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Chapter 2

ELEMENTS OF GROUP 2

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2.1 INTRODUCTION

Following the format adopted previously,[1] the chemistry of these elements is reviewed in sections which reflect topics currently of interest and importance. For those topics which are common to Group I and 2 elements, e.g. cation solvation, molten salts, polyether and related complexes, the published data are considered in the relevant section in Chapter 1. The topics unique to the Group 2 elements are discussed in this Chapter.

Record calcium isotope ($^{40}Ca/^{44}Ca$ and $^{40}Ca/^{48}Ca$) separations have been achieved with an ion exchange resin containing C222B cryptand anchor groups;[2] the data are such that the application of the technique for industrial scale chemical pre-enrichment of heavy calcium isotopes has been proposed.[2]

2.2 METALS AND INTERMETALLIC COMPOUNDS

The number of papers abstracted for this section has risen markedly this year owing to the publication of the proceedings of the 1980 International Symposium on the Properties and Applications of Metal Hydrides;[3] several of the contributions describe the hydrogenation/dehydrogenation characteristics for magnesium and for a number of Mg-rich intermetallic compounds, including Mg_2Ni and $Mg_{12}Ln$. A number of papers have also been published, in which aspects of the low temperature solid state chemistry of alkaline earth metal atoms are described. Consequently, in contrast to the earlier reviews, this part of the review is divided into a number of subsections relating to these topics.

2.2.1 Low Temperature Chemistry of Alkaline Earth Metal Atoms

The reactions of alkaline earth metal atoms with a number of organic moieties have been studied in cocondensation reactions at 77K.[4-6] The reactions of magnesium with a variety of organochlorine derivatives have been studied using i.r. techniques;[4] the nature of the intermediates and of the reaction mechanism is discussed. Hydrolysis of the highly reactive solids produced by reaction of calcium,[5] strontium[6] and barium[6] with dimethylether leads to a mixture of hydrocarbons which were identified by GCMS techniques as C_1-C_8 alkanes, alkenes and alkynes. It is assumed that a wide variety of organometallic compounds are formed during the cocondensation process. The ether oxygen atom probably serves as an activating point, oxidative insertion of M into C-O bonds yielding $CH_3\dot{O}MCH_3$ or CH_3MOMCH_3; to account for the hydrolysis products, extensive insertion of the M atoms into either C-C or C-H bonds must also be involved.[5,6]

Reaction of alkaline earth metal atoms (M=Mg,Ca,Sr) with methyl halides in argon matrices has given rise to a new chemical species which has been characterised as H_3CMX (M=Mg,Ca,Sr; X=Cl,Br,I);[7] no evidence was detected for a strong polar covalent C-M bond, suggesting the unsolvated Grignard reagent formed here has a structure other than that of the solvated solution species.[7]

2.2.2 Metallic Solutions

Thermodynamic parameters have been calculated by ab initio methods for liquid Mg-Al solutions[8] and for liquid binary solutions containing calcium.[9] The kinetics of the solution of cobalt in liquid calcium have been determined ($1273 \leqslant T/K \leqslant 1723$);[10] they are very similar to the cobalt grain boundary self diffusion kinetics.

2.2.3 Intermetallic Compounds

The Mg-Ga phase diagram ($0.00 \leqslant x_{Mg} \leqslant 0.40$) has been reinvestigated.[11] The enthalpies of formation of $MgGa_2$ (-9.844 kJ mol^{-1}) and of Mg_2Ga_5 (-8.548 kJ mol^{-1}) were determined by differential scanning calorimetry. A new metastable phase, m-$MgGa_2$, was found by solidification of an undercooled liquid solution. It is isostructural with $CaIn_2$; hexagonal, space group $P6_3/mmc$, a=434.3pm, c=698.2pm. The structural relationships between this phase, other phases of $CaIn_2$-type and stable $MgGa_2$ are discussed. The enthalpy of transformation between the two phases was calculated to be -0.440 kJ mol^{-1}.[11]

Several papers dealing with the chemistry of alkaline earth metal silicides and germanides have been published.[12-14] Thin layers (10-20μm) of Mg_2Si or Ca_2Si have been prepared on silicon substrates by reaction of the appropriate metal vapour with silicon wafers;[12] the layer thickness and the size of the crystallites may be controlled by the conditions of the preparation.[12]

A single crystal X-ray diffraction study of the high temperature-high pressure modification (α-$ThSi_2$-structure) of $BaGe_2$ has been performed; it is tetragonal, space group $I4_1/amd$, with a=476.9 and c=1473.7pm.[13]

$CaSi_2$ has been converted to a two-dimensional subsiliceous acid, $Si_6H_3(OH)_3$ (Kautskys' Siloxene) in a topochemical reaction, see equation (1), by a variety of acids under dry nitrogen at room

$$3CaSi_2 + 6HCl + 3H_2O \longrightarrow Si_6H_3(OH)_3 + 3CaCl_2 + 3H_2 \quad ...(1)$$

temperature.[14]

The dissolution of the Mg-Cd alloys in aqueous 0.5M $NaClO_4$ solutions ($298 \leq T/K \leq 348$) has been studied.[15,16] Selective dissolution of magnesium was observed, the solution process accelerating with increase in temperature and/or magnesium content of the alloy; cadmium was accumulated on the surfaces as a soft crystalline metallic film.[15] Anodic dissolution of the alloys at pH=5.5 led to the formation of Mg^{2+} ions; no evidence was observed for the formation of Cd^{2+} ions.[16] At low magnesium content ($0.0 \leq x_{Mg} \leq 0.074$) a continuous protective film of metallic cadmium is formed on the alloy surface.[15,16]

Structural characteristics of the intermetallic compounds, MCu (M=Sr,Ba),[17] $CaZn_3$,[18] Ca_4Hg_9[19] and $Ca_4(Hg,M)_9$ (M=Zn,Cd,Cu,Ag, Au)[19] have been obtained from X-ray diffraction studies; typical unit cell parameters are included in Table 1.

Table 1. Crystallographic parameters for a number of intermetallic Compounds.

Compound	Symmetry	Space Group	a/pm	c/pm	Ref.
MCu (M=Sr,Ba)*	hexagonal	$P6_3/mmc$	434.1	1538	17
$CaZn_3$	hexagonal	$P6_3/mmc$	916.8	732.7	18
Ca_4Hg_9	cubic(primitive)	-	1113	-	19
$Ca_4(Hg,M)$ (M=Zn,Cd,Cu, Ag,Au)*	cubic(primitive)	-	1100	-	19

* The crystallographic data refer to the element listed first.

An XPS study of $Be_{13}Ln$ (Ln=La,Ce,Gd) has confirmed the coexistence of Ce(III) ($4f'5d^o$) and Ce(IV) ($4f^o5d^o$) in $Be_{13}Ce$.[20] The relative quantities of the two oxidation states is temperature dependent; as the temperature is lowered to 100K, both the lattice parameter behaviour and the XPS spectra can be interpreted by assuming a slight increase in the Ce(IV)/Ce(III) ratio.[20]

The magnetic properties of $Mg_{17}Eu_2$ and of Mg_2Eu have been determined ($3.7 \leq T/K \leq 295$); both compounds contain Eu(II).[21] Above 50K both compounds exhibit Curie-Weiss behaviour; below 16K, $Mg_{17}Eu_2$ appears to be ferrimagnetically ordered, whereas below 30K, Mg_2Eu has an antiferromagnetic behaviour, despite the fact that the θ value is positive.[21]

2.2.4 Hydrogen Storage Applications of Magnesium and of Magnesium-rich Intermetallic Compounds

As indicated earlier, several papers dealing with the hydrogenation/dehydrogenation characteristics of magnesium,[22,23] of dilute magnesium alloys,[24] and of magnesium-rich intermetallic compounds[24-28] were presented at the 1980 International Symposium on the Properties and Applications of Metal Hydrides.[3]

Hydrogen absorption and desorption isotherms for commercially pure magnesium have been measured ($523 \leqslant T/K \leqslant 673$).[22] The kinetics of the desorption process were slower than those of the absorption process; the resultant hydride was close to stoichiometric MgH_2.[22] The effect of surface oxide[22] and of surface nickel[23] on the isotherms has been ascertained. Exposure of the magnesium surface to air does not impair the absorption ability of the metal; on the contrary, it appears that surface oxide plays an important role in the reaction.[22] The principal effect of surface nickel was to improve markedly the desorption kinetics;[23] unfortunately, the effect decayed rapidly with continued cycling, presumably because of sintering of the nickel on the magnesium surface.[23]

The rate of the reaction between hydrogen and magnesium containing small quantities of Al, Ga, In has been investigated and compared with that for pure magnesium;[24] the results were interpreted in terms of a three dimensional diffusion mechanism.

