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Chapter 2

ELEMENTS OF GROUP 2

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2.1 INTRODUCTION

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

An annual (1977) survey of the organometallic chemistry of magnesium[2] has been published, together with biannual (1977-78) surveys of organoberyllium[3] and of organo-calcium, -strontium, and -barium[4] chemistry. As expected, the organomagnesium chemistry survey is extensive;[2] topics discussed in detail include preparative techniques, spectroscopic and structural properties and reaction chemistry. Most activity in organoberyllium chemistry has been concentrated on theoretical calculations of both real and fanciful moieties; the results of but few experimental studies have been reported.[3] Progress in the organometallic chemistry of calcium, strontium and barium is very slow, presumably because application of such compounds in organic synthesis offers no advantages over that of analogous lithium and magnesium reagents.[4]

Improved analytical techniques for the extraction of micro-quantities of Sr[5] and for separation of trace amounts of Ra from milligram quantities of Ba[6] have been described.

2.2 METALS AND INTERMETALLIC COMPOUNDS

Electrical resistivity and thermoelectric power data for high purity liquid calcium and liquid strontium have been determined.[7]

The formation of non-crystalline solid phases in the Mg-Ga system has been observed.[8] A metastable orthorhombic crystalline phase has been detected as a decomposition product of the amorphous material; the structural relations between this phase and Mg_5Ga_2 are discussed.[8] $Ba_{10}Ga$ has been synthesised in the Ba-Ga system;[9] it has been shown to be isotypic with α-$Al_{10}V$. (Structural parameters: cubic, space group Fd3m, a_o=20.52Å).

Aspects of the structural chemistry of the alkaline earth metal disilicides and digermanides have been elucidated by Evers et al.[10,11] The composition ranges over which the solid solutions, $M_{1-x}Sr_xSi_2$ (M=Ca,Ba) and $BaSi_{2-y}Ge_y$, will adopt the $SrSi_2$-type structure have been defined;[10] although it can be prepared for the entire composition range of the $Ba_{1-x}Sr_xSi_2$ system (0<x<1.0), its range of existence is limited in the $Ca_{1-x}Sr_xSi_2$ system ($0.8<x<1.0$) and the $BaSi_{2-y}Ge_y$ ($0<y<1$) system. The superconducting transition temperatures of the α-$ThSi_2$ variants of $CaSi_2$, $SrSi_2$ and $BaGe_2$ have also been determined;[11] they increase from 1.37K ($CaSi_2$), through 3.1K ($SrSi_2$) to 4.93K ($BaGe_2$).

2.3 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

Owing to the marked decrease in the number of papers published this year, this section is comprised of only two subdivisions; these relate to the binary and ternary compounds of the alkaline earth metals, respectively. In the case of the ternary derivatives, the second metal is restricted to a transition metal, lanthanide or actinide.

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

2.3.1 Binary Derivatives

Thermodynamic parameters for a number of these compounds have been evaluated using either solution calorimetry[12-14] or vapour pressure measurement[15-20] techniques. The standard enthalpy of formation of the aqueous Mg^{2+} ion has been redetermined by independent authors by acid solution calorimetry of solid magnesium[12] and of anhydrous $MgCl_2$.[13] The data obtained are compared with that previously quoted by the NBS[21] in Table 1a; the three values are in excellent agreement. The standard enthalpy of

Table 1a. Standard Enthalpies of formation, ΔH_f^o/kJ mol^{-1}, of Mg^{2+}(aq), $MgCl_2$(c), BaH_2(c) and $Ba(OH)_2$(g).

	ΔH_f^o	Ref.
$\Delta H_f^o(Mg^{2+}, aq, 298.15K)$	$-(466.80 \pm 1.25)$	12
$\Delta H_f^o(Mg^{2+}, aq, 298.15K)$	$-(465.96 \pm 1.07)$	13
$\Delta H_f^o(Mg^{2+}, aq, 298.15K)$	-466.85	21
$\Delta H_f^o(MgCl_2, c, 298.15K)$	$-(644.28 \pm 0.69)$	13
$\Delta H_f^o(BaH_2, c, 298.15K)$	$-(191.2 \pm 3.8)$	15
$\Delta H_f^o(Ba(OH)_2, g, 1500K)$	$+(1014.2 \pm 18.8)$	20

Table 1b. Standard enthalpy, ΔH^{o}_{sub}/kJ mol^{-1}, and entropy, ΔS^{o}_{sub}/JK^{-1} mol^{-1}, of sublimation of SrF_2[16].

