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Chapter 2

ELEMENTS OF GROUP 2

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2.1 INTRODUCTION

The format adopted previously[1] for reporting the chemistry of these elements has been retained for the present review, the abstracted data being considered in sections which reflect topics currently of interest and importance. Some topics (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. The topics unique to the Group 2 elements are covered in this Chapter.

2.2 METALS AND INTERMETALLIC COMPOUNDS

Once again a significant number of the papers abstracted for this section involve the application of alkaline earth metals and their intermetallic derivatives (eg. Mg_2Ni, Mg_2Cu, $CaNi_5$) as hydrogen storage materials; to give appropriate coverage to this subject, the section has been subdivided as for the previous review.[1]

2.2.1 Structural and Thermodynamic Properties

Reanalysis of the X-ray data from the high pressure phase Be(II) has revealed an alternative to the previously accepted hexagonal cell (a = 432.8, c = 341.6pm);[2] it is a smaller orthorhombic cell (a = 216.8, b = 375.5, c = 341.6pm) with four Be atoms occupying the 4c positions ($x \sim 0.67$, $y \sim 0.82$, $z \sim 0.70$) of the $P2_12_12$ space group.

Activity data for liquid Mg-X (X = Si,Ge,Sn,Pb) binary systems have been calculated from the corresponding liquidus and vapour pressure data.[3] They are used to develop models for the structure of the liquid close to the Mg_2X composition; the most realistic scheme is that in which successive dissociation of the compounds occurs with the formation of the intermediate associate:

$$Mg_2X \longrightarrow Mg + MgX \longrightarrow Mg + X \qquad (X = Si,Ge,Sn,Pb) \qquad ...(1)$$

Collins et al have determined the structures of $Be_{17}Zr_2$,[4] $Be_{16}Re_{0.92}$[5] and $Be_{12}Mo$.[6] Schafer et al[7] have prepared $BaAl_2$ under high pressure (300×10^6Pa) - high temperature (1273K) conditions and, after quenching to ambient conditions, have determined its structure as a metastable phase. Pertinent crystallographic parameters for all four intermetallic compounds are collated in

Table 1.

Single crystal XRD data have been used to assess the charge density distribution in the Laves phases MgX_2 (X = Cu,Zn).[8] Electron transfer from Cu to Mg and from Mg to Zn was observed; difference Fourier syntheses also show that there are residual electrons at the centre of the Cu_4 or Zn_4 tetrahedra.

The electronic structures of Mg_3X_2 (X = Sb,Bi) have been calculated using an extended Hückel technique to facilitate interpretation of soft X-ray emission and X-ray photoemission spectroscopic data.[9]

Single crystal XRD structural data have been accumulated for a number of ternary intermetallics;[10-15] the compounds studied are listed in Table 1 together with pertinent crystallographic parameters. The ternary borides investigated by Jung[10] are members of the homologous series $M_nRh_{3n-1}B_{2n}$ (M = Ca,Sr) whose structures are built up by combining elements of the MRh_3B_2 and MRh_2B_2 (M = Ca,Sr) structures; viz., $M_2Rh_5B_4$ (M = Ca,Sr), $M_3Rh_8B_6$ (M = Ca,Sr), $Sr_5Rh_{14}B_{10}$ and $Ca_7Rh_{20}B_{14}$ are 1/1, 2/1, 4/1 and 6/1 combinations, respectively. The structures of the ternary aluminides were ascertained by Schafer et al[11-13] and that of $Mg_{28.4}Cu_{57.9}Si_{13.7}$ by a group of Japanese chemists; the structure of the latter is a variant of that of the Laves Phase of composition, Mg_2Cu_3Si.

2.2.2 Hydrogen Storage Applications

Imamura et al[16] have continued their investigation, first reported in the 1983 review,[17] of the hydriding characteristics of magnesium metal clusters formed by cocondensation of magnesium atoms and thf molecules at 77K. The results of hydrogen-deuterium isotope scrambling and surface modification experiments for both Mg-thf mixtures and Mg powder indicate that the higher activity of the former substrate is attributable to a rapid surface process.[16]

Hydrogenation of $MgCl_2$ suspensions in thf in the presence of a $CrCl_3$-$C_{14}H_{10}Mg$ catalyst has also been studied;[18] the products obtained include MgHCl, MgHCl,$MgCl_2$ and MgHCl,MgH_2.

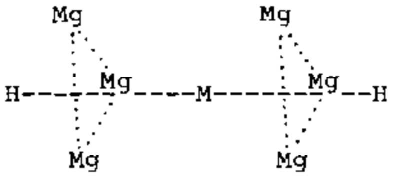
Both theoretical[19] and experimental[20-23] investigations of the hydrogenation of magnesium-containing alloys have been completed. The results of model calculations, based on extended Hückel MO theory, for the interaction of hydrogen atoms with a variety of

Table 1. Crystallographic parameters for diverse intermetallic compounds containing an alkaline earth metal.

Phase	Symmetry	Space Group	a/pm	b/pm	c/pm	Ref.
$Be_{17}Zr_2$	trigonal	$R\bar{3}m$	753.8	-	1101.5	4
$Be_{16}Re_{0.92}$	cubic	$F\bar{4}3m$	587.5	-	-	5
$Be_{12}Mo$	tetragonal	I4/mmm	725.1	-	423.4	6
$BaAl_2$	cubic	Fd3m	870.2	-	-	7
$CaRh_3B_2$	hexagonal	P6/mmm	555.1	-	291.9	10
$M_{0.66}Rh_3B_2$ (M=Sr,Ba)*	hexagonal	P6/mmm	566.8	-	281.5	10
$M_2Rh_5B_4$ (M=Ca,Sr)*	orthorhombic	Fmmm	546.0	972.7	1122.0	10
$M_3Rh_8B_6$ (M=Ca,Sr)*	orthorhombic	Fmmm	550.0	969.8	1704.7	10
$Sr_5Rh_{14}B_{10}$	orthorhombic	Fmmm	560.1	984.5	2890.3	10
$Ca_7Rh_{20}B_{14}$	orthorhombic	Fmmm	553.0	965.2	4042	10
$CaCr_2Al_{10}$	tetragonal	P4/nmm	1295.7	-	517.9	11
$Ca_4Cr_7Al_{48}$	trigonal	P3m1	1028.1	-	1157.9	12
$CaCu_4Al_8$	tetragonal	I4/mmm	882.3	-	515.1	11
$Ca_3Cu_2Al_7$	trigonal	$R\bar{3}m$	561.4	-	2585.3	11
$CaZn_2Al_2$	tetragonal	I4/mmm	412.7	-	1167.1	13
$Mg_{28.4}Cu_{57.9}Si_{13.7}$	cubic	$P4_132$	695.98	-	-	14
$Sr_6Al_2Sb_6$	orthorhombic	Cmca	2041.0	690.0	1350.1	15

*Several isostructural compounds were synthesised; the crystallographic data refer to the element listed first.

Mg_3MMg_3 clusters (1) have been presented;[19] they serve as a basis for qualitative speculation on the rates of hydriding and dehydriding of magnesium alloys and on the thermal properties of



M = Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu.