Hydrogenation/dehydrogenation characteristics of the binary intermetallic compounds Mg_2Ni,[24,25] Mg_3Al_2,[24] Mg_2Al_3,[24] Mg_2Cu,[24] MgCa,[24] $Mg_{12}Ln$ (Ln=La,Ce,mischmetal),[26] $Mg_{17}La_2$,[26] and $Mg_{41}Ce_5$.[26] Whereas Mg_2Ni yields Mg_2NiH_4 on hydrogenation, equation (2); Mg_3Al_2, Mg_2Al_3 and Mg_2Cu reversibly disproportionate to MgH_2 and the appropriate metal, equation (3); MgCa irreversibly disproportionates to MgH_2 and CaH_2, equation (4); and the intermetallic compounds containing lanthanide metals decompose during hydrogenation to give MgH_2 and LaH_3, equation (5).

$$Mg_2Ni + 2H_2 \longrightarrow Mg_2NiH_4 \qquad \ldots(2)$$

$$Mg_3Al_2 + 3H_2 \longrightarrow 3MgH_2 + 2Al \qquad \ldots(3)$$

$$MgCa + 2H_2 \longrightarrow MgH_2 + CaH_2 \qquad ...(4)$$

$$Mg_{17}La_2 + 20H_2 \longrightarrow 17MgH_2 + 2LaH_3 \qquad ...(5)$$

The effect of substitution of Mg by a first row transition metal (V-Zn) in $Mg_{12}Ce$[26,27] and by La in $MgNi_2$[28] has also been assessed in independent studies. Both sets of ternary compounds readily form hydrides at room temperature. $Mg_{11}CeM$ (M=V-Zn) evolve hydrogen, the desorption rate being markedly enhanced by the presence of the lighter transition metals (M=V-Ni);[26] $Mg_{1-x}La_xNi_2$, however, exhibit very low desorption rates, the hydrides showing a tendency to decompose into LaH_3, MgH_2 and Ni at elevated temperatures.[28] In a parallel study,[27] the structural chemistry which occurs on substitution of Mg by Ni, Cu and Zn in $Mg_{12}Ce$ has been ascertained. Substitution by Zn gives a single phase of formula $Mg_{11}CeZn$. For Ni and Cu, however, two-phase mixtures are obtained; substitution by Ni stabilises a $Mg_{17}Ce_2$-type phase in addition to Mg_2Ni, whereas substitution by Cu yields a $Mg_{12}Ce$-type phase containing a small amount of copper, in addition to Mg_2Cu.[27]

Aspects of the chemistry of Mg_2Ni[24,25,29] and of Mg_2NiH_4[24,25,29,30] were also reported at the Symposium.[3] The structural parameters of Mg_2Ni have been refined in a combined X-ray and neutron diffraction study;[25] pertinent unit cell parameters are included in Table 2. The solubility of hydrogen in Mg_2Ni has been studied and the relationship between the lattice parameters of Mg_2Ni and its hydrogen content ascertained.[24] Two independent crystallographic studies of Mg_2NiH_4 have confirmed the presence of two allotropic modifications of this material;[24,25] the crystallographic data, which are included in Table 2, are in exact agreement. The

Table 2. Crystallographic data for Mg_2Ni and for Mg_2NiH_4.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Ref.
Mg_2Ni (X-ray)	hexagonal	$P6_222$	521.6	-	1320	25
Mg_2Ni (neutron)	hexagonal	$P6_222$	519.8	-	1321	25
Mg_2NiH_4 (L.T)	orthorhombic	$P222_1$	1136	1116	912	24,25
Mg_2NiH_4 (H.T)	hexagonal	Fm3m	649	-	-	24,25

transition temperatures also agree, the value quoted by one group of authors, 508K,[25] lying within the range quoted by the other authors, 483-518K.[24] Hydrogen diffusion in $MgNiH_4$ has also been studied ($210 \leqslant T/K \leqslant 480$) using ^1H-nuclear spin lattice relaxation techniques.[30] Finally, the magnetic susceptibility of Mg_2Ni and of its hydrides has been measured as a function of field and temperature;[29] hydrogenation reduces the bulk susceptibility of Mg_2Ni.

2.3 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

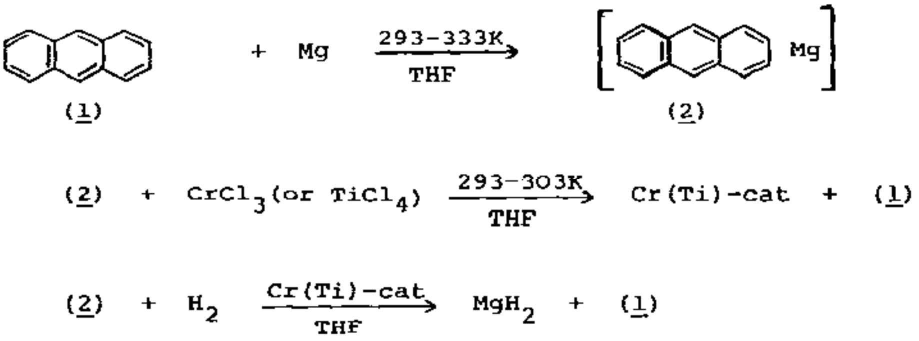
As for the 1979 review, there is a dearth of information relating to the binary derivatives of the alkaline earth metals. There has been a marked increase, however, in the number of papers abstracted for the ternary and quaternary derivatives. To accommodate this increase, this section is further subdivided than in previous reviews.

2.3.1 Binary Derivatives

Although many papers have been published in which the catalytic properties of the alkaline earth metal oxides are described, they are not considered here, since their content is of but marginal interest to the inorganic chemist.

An STO-3G basis set has been proposed for the main group elements of the third row of the Periodic Table (including calcium).[31] Equilibrium geometries calculated for CaF_2 using this minimal representation are in good agreement with available experimental data.

The chemistry of the alkaline earth metal hydrides has been reviewed.[32] MgH_2 has been catalytically synthesised (scheme 1) under extremely mild conditions via anthracene magnesium (2) as an intermediate.[33]



Scheme 1

The vapour pressure above Be_2C has been measured ($1388 \leqslant T/K \leqslant 1763$) using Knudsen-effusion mass spectrometry;[34] vaporisation occurs incongruently according to equation (6). The derived enthalpy of formation of $Be_2C(s)$ is : $\Delta H_f^{\ominus}(Be_2C,c,298.15K) = -(92.5 \pm 15.7)\,kJ\,mol^{-1}$.[34]

$$Be_2C(s) \longrightarrow 2Be(g) + C(s) \qquad \ldots(6)$$

Pauling[35] has challenged the earlier assertion of Vidal-Valat et al.[36] (reported in the 1979 review)[37] that the crystal structure of MgF_2 contains linear F-Mg-F "molecules". Pauling believes that it has a framework structure with each Mg atom forming six bonds with F atoms at the corners of a somewhat distorted octahedron; each F atom is bonded to the three nearest Mg atoms by a set of coplanar bonds with almost identical bond strength, r(Mg...F)=198.4, 199.4, 199.4pm.[35] Vidal-Valat et al.[38] have replied to Pauling's comment accepting that it is improper to speak of "molecules" in solid MgF_2. High temperature (1750K) gas phase electron diffraction studies of the molecular structure of MgF_2 have shown it to have a linear configuration in the gas phase with r(Mg...F)=177.0, r(F...F)= 343.6pm and ℓ(Mg...F)=8.9, ℓ(F...F)=16.3pm.[39]

The crystal structures of γ-$CaCl_2,4H_2O$,[40] $BaCl_2,2H_2O$[41] and $BaBr_2,2H_2O$[42] have been determined; pertinent unit cell parameters are included in Table 3.

Table 3. Crystallographic data for the monoclinic crystal structures of γ-$CaCl_2,4H_2O$,[40] $BaCl_2,2H_2O$[41] and $BaBr_2,2H_2O$.[42]

Compound	Space Group	a/pm	b/pm	c/pm	$\beta/^o$
γ-$CaCl_2,4H_2O$	$P2_1/c$	613.87	766.69	890.14	111.00
$BaCl_2,2H_2O$	$P2_1/c$	671.7	1090.0	969.6	132.7
$BaBr_2,2H_2O$	C2/c	1042.9	719.5	837.5	113.60

2.3.2 Ternary Silicides, Phosphides, Arsenides etc.

All the papers abstracted for this section describe the crystal structures of ternary compounds containing an alkaline earth metal and a transition metal; typical unit cell parameters for $BaNi_2Si_2$,[43] $CaCu_4P_2$,[44] SrM_2P_2 (M=Zn,Cd),[45] $BaCd_2X_2$ (X=P,As),[45] $BaMg_2P_2$,[45] MNi_2As_2 (M=Ca,Sr),[46] SrM_2As_2 (M=Zn,Cd)[47] and $CaMnBi_2$[48] are collected in Table 4.

