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Chapter 2

ELEMENTS OF GROUP 2

Peter Hubberstey

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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 presently of interest and significance. Some subjects (eg. complexes of crowns, cryptands and related molecules) are common to Group 1 and Group 2 elements, for these the published data are discussed in the appropriate section of Chapter 1. Other topics are unique to the Group 2 elements; for these the published data are covered in this Chapter.

A surprisingly small number of papers describing the chemistry of metals and intermetallic compounds has been abstracted this year. Consequently, it has been decided to omit this section from the present review, the few publications available being considered in other appropriate sections. In particular, those reporting aspects of the chemistry of hydrogen storage materials are discussed in the subsection for ternary derivatives.

Density data have been presented for liquid Mg-X (X = Ca,Sr,Ba) metallic solutions.[2] Positive excess densities were derived for all three systems indicating the formation of clusters. As for the corresponding enthalpy of mixing data, the maxima in the density-concentration isotherms occur at ~50 mole% Mg in the Mg-Ca solutions and at ~66 mole% Mg in the Mg-Sr and Mg-Ba solutions implying preferred packing (or perhaps complexes) with atomic ratios of 1:1 for the former and 2:1 for the latter systems.

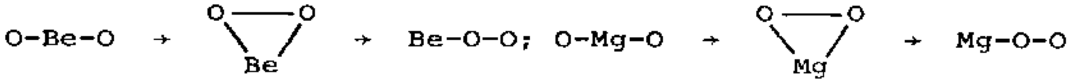
2.2 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

In view of the continuing low level of interest in these materials, the ideality of the 1985 review,[3] in which the abstracted papers are discussed under the two broad subject headings of 'binary derivatives' and 'ternary derivatives', has been retained. To avoid duplication with other Chapters of this review, the ternary compounds considered do not include those which contain a metal from the p-block of the Periodic Table.

2.2.1 Binary Derivatives

As for previous reviews, the many papers describing the catalytic properties of the alkaline earth metal oxides are not considered here, since they are of but peripheral interest to the inorganic chemist.

The potential surfaces for the singlet and triplet rearrangements:



have been studied by non-empirical Hartree-Fock methods with 4-31G and 6-31G**(beryllium)[4] and with 3-21G and DEHD + P(magnesium)[5] basis sets. Equilibrium geometric parameters of the isomers are collated in Table 1. For the singlet rearrangement, the minimum energy corresponds to the cyclic isomer. For the triplet rearrangements, however, the cyclic configuration does not even feature in the potential surface, the ground state isomer being the symmetrical linear OMO species.

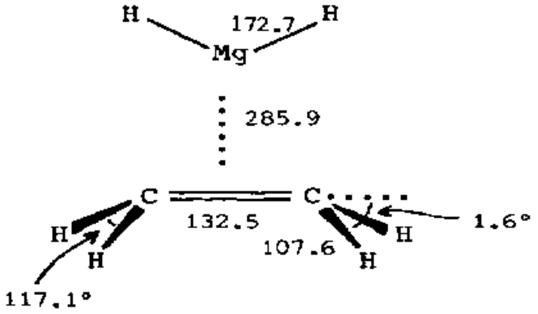
Ab initio theoretical calculations of the reactions of HF with Mg or Mg_2,[6] of HCl with Mg[6] and of C_2H_4 with MgH_2[7] have been completed. Comparison of the HF-Mg and HF-Mg_2 systems[6] indicated that simple Mg insertion into HF is energetically competitive with the side-on reaction of Mg_2 with HF and that radical formation is facilitated by involvement of a second Mg atom. Comparison of Mg insertion into HF and HCl[6] revealed similar transition state structures, that for the HCl-Mg system having the lower activation energy barrier. The potential energy

<u>Table 1.</u> Equilibrium geometric parameters for the isomers involved in the OMO → MOO (M = Be,Mg) rearrangements.[4,5]

Isomer*	r(M...O)/pm		r(O...O)/pm		θ(MOO)/°	
	Be	Mg	Be	Mg	Be	Mg
MOO (T)	140	179	130	130	-	-
MOO (S)	129	168	146	145	-	-
OMO (T)	145	190	-	-	-	-
OMO (S)	141	182	-	-	-	-
O-O \ / M (S)	144	177	159	175	67	59

*(S) and (T) represent singlet and triplet state, respectively.

curve for the insertion of C_2H_4 into MgH_2[7] exhibits a minimum corresponding to the formation of a weak π-complex (1). The dissociation energy of this complex, calculated using a 6-31G** basis set, is 22 kJ mol^{-1}. When correlation energies are included this increases to 29 kJ mol^{-1}.[7]



(1)

distances/pm.

A series of strontium polysulphides including SrS_2 has been prepared and characterised by XRD and vibrational (i.r. and Raman) spectroscopic analyses;[8] the data are compared with those for the corresponding barium derivatives.

Structural analyses have been reported for $MgCl_2,6H_2O$,[9] $MgCl_2$,4thf,[10] $MgCl_2$,2thf[10] and $MgBr_2$,5thf,$7H_2O$.[11] The structure of the hexahydrate, previously determined using X-ray diffraction methods, was re-examined using neutron diffraction methods to locate the hydrogen atoms.[9] The Mg and Cl atoms are located on a pseudo-3-fold symmetry axis and are bridged by water molecules forming a

$$Cl^- \cdot\cdot (H_2O)_3 \cdot\cdot Mg^{2+} \cdot\cdot (H_2O)_3 \cdot\cdot Cl^-$$

moiety with crystallographic point group symmetry 2/m. The oxygens of the six water molecules form an almost perfect octahedron about the Mg atom (205.7, 206.2pm) while the Cl atom is coordinated by eight hydrogens from eight water molecules (221-290pm) in a bicapped trigonal prismatic arrangement.[9]

The structures of the thf and thf-water adducts were investigated for the first time using X-ray diffraction methods.[10,11] $MgCl_2$,4thf,[10] which can be isolated from the $MgCl_2$-thf system at T < 301K, is a trans-dichlorotetrakis(thf)-

magnesium(II) complex; $MgCl_2$,2thf,[10] which is similarly prepared but at $T > 301K$, is a polymeric catena-di-μ-dichloro-trans-bis(thf)-magnesium(II) complex. $2MgBr_2$.5thf.$7H_2O$,[11] obtained by recrystallisation from thf of the product of the reaction of magnesium with bromine in ether containing 0.1 wt% H_2O, contains three crystallographically independent Mg atoms. Mg(1) is located in a general position; it is surrounded by three thf molecules (207.1-210.6pm) and three water molecules (204.8-206.6 pm) in the form of an octahedral meridional isomer. Mg(2) and Mg(3) are located at a centre of symmetry and on a 2-fold axis, respectively; they are each coordinated by two trans located thf molecules (r(Mg(2)...O) = 209.8pm; r(Mg(3)...O) = 208.1,213.1pm) and four water molecules (r(Mg(2)...O) = 206.7,207.5pm; r(Mg(3)...O) = 205.1,208.6pm).

Total lattice energy calculations have been performed for $CaCl_2,nH_2O$ (n = 0,2,4,6).[12] Two models based on either multipole moment calculations or a point charge evaluation of the electrostatic energy, were employed. The data are compared with the Born-Haber cycle lattice energies in Table 2. In keeping with the results of a recent study of $NaBr,2H_2O$[13] the calculated values are 3-4% lower than the experimental ones.[12,13]

<u>Table 2</u>. Lattice energy data for $CaCl_2,nH_2O$ (n = 0,2,4,6)[12] and $NaBr,2H_2O$.[13]

Halide	Lattice energy/kJ mol^{-1}		
	Calculated data		Experimental data
	Multipole moment	Point charge	Born-Haber
$CaCl_2$	-	-2159	-2232
$CaCl_2,2H_2O$	-2400	-2320	-2352
α-$CaCl_2,4H_2O$	-2233	-2297	-
β-$CaCl_2,4H_2O$	-2285	-2396	2470
γ-$CaCl_2,4H_2O$	-	-2354	-
$CaCl_2,6H_2O$	-2320	-2481	-2575
$NaBr,2H_2O$	- 802.7	- 805.1	- 841

2.2.2 Ternary Derivatives

A sintering technique ($620 < T/K < 770$; $40 < p/bar < 60$) has been used to prepare Mg_2CoH_5 and Mg_2CoD_5 as black crystalline solids.[14] At ambient temperatures, they adopt a tetragonally distorted CaF_2-type metal atom structure in which the hydrogens surround the Co atom in an ordered square pyramidal configuration (for Mg_2CoD_5; r(Co...D) = 159.0(axial), 151.5(equatorial)pm). At 488(5)K, the structure transforms into a disordered cubic modification. Pertinent unit cell parameters for both modifications of $MgCo_2D_5$ are collected in Table 3.

A novel electrochemical technique employing a low temperature molten salt galvanic cell of the type:

(-)Na | NaH in $NaAlEt_4$ (m.pt.=401K) | Metal alloy(hydride) (+)

has been developed to study and control hydrogen storage in ternary hydrides.[15] Thermodynamic data for the Mg-Ni-H, Mg-Cu-H and Mg-Al-H systems have been determined as a function of hydrogen content at 415 and 443K. They are in excellent agreement with data obtained by conventional P-T experiments. For example, $\Delta G^\circ_f(MgH_2,c,415K) = -20.1$ kJ mol^{-1} compared with literature values ranging from -17.6 to -20.9 kJ mol^{-1}.

Structural characterisation of the novel ternary borides, $Mg_2Ru_5B_4$ and $Mg_5Ru_{13}B_{11}$, prepared by high temperature reaction of the elements in sealed Ta crucibles, has been reported by Schweitzer and Jung;[16] pertinent unit cell parameters are included in table 3.