The Mg_3MMg_3 cluster showing axial approach of two hydrogen atoms.

(1)

doped magnesium hydrides. Those clusters containing Mg Ti V Cr Mn and Fe were found to be stable (with respect to the isolated atoms), while clusters containing Co Ni and Cu were unstable in this particular geometry (1). The presence of a second metal invariably decreased the work function of the Mg cluster; the introduction of hydrogen, however, increased its work function.[19]

The interaction of magnesium-copper[20] and magnesium-nickel[21] alloys containing hydride forming metals with hydrogen has been studied using XRD techniques; the initial phase compositions of the alloys and those of the hydrided products are summarised in Table 2. The introduction of these metals into the magnesium matrix invariably has a significant catalytic effect on the hydrogenation process.[20,21]

Table 2. Phase compositions of magnesium alloys before and after hydrogenation.[20,21]

Alloy	Initial Phase composition	Final Phase composition*
Mg-Cu-Ca	Mg_2Cu, Mg_2Ca, Mg	$MgCaH_4$, MgH_2, CaH_2, $MgCu_2$
Mg-Ni-Ca	Mg_2Ni, Mg_2Ca, Mg	$MgCaH_4$, Mg_2NiH_4, MgH_2
Mg-Ni-Sc	Mg_2Ni, $ScNi_2$, Mg	Mg_2NiH_4, MgH_2†
Mg-Ni-Y	Mg_2Ni, YNi_2, Mg	Mg_2NiH_4, MgH_2, YH_2
Mg-Ni-Ce	Mg_2Ni, $Mg_{12}Ce$, Mg	Mg_2NiH_4, MgH_2, CeH_3

*For some samples the products also contained some or all of the reactant phases; only novel phases are included here.

†Positive evidence for neither ScH_3 nor $ScNi_2H_x$ was obtained.

The kinetics of the hydrogenation of Mg_2Ni[22] and of the Mg-Mg_2Cu eutectic alloy ($x_{Cu} = 0.145$)[23] have been investigated. For Mg_2Ni, the rate-determining step was found to be dissociative chemisorption on nickel, involving heat transfer as a rate-delaying step.[22]

The hydriding characteristics of $CaNi_5$ have been the subject of both a thermodynamic[24] and a spectroscopic[25] analysis. Precise pressure-composition isotherms have been determined[24] for the α- and α'-phases of the $CaNi_5$-$H_2(D_2)$ systems. Interpretation of the results suggests that the hydrogen atoms are situated in a single type of interstitial site (maximum occupancy = 0.5H/$CaNi_5$) in the α-phase and in two types of interstitial site (maximum occupancy = 1.0H/$CaNi_5$ and 2.0H/$CaNi_5$) in the α'-phase.[24] Electron spectroscopy (Auger electron, X-ray photoelectron and u.v. photoemission) studies[25] of $CaNi_5$ and the related Haucke compounds $Ca_xEu_{1-x}Ni_5$ (x = 0.17, 0.75) indicate that their widely different hydriding characteristics are probably not dominated by electronic contributions (the band structures of these materials are almost identical) but are influenced by an increase in the size of the interstitial sites with increasing x and by the variation in the permeability of the passivation films formed on the surfaces of these compounds.[25]

Single crystal XRD studies have been performed for Mg_2FeH_6[26] and Mg_2NiH_4.[27-29] Prepared by a sintering technique at 773K and under (2-12) x 10^6Pa of hydrogen, Mg_2FeH_6 has a cubic (Fm3m) structure (K_2PtCl_6-type) with a_o = 644.3pm.[26]

Aspects of the structural chemistry of Mg_2NiH_4 (Mg_2NiD_4), ascertained from X-ray and neutron diffraction data, have been reported by three independent groups;[27-29] although broadly in agreement some of the details in the three papers differ slightly. Mg_2NiH_4 is polymorphic, existing in monoclinic, orthorhombic and cubic modifications. The pure monoclinic phase, which is the stable ambient temperature phase, has been prepared by hydriding a virgin sample of Mg_2Ni.[27] It converts irreversibly to the cubic modification at 518K[27] (508K)[28] and ambient pressure (10^5Pa). The third, orthorhombic, phase often contaminates samples of the monoclinic modification;[28] the experimental conditions required to synthesise a pure orthorhombic phase are unknown.[27] The orthorhombic phase transforms readily to the cubic polymorph at 508K and ambient pressure (10^5Pa)[27] and converts to the monoclinic phase on grinding at ambient temperature (298K) and pressure (10^5Pa);[28] it is stabilised by 10% substitution of Ni by Co.[28]

The monoclinic structure can be refined in either Cc space group with a = 1503.7, b = 641.1, c = 649.3pm, β = 118.8°[28] or C2/m space group with a = 1320.1, b = 640.7, c = 649.1, β = 93.21°[28] (a = 649.6, b = 641.2, c = 660.2pm, β = 93.23°).[29] The main peaks of the orthorhombic phase can be indexed with a = 657.2, b = 452.0, c = 456.0pm;[28] the presence of several weak peaks, however, indicates that longer range ordering exists and that the true unit cell is somewhat larger. The cubic phase can be refined in Fm3m space group with a = 653.0pm.[28]

The monoclinic polymorph consists of a 3-D network of distorted MgH_6 octahedra with shared vertices (average r(Mg...H) = 180pm);[27] the hydrogen atoms form square planar coordination spheres around the Ni atom (average r(Ni...H) = 156pm).[29] It can be considered to be constructed from alternating $CaTiO_3$- and ReO_3-type units. In the cubic polymorph, the metal atoms form a ccp CaF_2-type structure. At T = 513K, most of the hydrogen atoms are distributed among the 48h sites (x,x,0) [$x \sim 0.2$] for which the calculated Mg-H contact is 166pm; such a distance suggests a preferential Mg-H bond. At T>513K, the hydrogen atoms show no preference for 48h or 24e (x,0,0) sites.[27]

The electronic structures of the ternary hydrides, Mg_2FeH_6,[30] Mg_2NiH_4[31] and Ca_2RuH_6[30] have been studied using the augmented plane wave band structure method. Whereas the A_2BH_6 compounds were found to be semi-conductors,[30] Mg_2NiH_4 was found to be an insulator.[31]

2.3 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

The decrease in interest in these compounds noted in the 1983 review,[32] has not yet been reversed. Indeed so few papers have been abstracted this year that the various subsections included previously have been amalgamated under the two broad subject headings of 'binary derivatives' and 'ternary derivatives'. 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.

2.3.1 Binary Derivatives

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

Electronic and geometric structures and physicochemical properties of MO, $(MOH)^+$ and MOH (M = Be,Mg) have been calculated by ab initio SCF MO methods; pertinent data are summarised in Table 3.