2.3.3 Ternary Oxides and Chalcogenides

The only ternary compounds considered in this section are those containing an alkaline earth metal and either a transition or lanthanide metal. The synthesis of a number of novel ternary oxides has been reported.[49-61] These compounds are generally characterised using their crystallographic properties; these are summarised in Table 5. In general classical solid state reactions (e.g. high temperature reactions between alkaline earth metal oxides or oxysalts with transition metal oxides) were used as preparative routes. An interesting innovation, introduced by Muller-Buschbaum et al.,[55,58,59] is the use of a CO_2 laser to heat the reaction mixtures to the appropriate temperature.

Table 4. Crystallographic data for a number of silicides, phosphides, arsenides etc.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Reference
$BaNi_2Si_2$	orthorhombic	Cmcm	650	535	1133	43
$CaCu_4P_2$	rhombohedral	$R\bar{3}m$	403.6	–	2227.2	44
SrM_2P_2 (M=Zn,Cd)*	hexagonal	$P\bar{3}m1$	410.0	–	710.1	45
$BaCd_2X_2$ (X=P,As)*	hexagonal	$P\bar{3}m1$	440.2	–	755.7	45
$BaMg_2P_2$	hexagonal	$P\bar{3}m1$	436.7	–	758.0	45
MNi_2As_2 (M=Ca,Sr)*	tetragonal	I4/mmm	406.5	–	994.9	46
SrM_2As_2 (M=Zn,Cd)*	hexagonal	$P\bar{3}m1$	422.3	–	726.8	47
$CaMnBi_2$	tetragonal	P4/nmm	450	–	1108	48

*The crystallographic data refer to the element quoted first.

Several authors[62-68] have undertaken detailed studies of preparative routes to ternary oxides. Thus, Fotiev et al.[62-66] have considered the preparation of solid solutions of Ca in V_2O_5, of β-$Ca_xV_2O_5$ bronzes, of MV_2O_6, MV_2O_7 and $M_3V_2O_8$ (M=Mg,Ca) and of $CaFe_2O_4$ using classical solid state methods. The conditions for the hydrothermal synthesis

Table 5. Crystallographic data for a number of ternary oxides and chalcogenides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	$\beta/^{\circ}$	Ref.
$Sr_2Ti_6O_{13}$	monoclinic	C2/m	1525.0	376.9	916.4	99.15	49
$BaTi_8O_{16}$	monoclinic	C2	1420.9	297.1	998.1	133.5	50
$Mg_2Hf_5O_{12}$	rhombohedral	$R\bar{3}$	614.8	–	–	99.58	51
$BaV_{10}O_{15}$	orthorhombic	Ccmb	995.8	1161.8	941.0	–	52
$Ca_2Nb_2O_7$	monoclinic	$P2_1$	769.7	1338.5	550.2	98.34	53
$SrNb_6O_{16}$	orthorhombic	–	3715	3697	394.3	–	54
$Sr_2Fe_2O_5$	orthorhombic	Ibm2	566.1	1559.8	553.1	–	55
$BaRuO_3$	hexagonal	–	574.7	–	2160	–	56
Ba_2RuO_4	tetragonal	–	398.3	–	1342	–	56
Ba_3RuO_5	orthorhombic	–	891	448	686	–	56
$MgRh_2O_4$	cubic	Fd3m	849.1	–	–	–	57
$Sr_3La_4O_9$†	monoclinic	Cc	1165.7	734.8	1347.1	115.6	58
$Sr_3Nd_4O_9$†	monoclinic	Cc	1147.4	723.8	1324.6	115.6	59
$Ba_3M_4O_9$ (M=Sc,Gd, Tb,Dy,Ho, Er,Tm,Yb, Lu)*	hexagonal	–	579.7	–	475.2	–	60

*The crystallographic data refer to the element quoted first.

†These phases are metastable at room temperature; e.g. $Sr_3La_4O_9$ is only formed in the narrow temperature range from 2133 to 2173K.[58]

of highly dispersed $BaTiO_3$ have been defined;[67] the effect of temperature, pressure and duration of the hydrothermal process on the yield, degree of dispersion and structure of the $BaTiO_3$ product have been ascertained.[67] A mechanism for the synthesis ($873 \leq T/K \leq 973$) of $Mg_2Mo_3O_{11}$ from single crystal MgO and pelleted MoO_3 has been proposed;[68] it involves unidirectional transport of Mo(VI) via vacancies and of oxygen via the gas phase.[68]

Vibrational spectroscopic studies have been effected for $BaSc_2O_4$,[69] $Ba_2Sc_2O_5$,[69] $Ba_3Sc_4O_9$[69] and $MgRh_2O_4$;[57] the data suggest that the scandium atom in $BaSc_2O_4$ is 5-coordinate.[69] An i.r. study of the thermal decomposition of $MgCrO_4,5H_2O$[70] has shown that the pentahydrate dehydrates initially to $MgCrO_4$ which decomposes subsequently, in a single stage, forming $MgCr_2O_4$ and MgO.[70] The luminescence properties of $BaUO_4$ have also been ascertained.[71]

Thermodynamic parameters for the formation of Ba_2TiO_4,[72] $Ba_6Ti_{17}O_{40}$,[72] α-MgV_3O_8[73] and $BaUO_4$[74] have been presented. The Gibbs free energy of formation of Ba_2TiO_4 and $Ba_6Ti_{17}O_{40}$ (from the constituent oxides, BaO and TiO_2) have been calculated[72] from e.m.f. data on the basis of the corresponding Gibbs free energy of formation of $BaTiO_3$[75] : ΔG^o_{ox} $(Ba_2TiO_4, 673K) = -(182 \pm 3)kJ\ mol^{-1}$; ΔG^o_{ox} $(Ba_6Ti_{17}O_{40}, 673K) = -(1007 \pm 23)kJ\ mol^{-1}$. The value for Ba_2TiO_4 lies between the presently compiled value $-(197 \pm 16)kJ\ mol^{-1}$ and that $-(168 \pm 20)kJ\ mol^{-1}$ obtained recently from studies of the temperature dependence of equilibrium CO_2 pressures over reaction (6).

$$BaCO_3 + BaTiO_3 \rightleftharpoons Ba_2TiO_4 + CO_2 \qquad \ldots(6)$$

Thermodynamic characteristics of the oxidation of the vanadium bronze, α-$Mg_{1+x}(V_3O_8)_2$ have been determined by e.m.f. methods.[73] The enthalpy of formation and entropy of the bronze α-MgV_3O_8 are determined as : $\Delta H^o_f(\alpha\text{-}MgV_3O_8, c, 298K) = -(2917.53 \pm 0.45)kJ\ mol^{-1}$ and $S^o(\alpha\text{-}MgV_3O_8, c, 298K) = 226 \pm 9JK^{-1}mol^{-1}$.[73] The enthalpy of formation of $BaUO_4$, $\Delta H^o_f(BaUO_4, c, 298.15K) = -(1997.1 \pm 2.1)kJmol^{-1}$ has been recalculated from the results of an adiabatic calorimetric study $(5 \leq T/K \leq 350)$ of the heat capacity of $BaUO_4$.[74]

The ternary sulphide, $BaTiS_3$, has been synthesised and characterised by X-ray diffraction methods;[76] its unit cell has hexagonal symmetry, space group $P6_3/mmc$ with a=675.6 and c=579.8pm.

2.3.4 Ternary Halides

Phase relationships in the MCl-$SrCl_2$ (M=Na-Cs)[77] and in the MCl-$MgCl_2$ (M=Li-Cs)[78] systems have been elucidated using either d.t.a.[77] or Raman spectroscopic[78] methods. A number of compounds (K_2SrCl_4, $MSrCl_3$ (M=Rb,Cs) and MSr_2Cl_5 (M=K,Rb) were observed in the MCl-$SrCl_2$ (M=Na-Cs) systems.[77] The phase relationships between the various modifications of these compounds have been studied; pertinent unit cell parameters are included in Table 6.[77] Of the many compounds ($CsMg_3Cl_7$, $MMgCl_3$ (M=Na-Cs), M_2MgCl_4 (M=Na-Cs) and M_3MgCl_5 (M=K-Cs) formed in the MCl-$MgCl_2$ (M=Li-Cs) systems, only the two novel compounds, M_3MgCl_5 (M=K,Rb), and Cs_2MgCl_4 contain the discrete tetrahedral $MgCl_4^{2-}$ anion;[78] most of the other solids appear to contain distorted network octahedra with face, edge or corner shared chlorine atoms. All the solids melt to give the more stable $MgCl_4^{2-}$ moiety in the molten salt; in melts of high $MgCl_2$ concentration, evidence for equilibrium (7) was obtained. Further

$$2MgCl_4^{2-} \rightleftharpoons Mg_2Cl_7^{3-} + Cl^- \qquad ...(7)$$

evidence for the stability of the MX_4^{2-} species in the liquid phase has been obtained from a thermodynamic study of the NaF-BeF_2 system.[79] Enthalpy data ($298 \leqslant T/K \leqslant 1000$) for NaF, BeF_2, $NaBeF_3$ and Na_2BeF_4 suggest that BeF_3^- reacts with F^- on fusion to form the more stable BeF_4^{2-}.[79]