Crystallographic data have been published for metastable modifications of $SrCoO_3$[17] and $Ca_2Ta_2O_7$,[18] for the mixed valence strontium niobium oxides $Sr_5Nb_5O_{16}$ ($\equiv Sr_5Nb_3{}^{IV}Nb_2{}^{V}O_{16}$)[19] and $Sr_7Nb_6O_{21}$ ($\equiv Sr_7Nb_2{}^{IV}Nb_4{}^{V}O_{21}$),[20] and for the mixed alkaline earth metal derivative, $Ba_2SrLu_{22}O_{36}$;[21] they are collected in Table 3. Whereas the latter three oxides were obtained by Muller-Buschbaum et al[19-21] using classical solid state techniques the former two oxides were synthesised by independent groups of Russian authors[17,18] using less familiar methods. Metastable $SrCoO_3$ was prepared[17] by heating a mixture of $Sr(NO_3)_2$ and $Co(NO_3)_2$ in a stream of oxygen at 1173 and 1373K with subsequent stabilisation of the product at elevated temperature (1273K) and pressure (65×10^8 Nm^{-2}). When heated under ambient pressure conditions to

Table 3. Crystallographic parameters for diverse ternary hydrides, borides, and oxides.

	Symmetry	Space Group	a/pm	b/pm	c/pm	Ref
Mg_2CoD_5 (T=298K)	Tetragonal	P4/nmm	446.3	–	659.3	14
Mg_2CoD_5 (T=498K)	Cubic	–	654.3	–	–	14
$Mg_2Ru_5B_4$	Orthorhombic	Pbam	1000.0	837.6	295.4	16
$Mg_5Ru_{13}B_{11}$	Orthorhombic	Pbam	2190.1	996.7	294.7	16
$SrCoO_3$	Cubic	–	384.0	–	–	17
$Ca_2Ta_2O_7$	Orthorhombic	–	2675	770	550	18
$Sr_5Nb_5O_{16}$	Orthorhombic	$Pmn2_1$	399.2	3247.6	567.7	19
$Sr_7Nb_6O_{21}$	Rhombohedral	$R\overline{3}$	567.0	–	4836.4	20
$Ba_2SrLu_{22}O_{36}$	Hexagonal	$P6_3/m$	1760	–	333	21

$T > 883K$ it decomposes into SrO and Co_3O_4.[17] Samples of $Ca_2Ta_2O_7$ produced[18] by simultaneous precipitation of the appropriate hydroxide oxalates followed by heating at 1173–1373K for 8 hours contain two phases: the well known phase with the pyrochlore structure and the previously unknown metastable phase with a layer perovskite structure. Heat treatment of the two phase mixture results in the irreversible formation of the pyrochlore phase.[18]

The high temperature phases of $CaTa_2O_6$ and $CaTa_4O_{11}$ have been studied using high resolution transmission electron microscopy.[22] Comparison of the data with simulated images obtained using different values of crystal thickness and defocus shows the validity of the chosen computational method.

The oxygen deficient perovskite phase $SrFeO_{3-x}$ ($0.15 < x < 0.25$) has been characterised using ^{57}Fe Mössbauer spectroscopy, XRD and magnetic susceptibility measurements.[23] At low temperatures ($T < 550K$), there is evidence for the presence of three chemically distinct Fe atoms; at high temperatures ($T > 550K$), however, thermally activated electron transfer processes occur resulting in only one type of Fe atom.

Vibrational (i.r. and Raman) spectroscopic studies[24] of the Sr_3WO_6–Ba_3WO_6 system indicate the presence of five homogeneity ranges and confirm that a continuous series of solid solutions does not occur in this system.

The ternary halides considered in the papers abstracted for this review fall conveniently into two groups; those containing an alkali metal or ammonium cation together with the alkaline earth metal[25-28] and those containing a transition or lanthanide metal in addition to the alkaline earth metal.[29-31]

Dta studies of the LiCl-$BeCl_2$ system[25] have confirmed the presence of the compound, Li_2BeCl_4, which decomposes in a peritectic reaction at 623K. Physicochemical analysis (density, electrical conductivity) of the molten state indicate a complex structure for the fused salt.

The polymorphism of $KCaCl_3$[26] and of NH_4BeF_3[27] has been studied using XRD methods; novel details are given in Table 4. Single crystal studies of the high temperature phases of NH_4BeF_3 (NH_4BeF_3-II and NH_4BeF_3-I) indicate that the Be atoms retain the same tetrahedral coordination geometry through the high temperature transition. Neither the terminal Be-F bond (156.1, 158.5pm in II; 153.2, 156.6pm in I) nor the bridging Be-F bond (150.3, 150.8pm in II; 144.9, 144.9pm in I) nor the θFBeF angles (104.9-114.2° in II; 106.4-111.3° in I) change significantly. The major differences lie in the conformations of the $[BeF_3]_n$ chains, the N-H...F hydrogen bonding and the orientation of the NH_4^+ cations.[27]

A detailed study[28] using electrical conductivity, thermal, crystal-optical and XRD analyses of the NaCl-$KMgCl_3$ system has revealed the presence of $NaKMgCl_4$. Interplanar spacings are quoted for this material but no structural data.[28]

Thermodynamic data (298K) for the synproportionation of the KCl-MCl_2 (M = Mg,Ca) systems have been determined from e.m.f. data for a galvanic cell with solid electrolyte.[26] Enthalpy, entropy and free energy data for $KMCl_3$ (M = Mg,Ca)[26] are compared with similar earlier data[32,33] for other diverse $M_nM'Cl_{n+2}$ (M = K, Rb; M' = Ca-Sr) ternary halides in Table 5. With the exception of $RbSrCl_3$, the synproportionation is both exothermic and exoergic. For $RbSrCl_3$, an enthalpy loss is compensated by an entropy gain giving an exoergic process (Table 5).

Phase relationships in the MF_2 (M = Mg-Sr)-MnF_2[29] and MCl_2 (M = Sr,Ba)-$LnCl_3$ (Ln = La,Sm,Gd,Yb)[30] systems have been elucidated using d.t.a methods. Although compounds were not found in the

Table 4. The polymorphism of $KCaCl_3$[26] and of NH_4BeF_3[27] (Temperatures/K)

$$\begin{tikzcd} \mathrm{KCaCl_3}: & \mathrm{III} \arrow[r, shift left, "816"] & \mathrm{II} \arrow[l, shift left] \arrow[r, shift left, "907"] & \mathrm{I} \arrow[l, shift left] \end{tikzcd}$$

$$\begin{tikzcd} \mathrm{NH_4BeF_3}: & \mathrm{IV} \arrow[r, shift left, "253"] & \mathrm{III} \arrow[l, shift left, "245"] \arrow[r, "334"] & \mathrm{II} \arrow[r, shift left, "347"] \arrow[ll, bend left, "245"] & \mathrm{I} \arrow[l, shift left, "340"] \end{tikzcd}$$

Modification	Symmetry	Space Group	a/pm	b/pm	c/pm
$KCaCl_3$-III	orthorhombic	Pnma	756.1	1048.0	725.5
$KCaCl_3$-II	tetragonal	P4/mbm	755.3	-	535.0
$KCaCl_3$-I	cubic	Pm3m	536.5	-	-
NH_4BeF_3-II	orthorhombic	$P2_12_12_1$	566.1	460.0	1299.0
NH_4BeF_3-I	orthorhombic	Pmnb	574.3	464.3	1278.9

MF_2 (M = Mg,Ca)-MnF_2 systems, a single ternary halide, $SrMnF_4$, was discovered in the SrF_2-MnF_2 system;[29] it has a limited thermal stability range, existing between 960 and 1085K. Several diverse ternary chlorides were observed in the MCl_2 (M = Sr,Ba)-$LnCl_3$ (Ln = La,Sm,Gd,Yb) systems.[30] Positive evidence is provided for $BaLnCl_5$ (Ln = Sm,Gd), Sr_2LnCl_7 (Ln = Sm,Gd), Ba_2LnCl_7 (Ln = La,Sm, Gd,Yb) and Ba_3YbCl_9 all of which decompose in peritectic reactions. Circumstantial evidence is provided for Sr_2LnCl_7 (Ln = La,Yb), Sr_3YbCl_9 and Sr_4SmCl_{11}, which decompose in peritectic reactions, and for Ba_3SmCl_9 and Sr_4GdCl_{11} which decompose in peritectic reactions. Enthalpy of mixing data were also measured calorimetrically for the $SrCl_2$-$LnCl_3$ (Ln = La,Gd,Yb) systems;[30] the values are exothermic with minima close to $x_{SrCl_2} = 0.65$.

A single compound containing two alkaline earth metals, $CaBaCrF_7$, has been reported.[31] Characterised using XRD methods it is monoclinic, space group P2/n with a = 539.8, b = 542.2, c = 1900.6pm and β = 92.10°.

Table 5. Thermodynamic data (298K) for the formation of $M_nM'Cl_{2+n}$ by the synproportionation of MCl (M = K,Rb) and $M'Cl_2$ (M' = Ca-Sr).

Ternary Halide	ΔH°/kJ mol^{-1}	-TΔS°/kJ mol^{-1}	ΔG°/kJ mol^{-1}	Ref
$K_{0.5}SrCl_{2.5}$	-5.1	0	-5.1	32
$Rb_{0.5}SrCl_{2.5}$	-10.1	+1.0	-9.1	33
$KMgCl_3$	-8.7	-5.0	-13.7	26
$KCaCl_3$	-12.4	-2.9	-15.3	26
$RbMgCl_3$	-27.1	-1.8	-23.9	33
$RbCaCl_3$	-23.1	-2.8	-25.9	33
$RbSrCl_3$	+5.4	-6.4	-1.0	33

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

Approximately half of the papers abstracted for this section fall into one of three categories of current and specialized interest; namely, complexes of significance in bioinorganic chemistry, complex formation in solution and salts of carboxylic acids. Consequently, subsections covering these topics are included prior to subsections devoted to the individual alkaline earth metals. The latter are included to cover the remainder of the abstracted papers which report on diverse and fragmented topics; of these papers, those which allude to more than one alkaline earth metal are considered once only in the subsection devoted to the lightest element mentioned.