Extensive solid solutions have been observed in the SrI_2-BaI_2 system both at ambient and higher (2.0GPa) pressures.[34] The

Table 3. Structural properties for MO $(MOH)^+$ MOH (M = Be,Mg) molecular species calculated using ab initio SCF MO methods.[33]

Species	State	r(M...O)/pm	r(O...H)/pm	μ/D
BeO	$^1\Sigma^+$	132.1	-	-7.43
MgO	$^1\Sigma^+$	179.5	-	-8.44
$(BeOH)^+$	$^1\Sigma^+$	134.0	94.4	-5.41
$(MgOH)^+$	$^1\Sigma^+$	170.9	94.5	-7.77
BeOH	$^2\Sigma^+$	139.9	93.4	0.85
MgOH	$^2\Sigma^+$	177.4	94.1	-1.27

normal pressure phases of SrI_2 (SrI_2-type structure) and BaI_2 ($PbCl_2$-type structure) dissolve up to 20 mol.% BaI_2 and 40 mol.% SrI_2, respectively, whereas the high pressure phases of SrI_2 ($PbCl_2$-type variant) and BaI_2 (anti-Fe_2P structure) dissolve up to 15 mol.% BaI_2 and 60 mol.% SrI_2, respectively.

Single crystal XRD studies have been undertaken for the hydrated alkaline earth metal halides, $CaI_2.4H_2O$,[35] $CaI_2,6.5H_2O$[35] and $SrCl_2.6H_2O$;[36] whereas those of the calcium salts are novel investigations,[35] that of the strontium salt is a re-examination.[36] The structure of $CaI_2,4H_2O$[35] consists of centrosymmetric octahedral trans-configurated $CaI_2(H_2O)_4$ groups with r(Ca...I) = 312.7, r(Ca...O) = 229.9, 230.9pm. That of $CaI_2,6.5H_2O$[35] contains binuclear $Ca_2(H_2O)_{13}{}^{4+}$ cations and I^- anions; in the cations, two $Ca(H_2O)_8$ square antiprisms are connected by two common triangular faces with r(Ca...O) = 239-260pm. In the structure of $SrCl_2,6H_2O$,[36] infinite chains of 9-coordinate Sr atoms lie along the 3-fold axes of the trigonal P321 space group. Three water molecules are equatorially coordinated to each Sr atom, while the other six water molecules bridge to adjacent Sr atoms.

2.3.2 Ternary Derivatives

The structural chemistry of several novel ternary oxides[37-43] has been elucidated using XRD methods; pertinent crystallographic parameters are summarised in Table 4. Although the majority of these polytypes were prepared by classical solid state methods, $CaTa_2O_6$ and $Ba_3Lu_4O_9$ were synthesised by Muller-Buschbaum[37,43] using the CO_2 laser technique, and $SrTa_2O_6$ was obtained by Bayer and Gruehn[38] both by deposition from the vapour phase using Cl_2 as transporting agent and by crystallisation from B_2O_3 melts at T<1423K. The three barium ruthenates(IV) were generated, together with the Ba-rich compounds, Ba_9RuO_{11} and Ba_4RuO_6, for which XRD data could not be indexed, by a group of Russian authors[41] in a comprehensive study of the $BaO-RuO_2$ system.

Table 4. Crystallographic parameters for diverse ternary oxides and halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
$CaTa_2O_6$	cubic	Pm3	778	-	-		37
$Ca_{0.5}TaO_3$	cubic	Pm3m	388.9	-	-		37
$SrTa_2O_6$	orthorhombic		1100.6	763.8	562.2	-	38
Ba_2TiO_4	orthorhombic	$P2_1nb$	610.7	2295.2	1054.0	-	39
$Ba_6Ti_{17}O_{40}$	monoclinic	C2/c	988.7	1709.7	1891.8	98.72	40
$BaTi_4O_9$	orthorhombic	Pmmn	1452.7	379.4	629.3	-	40
Ba_3RuO_5	orthorhombic		888.0	449.0	688.0	-	41
Ba_2RuO_4	tetragonal		398.1	-	1344.0	-	41
$BaRuO_3$	hexagonal		574.5	-	2162.0	-	41
$Ba_4Ln_2O_7$[*]	tetragonal		436.6	-	2868.0	-	42
$Ba_3Ln_3O_{7.5}$[†]	tetragonal		438.6	-	1185.6	-	42
$Ba_3Lu_4O_9$	trigonal	R3	896	(α = 39.42°)	-	-	43
Cs_2BeCl_4	orthorhombic	Pnma	964.2	717.8	1246.8	-	44
$BaMnF_5$	orthorhombic	$P2_12_12_1$	1411.5	581.1	488.1	-	45

[*] Several isostructural compounds were studied (Ln = Gd-Lu,Y); the data refer to the yttrium derivative.

[†] Several isostructural compounds were studied (Ln = Ho-Lu,Y); the data refer to the yttrium derivative.

The structures of the novel MTa_2O_6 (M = Ca,[37] Sr[38]) polytypes differ considerably. The calcium tantalate(V)[37] is a cubic modification which, although similar in structure to $Ca_{0.5}TaO_3$, differs in the presence of an ordered distribution of Ca atoms. The strontium tantalate(V) is a low temperature orthorhombic modification which reverts irreversibly to the normal structure at T>1493K.

I.r. and Raman spectra of $M(VO_3)_2$ (M = Mg-Ba) have been recorded and assigned on the basis of their monoclinic C2/m structures by Fotiev et al.[44]

Two ternary halides, Cs_2BeCl_4[45] and $BaMnF_5$,[46] have been structurally characterised; pertinent unit cell parameters are included in Table 4.

Optical visible absorption spectra of doped samples of $CsMgX_3$ (X = Cl,Br) have been measured by two independent groups.[47-49] Gudel et al have investigated $V_2^{II}Cl_9^{5-}$ dimer formation in $CsMgCl_3$[47] and $Mn_2^{II}X_9^{5-}$ dimer formation in CsMgX (X = Cl,Br)[48] and McPherson et al have studied $Cu^IM^{III}Cl_9^{5-}$ (M = Cr,Mo,Ru,Rh) dimer formation in $CsMgCl_3$.[49] The absorption bands are assigned either to vanadium(II) or manganese(II) pair excitations[47,48] or to intermetallic Cu(I)→M(III) (M = Cr,Mo,Ru,Rh) charge transfer transitions.[49]

Analysis[50] of the liquidus curve for the $NaF-MgF_2$ system indicates that the melt probably contains MgF_4^{2-} anions rather than MgF_3^- (or Mg^{2+}) ions, despite the fact that the only ternary compound formed in the system is $NaMgF_3$.

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

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

2.4.1 Complexes of Significance in Bioinorganic Chemistry

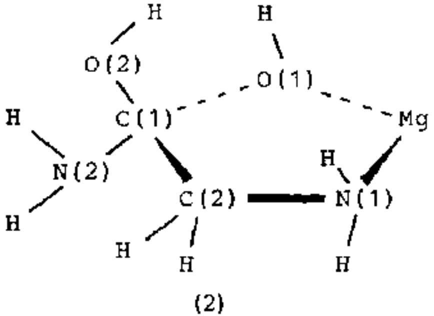
Diverse biologically active molecules are known to interact with alkaline earth metals; those which have been studied in 1984, however, fall into the three distinct categories of saccharides,[51-54] peptides[55,56] and nucleotides.[57-61]

Complex formation between Ca^{2+} ions and diverse monosaccharides has been studied in solution both spectroscopically[51] and calorimetrically.[52] The spectroscopic evidence[51] indicates that those sugars with pyranose structures bind Ca^{2+} ions strongly using three adjacent hydroxyl groups in the ax-eq-ax configuration; for those sugars with furanose structures, however, the spectra suggest that three cis hydroxyl groups are required for strong bonding to Ca^{2+} ion. The calorimetric data[52] indicate that the behaviour of D-glucose and D-fructose in the presence of Ca^{2+} ions cannot be differentiated, the free energy ($-5.4(4)$ $kJ.mol^{-1}$) and entropy ($0(8)$ $JK^{-1}mol^{-1}$) changes on formation of 1:1 complexes being identical.