Bond energies, equilibrium distances and compressibility data have been calculated for the perovskite, $KMgF_3$, within the framework of the quantum mechanical theory of ionic crystals; fairly good agreement with experimental data was achieved.[80] ^{133}Cs-n.m.r. spectra of $CsMF_3$ (M=Ca,Sr) have been measured in an attempt to elucidate the magnetic shielding of ^{133}Cs nuclei in ionic fluorides.[81]

Ternary halides containing an alkaline earth metal with a transition or lanthanide metal have been the subject of a small number of structural communications;[82-86] pertinent unit cell parameters are included in Table 6. Kieser and Greis[84-86] have studied Ba_2LnF_7 (Ln=Dy-Lu,Y) and $Ba_4Ln_3F_{17}$ (Ce-Nd, Sm-Lu,Y). The former are only stable above ~1213K but may be obtained by quenching after annealing for several days at 1223-1273K.[84] X-ray powder diffraction[85] and single crystal electron diffraction experiments[86] on typical examples of the latter, revealed a new type of fluorite-related superstructure of symmetry R3 or $R\bar{3}$ with $a_s=0.5\sqrt{14}\,a_F$ and $c_s=2\sqrt{3}\,a_F$ (z=42); no evidence for a superstructure with $a_s=3.5\sqrt{2}\,a_F$ and $c_s=4\sqrt{3}\,a_F$ (z=588), as reported by Russian workers,[87] was found.[86]

2.3.5 Quaternary Oxides

Kemmler-Sack[88-106] has produced a staggering 19 papers on quaternary oxides containing alkaline earth metals (principally barium) during the period of this review. The majority describe

Table 6. Crystallographic data for several ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref.
K_2SrCl_4	cubic	$I\bar{4}3d$	916	–	–	–	77
$MSrCl_3$ (M=Rb,Cs)*	cubic	Pm3m	563	–	–	–	77
$MSrCl_3$ (M=Rb,Cs)*	tetragonal	P4/mbm	792	–	562	–	77
$RbSrCl_3$	monoclinic	$P2_1/m$	793	1102	767	90.1	77
$CsSrCl_3$	orthorhombic	Pnma	792	1125	792	–	77
MSr_2Cl_5 (M=K,Rb)*	monoclinic	$P2_1/c$	897	785	1260	90.2	77
$MgSrF_4$	orthorhombic	Amam	391.7	1445.9	563.7	–	82
$MgLnF_4$ (Ln=Sm,Eu)*	orthorhombic	Amam	391.5	1444	566.1	–	82
$MgVF_4$	tetragonal	$P4_2/mnm$	472.2	–	314.8	–	83
Ba_2LnF_7 (Ln=Dy–Lu,Y)*	tetragonal	–	422.7	–	599.3	–	84

*The crystallographic data refer to the element listed first.

the synthesis and characterisation (principally structural and spectroscopic) of novel hexagonal stacking polytypes with rhombohedral layer structures. Structural analyses of oxides with 5L (sequence hhccc) : $Ba_5[BaMW_2\square O_{29/2}\square_{1/2}]$ (M(V)=Nb,Ta),[88] $Ba_5[BaM_2W\square O_{29}\square]$ (M(V)=Nb,Ta)[88] – 6L(sequence $(hcc)_2$) : $Ba_4[Sc_2Ru_2O_{12}]$,[89] $Ba_4[M_2Os_2O_{12}]$ (M(II)=Co,Ni),[90] $Ba_4[M_{4/3}Ru_{4/3}Ir_{4/3}O_{12}]$ (M(III)=La,Sc,In, Nd–Yb)[91] – 9L(sequence $(hhc)_3$) : $Ba_3[NbW\square O_{17/2}\square_{1/2}]$[92] – 12L(sequence $(hhcc)_3$) : $Ba_4[M_2W\square O_{12}]$ (M(V)=Nb,Ta,[93] $(Ba_3La)[M_3\square O_{12}]$ (M(V)=Nb,Ta),[93,94] $(Ba_3La)[MW_2\square O_{12}]$ (M(III)=Sc,In,Lu,Yb)[95] $(Ba_3La)[MReW\square O_{12}]$ (M(II)=Mg,Co,Ni Cu,Zn),[96] $(Ba_2La_2)[MW_2\square O_{12}]$ (M(II)=Mg,Co,Ni,Zn),[97,98] $Sr_{4-x}Ba_x[NiRe_2\square O_{12}]$,[99] – 18L(sequence $(hhcccc)_3$) : $Ba_6[MNb_4\square O_{18}]$ (M(IV)= Ti,Zr,Hf)[100] – 27L(sequence $(hhccchhcc)_3$) : $Ba_9[M_6W\square_2O_{27}]$ (M(V)= Nb,Ta)[101,102] – structures have been accomplished. The structures of the novel 6L, 9L and 27L stacking polytypes are shown in Figure 1;

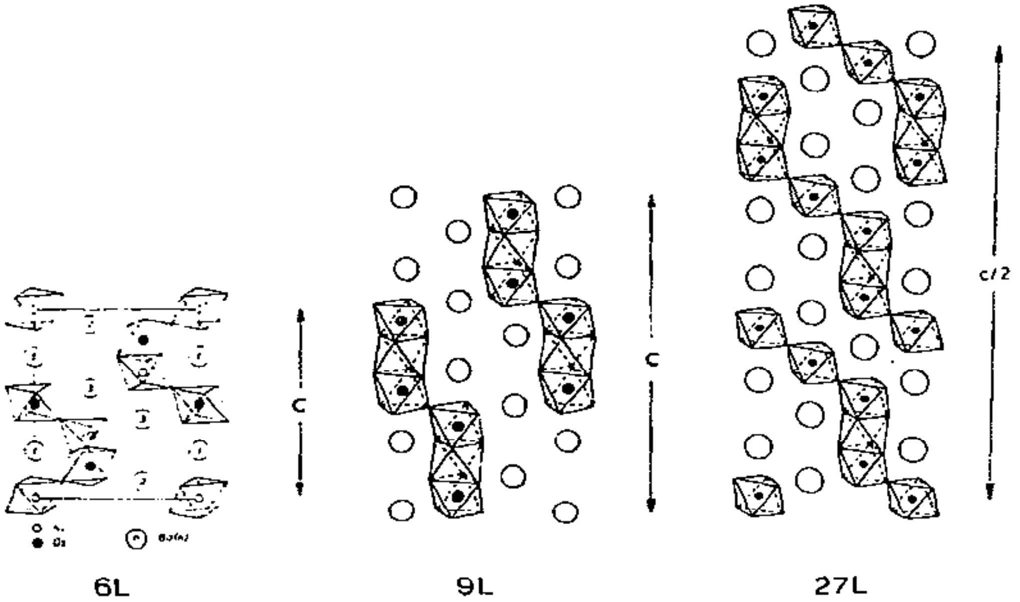


Figure 1. Hexagonal stacking polytypes with rhombohedral structures (reproduced by permission from Z. Anorg. Allg. Chem., 470(1980)95, 471(1980)102, 462(1980)166).

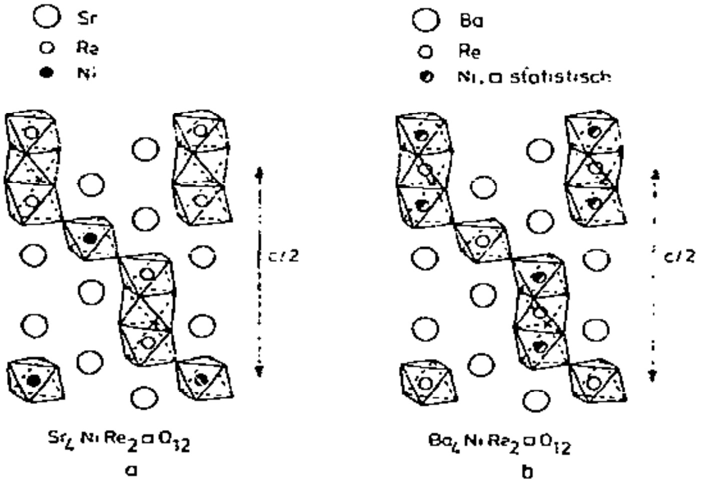


Figure 2. Polymorphism of the hexagonal 12L stacking polytypes for (a) $Sr_4[NiRe_2□O_{12}]$ and (b) $Ba_4[NiRe_2□O_{12}]$ (reproduced by permission from Z. Anorg. Allg. Chem., 469(1980)51).

Table 7. Crystallographic data for a number of hexagonal stacking polytypes with rhombohedral layer structures.