2.3.1 Complexes of Significance in Bioinorganic Chemistry

Biologically active ligands for which complexation of alkaline earth metals has been reported during 1985 can be categorised as either amino acids and peptides,[34-37] antibiotics,[38-42] nucleosides and nucleotides[43-45] or saccharides.[46-48]

Complex formation between alkaline earth metal cations and the amino acids, glycine,[34] leucine,[35] and hydroxy-L-proline[36] has been studied in the solid state. The isolation of the crystalline hydrates $BaI_2,n(CH_2(NH_2)COOH),2H_2O$ (n = 2,3), and $BaI_2,4(CH_2(NH_2)COOH),H_2O$ and $MgCl_2,2(CH_3)_2CHCH_2CH(NH_2)COOH,2H_2O$

from aqueous mixtures of BaI_2 and glycine[34] and of $MgCl_2$ and leucine[35] has been reported by Kydynov et al. The crystallisation of pentaaquobis(hydroxy-L-prolinato)calcium from aqueous solutions of $CaCl_2$ and hydroxy-L-proline at pH = 11 has been described by Kim et al.[36] Structural elucidation of the latter complex[36] has shown the Ca atom to be located in a 7-fold (distorted pentagonal bipyramidal) coordination sphere provided by the two carbonyl oxygens (233.0,236.7pm) and the two nitrogens (259.5,261.3pm) from the two amino acid residues and by three water molecules (234.5-245.2pm). Structural comparisons with eleven other calcium amino acid complexes indicate that binding of the Ca atom to nitrogen only occurs in crystals grown from solutions of $pH > 10$.[36]

Several cyclic octa- and decapeptides have been prepared and their ion selectivity in solvent polymeric membranes studied.[37] Cyclo$(-LPro-DLeu-)_5$ exhibits selectivity for Mg^{2+} over Ca^{2+} by a factor of ~100 but cyclo$(-LPro-LLeu-)_5$ is ineffective. The latter ionophore, however, exhibits selectivity for Mg^{2+} over Li^+, Na^+ and K^+ by factors of ~400, ~200 and ~10, respectively.[37]

The antibiotic calcimycine (A23187) has been shown to exhibit selectivity for Ca^{2+} over Mg^{2+} in a study of Ca^{2+}/Mg^{2+} transport across chloroform membranes.[38] The preferential movement of Ca^{2+} is attributed to the kinetics of the liberation process which is markedly different for the two ions.[38] A contemporary single crystal XRD study[39] of the structure of the 1:2 Mg^{2+} complex of calcimycine has revealed that the Mg^{2+} coordination geometry is markedly different from that in the corresponding Ca^{2+} complex providing a possible reason for the difference in the transport properties of the two ions. The Mg atom is located in a nearly perfect octahedral coordination sphere generated by two tridentate chelating antibiotic ligands (r(Mg...O(carboxyl)) = 199.0, 199.6pm; r(Mg...O(carbonyl)) = 206.0, 206.4pm; r(Mg...N) = 222.8, 223.5pm). The Ca atom, on the other hand, is situated in a 7-fold coordination geometry provided by two tridentate chelating antibiotic ligands (r(Ca...O(carboxyl)) = 227, 237pm; r(Ca...O(carbonyl)) = 228, 238pm; r(Ca...N) = 258, 269pm) and a single water molecule (238pm).

The polyene antibiotics, nystatin and amphotericin B, form both 1:1 and 1:2 complexes with Mg^{2+} and Ca^{2+};[40] their stability constants have been determined in aqueous solution containing 1% dmf by a solubility method.[41] I.r. and e.s.r. studies of the solid phases indicate that interaction occurs via the carboxylate group of the polyenes;[40] in this respect these complexes differ from those of Ni^{2+}, Cu^{2+} and Zn^{2+} which are thought to interact via the hydroxyamine group of the polyenes. The biological activities of the complexes with nystatin have also been evaluated in a flow microcalorimetric study.[42] They are all lower (per unit weight of complex) than that of nystatin itself; nevertheless, their enhanced solubilities over that of nystatin may yield higher overall bioactivities.[42]

The nucleoside, guanosine, forms two types of complex with the alkaline earth metal cations, Mg^{2+}, Ca^{2+} and Ba^{2+};[43] they have the general formulae $M(guanosine)_nX_2,yH_2O,zC_2H_5OH$ (where M = Mg, Ca, Ba; n = 1,2,4; X = Cl,Br,NO_3,ClO_4 and OH; y = 0-6; z = 0-2) and $M(guanosine\text{-}H)(OH),yH_2O$ (where M = Xa^{2+}, Ba^{2+}; (guanosine-H) = guanosine ionised at N_1; y = 1-3). Characterisation by ^1H n.m.r. and F.T. -i.r. spectroscopic methods indicates that metal binding occurs either through the N_7 site of the guanine moiety for the neutral nucleoside or through the O_6 site of the guanine moiety for the anionic nucleoside.[43]

Reaction of inosine-5'-monophosphate (5'-imp) with hydrated $MgCl_2$ at pH = 7.5 in the presence of NaOH yields, depending on molar ratios $Mg(5'\text{-imp}),5H_2O$ and $Mg_2(5'\text{-imp})_3,15H_2O$.[44] Since the F.T.-i.r. spectra ($1800 < \bar{\nu}/cm^{-1} < 400$) of $Mg(5'\text{-imp}),5H_2O$ and of $Mg_2(5'\text{-imp})_3,15H_2O$ show marked similarities with those of $M(5'\text{-imp}),5H_2O$ (M = Co,Ni) and with those of $Cd_2(5'\text{-imp})_3,12H_2O$ and $Ca(5'\text{-imp}),6.5H_2O$, respectively, it is concluded, by analogy with the known structures of the latter complexes, that the Mg atom in $Mg(5'\text{-imp}),5H_2O$ is N_7-bound with an indirect metal-phosphate and metal-carbonyl interaction through a coordinated water molecule, and that the Mg atom in $Mg_2(5'\text{-imp})_3,15H_2O$ binds directly to the phosphate and to the sugar moiety as well as to the N_7-site of the purine ring system.[44]

Analysis of ^{31}P n.m.r. chemical shift data evaluated for adenosine-5'-diphosphate (5'-adp) and nicotinamide adenine dinucleotide (nad) as a function of Mg^{2+} concentration at pH = 4 and for adenosine-5'-triphosphate (5'-atp) as a function of Mg^{2+}, Ca^{2+} and Ba^{2+} concentration at pH = 4 and pH = 5 has given the stability constants for the complexes to each phosphate moiety.[45] With the exception of Mg^{2+}-nad complexes, downfield chemical shifts are observed indicating that the alkaline earth metal is coordinated by two phosphate moieties; the upfield shift observed for Mg^{2+}-nad complexes suggests that the Mg atom only associates with one phosphate moiety at a time.

Interaction of Ca^{2+} with the two isomeric aldopentoses, D-(-)-ribose and D-(-)-arabinose in aqueous solution has been studied electrochemically.[46] D-(-)-ribose contains a sequence of hydroxyl groups which interacts specifically with the cation; the corresponding association constant (β_1) is 0.93.

Single crystal XRD studies have been completed for Calcium D-glucarate tetrahydrate[47] and for Calcium D-glycero-D-gulo-heptonate tetrahydrate.[48] Sheldrick et al[47] have redetermined the structure of the former compound and compared the results with those of the original study by Taga and Osaki.[49] The new data[47] show agreement with improved accuracy. Thus the Ca atom is located in a distorted square antiprismatic environment provided by two carboxyl and three hydroxyl oxygens of different anions and by three water molecules; all the Ca...O distances lie in the range 237-255pm (average 245pm). Taga, Osaki et al[48] have reported the novel structural elucidation of the latter compound. In this case, the Ca atom is located in a distorted dodecahedral coordination sphere generated by six oxygens (240.3-248.0pm) from three bidentate chelating anions (five hydroxyl and one carboxyl oxygen), one carboxyl oxygen (247.9pm) of a monodentate anion and a single water molecule (242.9pm).[48]

Table 6. Spectroscopic and Structural data for Adducts of Magnesium tetraphenylporphyrin with 1-(methyl)imidazole (1-MeIm), 4-picoline (4-pic) and piperidine (pip).[50]

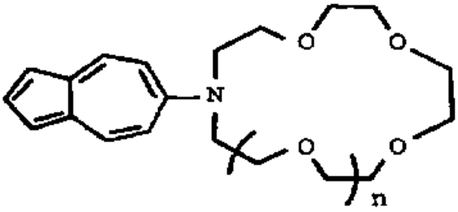
Adduct	Electronic Band Maximum/nm			r(Mg...N(ax))/pm
	KBr Disc	Nujol Mull	CH_2Cl_2 solution	
$Mg(tpp)(1\text{-}MeIm)_2$	634	640	627	229.7
$Mg(tpp)(4\text{-}pic)_2$	621	629	623	238.6
$Mg(tpp)(pip)_2$	619	624	620	241.9

Electronic spectral studies[50] of a series of six-coordinate magnesium tetraphenylporphyrin complexes $Mg(tpp)L_2$ (where tpp =

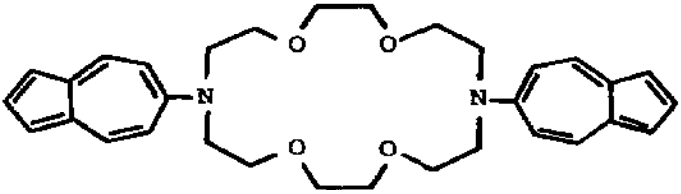
tetraphenylporphyrin, L = 1-(methyl)imidazole (1-MeIm), 4-picoline (4-pic) and piperidine (pip) which contain axial N-donor ligands weakly bound to magnesium at comparatively large distances indicate that the magnitudes of the red shifts for these entities correlate with the Mg...N(axial ligand) bond distance. The significance of these data, which are incorporated in Table 6, to the spectral properties of in vivo chlorophyll molecules is stressed.