The thermodynamics of complex formation between the biopolysaccharide, heparin, and Ca^{2+} ions have been determined[53] using potentiometric techniques in aqueous solution adjusted to $I = 0.3$ by MCl (M = Li,Na,K) or $MgCl_2$. When Ca^{2+} ions are in excess, complex formation was found to be dependent on the electrolyte cation, either one (in the presence of Na^+ or K^+) or two (in the presence of Li^+, Na^+ or Mg^{2+}) Ca^{2+} ions being coordinated to each tetrasaccharide unit of heparin. When heparin is in excess, however, Ca^{2+} ion bridge formation linking two tetrasaccharide units is also revealed in each system.[53]

Complex formation between riboflavin and, inter alia, Ca^{2+} ion has been investigated[54] spectroscopically (i.r. and u.v.-visible) in CH_3CN with $LiClO_4.3H_2O$ as supporting electrolyte. The spectra indicate that coordination occurs through the pyrimidine carbonyl and ribitol hydroxyl oxygen atoms.

Quantum mechanical calculations using the ab initio Hartree Fock MO method have been completed for peptide bond formation in the presence of Mg^{2+} ion[55] and for complex formation between the dipeptides, glycylproline or prolylglycine, and Ca^{2+} ion.[56] Two mechanisms were examined for the S_N2 reaction (i.e. two-step and concerted) between glycine and ammonia in the presence of Mg^{2+} ion.[55] The activation energies calculated for the Mg^{2+}-catalysed amide bond formation were substantially lower than those obtained for the uncatalysed and amine-catalysed reactions. The catalytic effect of the Mg^{2+} ion is to stabilise both the transition states and the intermediate; it is attributed to the neutralisation of the developing negative charge on the electrophile and formation of a conformationally flexible non-polar five membered chelate ring structure (2).



(2)

Bond distances/pm		Bond angles/°	
Mg...O(1)	180.1	MgO(1)C(1)	117.7
O(1)...C(1)	149.3	O(1)C(1)C(2)	105.6
C(1)...C(2)	158.1	C(1)C(2)N(1)	112.2
C(2)...N(1)	152.2	C(2)N(1)Mg	105.3
N(1)...Mg	194.8	N(1)MgO(1)	89.9

The stabilities of various geometrical forms of the complexes of Ca^{2+} ion with both neutral (Zwitterionic) and anionic glycylproline and prolylglycine were determined to assess the different binding sites of these aliphatic dipeptides.[56] The configuration with the greatest stability was that in which the Ca^{2+} ion is coordinated by both oxygen atoms of the carboxyl group.

The structural chemistry of the binary compounds formed between xanthosine-5'-monophosphate(5'-xmp) and Mg^{2+} ions,[57] thymidine-5'-monophosphate (5'-tmp) and Ca^{2+} ions,[58] deoxyadenosine-5'-monophosphate (5'-damp) and Ca^{2+} ions[59] and of the ternary compounds formed between adenosine-5'-triphosphate (5'-atp), bis(2-pyridyl)amine (bipyam) and Mg^{2+} or Ca^{2+} ions,[60] has been elucidated using a variety of techniques. Spectroscopic and chemical evidence obtained by Tajmir-Riahi and Theophanides[57] suggest that whereas the cation in Mg[5'-xmp],$4H_2O$ binds to the phosphate moiety as well as the N(7) atom of the purine ring, that in Mg[5'-xmp],$9H_2O$ only interacts with the N(7) atom of the purine ring; presumably the extra water molecules replace the phosphate moiety in the cation coordination sphere.

Sato has completed single crystal XRD studies of Ca[5'-tmp],$2H_2O$[58] and of Ca[5'-damp],$5H_2O$.[59] In the former structure[58] the Ca^{2+} ion interacts with three phosphate oxygen atoms, two sugar oxygen atoms, one oxygen atom of the thymine base and a single water molecule; in the latter structure,[59] the Ca^{2+} ion interacts with four phosphate oxygen atoms and three water molecules. The CaO_7 coordination spheres in both complexes are irregular with fairly wide-ranging Ca-O distances (229.1-255.5pm in the 5'-tmp derivative and 230.2-258.1pm in the 5'-damp derivative).

The crystal and molecular structures of the ternary complexes formed between 5'-atp, bipyam and M^{2+} (M = Mg,Ca) have been elucidated by Cini et al.[60] They contain $[M(H_2O)_6]^{2+}$ cations, $[M(5'\text{-Hatp})_2]^{4-}$ anions, uncoordinated Hbipyam^+ cations and several free water molecules and are best formulated as $[Mg(H_2O)_6][\text{Hbipyam}]_2[Mg(5'\text{-Hatp})_2],12H_2O$ and $[Ca(H_2O)_6][\text{Hbipyam}]_2[Ca(5'\text{-Hatp})_2],9H_2O$. The $[M(H_2O)_6]^{2+}$ cations have a distorted octahedral geometry; the metal atoms lie on a 2-fold axis with Mg-O and Ca-O distances averaging 212(6) and 240(7)pm, respectively.

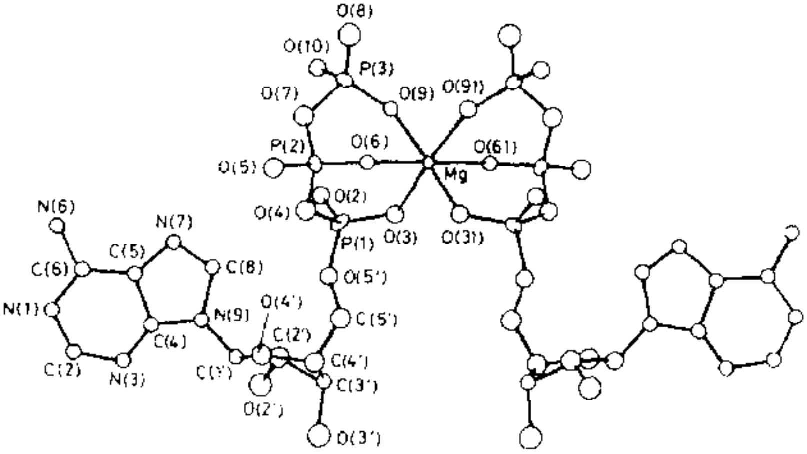


Figure 1. Molecular structure of the $[Mg(5'\text{-Hatp})_2]^{4-}$ anion in the $[Mg(H_2O)_6][\text{Hbipyam}]_2[Mg(5'\text{-Hatp})_2],12H_2O$ ternary complex (reproduced by permission from J. Chem. Soc., Dalton Trans., (1984)2467).