Compound	Space Group	a/pm	c/pm	Reference
$Ba_5[BaMW_2\square O_{29/2}\square_{1/2}]$ (M=Nb,Ta)	$P\bar{3}m1$	601	1240	88
$Ba_5[BaM_2W\square O_{29}\square]$ (M=Nb,Ta)	$P\bar{3}m1$	603	1240	88
$Ba_4[Sc_2Ru_2O_{12}]$	$P\bar{3}m1$	579	1422	89
$Ba_4[M_2Os_2O_{12}]$ (M=Co,Ni)	$p\bar{3}m1$	573	1408	90
$Ba_4[M_{4/3}Ru_{4/3}Ir_{4/3}O_{12}]$ (M=La,Sc,In,Nd-Yb)	$P\bar{3}m1$	595	1500	91
$Ba_3[NbW\square O_{17/2}\square_{1/2}]$	$R\bar{3}m$	588	2090	92
$Ba_4[M_2W\square O_{12}]$ (M=Nb,Ta)	$R\bar{3}m$	577	2800	93
$(Ba_3La)[M_3\square O_{12}]$ (M=Nb,Ta)	$R\bar{3}m$	575	2810	93,94
$(Ba_3La)[MW_2\square O_{12}]$ (M=Sc,In,Lu,Yb)	$R\bar{3}m$	572	2780	95
$(Ba_3La)[MReW\square O_{12}]$ (M=Mg,Co,Ni,Cu,Zn)	$R\bar{3}m$	567	2760	96
$(Ba_2La_2)[MW_2\square O_{12}]$ (M=Mg,Co,Ni,Zn)	$R\bar{3}m$	566	2740	97,98
$Sr_4[NiRe_2\square O_{12}]$	$R\bar{3}m$	553	2670	99
$Ba_4[NiRe_2\square O_{12}]$	$R\bar{3}m$	577	2800	99
$Ba_6[MNb_4\square O_{18}]$ (M=Ti,Zr,Hf)	$R\bar{3}m$	577	4240	100
$Ba_9[M_6W\square_2O_{27}]$ (M=Nb,Ta)	$R\bar{3}m$	579	6340	101,102

* The crystallographic data refer to the element listed first.

those of the 12L, 18L and 24L stacking polytypes are shown in the 1979 review.[107] Pertinent unit cell parameters are collected in Table 7. The $Sr_{4-x}Ba_x[NiRe_2\square O_{12}]$ system[99] exhibits two different 12L stacking polytypes, $Sr_4[NiRe_2\square O_{12}]$ and $Ba_4[NiRe_2\square O_{12}]$. Both crystallise in the space group $R\bar{3}m$ with the same sequence of the close packed AO_3 sheets – $(hhcc)_3$. They differ in the distribution of the rhenium and nickel atoms and of the vacancies; the differences are clearly shown in Figure 2.[99] Vibrational spectroscopic studies of the 6L(sequence $(hcc)_2$) : $Ba_4[Sc_2Ru_2O_{12}]$,[89] $Ba_4[M_2Os_2O_{12}]$ (M(II)=Co,Ni)[90] and of the 12L(sequence $(hhcc)_3$) stacking polytypes[93]: $Ba_4[M_2W\square O_{12}]$ (M=Nb,Ta), $Ba_4[CeW_2\square O_{12}]$ and $(Ba_3La)[Nb_3\square O_{12}]$, have been undertaken and factor group analyses completed.

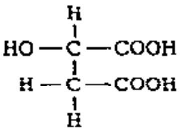
Kemmler-Sack[103-6] has also synthesised and characterised A_2BUO_6 (A,B=Ca,Sr,Ba),[103] $Ba_2[Zr_{3/4}\square_{1/4}SbO_6]$,[104] $Ba_2[Ce_{3/4}\square_{1/4}SbO_6]$,[105] and $Ba_2[M^{I}_{1/2}M^{III}_{1/2}TeO_6]$ (M(I)=Li,Na; M(III)=Sc,Y,La,Pr-Ho).[106] Russian workers have prepared the quaternary oxides, $Ba_6Ti_2Nb_8O_{30}$,[108] $BaLa_2Ti_2O_8$,[109] $BaLn_2Ti_3O_{10}$ (Ln=La,[109] Pr-Eu[110]), $BaLn_2Ti_4O_{12}$ (Ln-La,[109] Pr-Gd[110]) and $BaNd_2Mo_4O_{16}$;[111] they have been characterised by X-ray diffraction methods.[108-111]

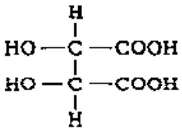
2.4 COMPOUNDS OF THE ALKALINE EARTH METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS

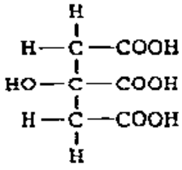
In general, the recently reported chemistry of these compounds is considered in subsections devoted to individual alkaline earth metals; data pertinent to several elements are discussed once only, in the subsection of the lightest metal considered. There are, however, two subsections in which recent advances in the fields of alkaline earth metal derivatives of carboxylic acids and of nucleosides, nucleotides and other compounds of biological significance are described.

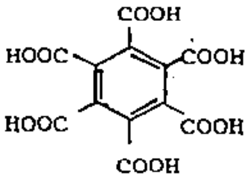
2.4.1 Salts of Carboxylic Acids

Particular interest has been shown in the salts of hydroxycarboxylic acids.[112-116] Complex formation between alkaline earth metal cations and malic acid,[112,113] tartaric acid[112] and citric acid[114] has been evaluated in aqueous solution. Potentiometric titrations (I=0.5M, $NaClO_4$; T=298K) have shown that malic acid (H_2L) complexes with Be^{2+} to form BeL, $[Be_3(OH)_3L]^+$, $[Be_3(OH)_3L_2]^-$ and $[Be_3(OH)_3L_3]^{3-}$; tartaric acid (H_2L), however, yields BeL, $[BeL_2]^{2-}$, $[Be_3(OH)_3L]^+$,


Malic Acid


Tartaric Acid


Citric Acid


Mellitic Acid

$[Be_3(OH)_3(H_{-1}L)]$ and $[Be(H_{-1}L)_2]^{4-}$ complex species.[112] Thermochemical studies (I=1.0M, $NaNO_3$; T=298K) have given the stability order of the ML complexes formed between malic acid (H_2L) and M^{2+} (M=Mg-Ba) cations:[113]

$Mg < Ca > Sr > Ba$

The sequence appears to be determined by enthalpy factors; the peculiar position of Mg^{2+} is thought to be caused by the difficulty of stable bond formation between Mg^{2+} and polydentate anions.[113] The formation constants of the complexes ($[MH_2L]^+$, MHL, $[ML]^-$) formed between citric acid (H_3L) and M^{2+} (M=Mg-Ba) have been redetermined (298K) from pH titration data.[114]

The crystal structures of the two malic acid derivatives, Magnesium (+)-malate, pentahydrate[115] and calcium di(hydrogen-l-malate), hexahydrate[116] have been determined from single crystal X-ray diffraction studies. Although the coordination geometries of the two cations in these salts are different - that for Mg^{2+} is slightly distorted octahedral whereas that for Ca^{2+} is square antiprismatic - the chemical environments are quite similar. Thus, the six oxygen atoms coordinating the Mg^{2+} cation are donated by a single bidentate malate ion (one carboxylato oxygen, and one hydroxyl oxygen) and four water molecules, r(Mg...O)=202.0-211.2pm,[11] whereas the eight oxygen atoms surrounding the Ca^{2+} cation are provided by four monodentate malate ions (two carboxylato oxygens and two hydroxyl oxygens) and four water molecules, r(Ca...O)= 241.4-259.5pm.[116]

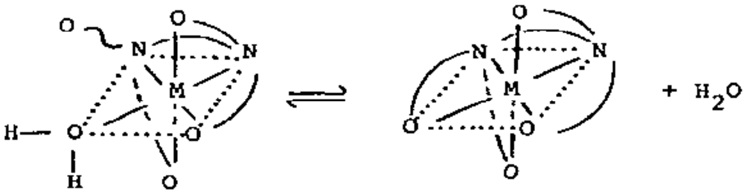
Structural studies have been completed on a number of carboxylates; these include calcium formate (β- and δ- modifications),[117] the mixed crystal between calcium and strontium formate,[117] dicalcium mono barium hexapropionate,[118] calcium succinate trihydrate,[119] and dicalcium dihydrogen mellitate, nonahydrate.[120] The results of two independent studies of the structure of β-$Ca(HCOO)_2$ have been reported in a collaborative paper.[117] The two sets of data are in agreement; the Ca^{2+} cations are coordinated by four monodentate formate anions in a square plane, r(Ca...O)=231.1, 236.4pm, and two bidentate formate anions in the corresponding apical positions, r(Ca...O)=248.4, 294.4pm.[117] The tetragonal mixed crystal between $Ca(HCOO)_2$ and $Sr(HCOO)_2$ has been prepared; it has the same structure as β-$Ca(HCOO)_2$.[117] The structure of δ-$Ca(HCOO)_2$ has also been considered; it is disordered but can be derived from that of β-$Ca(HCOO)_2$.[117]