2.3.2 Complex Formation in Solution

Lohr[51] has discovered that complexation of Ba^{2+} by the novel 6-aminoazulene coronand (2) in CH_3CN results in a colour change from yellowish-orange to blueish-violet. None of the other alkaline earth metals nor any of the alkali metals has such a marked effect. Similarly neither of the other two ligands synthesised in this work (3,4) exhibit comparable behaviour. The observed band shift is discussed in the context of the dipole moment changes which result from the excitation of the azulene system from the ground to the photoexcited state.[51]



n = 2 (2)
n = 1 (3)



(4)

Complexation of Mg^{2+} by phenanthraquinone semicarbazone has been studied by a pH-potentiometric method;[52] the stability constant of the resultant complex was found to be lower than those of the corresponding complexes of Mn, Co, Ni, Cu, Zn and Cd.

In an extensive series of papers,[53-63] several Russian authors have published data on the interaction, in aqueous or ethanolic

Table 7. Complex formation between alkaline earth metal salts and species derived from urea, thiourea and formamide; systems studied and products formed.

Salt	Ligand (L)	Solvent	T/K	Complex	Ref
$MgCl_2$	$NH_2CONHCH_2OH$	H_2O	303		53
$MgCl_2$	$(NH_2CONH)_2CH_2$	H_2O	303	$2MgCl_2,3L,12H_2O$	53
$MgCl_2$	$PhCONH_2$	EtOH	298	$MgCl_2,10L,6H_2O$	54
				$MgCl_2,2L$	
$MgSO_4$	$NH_2CONHCH_2OH$	H_2O	303		53
$MgSO_4$	$(NH_2CONH)_2CH_2$	H_2O	303	$MgSO_4,10L,7H_2O$	53
$Mg(NO_3)_2$	CH_3CONH_2	H_2O	298	$Mg(NO_3)_2,6L,2H_2O$	55
				$Mg(NO_3)_2,4L,2H_2O$	
$Mg(NO_3)_2 + Ca(NO_3)_2$	$CO(NH_2)_2$	H_2O	298	$Mg(NO_3)_2,4L,2H_2O$	56
				$Mg(NO_3)_2,2L,6H_2O$	
				$Ca(NO_3)_2,L,3H_2O$	
				$Ca(NO_3)_2,4L$	
$Mg(CH_3COO)_2$	$CO(NH_2)_2$	H_2O	298	$Mg(CH_3COO)_2.2L$	57
$Mg(CH_3COO)_2$	$CO(NH_2)_2$	H_2O	323	$Mg(CH_3COO)_2,2L$	58
$Mg(CH_3COO)_2$	$HCONH_2$	H_2O	298	$Mg(CH_3COO)_2,4L$	59
				$Mg(CH_3COO)_2,L$	
$Mg(CH_3COO)_2$	CH_3CONH_2	H_2O	303	$Mg(CH_3COO)_2,2L$	60
$Ca(CH_3COO)_2$	$CO(NH_2)_2$	H_2O	298	$Ca(CH_3COO)_2,L$	57
$Ca(CH_3COO)_2$	$HCONH_2$	H_2O	298	$Ca(CH_3COO)_2,L$	61
$Ca(CH_3COO)_2$	CH_3CONH_2	H_2O	303		62
$Ca(CH_3COO)_2$	$CH_3CONHCONH_2$	H_2O	303		62
$Ca(CH_3COO)_2$	$CS(NH_2)_2$	H_2O	303		62
$Ca(CH_3COO)_2$	$NH_2CSNHNH_2$	H_2O	303		62
$Sr(CH_3COO)_2$	$CO(NH_2)_2$	H_2O	298		57
$Ba(CH_3COO)_2$	$CO(NH_2)_2$	H_2O	298		57
$Mg(CH_3COO)_2 + Ca(CH_3COO)_2$	$CO(NH_2)_2$	H_2O	298	$Mg(CH_3COO)_2,2L$	63
				$Ca(CH_3COO)_2,L$	63

solution, between alkaline earth metal salts and species derived from urea, thiourea and formamide. Solid products were characterised using chemical, thermogravimetric and crystal-optical analyses, and by XRD and i.r. spectroscopic methods. The systems studied and complexes formed therein are listed in Table 7.

2.3.3 Salts of Carboxylic Acids

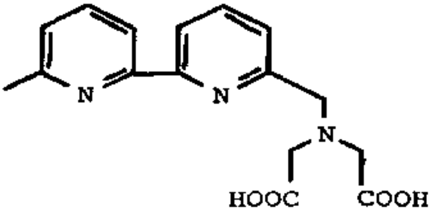
This subsection has been introduced this year to collate the growing number of publications in which alkaline earth metal salts of carboxylic and related acids are discussed. Topics of principal interest include complexation in solution [64-68] and structure in the solid state.[69-74]

Multinuclear (^{9}Be and ^{13}C) n.m.r. spectroscopy[64] of solutions containing Be^{2+} and malonic acid anion at different pH shows the formation of three successive complexes; $[CH_2(COO)_2]Be$, $\{[CH_2(COO)_2]_2Be\}^{2-}$ and $\{[CH_2(COO)_2]_3Be_3(OH)_3\}^{3-}$.

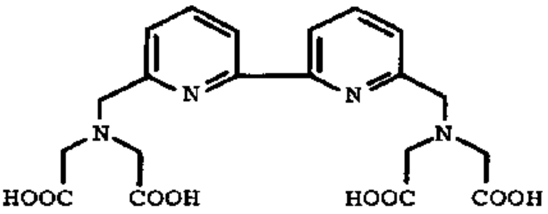
Stability constants of complexes of Mg^{2+} with orotic acid dianion and various aminoacid anions have been determined at 20°C and I = 0.15M(NaCl) using pH-potentiometric methods;[65] similar data for mixed ligand complexes containing both orotic acid dianion and an aminoacid anion were also determined under identical conditions.

Calcium and magnesium salts of pantoic acid (2,4-dihydroxy-3,3-dimethylbutan-1-oic acid) have been formed in both aqueous solution and the solid phase.[66] Their reaction with 4-aminobutan-1-oic acid yields the butyrolactam adduct $[HOCH_2CMe_2CH(OH)CO_2]_2Ca$, $2H\overline{N(CH_2)_3C}O$; it is thought the formation of these adducts may hinder the synthesis of biologically active materials by condensation of salts of pantoic acid with 4-aminobutan-1-oic acid.[66]

The novel reagents (<u>5</u>)-(<u>11</u>) have been synthesised and their complexation of M^{2+} (M = Mg-Ba) studied.[67,68] The selectivity of (<u>5</u>) and (<u>6</u>) for M^{2+} (M = Mg-Ba) and the stabilities of the complexes so formed were determined by potentiometric titration[67] and compared to those of edta and other complexing agents. The complexes of (<u>6</u>) with all four cations have comparable stability to the corresponding complexes of edta; they exhibit a pronounced selectivity towards Ca^{2+}. The stability constants of the Mg^{2+} and Ca^{2+} complexes of (<u>5</u>) are of normal magnitude (complexation of (<u>5</u>) with Sr^{2+} and Ba^{2+} was not studied).[67] The complexation of



(5)



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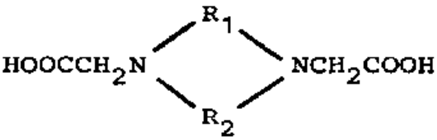


	R_1	R_2
(7)	$-CH_2CH_2-$	$-CH_2CH_2-$
(8)	$-CH_2CH_2CH_2-$	$-CH_2CH_2CH_2-$
(9)	$-CH_2CH_2-$	$-CH_2CH_2OCH_2CH_2-$
(10)	$-CH_2CH_2CH_2-$	$-CH_2CH_2OCH_2CH_2-$
(11)	$-CH_2CH_2CH_2-$	$-CH_2(CH_2OCH_2)_2CH_2-$

M^{2+} (M = Mg-Ba) by (7)-(11) was investigated using thermometric titrimetric methods.[68] In general their affinity for a given cation decreases with increase in macrocycle size or increase in the number of macrocycle donor oxygen atoms; all five complexing agents exhibit selectivity between cations.[68]

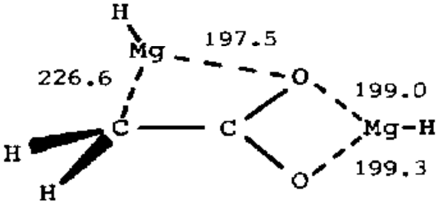
Single crystal XRD studies have been completed for derivatives of formic,[69] acetic,[70] α-methylmalonic[71] and nicotinic[72,73] acids. In the structure of distrontium(II)copper(II) formate octahydrate[69] the Sr atom is surrounded by nine oxygens provided by four water molecules (262-281pm) and three formate anions, two bidentate (254,267pm) and one monodentate (262pm). The stereochemistry of the cation is distorted monocapped square antiprismatic with loose overall C_{4v} symmetry. The Ca atom in (acetylacetonato)calcium(II)acetate dihydrate[70] is located in a distorted dodecahedral arrangement of eight oxygens provided by two water molecules (248.4,251.1pm), three acetate anions, one bidentate (253.1,259.5pm) and two monodentate (233.2,236.5pm) and a chelating acetylacetonato ligand (238.7,239.2pm).