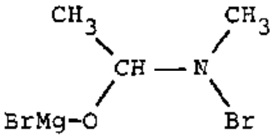
In the $[M(5'\text{-Hatp})_2]^{4-}$ unit (Figure 1), the metal atom has octahedral coordination geometry and is located on a 2-fold axis. The two $(5'\text{-Hatp})^{3-}$ anions interact with the metal atom via the α, β, and γ phosphate oxygen atoms (Figure 1). The MgO_6 coordination polyhedron is almost regular with an average Mg-O distance of 206(2)pm; the CaO_6 coordination polyhedron, however, is a little more distorted with an average Ca-O distance of 228(2)pm. No association occurs between the metal atoms and either the nitrogen atoms of the purine system or the sugar oxygen atoms.[60]

An ab initio MO theoretical study[61] of phosphate interaction with Mg^{2+} predicts that the addition of two water molecules to the system does not affect the geometry of the magnesium phosphate complex. Implications for the association of alkaline earth metal cations with nucleotides and their derivatives are discussed.[61]

2.4.2 Complex Formation in Solution

At least three complexes (BeL^+, Be(OH)L and BeL_2) have been detected[62] by spectrophotometric and luminescence methods when Be^{2+} ions are treated with either 2-(o-hydroxyphenol)benzoxazole or 2-(o-hydroxyphenyl)benzothiazole. Where possible stability constants were calculated.[62] Stability constants have also been determined[63] for complexes formed between dithiodiproprionic acid and methylenebis(thioacetic) acid and, inter alia, Be^{2+} ions.

The reaction between anhydrous $MgBr_2$ and N-methylacetamide in CCl_4 has been studied by i.r. spectroscopy;[64] the variation in the spectra as a function of time has been followed, the final spectrum being attributed to an addition product (3).



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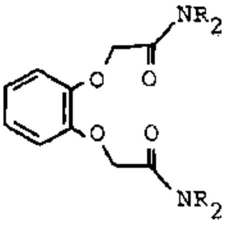


(4)

The chelation ability and coordination modes of a series of 1,2- and 1,3-phenylenedioxydiacetamides for Ca^{2+} ions have been systematically studied using spectroscopic (i.r. ^{1}H- and ^{13}C-nmr) techniques.[65] Only the 1,2-phenylenedioxydiacetamides (4) function as ligands; they act as tetradentate chelating ligands, forming 2:1 complexes using all four oxygen atoms to bind the Ca^{2+} ion.

2.4.3 Beryllium Derivatives

Structural analyses have been completed on a number of diverse beryllium derivatives.[66-72] The previously reported[73,74] "slip sandwich" geometry of dicyclopentadienylberyllium (Figure 2) has been confirmed in a redetermination[66] of its structure at 128K. The Be atom is disordered between two equivalent sites in which it is centrally (η^5-) bonded to one ring and peripherally (η^1-) bonded to the other (Figure 2). Analysis of the molecular geometry suggests that the peripherally bonded ring is attached to the Be atom with a basically sp^2 hybridised carbon. This indicates only slight perturbation of the ring's delocalised π-system and accounts for the recently reported[75] Raman spectrum

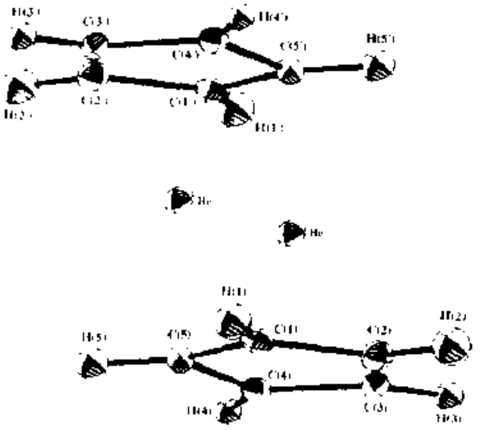
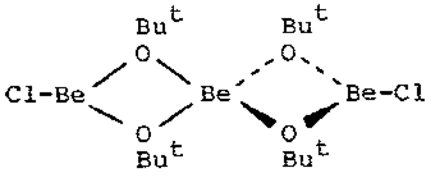


Figure 2. Lateral view of the structure of the beryllocene molecule determined at 128K showing the "slip-sandwich" structure (reproduced by permission from Austral. J. Chem., 37(1984)1601).

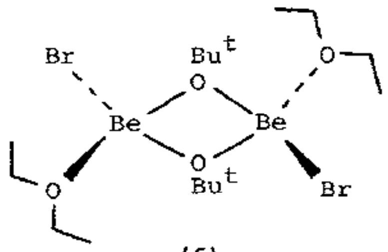
which was thought to be inconsistent with an η^1-C_5H_5 ring. In an independent i.r. solution (CS_2, C_6D_{12}, $CDCl_3$) study[67] of dicyclopentadienylberyllium evidence is given for both η^5- and η^1-attachment of the C_5H_5 rings to the Be atom. For cyclopentadienylberyllium chloride and bromide, η^5-attachment of the C_5H_5 ring is confirmed using comparable i.r. data.[67]

Electron diffraction data[68] for gaseous $Be_4O(NO_3)_6$ at ~430K are consistent with a T symmetry model for the molecule, the spatial arrangement of atoms in gaseous $Be_4O(NO_3)_6$ being generally very similar to that in solid $Be_4O(CH_3CO_2)_6$. The principal geometrical parameters refined to: r(Be...O(central μ_4-oxygen atom)) = 166.5pm, r(Be...O(nitrate oxygen atoms)) = 162.0pm, r(N...O(coordinated oxygen atom)) = 129.8pm, r(N...O(terminal oxygen atom)) = 118.5pm, ∠ONO = 117.0°, η(the angle of rotation of the NO_3 group about the 2-fold axis) = 25.2°.

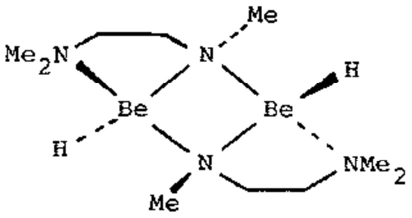
Single crystal XRD studies have shown that whereas $[Be_3Cl_2(OBu^t)_4]$ (5)[69] is monomeric, $[BeBr(OBu^t),Et_2O]_2$ (6),[70] $[BeH(Me_2NCH_2CH_2NMe)]_2$ (7) and $[Be(MeC{\equiv}C)_2,Me_3N]_2$ (8)[72] are dimeric. In the unit cell of (5),[69] the molecule lies at the intersection of two perpendicular mirror planes. The two chlorine and three



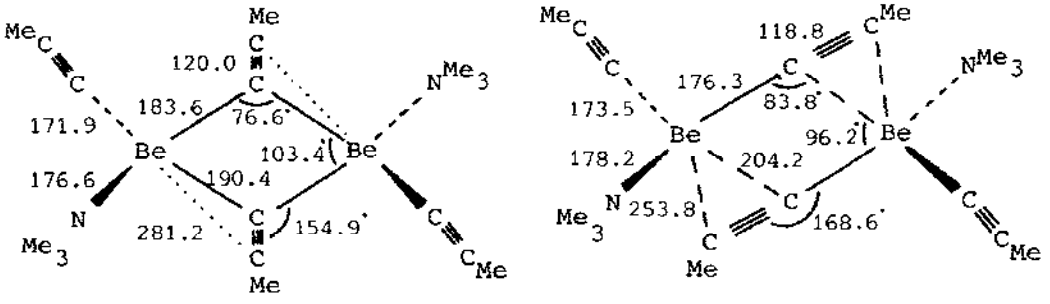
(5)



(6)



(7)



(a) (b)

distances/pm.