	ΔH^{o}_{sub}(1611K)	ΔS^{o}_{sub}(1611K)
Second Law	442.8	208.4
Third Law	444.4	209.4

formation of anhydrous $MgCl_2$ has also been derived from the $MgCl_2$ solution data.[13] It is quoted in Table 1a together with the corresponding values for crystalline BaH_2 and gaseous $Ba(OH)_2$ which were derived from the results of a study ($1008<T/K<1223$) of equilibrium hydrogen pressures in the Ba-H_2 system[15] and a transpiration study ($1443<T/K<1593$) of the hydrolysis of BaO (equation(1)),[20] respectively.

$$BaO(s) \ + \ H_2O(g) \longrightarrow Ba(OH)_2(g) \qquad \ldots (1)$$

Hydrolysis of Be^{2+} in both aqueous solution and H_2O-dioxane mixtures has been studied calorimetrically at 298K.[14] Thermodynamic data for the formation of a number of $Be_q(OH)_p^{(2q-p)+}$ complexes have been reported.

The standard enthalpy and entropy of sublimation of SrF_2 have been calculated from data obtained in a vapour pressure study of SrF_2 ($1529<T/K<1693$);[16] the data are tabulated in Table 1b. The melting point of SrF_2 (1736±7K) has been measured by DTA techniques.[16]

Schafer and Wagner have undertaken a Knudsen-mass-spectrometric study of the vapour in equilibrium with solid $MgCl_2$[17] and with $MgCl_2$-NaCl[18] and $MgCl_2$-$ScCl_3$[19] mixtures. The vapour consists not only of monomers, dimers and trimers of the constituent chlorides, but also of 1:1 1:2 and 2:1 complexes; derived thermodynamic data are collected in Table 2.

Gaseous electron diffraction studies of $MgCl_2$,[22] CaI_2[23] and SrI_2[23] have shown that the molecules are effectively linear with $r(Mg...Cl) = 2.185$, $r(Ca...I) = 2.866$, $r(Sr...I) = 3.009$Å. The fundamental stretching vibrational frequencies of gaseous MX_2 molecules (including M=Be,Mg,Ca,Sr,Ba) have been correlated empirically with their internuclear distances.[24]

Table 2. Thermodynamic data for a number of gas phase equilibria involving $MgCl_2$.

Reaction	ΔH_r^o(298K)	ΔS_r^o(298K)
$MgCl_2(s) \rightarrow MgCl_2(g)$	251.5	190.8
$2MgCl_2(s) \rightarrow Mg_2Cl_4(g)$	328.4	256.1
$2MgCl_2(g) \rightarrow Mg_2Cl_4(g)$	-174.5	-125.5
$MgCl_2(g) + Mg_2Cl_4(g) \rightarrow Mg_3Cl_6(g)$	-191.6	-155.2
$0.5Na_2Cl_2(g) + 0.5Mg_2Cl_4(g) \rightarrow NaMgCl_3(g)$	-23.8	3.8
$Na_2Cl_2(g) + 0.5Mg_2Cl_4(g) \rightarrow Na_2MgCl_4(g)$	-130.1	-
$2NaMgCl_3(g) \rightarrow Na_2Mg_2Cl_6(g)$	-187.4	-
$0.5Mg_2Cl_4(g) + 0.5Sc_2Cl_6(g) \rightarrow MgScCl_5(g)$	-2.9	8.4
$MgCl_2(g) + ScCl_3(g) \rightarrow MgScCl_5(g)$	-190.4	-118.0
$Mg_2Cl_4(g) + ScCl_3(g) \rightarrow Mg_2ScCl_7(g)$	-207.1	-
$MgCl_2(g) + Sc_2Cl_6(g) \rightarrow MgSc_2Cl_8(g)$	-206.7	-