The crystal structures of the magnesium and calcium salts of α-methylmalonic acid, $[CH_3CH(COO)_2]Mg,4H_2O$ and $\{[CH_3CH(COO)_2]Ca\}_3,4H_2O$, are quite different;[71] whereas the former contains only one Mg atom the latter contains three Ca atoms, two of which are symmetry related. The coordination geometry of the Mg atom, which is located on a mirror plane of symmetry, is octahedral with four water molecules (205.0-206.9pm) and a chelating ($\overline{\text{Ca-O-C-C-C-O}}$) bidentate malonate anion (206.3pm).[71] The two symmetry related Ca atoms are surrounded by seven oxygens provided by a water molecule (238.4pm), and four malonate anions, one chelating bidentate (236.2,238.6pm), one regular bidentate (248.1,256.6pm) and two monodentate (231.6,237.1pm); the coordination polyhedron is best described as distorted capped octahedral.[71] The third Ca atom is located in a special position and is coordinated by eight oxygens provided by two water molecules (243.1pm) and four malonate anions, two bidentate (250.3,255.9pm) and two monodentate (235.5pm); the coordination geometry is pseudo-octahedral, the axial positions being occupied by the bidentate ligands.[71]

Quantum-mechanical calculations have been performed on the coordination of Mg^{2+} and Ca^{2+} by malonate anion;[75] although generally similar, the magnesium complexes are more tightly bound than the calcium salts. The calculated calcium malonate structure is in substantial agreement with recent XRD data on the calcium salt of α-ethylmalonic acid[74] in which the eight coordinate Ca atom is surrounded by four water molecules and two malonate anions, one chelating bidentate and one regular bidentate.

As for the salts of α-methylmalonic acid, the magnesium and calcium derivatives of nicotinic acid are structurally dissimilar.[73,74] Whereas the Ca atom in calcium(II) nicotinate, pentahydrate[73] is located on a 2-fold symmetry axis and is surrounded by two water molecules (240.2pm) and four carboxyl moieties, two bidentate (241.2,279.7pm) and two monodentate (234.5pm), the Mg atoms in magnesium(II) nicotinate decahydrate[73] and magnesium(II)nicotinate tetrahydrate[74] are surrounded either solely by six water molecules (200.9-209.6pm)[73] or by four water molecules and two nitrogen atoms of separate anions.[74] The absence of carboxyl moieties in the Mg coordination sphere is attributed, by Lenstra et al,[74] on the basis of quantum mechanical calculations, to polarisation effects around the Mg atom.

Ab initio MO calculations within the 3-21G basis set and semi-empirical MNDO calculations indicate that monomeric bis(magnesyl) derivatives of acetic acid (an Ivanoff reagent) favour the 1,3-1,3' doubly bridged structure generally found in metallated Y conjugated dianion systems;[76] in the minimum energy 3-21G structure (12), one Mg-H moiety is roughly in the carboxylate plane while the second is involved in π-enolate bridging.



(12)

distances/pm.

2.3.4 Beryllium Derivatives

Single crystal XRD studies have been completed for bis(acetylacetonato)beryllium(II) at 119K[77] and for (η^5-cyclopentadienyl)beryllium(II) chloride at 298K.[78] The structure of the acetylacetonato complex[77] contains two independent but similar molecules in which the Be atoms are chelated in a distorted tetrahedral arrangement by the two ligands (r(Be(1)...O) = 161.4-162.3pm; r(Be(2)...O) = 160.7-162.6 pm). These data confirm the 298K structure which is in excellent agreement with that in the gas phase.[77] The structure of the η^5-cyclopentadienyl complex[78] is also the same as that in the gas phase; within the limits of experimental error the molecule possesses a C_5 symmetry axis which passes through the centroid of the ring (r(Be...C) = 186.7-187.5pm) and the chlorine atom (186.9pm).[78]

In the third and final paper to be abstracted for this subsection, the dipolar nature of bis(η^5-cyclopentadienyl)-beryllium(II) is confirmed using the results of a microdielectric loss study of solutions in cyclohexane, decalin, benzene and 1,4-dioxane.[79] The dielectric absorption is interpreted to suggest rocking movements of the cyclopentadienyl groups synchronous with the oscillation of the beryllium atom between two equivalent positions in an η^5,σ structure.[79]

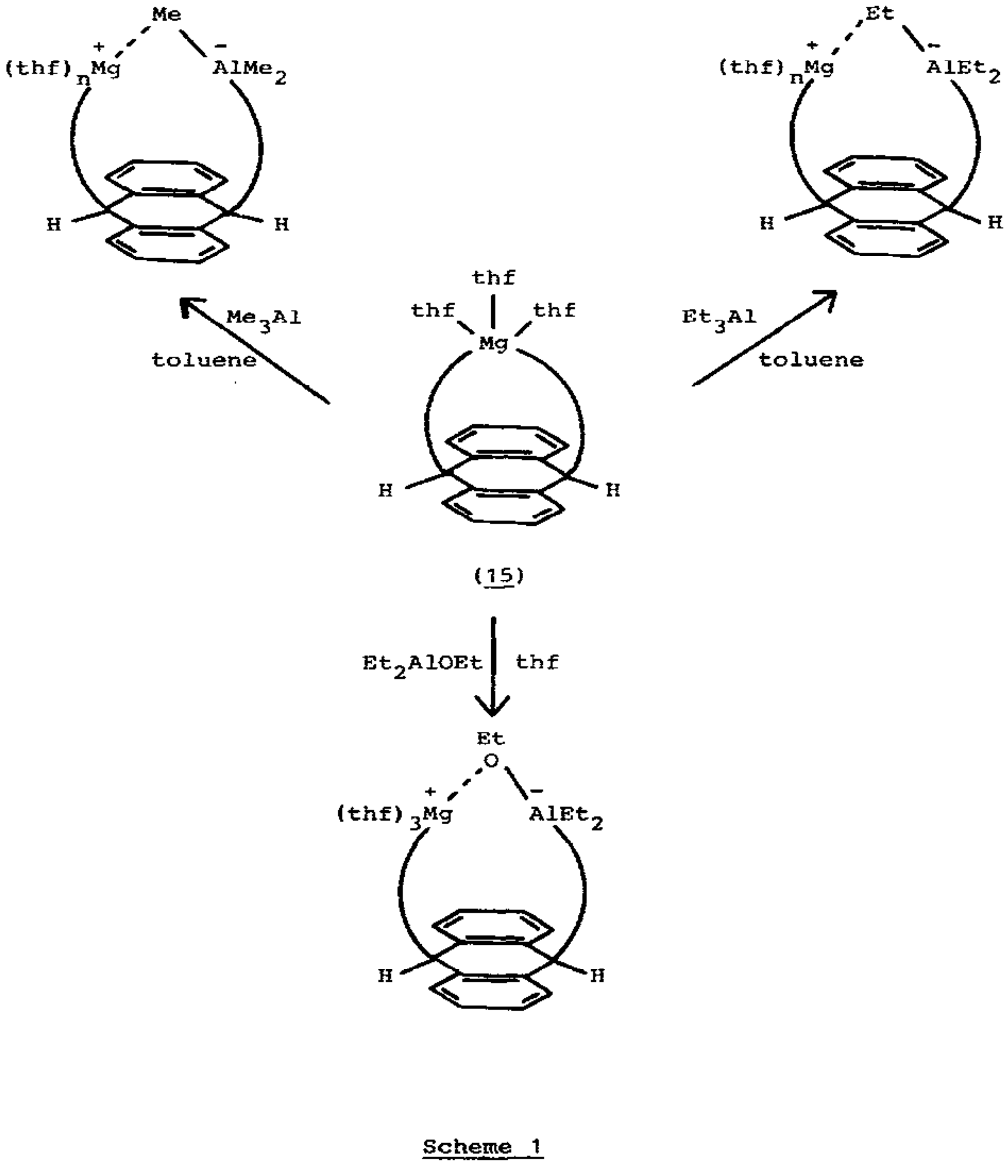
2.3.5 Magnesium Derivatives

Some of the more fascinating developments in recent alkaline earth metal research have centered on the synthesis, characterisation and reaction chemistry of magnesium-anthracene derivatives.[80-84] Lehmkuhl et al[80] have reported that reaction of anthracene (13) and of 9,10-bis(trimethylsilyl)anthracene (14) with metallic magnesium yields thf solvates of 9,10-dihydro-9,10-anthrylenemagnesium(II) (15) and of 9,10-bis(trimethylsilyl)-9,10-anthrylenemagnesium(II) (16) respectively. Their structural analysis of (16) revealed[81] that the Mg atom forms an intramolecular bridge between the 9- and 10-positions of the anthrylene system (223.3,223.4pm); the pseudo tetrahedral coordination sphere of the Mg atom is completed by the oxygens of the two thf solvate molecules (199.7,202.1pm).

