom is bis(chelated) by the two anions, which coordinate via the carbanion carbon and the ether oxygen, in a distorted tetrahedral geometry.

The anions are totally independent of the Mg atoms in the structures of $[Mg(H_2O)_6](N_3)_2$ (21)[93] and $[Mg(CH_3.NH.CO.CH_3)_2(H_2O)_4](NO_3)_2$ (22).[94] In both cations (Figure 2), the Mg atoms are located in tetragonally elongated octahedral coordination spheres; that of (21) has 4-fold symmetry whereas that of (22) has a centre of symmetry.

Reaction of bis(4-alkoxybutyl)- and bis(N,N-dialkylaminoalkyl)-magnesium derivatives with diethylmagnesium leads to ethyl(4-alkoxybutyl)- and ethyl(N,N-dialkylaminoalkyl)magnesium derivatives.[95] Structural analysis has shown that ethyl(3-N,N-dimethylaminopropyl)magnesium (23) and ethyl(3-N-cyclohexyl-3-N-methylaminopropyl)magnesium (24) are dimeric with planar Mg_2C_2 rings with bridging α-carbons (Figure 2);[95] the pseudo-tetrahedral coordination geometries of the Mg atoms are completed by the intramolecularly bonded pendant amino groups and the ethyl anion.

Treatment of $HN(SiMe_3)_2$ in heptane with dialkylmagnesiums result in the initial formation of $[(Me_3Si)_2NMgCH(CH_3)CH_2CH_3]_2$ (25) followed by $[\{(Me_3Si)_2N\}_2Mg]$.[96] The structure of the intermediate (25) (Figure 2) is that of a dimer based on a planar Mg_2N_2 ring with bridging amido nitrogens and with 222 symmetry; the trigonal coordination of the Mg atom is completed by the s-butyl anion.

The bromomagnesium enolate of t-butyl ethyl ketone (26), prepared by the reduction of $^{t}Bu.CO.CH(Br)CH_3$ with magnesium metal in ether, crystallises with a dimeric structure based on a slightly puckered Mg_2O_2 ring with bridging enolate oxygens (Figure 2);[97] the Mg atom is further coordinated by the bromine and ether oxygen to give an approximately tetrahedral coordination geometry.

^{1}H-n.m.r. studies of the interaction of bis(4-methylphenyl) magnesium (Ar_2Mg) with C221 in benzene suggest the formation of the ions $[C221MgAr]^+$ and $[MgAr_3]^-$;[98] addition of Ar_2Mg to benzene solutions of 15C5, however, is thought to generate moleular $[15C5MgAr_2]$ complexes without the accompanying formation of disproportionation products.

Complexes of M^+ (M = Mg-Ba) with 1,3-bis(2-hydroxyphenyl)-1,3-propanedione of stoichiometry ML_2,xH_2O have been synthesised.[99] Conductivity, spectral and thermal studies indicate a difference in coordination mode between Mg and the other metals although all four complexes exhibit non-ionic behaviour. It is suggested that the magnesium derivative adopts a similar molecular structure to that of $ZnL_2,2EtOH$ in which the anion acts as a bidentate chelating ligand forming a square planar $ZnO_4(MgO_4)$ unit which has $EtOH(H_2O)$ molecules lying in the axial positions.[99]

Treatment of a suspension of the bis(diglyme) adduct of magnesium octahydrotriborate in benzene with ammonia gave $[Mg(NH_3)_6](B_3H_8)_2$.[100] Thermal studies showed the product to be stable upto 373K; at higher temperatures it decomposes to form the hydroborate, borazine and hydrogen:[100]

$$3[Mg(NH_3)_6](B_3H_8)_2 \xrightarrow{T\sim 403K} 3Mg(BH_4)_2.2NH_3 + 2B_3N_3H_6 + 6/n(BNH)_n + 21H_2$$

The magnesium cyanurates $Mg(H_2C_3N_3O_3)_2.3H_2O$ and $Mg_3(C_3N_3O_3)_2.8H_2O$ decompose similarly, the only difference being the conversion of the acid salt to the normal salt at 533-563K. [101] Dehydration of the normal salt occurs at 453-503K. It then dissociates at 583-593K with simultaneous formation of magnesium cyanate and isocyanate which decompose forming MgO at 643-673K and 753-773K respectively.[101]

2.3.7 Calcium, Strontium and Barium Derivatives

All bar one of the papers abstracted for this subsection describe the synthesis and structural characterisation of novel complexes. In the exception,[102] spectroscopic (i.r., visible, ^{1}H and ^{11}B n.m.r.) data are reported for

$\{(CH_3)_3N.BH_2.CO_2\}Ca(NO_3).(CH_3)_2CO.0.5H_2O$, prepared by reaction of $Ca(NO_3)_2$ with $\{(CH_3)_3N.BH_2.CO_2\}Na.0.25CH_3OH$; they suggest that the trimethylamine-boranecarboxylato ligand functions as a bidentate chelating ligand.