(8)

Be atoms lie along the intersection of these planes and are colinear. Adjacent Be atoms are bridged by two $-OBu^t$ anions, such that the $Be(\mu\text{-}OBu^t)_2Be$ moieties are at right angles giving a near tetrahedral coordination to the central Be atom, r(Be...O) = 164pm. The terminal Be atoms are trigonal planar, bonding to the bridging oxygen atoms (r(Be...O) = 154pm) and terminal chlorine atoms (r(Be...Cl) = 188pm). The shorter Be(sp^2)-O (154pm) than Be(sp^3)-O (164pm) distances and the relatively short Be-Cl distances (typically 196pm) are indicative of the presence of π-bonding around the 3-coordinate Be atoms.[69]

In the presence of ether, the corresponding bromide forms a dimeric structure (6) based on a centrosymmetric Be_2O_2 ring.[70] The distorted tetrahedral Be coordination sphere is generated by the two oxygen atoms of the bridging $-OBu^t$ anions (160,163pm), the oxygen atom of the ether molecule (165pm) and a bromine atom (219pm). The corresponding magnesium compound[76] has an analogous structure with r(Mg...OBu^t) = 191,191, r(Mg...OEt_2) = 201 and r(Mg...Br) = 243.5pm.

The dimeric structure of (7)[71] is similar; it is based on a centrosymmetric Be_2N_2 framework; the Be atom achieves a coordination number of 4 by virtue of the two bridging nitrogen atoms (174.6,174.7pm), a hydrogen atom (139pm) and the second nitrogen atom of the amido ligand (181.4pm).

Crystals of (8)[72] contain two independent centrosymmetric dimers in which μ-alkynyl groups exhibit quite different types of interaction with the Be atoms. In (8a), the μ-alkynyl groups function as one electron donors leading to a predominantly electron deficient Be_2C_2 ring in which significant cross-ring Be-Be bonding occurs giving a short Be-Be contact (231.9pm). In (8b), the ring is effectively electron precise with the μ-alkynyl groups acting as three electron (σ,π) donors with a longer associated Be-Be distance (254.9pm). Pertinent geometrical data for both dimers are included in the appropriate diagrams.[72]

Reaction of 1:1 molar ratios of $BeCl_2$ (or $MgCl_2$) and $Ph_3As{=}CH_2$ also yields[77] a dimeric beryllium(magnesium) species, in this case a cation, $[Ph_3AsCH_2M(\mu\text{-}Cl_2)MCH_2AsPh_3]^{2+}$ (M = Be,Mg) which is based on a M_2Cl_2 (M = Be,Mg) framework. Although thermally stable, they are hygroscopic. Whereas the Be complex dissolves readily in HNO_3 and HCl, the Mg complex is soluble in dmf, dmso, CH_3OH and water; they are both slightly soluble in CH_2Cl_2 and $CHCl_3$.[77]

Vibrational (i.r. and Raman) spectroscopic studies[78] of alkaline beryllate solutions have been effected; both aquo, $[Be(H_2O)_4]^{2+}$, and hydroxo, $[Be(OH)_4]^{2-}$, complexes were detected in solution. The two species were characterised by bands at 520cm^{-1} and in the range 870-900cm^{-1} ($[Be(H_2O)_4]^{2+}$) and by bands in the range 700-750cm^{-1} ($[Be(OH)_4]^{2-}$).[78]

2.4.4 Magnesium Derivatives

Since organomagnesium chemistry is reviewed elsewhere it is generally ignored here. Consequently, of the plethera of papers published during 1984 which describe the chemistry of this element, but few have been abstracted for this subsection; those included, however, cover a diversity of interests with no obvious recurrent theme.

The reaction of Mg atoms, Mg_2 dimers and Mg_3 trimers with CH_3Br in cryogenic (Ar) matrices has been studied[79] using u.v.-visible spectroscopic and matrix-gas replacement techniques. At high dilution Mg atoms are totally inert; Mg clusters, however, react by an oxidative-additive mode:

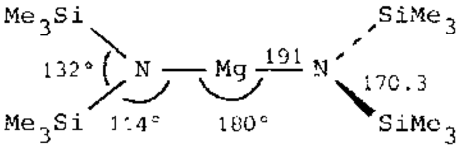
$$(Mg)_n + CH_3Br \rightarrow CH_3(Mg)_nBr \qquad \ldots(2)$$

The higher reactivity of the Mg clusters is attributed to a greater thermodynamic stability of the cluster Grignard product, steric/orbital considerations and a lower ionisation potential of Mg clusters.[79]

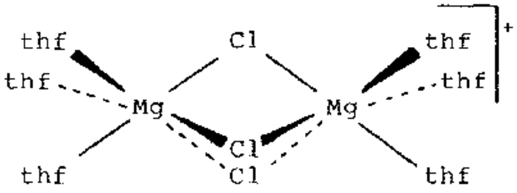
The amido complexes $M_2[Mg(NH_2)_4]$ (M = K,Rb) have been prepared[80] by reaction of the metals with liquid ammonia at high temperature (423K) and pressure (200 MPa). XRD studies have shown that they are isotypic; single crystal data for $K_2[Mg(NH_2)_4]$ indicate that the Mg atom is tetrahedrally surrounded by four NH_2^- anions (r(Mg...N) = 204-209; r(Mg...H)>243pm) and that the two crystallographically distinct alkali metal atoms are located in rectangularly monocapped trigonal prisms afforded by NH_2^- anions (r(K(1)...N) = 284.9-333.4; r(K(2)...N) = 300.5-331.9; r(K...H)>276pm).[80]

Electron diffraction data for gaseous $[Mg\{N(SiMe_3)_2\}_2]$[81] at 400K are consistent with a monomeric model (9). Significant structural features are the linear NMgN arrangement and the staggered $Si_2NMgNSi_2$ backbone. Minor torsional distortions lower the overall symmetry of the molecule from D_{2d} to S_4.[81]

The cation, $[Mg_2Cl_3,(thf)_6]^+$ (10), has been structurally characterised by two independent groups;[82,83] a Dutch group[82] observed it in the product, $[Mg_2Cl_3(thf)_6]^+[TiCl_3(PhC{=}CPh)_2]^-$, of the reaction of $[TiCl_3(thf)_3]$, diphenylacetylene and Pr^iMgCl in thf and a Polish group[83] found it in the product $[Mg_2Cl_3(thf)_6]^+[TiCl_5(thf)]^-$ of the direct reaction of $[MgCl_2(thf)_2]$ and $[TiCl_4(thf)_2]$ in thf. The details of the two structure determinations are very similar. The cation (<u>10</u>) contains two symmetry unrelated Mg atoms bridged by three chlorine atoms, r(Mg(1)...Cl) = 248-251 (249.7-251.1); r(Mg(2)...Cl) = 247-251 (251.2-251.5pm); each Mg atom has three terminal thf molecules to complete their distorted octahedral coordination spheres, r(Mg(1)...O) = 207-210 (206.6-208.5); r(Mg(2)...O) = 204-211 (204.1-210.2pm). [Polish data[83] are given in parentheses].