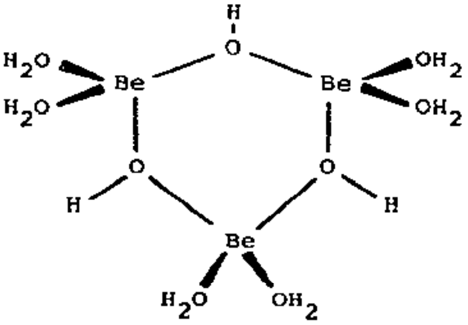
Several papers[25-28] have been published in which aspects of the chemical crystallography of alkaline earth metal halides are discussed. A neutron diffraction investigation[25] of MgF_2 has been effected at 52 and 300K to obtain more reliable values for the position of the F^- anion and for the anisotropic thermal parameters. The coordinates of F^- were independent of temperature corresponding to r(Mg...F)=1.979 and 1.984Å at 52 and 300K, respectively. Strong anisotropy of the vibrations of F^- was observed at 300K indicating strong excitation of a libration-like mode of the MgF_2 molecule.[25] High pressure studies have yielded new polymorphs of MX_2 (M=Ca,Sr; X=Cl,Br)[26] and of SrI_2,[27] which could be quenched and characterised by X-ray diffraction methods; single crystal studies show the SrI_2 phase to be of the $PbCl_2$-type. The crystal structures of, inter alia, MFBr (M=Sr,Ba) have been refined from single crystal X-ray diffraction data;[28] the analysis of the structural parameters of these mixed halides shows the influence of different bonding types on the geometry of the PbFCl-type structure.

$MgCl_2$, when vigorously milled with an aromatic or polymeric material, e.g. naphthalene, durene or polyethylene, formed complexes containing a substantial concentration of free radicals some of which were highly coloured and all of which were typified by intense e.s.r. spectra.[29] The most striking feature of the complexes is their stability. The radicals were not affected by O_2, CO_2, H_2 or Cl_2; most dry solvents had no effect or simply dissolved away the excess of polymeric material, leaving the radicals stabilised on the support. Only water and the lower alcohols succeeded in dissolving away the support and destroying the complex. $MgBr_2$, MgI_2 and $MnCl_2$ were also shown to function as supports but were not as effective as $MgCl_2$.[29]

The preparation and characterisation of MgX_2 (X=O,S,Se,Te) has been undertaken.[30] Structural data for the FeS_2-pyrite type phases, MgO_2, (a=4.8441Å) and $MgTe_2$ (a=7.0212Å) have been reported; the Mg^{2+} cations are approximately octahedrally coordinated by X atoms with r(Mg...O)=2.083, r(O...O)=1.487Å, and r(Mg...Te)=2.941, r(Te...Te)=2.736Å, respectively.[30]

Interest in the chemistry of the hydrated binary halides has been maintained during 1979. Analysis of the X-ray diffraction data from liquid $CaCl_2,6H_2O$[31] indicates that (i) the liquid is characterised by a middle range order involving cation-cation correlations and (ii) the liquid retains some features of the hydrated crystal lattice structure.

Phase relationships in the $BeCl_2$-H_2O,[32] $CaCl_2$-H_2O,[33] $SrCl_2$-H_2O[34] and $BaCl_2$-H_2O[35] binary systems, the $CaCl_2$-$SrCl_2$-H_2O[36], ternary system and the $CaCl_2$-$SrCl_2$-$BaCl_2$-H_2O[36,37] quaternary system have been elucidated. The results of an investigation of the compound which is formed by direct hydration of $BeCl_2$ are consistent with the formulation $([Be(OH)(H_2O)_2]^+Cl^-)_n$;[32] a cyclic trimer (1) is assumed and a simplified coordinate analysis is performed to



(1)

support these assignments. The crystal structure of α-$CaCl_2.4H_2O$ has been redetermined[33] (triclinic, space group $P\bar{1}$, a=6.5932, b=6.3673, c=8.5606Å, α=97.83, β=93.50, γ=110.58°); the calcium coordination has been shown to be 7-fold and not 6-fold as described in a previous study;[38] the coordination sphere comprises three chlorine atoms, r(Ca...Cl)=2.845 to 2.933Å and four oxygen atoms, r(Ca...O)=2.354-2.468Å.

Thermal decomposition of $SrCl_2.6H_2O$ leads to $SrCl_2$ via $SrCl_2.2H_2O$ and $SrCl_2.H_2O$; at high temperatures (>878K) and in the presence of water, $SrCl_2$ reacts to form Sr_4OCl_6.[34] Similarly, thermal decomposition of $BaCl_2.2H_2O$ leads to $BaCl_2$ via $BaCl_2.H_2O$ and $BaCl_2.\frac{1}{2}H_2O$.[35] All products and intermediates have been characterised by X-ray diffraction, i.r., Raman and DTA techniques.