Wei et al.[103,104] have published the crystal and molecular structures of a series of triglyme and tetraglyme complexes of $M(SCN)_2$ (M = Ca-Ba). In $[(triglyme)Ca](SCN)_2.H_2O$,[103] the Ca atom is equatorially coordinated by the four oxygens of the triglyme ligand and the nitrogen of one of the anions; its pentagonal bipyramidal coordination geometry is completed by the nitrogen of the other anion and the water molecule. The 8-fold coordination of the Sr atom in $[(triglyme)Sr](SCN)_2.2H_2O$,[103] is approximately square pyramidal with the triglyme ligand folded such that its four oxygens provide one face of the coordination sphere, the other face being formed by the two anion nitrogens and the two water molecules. In the three tetraglyme complexes, $[(tetraglyme)Ca](SCN)_2.H_2O$,[104] $[(tetraglyme)Sr](SCN)_2.H_2O$,[104] and $[(tetraglyme)Ba](SCN)_2.2H_2O$,[104] the five oxygens of the tetraglyme ligand coordinate the cation equatorially, the degree of opening of the ligand increasing with increasing size of the cation from Ca to Ba. The coordination geometries of the alkaline earth metal atoms are completed by two anion nitrogens on one side and either one or two water molecules on the other side giving 8-coordinate Ca and Sr atoms and 9-coordinate Ba atoms. Details of the metal coordination spheres in the two triglyme and three tetraglyme complexes are collected in Table 9.

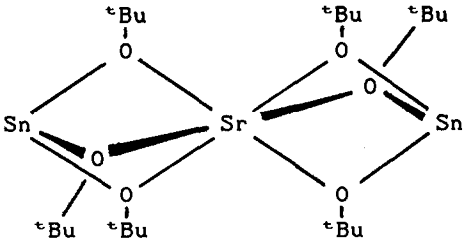
The Sr atom in the similar complex $[(tetraethyleneglycol)Sr\text{-}\{3,5\text{-}(NO_2)_2C_6H_3CO_2\}_2.H_2O$[105] has a slightly expanded, 9-fold, coordination polyhedron. It comprises the five oxygens of the tetraethyleneglycol ligand (Sr...O = 262.3-274.0pm), two oxygens of one anion (Sr...O = 255.7,298.4pm), an oxygen from a centrosymmetrically related anion (Sr...O = 247.8pm) and a water molecule (Sr...O = 256.9pm). A 9-coordinate Sr atom also occurs in the crystal and molecular structure of strontium squarate trihydrate.[106] The Sr atom is located on a 2-fold axis of symmetry in a distorted monocapped square antiprismatic geometry by six oxygens of the squarate dianions (Sr...O = 253.7,267.4,284.9pm) and three water molecules (Sr...O = 254.5, 267.7,267.7pm).

Table 9. Interatomic distances/pm in the metal coordination spheres of hydrated triglyme[103] and tetraglyme[104] complexes of $M(SCN)_2$ (M = Ca,Sr,Ba).

	r(M..polyether O) min.	r(M..polyether O) max.	r(M..water O)	r(M...N)
$[(triglyme)Ca](SCN)_2.H_2O$	243.3	247.9	236.0	238.9,239.7
$[(triglyme)Sr](SCN)_2.2H_2O$	262.8	269.0	256.5,265.7	259.0,261.3
$[(tetraglyme)Ca](SCN)_2.H_2O$	246.5	250.3	242.2	244.4,248.8
$[(tetraglyme)Sr](SCN)_2.H_2O$	261.7	265.2	258.4	258.8,263.8
$[(tetraglyme)Ba](SCN)_2.2H_2O$	286.1	290.1	273.9,282.0	281.2,282.4

Hummel and Wolf have reported the isotypic structures of calcium[107] and strontium[108] 1,1-dicyanoethylene-2,2-dithiolate pentahydrate, produced by addition of $M(NCS)_2$ to an ethanol solution of $Na_2[S_2C=C(CN)_2]$ previously prepared by reaction of CS_2 with maleonitrile in the presence of sodium ethoxide in ethanol. The metal atoms are coordinated by six water molecules (Ca...O = 236.7-252.4; Sr...O = 258.0-270.1pm), and two anion nitrogens (Ca...N = 254.9,272.2; Sr...N = 272.6,299.6pm) in a bicapped trigonal prismatic arrangement. The six oxygen atoms form the trigonal prism, with the two nitrogens located on two of the rectangular faces; a third, quite remote, nitrogen is situated above the other rectangular face. Of the six oxygens, two are coordinated to two different Ca atoms forming dimeric units.

Reaction of tin-di-tert-butoxide in benzene solution with strontium and barium tert-butoxide, which are insoluble in benzene, leads to $[Sn(O^tBu)_3M(O^tBu)_3Sn]$ (M = Sr,Ba);[109] magnesium and calcium tert-butoxides do not react, even in refluxing benzene. The two products have been characterised spectroscopically and structurally. They are isotypic; the structure of the strontium derivative (27) has been determined by single crystal X-ray structure analysis. The Sr atom, situated at a centre of inversion, is surrounded by oxygens of six alkoxide anions in a distorted octahedral array; the Sn atoms are coordinated in a trigonal pyramidal geometry by the oxygen atoms of the alkoxide anions which bridge to the Sr atoms.