The structure of, and disorder in, $Ca_2Ba(CH_3CH_2COO)_6$ have been studied.[118] The Ca^{2+} cation is coordinated by six monodentate propionate anions, r(Ca...O)=225.3pm, forming a trigonal antiprismatic coordination geometry; the Ba^{2+} cations, however, are octahedrally surrounded by six bidentate propionate anions, r(Ba...O)=296.5pm, giving 12 fold coordination.[118]

The distorted bicapped trigonal prismatic geometry of the Ca^{2+} cations in $Ca(CH_2COO)_2.3H_2O$ is composed of eight oxygen atoms contributed by two near symmetrical bidentate succinates, two monodentate succinates and two water molecules, r(Ca...O)=234.5-256.2pm.[119]

Two crystallographically independent Ca^{2+} cations exist in the structure of $Ca_2[C_{12}H_2O_{12}],9H_2O$; they are 7 and 8 coordinate, respectively.[120] The primary binding between the Ca^{2+} cations and the mellitate acid anions is through the formation of a four membered chelate ring utilising a bidentate carboxylate group; the Ca^{2+} coordination is completed by two monodentate (bridging) carboxylate groups and either three or four water molecules, r(Ca...O)=234.6-263.5pm.

Ultrasonic absorption has been measured in aqueous solutions of 1:1 complexes of EDTA with M^{2+}(M=Ca,Sr,Ba);[121] the absorption observed was attributed to the configurational change reaction (8)



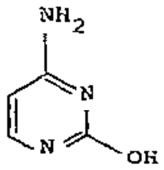
...(8)

which involves oscillation between a penta- and a hexadentate EDTA ligand. The kinetic data were discussed in relation to the coordinated water substitution rate constants of the M^{2+} cations using a step-by-step mechanism.[121] The stability constants of the M^{2+} (M=Mg-Ba) complexes, ML and ML_2 of d,ℓ-1,2-diaminopropionic-N,N,N',N'-tetraacetic acid have been determined by potentiometric pH titration.[122]

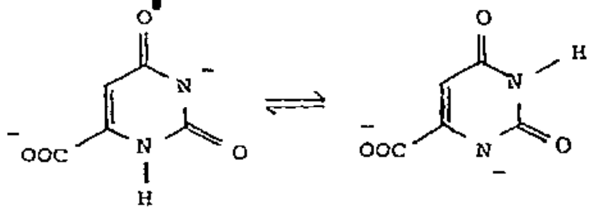
2.4.2 Complexes of significance in Bio-Inorganic Chemistry

This section has been introduced into the review to accommodate the increasing awareness and interest in the role of alkaline earth metal cations in biological systems; complexes with nucleosides, nucleotides and other biologically important molecules have been studied.

The crystal and molecular structure of the 1:1:1 $CaCl_2$:cytosine.H_2O complex has been elucidated;[123] it is the first example of a compound with direct binding of Ca^{2+} to a cytosine base. The Ca^{2+} cation is in a pentagonal bipyramidal environment; it is coordinated in the equatorial plane by two chlorine atoms, r(Ca...Cl)=279.3, 281.8pm, the nitrogen, r(Ca...N)=257.1pm, and oxygen, r(Ca...O)=257.2pm, atoms of a cytosine base and the oxygen atom, r(Ca...O)=239.8pm, of an adjacent cytosine base. The two axial positions are occupied by a chlorine atom, r(Ca...Cl)=271.4pm, and the water oxygen atom, r(Ca...O)=233.2pm.[123] The tautomeric equilibrium, (2)⇌(3), of the orotic acid dianion, is markedly affected by the presence of either Mg^{2+} or Ca^{2+} owing to the specific complexation of the N(3)-H tautomer (3);[124] estimates of the complex formation constants for both cations have been determined.

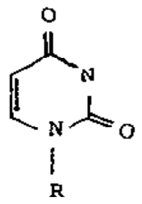


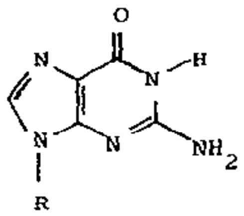
(1)
cytosine

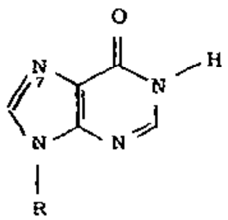


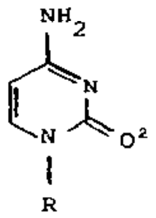
(2) (3)
tautomers of the orotic acid dianion

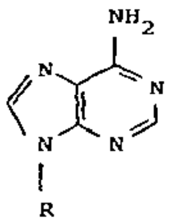
The complexation of $M(NO_3)_2$ (M=Mg-Ba) by several nucleosides (the molecular formulae of uridine, adenosine, cytidine are shown below) in DMSO has been studied using Raman and ^{13}C-n.m.r.

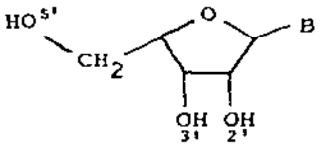

uridine


guanosine


inosine


cytidine


adenosine



ribose

R = ribose ; B = base

techniques.[125] The results suggest that the M^{2+} (M=Mg-Ba) cations have a lower affinity for nucleosides than suggested previously; of the common nucleosides, cytidine has the greatest affinity for M^{2+} which appear to bind to the base oxygen atom O(2).[125]

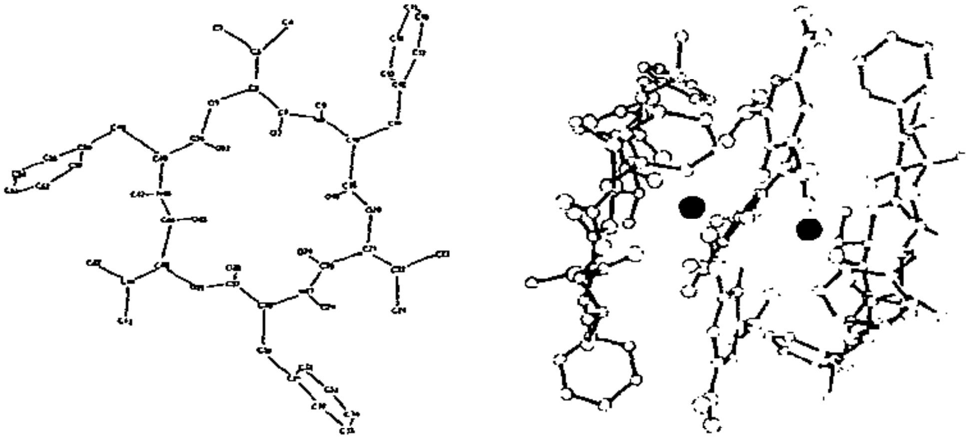
Binding of Ca^{2+} and of Ba^{2+} to nucleotides has been considered in structural investigations of a hydrated calcium salt of inosine-5'-monophosphate[126] and of a hydrated barium salt of cytidine-5'-monophosphate.[127] (The molecular formula of the parent nucleosides are shown above). In the structure of Ca[5'-IMP].6.5H$_2$O,[126] the two crystallographically independent Ca^{2+} cations are directly coordinated to only one of the two crystallographically independent nucleotides. This nucleotide directly binds one Ca^{2+} cation through N(7) of the purine ring, and the other Ca^{2+} cation through O(2') and O(3') of the ribose function and through O(2) of the phosphate moiety; the seven-fold coordination spheres of both Ca^{2+} cations are completed by oxygen atoms from water molecules. The second nucleotide forms only outer-sphere, water-mediated contacts with Ca^{2+} cations.