In the $CaCl_2$-$SrCl_2$-H_2O ternary system,[36] two stoichiometric compounds, α-$CaCl_2.4H_2O$ and $SrCl_2.2H_2O$ were observed together with the $[Sr_{1-x}\ Ca_x]Cl_2.6H_2O$ solid solution. These materials were also isolated from the $CaCl_2$-$SrCl_2$-$BaCl_2$-H_2O quaternary system[36,37] together with the compounds, $2BaCl_2.H_2O$, $BaCl_2.H_2O$ and $BaCl_2.2H_2O$.

Structural investigations of the pyridine and urea solvates, $MgCl_2.4C_6H_5N$[39], $MgBr_2.10CO(NH_2)_2$,[40] $MgI_2.2H_2O.6C_6H_5N$,[41] and $BaBr_2.3CO(NH_2)_2$[42] have also been undertaken. For the magnesium derivatives, the cations are effectively octahedrally coordinated; the structures contain trans-$[Mg(py)_4Cl_2]$, $[Mg(urea)_6]^{2+}$ and trans-$[Mg(py)_4(H_2O)_2]^{2+}$ moieties, respectively, with r(Mg...N)=2.26-2.28Å, r(Mg...Cl)=2.463, 2.483Å,[39] r(Mg...O)=2.054-2.084Å,[40] and r(Mg...N)=2.20-2.28Å, r(Mg...O)=2.00,2.12Å,[41] respectively.

2.3.2 Ternary Derivatives

The structural properties of $MgNiH_4$ have been investigated over a wide temperature range ($298<T/K<773$).[43] Two structural forms have been identified; the low temperature orthorhombic variant (space group $P222_1$, a=11.36, b=11.16, c=9.12Å) is transformed at T=483-518K (ΔH^{o}_{trans} = 6.7 ± 0.4 kJ mol^{-1}) into a cubic variant (pseudo-CaF_2, a=6.490Å)[43].

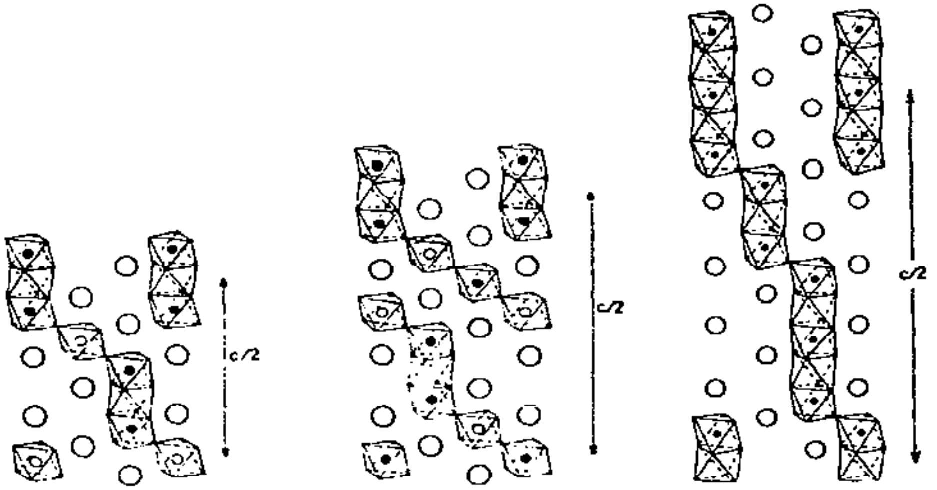
$MgZnH_4$ has been prepared as a THF-disolvate, $MgZnH_4.2THF$, by a variety of synthetic routes utilising either highly reactive MgH_2 (prepared by reaction of Et_2Mg or Ph_2Mg with $LiAlH_4$ in ether) and ZnH_2 (prepared by reaction of Ph_2Zn, Me_2Zn or $ZnBr_2$ with $LiAlH_4$ in ether). The disolvate has been characterised by complete elemental analysis, X-ray diffraction and DTA-TGA studies.[44]