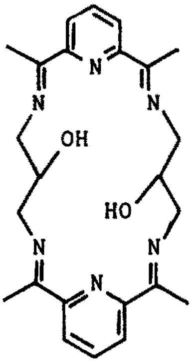
r(Sr...O) = 252.3pm
r(Sn...O) = 207.8pm

(<u>27</u>)

The remaining three papers[110-112] abstracted for this subsection, report the structural characterisation of six barium complexes. In the structure of $Ba(O_2CCH_2NHCS_2).3H_2O$[110] the Ba atom is surrounded by two sulphurs (Ba...S = 325.4,337.6pm), and seven oxygens, three of which belong to anions (Ba...O = 268.8-284.5pm) and the remainder to water molecules (Ba...O = 279.5-287.1pm).

The crystal and molecular structures of $Ba(en)_{4.5}Te_3$ (<u>28</u>) and $Ba(en)_3Te_3$ (<u>29</u>) are surprisingly different.[111] Whereas (<u>28</u>) is built up of separate $[Ba_2(en)_9]^{4+}$ cations and Te_3^{2+} anions, (<u>29</u>) adopts a molecular structure in which Te_3 units link together $Ba(en)_3$ moieties to give a polymeric arrangement.[111] In (<u>28</u>),[111] the Ba atoms are coordinated by four bidentate en ligands (Ba(1)...N = 294.1-308.7;Ba(2)...N = 290.9-301.7pm) and are connected into pairs by a further en molecule (Ba(1)...N = 299.6;Ba(2)...N = 314.8pm) to give the dinuclear $[(en)_4Ba(en)Ba(en)_4]^{4+}$ cation. The two Te_3^{2-} anions are remote from the cation and are bent with relatively short internuclear distances (Te...Te = 272.1-273.1pm; TeTeTe = 110.9,112.2°). In (<u>29</u>),[111] the Ba atom is surrounded by the three bidentate en ligands (Ba...N = 289.5-297.5pm), by a Te_3^{2-} anion which lies perpendicular to the Ba atom (Ba...Te = 360.5,376.0,380.5pm) and by one of the tellurium atoms of the symmetry related Te_3^{2-} anion (Ba...Te = 391.6pm). The Te_3^{2-} anion is quite severely bent and is considerably more asymmetric (Te...Te = 273.9,278.5pm; TeTeTe = 105.7°).

Finally, a group at Sheffield has prepared several barium complexes of tetraimine Schiff base macrocycles, of which three, $[($<u>30</u>$)Ba]^{2+}(ClO_4)_2.2H_2O$ (<u>33</u>), $[($<u>31</u>$)Ba]^{2+}(ClO_4)_2$ (<u>34</u>) and $[($<u>32</u>$)Ba]^{2+}(ClO_4)_2.EtOH$ (<u>35</u>), have been structurally characterised.[112] In (33), the six nitrogens of the macrocycle occupy one coordination hemisphere of the Ba atom (Ba...N = 291.4-296.3pm); the other coordination hemisphere contains five oxygens comprising the two substituent hydroxyl groups (Ba...O = 279.5, 280.2pm), two water molecules (Ba...O = 282.5,292.7pm) and, at a greater distance, a water molecule of an inversion related complex (Ba...O = 316.0pm) thus giving a weak dimerisation across (0,0,0). Although the two ClO_4^- anions are not directly coordinated to the Ba atom in this molecule, they are in the structure of the closely related species (34). Thus, in (34) the heteroatoms of the macrocycle, with the exception of the substituent hydroxyl oxygens, occupy one coordination hemisphere of the Ba atom (Ba...N = 297.2-308.2; Ba...O = 289.9,294.3pm) while the other hemisphere contains the two substituent hydroxyl oxygens (Ba...O = 283.7, 288.8pm), and the four oxygens of two approximately symmetrically bidentate ClO_4^- anions (Ba...O = 287.5-297.9pm). The much larger macrocycle cavity of (32) results in an asymmetrically positioned Ba atom and a planar skeleton in the structure of (35). Thus, the Ba atom is accommodated at one end of the cavity 34pm above an approximately planar 5-coordinate environment generated by two nitrogens (Ba...N = 297.1,299.8pm) and three oxygens (Ba...O = 263.2,271.1,282.2pm) of the ring; it is further coordinated on one side by the ethanol molecule (Ba...O = 263.2pm) and a bidentate anion (Ba...O = 286.7,299.3pm) and on the other side by a bidentate anion (Ba...O = 289.2,300.6pm).



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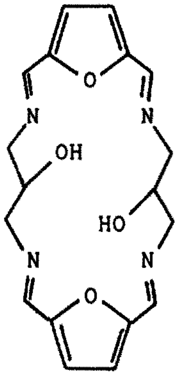

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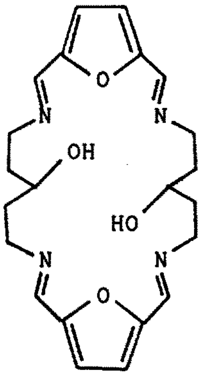

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