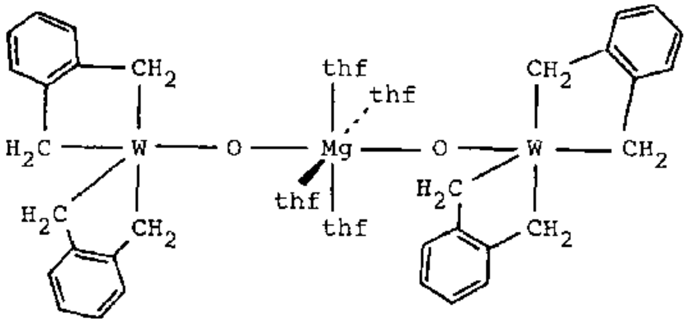


distances/pm
r(Si...C) = 188.6pm
∠NSiC = 116.4°
(<u>9</u>)



(<u>10</u>)

The structures of two heterobimetallic complexes containing magnesium have been elucidated.[84,85] Reaction of $MgCl_2$ with $FeCl_3$ in thf yields $[MgCl(thf)_5][FeCl_4]$ which is reduced in the presence of thf to form the Mg-Fe complex, $[Cl_2Fe(\mu\text{-}Cl_2)Mg(thf)_4]$ (<u>11</u>).[84] Crystallographic studies of (<u>11</u>) have shown it to contain pseudotetrahedral $FeCl_4$ units (r(Fe...Cl) = 222.8,237.7pm) and pseudooctahedral $MgCl_2(thf)_4$ units (r(Mg...Cl) = 250.1pm; r(Mg...O) = 207.3,211.1pm) which edge share a pair of bridging chlorine atoms.[84] Reaction of $WOCl_4$ with either the diGrignard reagent $o\text{-}C_6H_4(CH_2MgCl)_2$ or $[Mg(CH_2C_6H_4CH_2\text{-}o)(thf)]$ in thf yields either the trischelate $[W(CH_2C_6H_4CH_2\text{-}o)_3]$ or the Mg-W complex, $[\{W(CH_2C_6H_4CH_2\text{-}o)_2\}(\mu\text{-}O)Mg(thf)_4(\mu\text{-}O)\{W(CH_2C_6H_4CH_2\text{-}o)\}]$ (<u>12</u>).[85] Structural elucidation of (<u>12</u>) has shown the Mg atom to be located at the inversion centre and to be octahedrally coordinated by the two bridging oxygen atoms (207pm), and four thf oxygen



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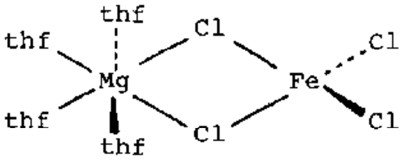


(11)

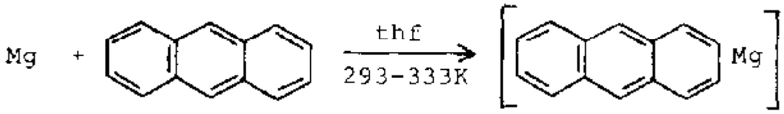
atoms (209,211pm). The five-coordinate W atom environment is highly distorted owing to a very short W-O bridging contact (171pm) and the restrictions associated with the presence of two chelating ligands (r(W...C) = 214-218pm).[85]

Hydrated alkaline earth metal (Mg-Ba) salts of $(CH_2COOH)_2$[86] and $HOCH[CH_2N(CH_2PO_3H_2)_2]_2$[87] have been synthesised and their thermal properties ascertained using dta, tga and XRD methods. The carboxylates, $M(CH_2COO)_2,nH_2O$ (Mg, n=4; Ca, n=1.5) decompose via the anhydrous salt and the carbonate to the oxide; the decomposition of the anhydrous salts $M(CH_2COO)_2$ (M = Sr,Ba), however, proceeds no further than the carbonate.[86] The phosphates, $M_4\{HOCH[CH_2N(CH_2PO_3)_2]_2\}$ (Mg, n=8; Ca, n=4; Sr, n=6; Ba, n=8) dehydrate in either a single stage (Mg,Ca,Sr) or a two stage (Ba) process eventually forming the anhydrous salts. Further decomposition was not studied.[87]

The structure of magnesium bis(hydrogen maleate)hexahydrate has been ascertained by single crystal methods.[88] The Mg atom is located at an inversion centre and is coordinated by a slightly distorted octahedron of water molecules (203.6-205.9pm); bonding to the carboxylate anion is through the water molecules via strong hydrogen bonds.[88]

The magnesium-anthracene (1/1) complex crystallises from thf with three solvate molecules.[89] Multinuclear nmr (^1H, ^{13}C)

studies[89] indicate that, in thf solution, magnesium, anthracene and the complex exist in a temperature dependent, reversible equilibrium:



...(3)

the formation of the complex being favoured at lower temperatures. The data also show that the Mg atom interacts most strongly with the 9,10-positions of the aromatic ring system.[89] Reaction of the complex with dialkyl aluminium hydrides in thf yields magnesium μ-(9,10-dihydro-9,10-anthrylene)-dialkylhydridoaluminates;[90] similar products are obtained with aluminium trihydride and with ethoxydiethylaluminium. The structures of these compounds when dissolved in thf were determined by nmr spectroscopy.[90] An XRD study[90] of the diethylhydridoaluminate (Figure 3) showed that Mg and Al occupy axial positions in a 9,10-dihydro-9,10-anthrylene system, r(Mg...C) = 219.5, r(Al...C) = 203.6pm; and are bridged by the hydrogen atom, r(Mg...H) = 196, r(Al...H) = 162pm. The five-fold coordination polyhedron of the Mg atom (Figure 3) is completed by the oxygen atoms of three thf molecules (205.8-210.6pm) and the four-fold coordination sphere of the Al atom (Figure 3) is completed by the carbon atoms of the two ethyl moieties (198.0;198.4pm).[90]

2.4.5 Calcium Derivatives

A total of eleven papers have been abstracted for this subsection. They all describe the results of single crystal XRD studies; eight carboxylates,[91-97] one sulphonate,[98] and three other more diverse materials[99-101] have been studied. Pertinent features of the Ca atom coordination polyhedra in the organic salts[91-98] are summarised in Table 5. The CaO_7 coordination sphere in $Ca(HPO_3H)_2,H_2O$[99] is generated by six oxygen atoms from phosphate anions (average r(Ca...O) = 241.3pm) and a single water molecule (r(Ca...O) = 237.7pm) arranged in a distorted mono-capped trigonal prismatic geometry. A seven-coordinate Ca atom is also found in the structure of $CaTl_2Cl_{10},7H_2O$;[100] each Ca atom is surrounded by seven water molecules (average r(Ca...O) = 240.1 pm) disposed in a rectangularly capped trigonal prismatic geometry. In the structure of the $CaCl_2$-sarcosine (1/3) adduct,[101] the Ca