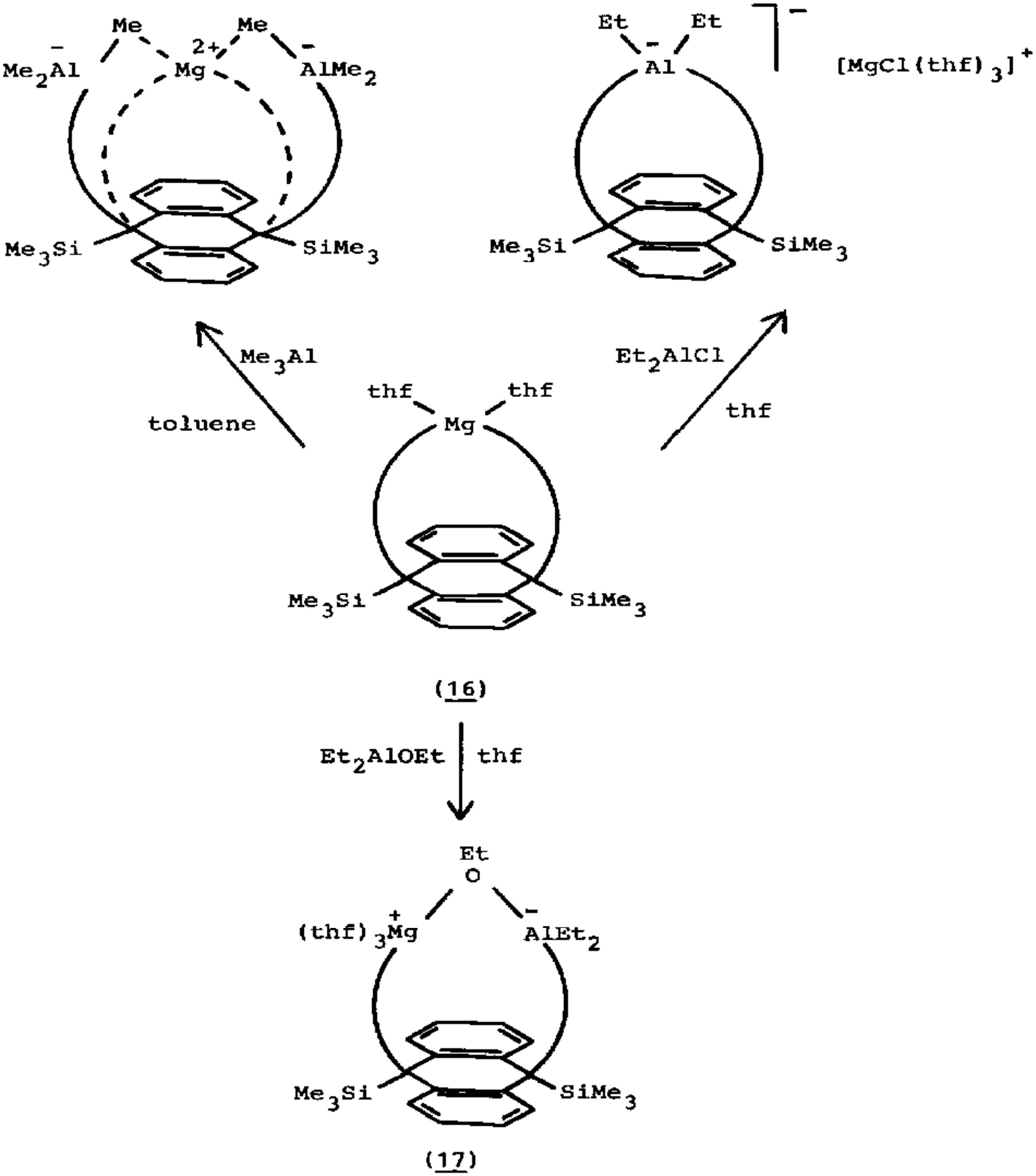
Bogdanovic et al[83] have also reported the structure of the 1,4-dimethyl derivative of (15). It contains two crystallographically independent molecules of very similar geometry. Again the Mg atoms form a intramolecular bridge between the 9- and 10-positions of the anthrylene system ($r(Mg...C)_{av}$ = 232pm); in this structure, however, they are located in a 5-fold coordination sphere completed by the oxygens of three thf molecules.

Lehmkuhl et al[80,82] have also shown that the anthrylenemagnesium derivatives react with organoaluminium compounds according to schemes 1 and 2. Structural analysis of the tris(thf) solvate of the adduct formed between Et_2AlOEt and 9,10-bis(trimethylsilyl)-9,10-anthrylenemagnesium (17)[82] indicates that both Mg and Al atoms occupy axial positions in the 9,10-anthrylene group. The Mg atom occupies a distorted trigonal bipyramidal coordination sphere with bonds to C9 and to the oxygens of the Et_2AlOEt moiety and of the three thf molecules; the Al atom is located in a distorted tetrahedral environment generated by C(10), and the three ligating atoms of the Et_2AlOEt moiety (Details of the structure are not given as the refinement only proceeded to R = 0.121).[82]

Bogdanovic et al[83] have obtained hexakis(thf)tri-μ-chlorodimagnesium(II) anthracenide from (15) by reaction with $MgCl_2$ and anthracene in thf. They have also synthesised it by direct


Me
(thf)$_n$Mg$^+$
AlMe$_2^-$
H
H
Et
(thf)$_n$Mg$^+$
AlEt$_2^-$
H
H
Me$_3$Al
toluene
thf
thf
thf
Mg
Et$_3$Al
toluene
H
H
(15)
Et$_2$AlOEt
thf
Et
O
(thf)$_3$Mg$^+$
AlEt$_2^-$
H
H

Scheme 1


Me
Me
2+
Me$_2$Al
Mg
AlMe$_2$
Me$_3$Si
SiMe$_3$
Et
Et
Al
[MgCl(thf)$_3$]$^+$
Me$_3$Si
SiMe$_3$
Me$_3$Al
toluene
Et$_2$AlCl
thf
thf
thf
Mg
Me$_3$Si
SiMe$_3$
(16)
Et$_2$AlOEt
thf
Et
O
(thf)$_3$Mg
AlEt$_2$
Me$_3$Si
SiMe$_3$
(17)

Scheme 2

reaction of Mg, $MgCl_2$ and anthracene in thf. Their single crystal XRD examination has shown it to contain an isolated anthracene radical anion thereby confirming u.v. and e.s.r. data. The cation contains two Mg atoms bridged by three chlorines, the pseudooctahedral geometries of the Mg atoms being completed by three thf molecules; its structure is very similar to those of the $[Mg_2Cl_3(thf)_6]^{2+}$ cations reported in the 1984 review.[85]

Bogdanovic[84] has also reviewed the role of complexes such as ($\underline{15}$)

$$(\underline{13}) + \text{Mg} \xrightarrow[\text{thf}]{20-60^{\circ}\text{C}} (\underline{15})$$

$$(\underline{15}) + \text{CrCl}_3(\text{TiCl}_4) \xrightarrow[\text{thf}]{20-30^{\circ}\text{C}} \text{Cr(Ti) - catalyst} + (\underline{13})$$

$$(\underline{15}) + \text{Cr(Ti)-catalyst} + \text{H}_2 \xrightarrow[\text{thf}]{20-30^{\circ}\text{C}} \text{MgH}_2 + (\underline{13})$$

Scheme 3

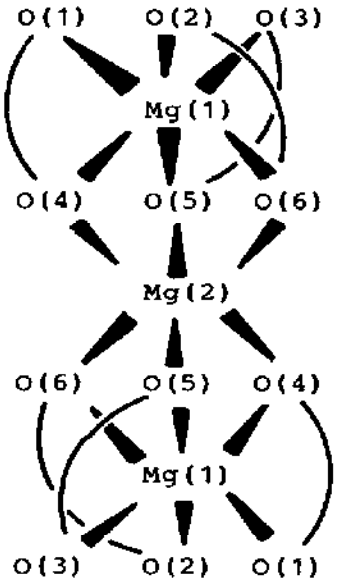
and ($\underline{16}$) in the catalytic formation of MgH_2 according to scheme 3. Samples of MgH_2 so produced are highly reactive and can be used as both a hydrogenating agent and a high temperature hydrogen storage material.[84]

Several η^5-cyclopentadienyl derivatives of magnesium have been synthesised and characterised.[86,87] The molecular structure of $(\eta^5-C_5H_5)Mg(CH_2CMe_3)$, determined by gas phase electron diffraction methods,[86] is such that the Mg...C bond distances (r(Mg...C(neopentyl)) = 212(2)pm; r(Mg...C(cyclopentadienyl)) = 232.8(7)pm) are indistinguishable from those in $(Me_3CCH_2)_2Mg$ and $(\eta^5-C_5H_5)_2Mg$, respectively. The low-temperature thf solution structure of $(\eta^5-C_5H_5)Mg(CH_2CMe{=}CH_2)$, elucidated by multinuclear (^1H and ^{13}C)n.m.r. spectroscopic methods,[87] is such that the allyl moiety is σ-bonded to the Mg atom. As the temperature is increased the molecule becomes fluxional; the activation parameters $E_a = 54.4\ kJ.mol^{-1}$, $\Delta S^{\ddagger} = 27.2\ JK^{-1}mol^{-1}$ were obtained from line shape analysis of the $^{13}C\{^1H\}$ spectra.[87]

Ab initio MO calculations on $(\eta^5-C_5H_5)MgH$ have given an optimum perpendicular metal-ring distance (201pm) which is shorter (2pm) than that (203pm) calculated similarly for $(\eta^5-C_5H_5)_2Mg$.[86] Metal-ring bonding is affected by stabilisation of the ring e_1 and a_1 π-orbitals through interactions with magnesium $3p_x$, $3p_y$ and 3s orbitals respectively. The integrated dipole moment is 1.13D with the negative pole at the hydrogen atom.[86]

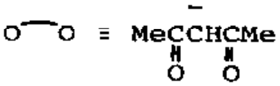
Single crystal XRD studies have been completed successfully for a number of diverse magnesium-containing species. Two are trimeric, bis(acetylacetonato)magnesium(II) (18)[88] and bis{(diethoxyphosphinyl)acetonato}magnesium(II) (19),[88] one is dimeric, 1,2-bis(trimethylsilylamido)benzenemagnesium(II)-diethyl ether (1/1) solvate (20),[89] while the remainder are monomeric, dibromotetrakis(5,7-dihydrodibenz[c,e]oxepin)magnesium(II)-toluene (1/2) solvate (21)[90] and 2-pivaloyl-1,2,3,4-tetrahydroisoquinoline-1-magnesium(II)bromide-thf (1/3) solvate (22).[91] In the centrosymmetric trimeric structures of (18) and (19)[88] each Mg atom is coordinated by six oxygen atoms with a distorted octahedral geometry; structural details are given in the diagram. The centrosymmetric dimeric structure of (20)[89] is based on a Mg_2N_2 ring, each bis(amido) ligand providing one bridging nitrogen (208.2pm). The other nitrogen (199.7pm) also ligates the Mg atom forming a chelate ring, and together with the oxygen (204.1pm) of the solvate molecule, completes its distorted tetrahedral geometry. In the monomeric structure of (21)[90] the Mg atom lies on a crystallographic 2-fold axis in a distorted octahedral coordination polyhedron generated axially by the trans-located bromines (262.3pm) and equatorially by the oxygens of the four oxepin ligands (212.7-218.3pm); the solvate molecules do not ligate the Mg atom. The Mg atom in the structure of (22)[91] lies in a pseudo-equatorial position of the tetrahydroisoquinoline ring system and is σ-bonded to the 1-position (224.5pm). Chelation is effected by the carbonyl oxygen of the pivaloyl moiety (204.9pm) and the six-fold coordination of the Mg atom is completed by the bromine (262.2pm) and the three thf oxygens (213.6,214.6,223.6pm). As expected the bromine occupies the position trans to the most electronegative ligand, the carbonyl oxygen.[91]