In the structure of Ba[5'-CMP],8.5H_2O, both crystallographically independent nucleotides bind directly to the three crystallographically independent Ba^{2+} cations.[127] Nucleotide A binds to one Ba^{2+} cation through the carbonyl oxygen of the purine ring, O(2); the 8-fold coordination sphere of this Ba^{2+} cation is completed by seven water molecules. Two nucleotide A residues also bind to a Ba^{2+} cation using the cis-hydroxyl groups of the ribose moiety; the 9-fold coordination of this Ba^{2+} cation is completed by five water molecules. The third Ba^{2+} cation is in a very similar environment, its 9-fold coordination being generated by four hydroxyl groups of two nucleotide B residues and five water molecules.[127]

A Raman study of the binding of guanosine-5'-monophosphate to, inter alia, Mg^{2+} and Ca^{2+} in aqueous solution has been undertaken.[128] Neither cation substantially perturbs the position or the intensity of the Raman bands of 5'-GMP and hence are thought to bind to the 5'-GMP either through weak ionic M^{2+}-phosphate oxygen interactions or by hydrogen bonding.[128]

The interactions of alkaline earth metal cations with antibiotics have been the subject of two separate studies.[129,130] The complexation of Ca^{2+} with the bleomycin antibiotics has been monitored by a combination of potentiometric, fluorescence and n.m.r. methods.[129] It is concluded that on complex formation, a single proton is displaced from the α-amino group of the diaminoproprionamide residues of the antibiotics.[129]

The crystal structure of the complex between the antibiotic beauvericin (Bv) and barium picrate has been determined by single-crystal X-ray diffraction methods.[130] The molecular unit is complex, having a $[Bv.Ba.Pic_3.Ba.Bv]^+.Pic^-$ formulation. The structure (Figure 3) is thus a modification of a "sandwich" complex with the important addition of three picrate molecules involved in the coordination to the Ba^{2+} cations. The 9-fold coordination of each Ba^{2+} cation is provided by the three amide group oxygens from beauvericin, r(Ba...O)=264-277pm, and three phenolic, r(Ba...O)=272-278pm, and three nitro group oxygens, r(Ba...O)= 296-307pm (considerably weaker bonds) from the picrates (Figure 3). The intimate involvement of the picrate anions in the Ba^{2+} coordination explains observations that the cation specificity of beauvericin in membrane transport depends on the species of anions present.[130]



(a) (b)

Figure 3. (a) Molecular formula and numbering scheme of beauvericin, and (b) partial structure of the beauvericin-barium picrate complex showing the $[Bv.Ba.Pic_3.Ba.Bv]^+$ molecular unit (reproduced by permission from J. Amer. Chem. Soc., 102(1980)2704).

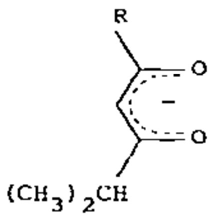
2.4.3 Beryllium Derivatives

^1H and ^9Be-n.m.r. spectroscopic studies[131] of the hydrolysis of the $[Be(H_2O)_4]^{2+}$ cation in concentrated aqueous solution have demonstrated the intermediate formation of the species, $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$ (cf. the related species formed between Be^{2+} and malic and tartaric acid in aqueous solution in section 2.4.1); the Be^{2+} ion remains in an essentially regular BeO_4 tetrahedral environment in all the species observed.[131]

UPS (HeI) of CpBeX ($X=-CH_3$, $-C{\equiv}CH$, $-C{\equiv}C-CH_3$, -Cl, -Br) have been recorded and interpreted with the help of CNDO-type calculations.[132]

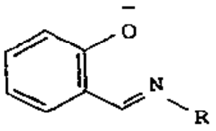
Complex formation between Be^{2+} (and, in some cases, the heavier alkaline earth metal cations) and several diverse ligands has been studied using a variety of techniques.[133-137] Vibrational spectroscopic studies of the Be^{2+} complexes with $N(CH_2COOH)_{3-x}(CH_2PO_3H_2)_x$ ($0 \leq x \leq 3$) have shown that chelate rings, typical of normal complexes, are not formed, but that the Be^{2+} cation is octahedrally coordinated by unidentate ligands and water molecules.[133] Although the formation of the N-Be bond is preferred in the case of $N(CH_2COOH)_3$, for those ligands containing phosphonic acid groups O(phosphonic acid) - Be bonds are always formed; it is concluded that a much greater negative charge resides on the phosphonic acid group oxygen atoms than on the carboxyl group oxygen atoms.[133]

Variable temperature ^1H-n.m.r. studies of the complexes formed between the bidentate ligands (4)[134] and (5)[135] and M^{2+} (M=Be-Ca,Ba) indicate that a pseudo-tetrahedral D_{2d} idealised structure is favoured for both series of complexonates.[134,135] The formation of 1:1 and 1:2 complexes of Be^{2+} with a series of N-o-tolylbenzohydroxamic acids (6) has also been studied at 298 and 308K.[136]



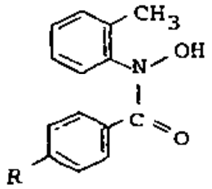
R=$-CH_3$; $-C_6H_5$

(4)



R= $-CH_3$; $-CH(CH_3)_2$

(5)



R= $-H$;$-CH_3$;$-OCH_3$;$-Cl$

(6)

Reactions of beryllium and magnesium acetylacetonates with biguanide $[H_2N-C(=NH)-N=C(-NH_2)_2]$ or N'-amidinoisourea $[H_2N-C(=NH)-N=C(-OH)-NH_2]$ in dry ethanol have produced complexes with multidentate Schiff base ligands.[137] Characterization of the products suggests that the Be^{2+} and Mg^{2+} complexes are 4- and 6-coordinate, respectively.

Prolonged heating of $(CH_3)_2Bi$ with $[(CH_3)_2SiO]_4$ in toluene yields $CH_3[(CH_3)_3SiO]Be$, which is tetramic in solution.[138] Although the pure complex, $CH_3BeN(CH_3)CH_2CH_2(C_5H_4N)$ was isolated from the reaction of $(CH_3)_2Be$ with $HN(CH_3)CH_2CH_2(C_5H_4N)$, a corresponding beryllium-phosphine complex could not be isolated from the reaction of $(CH_3)_2Be$ with $(CH_3)_2PH$, despite the fact that methane is formed during the reaction.[138] The reactions of CH_3BeH with pyridine and related species have also been examined.[138]

Reaction of $BeCl_2$ with anthracene radical anion in THF yields a crystalline polymeric organometallic compound.[139] Hydrolysis of this highly reactive product gives 9,9',10,10'-tetrahydro-9,9'-bianthryl; hydrolysis with D_2O affords exclusively the trans-10-d,-

trans-10'-d product. The structure of the beryllium polymer as hypothesised on the basis of these results is shown in Figure 4. Reaction of $BeCl_2$ with anthracene dianion in THF leads to cleavage of the solvent and formation of cis-9,10-dihydro-9,10-bis(4-hydroxybutyl)anthracene.[139]

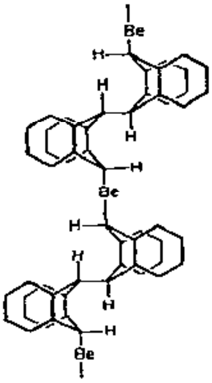


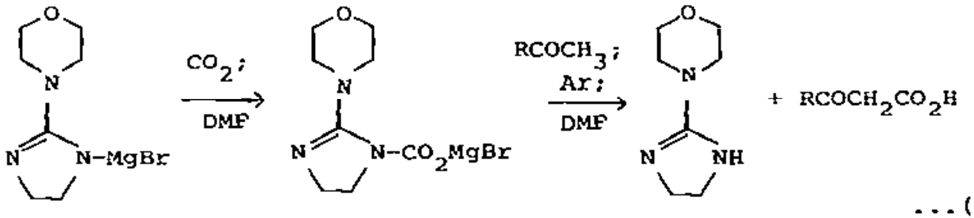
Figure 4. Hypothesised structure of the beryllium polymer formed on reaction of $BeCl_2$ with anthracene radical anion (reproduced by permission from J. Organomet. Chem., 197(1980)123).

2.4.4 Magnesium Derivatives

Although there are a vast number of publications dealing with magnesium chemistry, those abstracted for this review are relatively few in number, emphasis being placed on the inorganic chemistry of magnesium. The organometallic chemistry of magnesium, which accounts for the majority of these papers, is generally ignored since it is raviewed in detail elsewhere. An exception to this omission is a comprehensive study of the mechanism of the formation of Grignard reagents by Whitesides et al.[140-144] They have measured the kinetics of the reaction in diethyl ether of magnesium with alkyl chlorides,[140,141] alkyl bromides,[140,142] alkyl iodides[140] and aryl bromides.[143] It is concluded that the rate of the reaction of the organic halides with magnesium is proportional to halide concentration and magnesium surface area.[140] The rate-structure profile for the reductive cleavage of the carbon-halogen bond by magnesium is compared to that of tri-n-butyltin hydride and lithium-4,4'-dimethylbenzophenone ketyl.[141,143] Whitesides et al.[144] have also put forward evidence for the formation of alkyl radicals as intermediates in the preparation of Grignard reagents. ^{1}H-n.m.r. studies of the Grignard reaction and related reactions have also indicated that alkyl radicals are generated in the Grignard reaction proper, rather than in unrelated side reactions such as Wurtz coupling or metal-halogen exchange.[145]

The molecular structure of $((CH_3)_3CCH_2)_2Mg$ has been determined by gas phase electron diffraction.[146] It has a linear C-Mg-C bridge (C-Mg-C = 180°) with $r(Mg...C)=212.6$ and $\ell(Mg...C)=8.6$pm; other significant structural parameters are Mg-C-C = 118.3° and $r(C...C)=154.1$pm.[146] The solution structure of allyl magnesium bromide has been inferred from a ^{13}C-n.m.r. study of a number of deuterium-free and monodeuterated allylmagnesium bromide derivatives in THF and in diethyl ether.[147] It is concluded that it has a mono-hapto ("σ-compound") structure in contrast to allyllithium which has a bihapto ("π-compound") structure (section 1.6.6).[147]

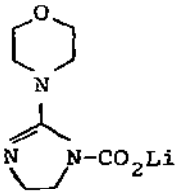
The magnesium complex (7) has been found to undergo fixation of CO_2;[148] the resulting complex (8) readily transfers the carboxylato group to active methylene compounds (eg. $C_6H_5COCH_3$ - equation (9)).