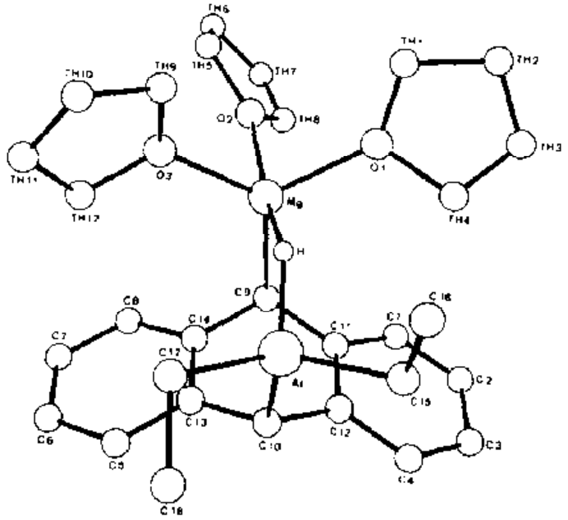


Figure 3. Molecular structure of magnesium-μ-(9,10-dihydro-9,10-anthrylene)-diethylhydridoaluminate (reproduced by permission from Chem. Ber., 117(1984)389).

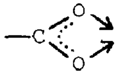
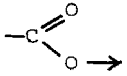
atom is located in a slightly distorted CaO_6 octahedral unit, the oxygen atoms being provided by six separate sarcosine molecules (CH_3NHCH_2COOH), r(Ca...O) = 229.4-238.7pm. Temperature dependent studies have shown that (i) the mirror symmetry of the paraelectric phase (>127K) is lost in the ferroelectric phase (<127K) and (ii) some disordered motion such as a reorientational motion of the CaO_6 octahedra occurs in the paraelectric phase.[101]

2.4.6 Strontium and Barium Derivatives

The traditional dearth of papers for this subsection has been maintained. Only four papers have been abstracted; they describe the crystal and molecular structures of one strontium[102] and three barium[103-105] derivatives. The structure of strontium digold octaacetate dihydrate[102] consists of isolated $SrAu_2(CH_3COO)_8$ units (13) with crystallographic symmetry 2. The coordination geometry is square planar at Au (r(Au...O) = 197.4-199.2pm) and square antiprismatic at Sr (r(Sr...O) = 254.8-259.6pm). The C-O bond lengths indicate covalent Au-O but electrostatic Sr-O interactions.[102]

Poonia et al[103-105] have reported structural data for the three barium derivatives, tetraaquabis(1,10-phenanthroline)barium(II)

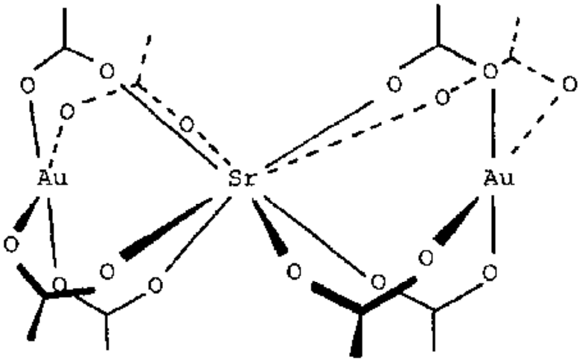
Table 5. Pertinent features of the Ca atom coordination polyhedra in various carboxylate[91-97] and sulphonate[98] salts.

Salt	Coordination* Polyhedron	r(Ca...O)			Ref.
				H_2O	
$Ca(CH_3COO)_2,H_2O$	$Ca(1)O_7$-D_{5h}	2; 246.0,249.0	3; 230.1-250.3	2; 236.0,236.8	91
	$Ca(2)O_8$-irregular	4; 239.9-293.3	4; 227.0-249.6	-	
$CaH(CH_3COO)_2,H_2O$	$Ca(1)O_7$-D_{5h}	2; 251.0-252.4	4; 235.2-242.4	1; 237.5	92
	$Ca(2)O_8$-D_{2d}	4; 251.0-259.4	3; 234.7-238.8	1; 237.2	
$Ca_2Ba[(CH_2)_2CHCOO]_6$	CaO_6-D_{3d}	$228.9^{\dagger}$			93
	BaO_{12}	$300.8^{\dagger}$			
$Ca_2Ba[(CH_3)_2CHCOO]_6$	CaO_6-D_{3d}	$225.3^{\dagger}$			93
	BaO_{12}	$296.5^{\dagger}$			
$Ca[HC(OH)COO]_2,3H_2O$	CaO_7-irregular	4; 221.4-241.9	1; 239.6	2; 236.1,238.4	94
$Ca_2[\overline{CH(COO)\{CH(COO)_3\}O}],2H_2O$	$Ca(1)O_8$-irregular	2^{x}	1^{x}	3^{x}	95
	$Ca(2)O_8$-irregular	2^{x}	1^{x}	3^{x}	
$Ca[2\text{-}FC_6H_4COO]_2,2H_2O$	CaO_8-D_{2d}	4; 246.3-262.9	2; 236.0	2^{x}	96
$Ca[2\text{-}OH\text{-}3,6\text{-}Cl\text{-}C_6H_2COO]_2,2H_2O$	CaO_8-D_{4d}	6; 251.6-251.7	2; 237.2	2; 241.4	97
$Ca[4\text{-}NH_2C_{10}H_6SO_3]_2,8H_2O$	CaO_7-D_{5h}	-	-	7; 237.5-243.5	98

* D_{5h}-distorted pentagonal bipyramid; D_{4d}-distorted square antiprism; D_{3d}-distorted trigonal antiprism; D_{2d}-distorted dodecahedral.

† Average values.

x Bond distances are available as supplementary material.



The AuO_4 rings are rotated by 45° relative to each other to give D_{4d} symmetry at the Sr atom.

(13)

(14),[103] bis(2,4-dinitrophenolato)bis(triethanolamine)barium(II) (15)[104] and bis(2-nitrophenolato)barium(II) (16).[105] Markedly different coordination polyhedra are found in the three compounds; that in (14) is a distorted cubic BaO_4N_4 arrangement, that in (15) is a monocapped distorted cubic BaO_7N_2 geometry, and that in (16) is a distorted one side bicapped square antiprismatic BaO_{10} configuration. The Ba atom in (14)[103] is located at the inversion centre of the $P\bar{1}$ space group; it is surrounded by four nitrogen atoms from two 1,10-phenanthroline ligands (294.0,294.5 pm) and four oxygen atoms from water molecules (276.3,277.8pm). The Ba atom in (15)[104] is bonded to the eight heteroatoms of the two triethanolamine ligands (r(Ba...O) = 270.3-289.4; r(Ba...N) = 300.0,303.6pm) and to a single oxygen atom of one of the dinitrophenolate anions (278.5pm). The Ba atom in (16)[105] lies on a 2-fold axis and is coordinated to four phenolic (271.1,272.2 pm) and six nitro (290.0-311.7pm) oxygen atoms.

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