Three heterobimetallic complexes containing magnesium,



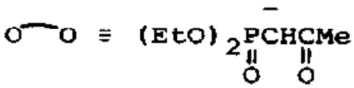
(18),(19)

(18)



$\overset{\frown}{O\quad O} \equiv \mathrm{Me}\underset{\underset{O}{\|}}{\mathrm{C}}\overset{-}{\mathrm{CH}}\underset{\underset{O}{\|}}{\mathrm{C}}\mathrm{Me}$

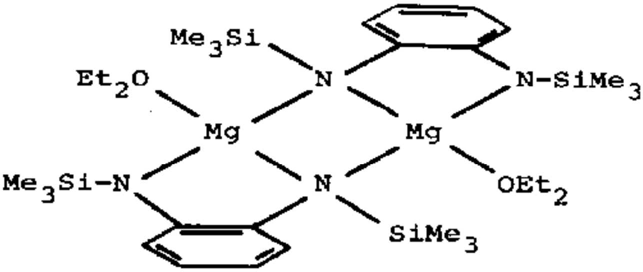
(19)



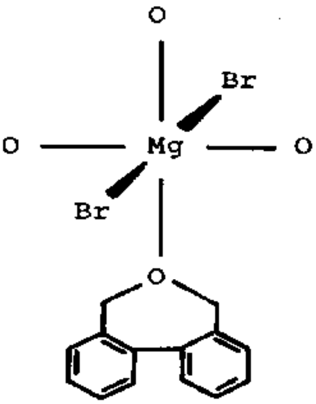
$\overset{\frown}{O\quad O} \equiv (\mathrm{EtO})_2\underset{\underset{O}{\|}}{\mathrm{P}}\overset{-}{\mathrm{CH}}\underset{\underset{O}{\|}}{\mathrm{C}}\mathrm{Me}$

	(18)	(19)
r(Mg(1)...O(1)) =	202.4	199.1
r(Mg(1)...O(2)) =	202.9	203.1
r(Mg(1)...O(3)) =	201.9	201.6
r(Mg(1)...O(4)) =	214.9	212.4
r(Mg(1)...O(5)) =	214.3	213.0
r(Mg(1)...O(6)) =	212.2	209.5
r(Mg(2)...O(4)) =	207.5	208.5
r(Mg(2)...O(5)) =	208.2	208.3
r(Mg(2)...O(6)) =	209.1	211.0

Distances/pm

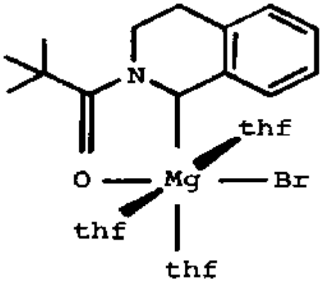


(20)



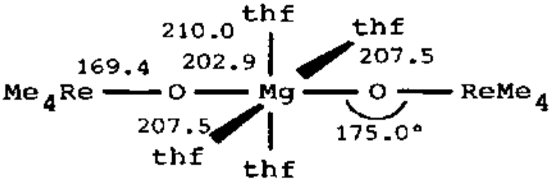
(21)

To aid clarity only one of the four oxepin ligands is shown in full

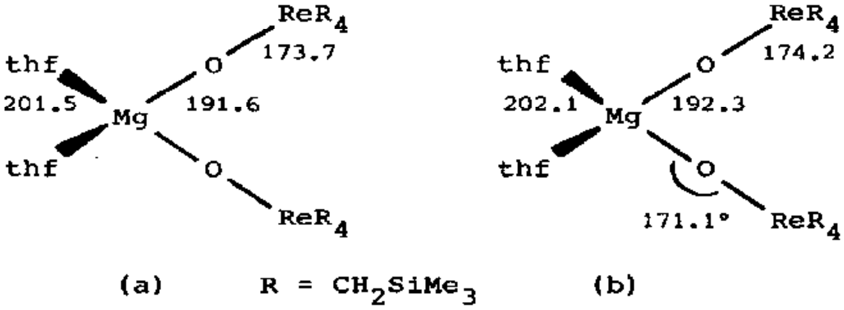


(22)

$(Me_4ReO)_2Mg(thf)_4$ (23),[92] $(\{Me_3SiCH_2\}_4ReO)_2Mg(thf)_2$ (24)[92] and $Cu_4MgPh_6.Et_2O$ (25)[93] have been structurally characterised. The diamagnetic Re(V) complexes, (23) and (24),[92] synthesised by reaction of Grignard reagents with Re_2O_7, $(Me_3NH)ReO_4$, $ReOCl_4$ or $ReOCl_3(PPh_3)_2$, consist of Mg atoms coordinated by thf molecules and R_4ReO^- (R = Me or Me_3SiCH_2) anions. Whereas the coordination geometry of the Mg atom in (23), which is located at a centre of symmetry, is pseudo-octahedral, that of the two crystallographically distinct Mg atoms in (24), which lie on 2-fold symmetry axes, is pseudo-tetrahedral; pertinent structural details are quoted on the schematic diagrams.[92]



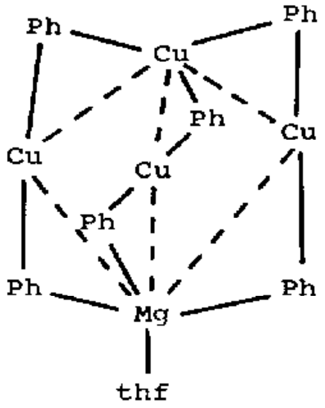
(23)



(24) distances/pm.

The copper(I) complex (25), prepared from CuBr and $MgPh_2$ in Et_2O, consists of a Cu_4Mg pentagonal bipyramidal cluster, $r(Mg...Cu)_{av}$ = 275.4pm, with phenyl groups bridging between the axially and equatorially located metal atoms, $r(Mg...C)_{av}$ = 235pm. The distorted tetrahedral geometry at the Mg atom is completed by the oxygen of the thf molecule, r(Mg...O) = 204.6pm.

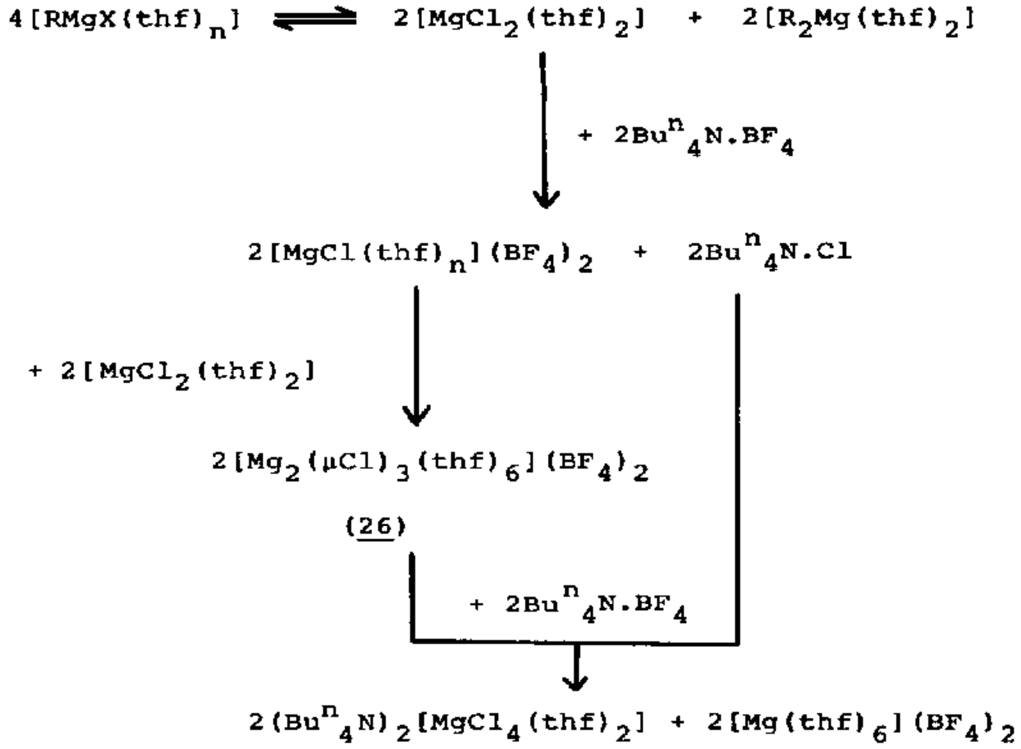
A limited number of papers[94-96] have been published in which facets of Grignard Reagents of interest to the inorganic chemist are described. Electrochemical oxidation of magnesium into CH_3CN