Ternary halides containing the alkaline earth metals have been the subject of a small number of papers.[45-49] The crystal structure of $(NH_4)_2BeF_4$ has been shown to be orthorhombic, space group Pnma, with a=7.6367, b=5.9072, c=10.4316Å.[45] The BeF_4^{2-} tetrahedron is almost regular; the average r(Be...F) after correction for thermal vibration is 1.551Å and the average F-Be-F angle is 109.5°. The NH_4^+ tetrahedron is not regular.[45] The thermal decomposition $(373<T/K<453,\ 1\times10^{-3}<P_{H_2O}/Nm^{-2}<2.7\times10^3)$ of $(NH_4)MgCl_3.6H_2O$ has been elucidated.[46] At low temperatures $MgCl_2.2H_2O$ is formed by a phase boundary controlled process. At higher temperatures, and low water vapour pressures, $MgCl_2$ is formed in a single stage; intermediate temperatures and water vapour pressures cause the latter reaction to proceed in two stages both of which are controlled by phase boundary processes.[46]

When introduced into crystals of $CsMgX_3$ (X=Cl,Br) trivalent ions tend to cluster in pairs which act as magnetic dimers.[47,50] The e.p.r. spectra of the Cr(III)-Cr(III) and Mo(III)-Mo(III) pairs have been carefully analysed in terms of exact solutions of a spin Hamiltonian written for systems which contain two magnetically coupled S=3/2 ions.[47]

The polymorphism of $MNbF_7$(M=Mg,Ca) has been studied in detail;[48] the fluorides adopt both f.c.c. structures (isostructural with $NaNbF_6$) and rhombohedral structures (isostructural with $LiNbF_6$) which are characterised by the presence of interstitial F^- anions. Phase relationships (limiting solubilities, thermal stabilities) in the CaF_2-MF_3 (M=Y, La-Lu) systems have also been assessed;[49] in general, the phases are non-stoichiometric with statistical distributions of various valency cations on the lattice sites of the CaF_2 and LaF_3-structure types.

The principal contribution to the chemistry of ternary and higher oxides of the alkaline earth metals has been made by Kemmler-Sack and his co-workers. In an extensive series of papers he has described the synthesis and characterisation (principally structural and spectroscopic) of a number of novel hexagonal stacking polytypes with rhombohedral layer structures. Structural analyses of oxides with 6L($Ba_4[W_{8/3}\square_{4/3}O_{12}]$),[51,52] 12L($Ba_4[MReW\square O_{12}]$, M=Sc,In,Lu,Yb),[53] 18L($Ba_4[M_{4/3}W\square_{2/3}O_{12}]$, M=Y, Gd-Lu),[54] and 24L($Ba_4[ReW_{3/2}\square_{3/2}O_{12}]$)[55] structures have been accomplished. The structural properties of these various stacking polytypes are shown in Figure 1 and unit cell parameters are



12L 18L 24L

Figure 1. Hexagonal stacking polytypes with rhombohedral structures. (Reproduced by permission from Z.Anorg. Allg.Chem., 448(1979)119, 451(1979)129).

collected in Table 3. Vibrational spectroscopic studies of 5L(Ba$_4$[M$_{16/5}\square_{4/5}$O$_{12}$], M=Nb,Ta),[56] of 12L(Ba$_4$[MRe$_2\square$O$_{12}$], M=Mg, Ca,Co,Zn,Cd and Ba$_4$[M$_{2/3}$Re$_2\square_{4/3}$O$_{12}$], M=Sc,Y,Pr,Sm-Lu)[57] and of 24L(Ba$_4$[ReW$_{3/2}\square_{3/2}$O$_{12}$] and Ba$_4$[Re$_{3/2}$Nb$_{1/2}\square_{3/2}$O$_{12}$])[56] variants have been undertaken and factor group analysis completed. Kemmler-Sack et al. have also shown that oxides with composition Ba$_4$[M$_{4/3}$Te$_2\square_{2/3}$O$_{12}$], (M=Y,Pr,Nd,Sm-Lu) crystallise with a cubic perovskite lattice;[58] the unit cell parameters decrease with decreasing size of M(III) from Pr(III) (a=8.52Å) to Y(III) (a= 8.33Å). They have also undertaken vibrational analysis of the ordered perovskites Ba$_4$[M$_2$Re$_2$O$_{12}$] and Sr$_4$[M$_2$Re$_2$O$_{12}$] (M=Li,Na).[59]