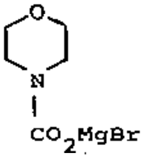
(7) (8)

...(9)

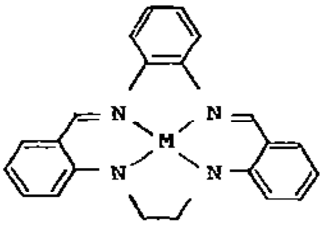
The transcarboxylating ability of (8) has been compared with those of (9) and (10).[148]



(9)



(10)



(11) M=2H; (12) M=Mg; (13) M=VO

The neutral Mg(II) complex (12) has been prepared by reaction of the planar conjugated macrocyclic ligand (11) with Grignard reagents in diethyl ether.[149] It is susceptible to hydrolysis (yielding the free ligand) and readily undergoes a transmetallation reaction to give a square pyramidal oxovanadium(IV) complex (13), the structure of which has been determined by X-ray crystallography.[149]

The magnesium amides, $Mg(NHi\text{-}Pr)_2$, $Mg(N(C_2H_5)_2)_2$ and $Mg(NC_5H_{10})_2$ have been prepared by direct synthesis from magnesium and the appropriate amine, at high temperature and under a hydrogen overpressure.[150] Under identical conditions, $t\text{-}BuNH_2$ gave $NMg_6(NHt\text{-}Bu)_9$ and an insoluble material, probably $(MgNR)_x$.[150] The structure of $NMg_6(NHt\text{-}Bu)_9$ (Figure 5) has been elucidated by single crystal X-ray diffraction methods. It consists essentially of a nitride atom surrounded by six approximately equidistant magnesium atoms, r(Mg...N)=213.3-217.4pm., which are disposed in a nearly perfect trigonal prismatic geometry. In addition to the nitride atom, each magnesium atom is tetrahedrally coordinated to three bridging nitrogen atoms, r(Mg...N)=204.3-212.5pm., giving rise to nine four membered $\overline{\text{Mg-N(nitride)-Mg-N}}$(bridging) approximately planar rings (Figure 5).[150]

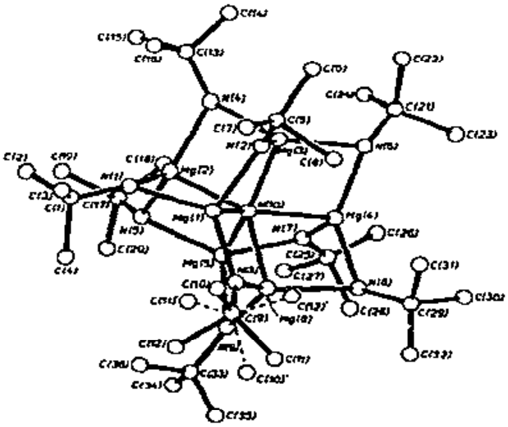


Figure 5. Perspective view of the $NMg_6(NHt\text{-}Bu)_9$ molecule (reproduced by permission from J. Organomet. Chem., 190(1980)229).

Dimethylmagnesium.(TMEDA) has been prepared from $(CH_3)_2Mg$ and TMEDA.[151] It has been studied by X-ray diffraction methods; the magnesium atom is tetrahedrally coordinated by two methyl groups, r(Mg...C)=216.6pm, and the bidentate TMEDA chelating ligand, r(Mg...N)=222.7, 225.7pm. The structure is very similar to that of $(C_6H_5)_2$Mg.TMEDA.[151]

The crystal structures of $[Mg(urea)_4(H_2O)_2]Br_2$[152] and of $[Mg(H_2O)_6]_2[CaCl_6]$ (tachyhydrite)[153,154] have been determined. In the urea complex, the Mg^{2+} cation is octahedrally surrounded by six oxygen atoms, provided by four urea molecules, r(Mg...O)=205.0, 207.8pm., and two water molecules, r(Mg...O)=210.8pm.[152] The structure of tachyhydrite, which was determined by two independent groups of authors,[153,154] is composed of $[Mg(H_2O)_6]$ and $[CaCl_6]$ octahedra. The internuclear distances differ but marginally between the determinations : r(Mg...O)=205.5, 205.9[153] (205.9, 206.2),[154] r(Ca...Cl)=275.0[153] (275.2)[154]pm.

2.4.5 Calcium, Strontium and Barium Derivatives

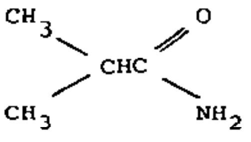
The geometries of some 150 examples of $Ca^{2+}...H_2O$ interactions in crystalline hydrates have been reviewed.[155] The Ca^{2+} cation generally lies near the plane bisecting the H_2O molecule, although the angle, θ, between the Ca...O vector and the H_2O dipole vector covers a wide range. There is an apparent correlation between r(Ca...O) and θ; examples with small r values have Ca^{2+} cations more nearly colinear with the H_2O dipole. It is concluded that the Ca...O interactions involve factors that impose significant constraints on the geometries of the resultant complexes.[155]

The crystal structure of trisglycine calcium bromide has been elucidated.[156] It contains two crystallographically independent Ca^{2+} cations, both of which are coordinated by six oxygen atoms (of the glycine (NH_2CH_2COOH) moieties), r(Ca...O)=234-272 (232-257)pm and one bromine anion, r(Ca...Br)=292(302)pm. The two Ca^{2+} coordination polyhedra are linked by an edge to form distorted pentagonal bipyramids.[156]

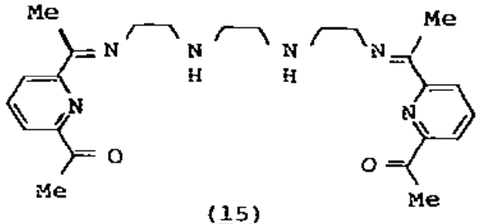
$M(OH)_2.nH_2O$ (M=Sr, n=1,8; M=Ba, n=1,3,8) have been synthesised and characterised by X-ray diffraction methods.[157]

The extraction of Ba^{2+} from nitric acid solutions into nitrobenzene containing $H^+[(\pi-(3)-1,2-B_9C_2H_{11})_2Co]^-$ has been studied and compared with that of the lighter alkaline earth metals.[158] The average hydration number of Ba^{2+} in the organic phase was determined as 11.5±1; the individual extraction constants for the alkaline earth (and alkali) metal cations correlate well with their hydration numbers.[158]

Single crystal X-ray diffraction studies have been completed for the two barium complexes, $[Ba(\underline{14})_4(ClO_4)_2(H_2O)]$[159] and $[Ba(\underline{15})(ClO_4)_2]$.[160] Analysis of the structure of the dimethyl-

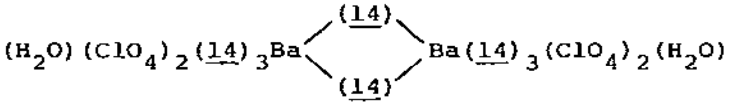


(14)



(15)

acetamide complex[160] shows that it is a binuclear centrosymmetric moiety with the following formulation:



$$(H_2O)(ClO_4)_2(\underline{14})_3\mathrm{Ba}\overset{(\underline{14})}{\underset{(\underline{14})}{\qquad}}\mathrm{Ba}(\underline{14})_3(ClO_4)_2(H_2O)$$

Thus the Ba^{2+} cations are coordinated by eight oxygen atom provided by five amide residues (two bridging, three terminal) r(Ba...O)= 264.1-276.2pm, two perchlorate anions, r(Ba...O)=274.8,288.6pm and one water molecule, r(Ba...O)=272.9pm.[159] In the centrosymmetric diketone structure,[160] the Ba^{2+} cation is 10-coordinate, being bonded to all eight donor atoms of the diketone (15) r(Ba...O)= 281pm, r(Ba...N)=287-292pm, and to two oxygen atoms of ClO_4^- anions, r(Ba...O)=288pm. The conformation of the ligand is such that the two planar keto-pyridylimine residues are inclined at 80.2° to each other forming a cleft in which the two ketonic carbon atoms are separated by 5.21Å. It is suggested that the failure of (15) to ring close in the reaction of $[Ba(\underline{15})(ClO_4)_2]$ with a range of primary diamines of varying chain length, is due to a steric barrier to the entry of the difunctional nucleophile into the cleft.[160]

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