(25)

solutions containing alkyl or aryl halides (RX) and 2,2'-dipyridyl (bipy) affords [RMgX,bipy];[94] with α,ω-dihalides (XR'X) the products are [R'Mg_2X_2,2bipy]. The synthesis is equally effective with alkyl or aryl derivatives and with chlorides, bromides or iodides. The products show none of the typical reactions of Grignard reagents other than alkene elimination with mineral acids.[94] Reaction of aryl magnesium halides (RMgX) or magnesium halides (MgX_2,nEt_2O) with aryl lithium derivatives (RLi) in ether or thf yields [$R_2Mg(Et_2O)_2$] or [$R_2Mg(thf)_2$].[95] Desolvation of the ether adducts, but not the thf adducts, can be achieved. Mixed diaryl magnesium-thf adducts, although coordinatively saturated have multinuclear (^1H and ^{13}C) n.m.r. spectra which suggest fluxionality.[95] Reaction of Grignard reagents with $Bu^n{}_4N.BF_4$ leads to the formation of [$R_2Mg(thf)_2$], $(Bu^n{}_4N)_2[MgCl_4(thf)_2]$ and $[Mg(thf)_6](BF_4)_2$ according to scheme 4.[96] The results suggest that the tri-μ-chlorohexakis(thf)dimagnesium(II) cation (26) is an important intermediate.[96]

The twelve complexes, $MgCl_2$,$nRAlCl_2$ (n = 1, R = Cl_2AlCH_2; n = 1.5, R = C_4H_9, C_8H_{17}; n = 2, R = CH_3, C_2H_5), $CaCl_2$,$nC_2H_5AlCl_2$ (n = 1,2,4), CaX_2,$2C_2H_5AlX_2$ (X = Br, I) and MCl_2,$3C_2H_5AlCl_2$ (M = Sr, Ba) have been synthesised[97] by addition of the appropriate anhydrous alkaline earth metal halide to the corresponding alkyl aluminium halide either neat or in n-heptane solution. For some systems, it was necessary to heat and stir the mixture. From their chemical and physical characterisation, a salt-like structure is postulated for these materials.[97] Reaction of the



Scheme 4

tetrabasic 1-hydroxy-3-(dimethylamino)propylidene-1,1-diphosphonic acid (H_4A) with Mg^{2+} and Ca^{2+} has yielded the six complexes $Mg_3(HA)_2,nH_2O$ (n = 1,6,10) and $Ca_3(HA)_2,nH_2O$ (n = 1,5,8).[98] Although the free acid adopts the betaine structure, i.r. and ^1H n.m.r. data suggest that the complexed anion contains deprotonated nitrogen atoms which can interact with the cations.[98]

Exchange of d.m.f. in $[15C5Mg(dmf)_2]^{2+}$, studied[99] using ^1H n.m.r. techniques in inert solvents (CD_3NO_2), is 10^4x slower than in $[Mg(dmf)_6]^{2+}$; the difference is attributed to an increased attraction between Mg^{2+} and dmf caused by coordination of 15C5.

2.3.6 Calcium, Strontium and Barium Derivatives

The traditional lack of interest in strontium and barium chemistry has now encompassed calcium chemistry, a total of only six papers being abstracted for this combined subsection. Once again structural chemistry dominates, the crystal and molecular structures of three calcium,[100] one strontium[101] and three barium derivatives[102-104] having been reported. In the sixth paper[105] a description of the thermal decomposition of the acid cyanurate monohydrates of all three alkaline earth metals, $M(HC_3N_3O_3).H_2O$ (M = Ca-Ba), is given. The first three stages of the decomposition are identical for all three metals $M(NCO)_2$ being formed via $M(HC_3N_3O_3)$ and $M_3(C_3N_3O_3)_2$ (Table 8). In the fourth stage of the decomposition, however, the barium salt behaves differently owing to the high temperatures involved; barium silicate and barium cyanide are formed:

$$Ba(NCO)_2 + SiO_2 \rightarrow BaSiO_3 + CO + N_2 + C \qquad ...(1)$$

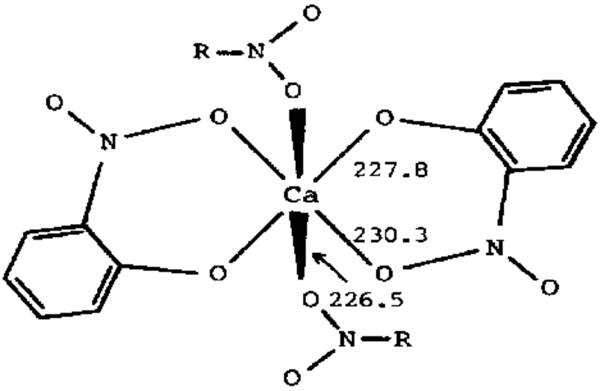
$$Ba(NCN) + C \rightarrow Ba(CN)_2 \qquad ...(2)$$

in addition to the cyanamide produced from the calcium and strontium salts (Table 8).

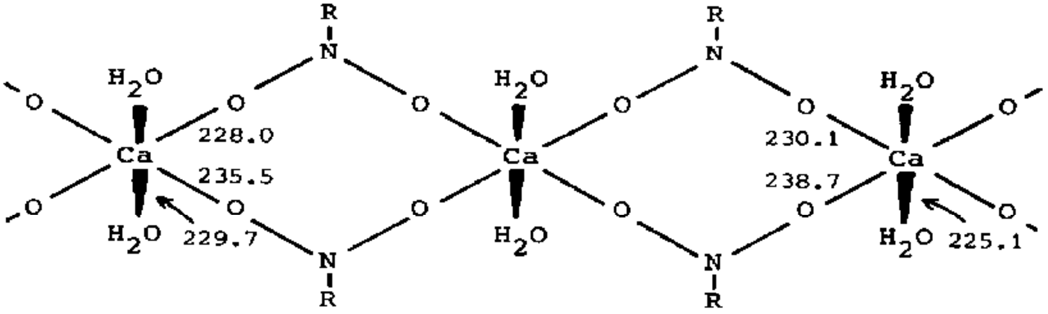
Table 8. Decomposition Products and Temperatures for $M(HC_3N_3O_3).H_2O$ (M = Ca-Ba).[105]

Decomposition Product	Decomposition Temperatures/°C		
	Calcium	Strontium	Barium
$3M(HC_3N_3O_3).H_2O$			
$\downarrow -3H_2O$	110-150	200-250	260-280
$3M(HC_3N_3O_3)$			
$\downarrow -3HNCO$	240-280	310-380	380-470
$M_3(C_3N_3O_3)_2$ $\downarrow$ $3M(NCO)_2$	340-450	430-460	525-575
$\downarrow -3CO_2$	580-670	600-680	700-740
$3M(NCN)$			

The anions of the three structurally characterised[100] calcium salts, catena-bis-μ-(picolinato-N-oxide)calcium(II) (27), catena-diaqua-μ-(nicotinato-N-oxide)calcium(II) (28) and catena-diaqua-μ-(isonicotinato-N-oxide)calcium(II) (29), are geometrical isomers. Although the centrosymmetric pseudo-octahedral Ca atom coordination polyhedra of (28) and (29) are similar, that of (27) is markedly different; whereas picolinato-N-oxide can chelate the



(27) R = o-PhO$^-$ distances/pm.



(28) R = m-PhO$^-$

(29) R = p-PhO$^-$

distances/pm; LHS refer to (28)
RHS refer to (29)

Ca atom, neither of the other two anions is capable of so doing. The Ca atom in (27) is surrounded by six oxygens provided by two chelating anions and by two nitro groups of two symmetry related anions; those in (28) and (29) are coordinated by six oxygens of two water molecules and of four nitro-groups which bridge through the other oxygen to symmetry related Ca atoms.[100]

Two crystallographically distinct Sr atoms occur in the crystal structure of $[Sr(en)_4]_2(As_3Se_6)Cl$.[101] Sr(1) is coordinated by three chelating and two bridging en ligands leading to the formation of $[Sr(en)_4]_n^{2+}$ chains; the eight-fold coordination geometry is approximately square antiprismatic with r(Sr...N) = 270-277pm. Sr(2) is coordinated by four chelating en ligands to give discrete $[Sr(en)_4]^{2+}$ units; the eight-fold coordination geometry has C_s symmetry with r(Sr...N) = 267-293pm.[101]

The analogous barium salts, $Ba[O(S)C{=}C(CN)_2],4H_2O$ (30)[102] and $Ba[S_2C{=}C(CN)_2],3H_2O$ (31)[103] have been similarly synthesised by metathesis of $K_2[O(S)C{=}C(CN)_2],H_2O$ $\{Na_2[S_2C{=}C(CN)_2]\}$, prepared by reaction of COS $\{CS_2\}$ with maleonitrile in the presence of KOEt {NaOEt} in ethanol, with $Ba(NCS)_2,3H_2O$ in ethanol. Although similar distorted tricapped trigonal prismatic coordination geometries are found for the Ba atoms in the two salts, the overall structures are considerably different; whereas (30) is monomeric, (31) is dimeric based on a centrosymmetric Ba_2O_2 ring. The Ba atom in (30) is surrounded by six oxygens provided by five water molecules (271.9-288.8pm) and a monodentate monothiolate moiety (281.1pm) and three nitrogens from the cyano moieties of three separate anions (285.5-304.3pm);[102] that in (31) is surrounded by four oxygens provided by two bridging (282.0,286.6pm) and two terminal (281,286pm) water molecules, three nitrogens from the cyano moieties of three separate anions (284-304pm) and two sulphurs of a bidentate dithiolate group (324.3,326.3pm).[103]

The Ba atoms in the crystal structure of bis(triethanolamine)bis-(2,4,6-trinitrophenolato)barium(II)[104] lie on 2-fold axes of symmetry and are surrounded by a nitro oxygen of two symmetry related anions (314.2pm) and by the nitrogen (303.0pm) and three oxygens (272.8-281.0pm) of two similarly related ligands in a distorted bicapped cubic ten-coordinate arrangement. The ligands are disordered over two positions which are approximately related by pseudo-mirror planes which include the nitrogen atom and each of the three terminal carbon atoms.

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