The conditions for the preparation of Ca$_2$Ti$_5$O$_{12}$,[60] M$_2$V$_6$O$_{16}$ and M$_2$V$_{12}$O$_{31}$ (M=Mg,Ca,Sr,Ba),[61] CaNbO$_3$,[62] Ba$_6$Nb$_2$O$_{11}$,[63] Ba$_5$Nb$_2$O$_{10}$,[63] Ba$_4$Nb$_2$O$_9$,[63] Ba$_3$Nb$_2$O$_8$,[63] BaNb$_2$O$_6$,[63] MgFe$_2$O$_4$,[64] Sr$_2$Os$_2$O$_{6.4+0.2}$[65] and MUO$_4$(M=Ca,Sr,Ba)[66] have been defined. The effect of molten salts, e.g. M$_2$CO$_3$ or MCl (M=Na,K), on the preparation of alkaline earth metal titanates and zirconates by reaction of MCO$_3$ (M=Ca,Sr,

Table 3. Unit cell parameters for a number of hexagonal stacking polytypes with rhombohedral layer structures.

Oxide	Space Group	a/Å	c/Å	Reference
$Ba_4[W_{8/3}\square_{4/3}O_{12}]$	$R\bar{3}c$	10.13	13.96	51,52
$Ba_4[ScReW\square O_{12}]$	$R\bar{3}m$	5.75	27.80	53
$Ba_4[InReW\square O_{12}]$	$R\bar{3}m$	5.78	27.90	53
$Ba_4[LuReW\square O_{12}]$	$R\bar{3}m$	5.81	28.05	53
$Ba_4[YbReW\square O_{12}]$	$R\bar{3}m$	5.81	28.06	53
$Ba_4[Lu_{4/3}W_2\square_{2/3}O_{12}]$	$R\bar{3}m$	5.84	42.56	54
$Ba_4[ReW_{3/2}\square_{3/2}O_{12}]$	$R\bar{3}m$	5.81	55.52	55

Ba) with TiO_2 or ZrO_2 has been assessed;[67] the molten salts were found to have an appreciable accelerating action. Reaction of titanium and zirconium hydroxides with aqueous solutions of barium and sodium hydroxides yields amorphous mixed hydroxides with M(II)/M(IV) ratios between 0.9 and 1.5;[68] on ageing crystallisation leads to the hydrated titanates and zirconates. The thermodynamic characteristics of possible redox processes in the $MgO-V_2O_5-VO_2$ system have been elucidated using e.m.f. and X-ray diffraction techniques.

Structural properties of a number of ternary oxides[60,65,70-76] have been evaluated; relevant unit cell parameters are collected in Table 4. X-ray diffraction studies of CaO-MnO samples,

Table 4. Unit cell parameters for a number of ternary oxides.

Oxide	Symmetry	Space Group	a/Å	b/Å	c/Å	β/°	ref.
$Ca_2Ti_5O_{12}$	cubic	-	4.31	-	-	-	60
$Ba_2Ti_{5.5}O_{13}$	monoclinic	C2/m	15.160	3.893	9.093	98.6	70
$BaMn_2O_3$	orthorhombic	Immm	10.967	4.385	3.552	-	71
$\alpha-BaCr_2O_7$	monoclinic	C2/c	16.31	16.67	9.474	95.53	72
$Sr_2Os_2O_{6.4\pm0.2}$	cubic	-	10.340	-	-	-	65
Sr_2CrMnO_6	hexagonal	$P\bar{3}$	5.416	-	6.640	-	73
$BaFe_{1.5}Al_{0.5}O_4$	hexagonal	$P6_3$	10.81	-	8.707	-	74

prepared by thermal decomposition of mixed carbonates, have confirmed the presence of a single phase of rock salt structure ($Ca_{1-x}Mn_xO$) across the entire composition range.[75] High temperature X-ray diffraction analyses have revealed that whereas $Ca_2Fe_2O_5$ retains its orthorhombic oxygen-deficient perovskite structure up to ca.1373K, $Sr_2Fe_2O_5$ undergoes a transition to a cubic oxygen-deficient perovskite structure at ca.973K.[76]

The vibrational spectra (i.r. and Raman) of a number of alkaline earth metal uranates[77] and of MGd_2O_4 (M=Sr,Ba)[78] and the magnetic behaviour of $MFeO_4$(M=Sr,Ba)[79] and of $BaRuO_3$[80] have been examined and discussed in terms of their structures. Standard thermodynamic parameters of formation of barium tungstates have been ascertained from electrochemical measurements ($1000<T/K<1400$);[81] data are collected in Table 5.

Table 5. Standard thermodynamic parameters of formation of several barium tungstates.[79]

Oxide	ΔH_f^o(298.15K) kJ mol^{-1}	ΔG_f^o(298.15K) kJ mol^{-1}	ΔS_f^o(298.15K) JK^{-1} mol^{-1}
$BaWO_4$	-(1680.1 ± 10.5)	-(1573.4 ± 10.9)	151.5 ± 7.5
Ba_2WO_5	-(2367.7 ± 10.5)	-(2225.7 ± 12.5)	201.7 ± 6.7
Ba_3WO_6	-(3008.3 ± 12.5)	-(2835.5 ± 13.4)	268.4 ± 9.6

2.4 COMPOUNDS CONTAINING ORGANIC OR COMPLEX IONS

In general, the recently reported chemistry of these compounds is considered in subsections devoted to individual alkaline earth metals; data pertinent to several elements are discussed once only, in the subsection of the lightest metal considered. There is, however, an initial subsection in which recent advances in the field of alkaline earth metal salts of carboxylic acids are described.

2.4.1 Salts of Carboxylic Acids

Particular interest has been shown in the salts of hydroxycarboxylic acids,[82-86] presumably because of their unusual affinities for alkaline earth metal ions in aqueous solution. The complexation of Be^{2+} with 3-hydroxybutanoic acid,[82] 2-hydroxy, 2-methylpropanoic acid,[82] and 4- and 6-hydroxysalicylic acids[83] in aqueous solutions has been studied potentiometrically; complex formation is found to be very sensitive to the pH of the system.

The crystal structures of three hydroxycarboxylates, magnesium malate pentahydrate,[84] calcium di-DL-glycerate dihydrate,[85] and calcium bromide D-pantothenate[86] have been elucidated. Whereas

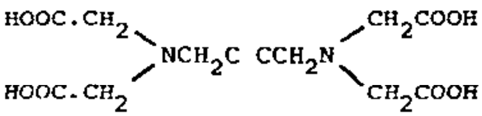
$HOOCCH(OH)CH_2COOH$	$CH_2(OH)CH(OH)COOH$	$CH_2(OH)C(CH_3)_2CH(OH)C(=O)\cdot$ $NHCH_2CH_2COOH$
Malic acid	Glyceric acid	Pantothenic acid
$HOOCCH(SH)CH_2COOH$	$HOOCCH(NH_2)CH_2CH_2COOH$	
Thiomalic acid	Glutamic acid	

the Mg^{2+} ion is six-coordinate, the Ca^{2+} ions in both salts are seven-coordinate. The approximately octahedral coordination sphere of Mg^{2+} in the malate is formed by two oxygen atoms of a chelating carboxylate anion and four water oxygen atoms, $r(Mg...O)=2.045-2.125$Å.[84] The Ca^{2+} coordination shell in the glycerate is effectively pentagonal bipyramidal, two chelating carboxylate anions, one monodentate carboxylate anion and two water molecules providing the seven oxygen atoms, $r(Ca...O)=2.346-2.443$Å.[85] The Ca^{2+} coordination shell in the pantothenate is composed of six oxygen atoms from three carboxylate anions (one tridentate, one bidentate and one monodentate), $r(Ca...O)=2.291-2.613$Å and a single bromine atom, $r(Ca...Br)=2.887$Å.[86]

Six-coordinate Ca^{2+} ions are found in the crystal structure of calcium di-L-glutamate tetrahydrate.[87] The α-amino acid binds to the Ca^{2+} ion using oxygen atoms from both carboxyl groups, the distorted octahedral Ca^{2+} coordination polyhedron being composed of four oxygen atoms from independent carboxylate anions and two water oxygen atoms, $r(Ca...O)=2.292-2.348$Å.

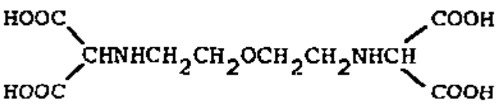
Solid state 1:1 salts of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} with thiomalic acid have been isolated and characterised by elemental analysis, i.r. spectra and thermal studies;[88] the latter show that desulphurisation preceeds decarbonylation leading to the formation of metal carbonates in all cases, except the magnesium salt for which MgO is the end product.

Complexation of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} with 1,4-diaminobut-2-ynetetraacetic acid (2)[89] and with [bis(2-aminoethyl)ether]-N,N'-dimalonic acid (3)[90] in aqueous solution have been studied using potentiometric techniques at 298K; the stabilities of the resultant



$(HOOC.CH_2)_2NCH_2C\ \ CCH_2N(CH_2COOH)_2$

(2)

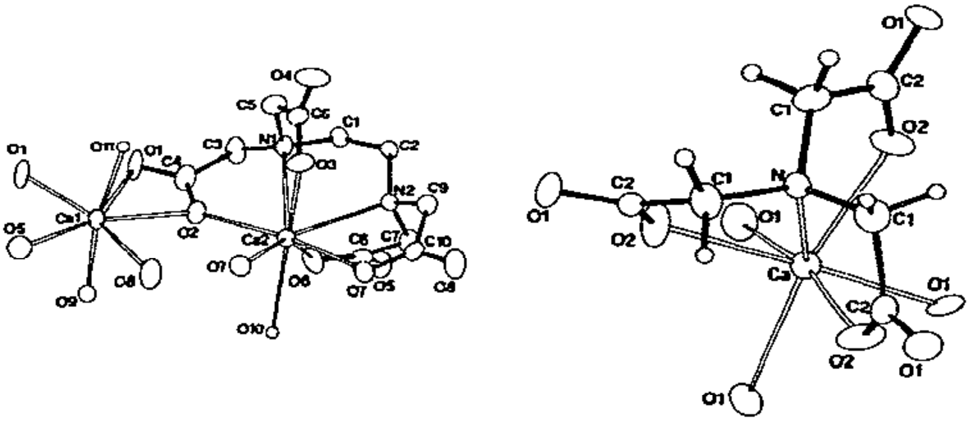


$(HOOC)_2CHNHCH_2CH_2OCH_2CH_2NHCH(COOH)_2$

(3)

complexes have been established and the influence of the structures of the hydrocarbon chains discussed.

The structural characteristics of calcium ion binding to the aminocarboxylates, ethylenediaminetetraacetate (EDTA) and nitrilotriacetate (NTA) have been assessed[91] in a single crystal X-ray diffraction study of Ca[CaEDTA].$7H_2O$ and Na[CaNTA]. The coordination polyhedra of the Ca^{2+} ions in these two moieties are shown in Figure 2. In Ca[CaEDTA].$7H_2O$, there are two crystallographically distinguishable Ca^{2+} ions (Figure 2a). Ca(2) is coordinated by a hexadentate EDTA molecule, r(Ca...O)=2.370-2.473Å, r(Ca...N)= 2.623, 2.711Å, the square antiprismatic 8-fold coordination being completed by a water molecule, r(Ca...O)=2.470Å, and a symmetry related EDTA oxygen atom, r(Ca...O)=2.526Å. Ca(1) has a pentagonal bipyramidal 7-fold coordination sphere furnished by five oxygen



(a) (b)

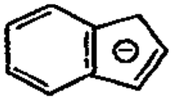
<u>Figure 2.</u> The Ca^{2+} coordination polyhedra in (a) Ca[CaEDTA].$7H_2O$ and (b) Na[CaNTA]. (Reproduced by permission from Inorg.Chem., 18(1979)2674).

atoms from four different but symmetry related EDTA ligands, r(Ca...O)=2.327-2.581Å, and two water molecules, r(Ca...O)=2.355, 2.363Å.[91] The 7-fold coordination of the Ca^{2+} ion in Na[CaNTA] (Figure 2b) is in the form of a capped trigonal antiprism which consists of the tetradentate NTA ligand, r(Ca...O)=2.365Å, r(Ca...N)=2.629Å and three non-chelated oxygen atoms from symmetry related NTA ligands, r(Ca...O)=2.392Å. The sodium atoms, solely serve to balance the charge; they are in a trigonal antiprismatic coordination environment of six oxygen atoms from six symmetry related NTA ligands, r(Na...O)=2.349, 2.431.[91]

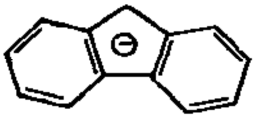
2.4.2 Beryllium Derivatives

Haaland and Lusztyk[92-94] have reported the results of an extensive study of the molecular structure of beryllocene, Cp_2Be. Novel gas phase electron diffraction[92] and He(I) photoelectron spectroscopic[93] data are presented together with liquid (338K) and solid phase (113,298K) Raman spectroscopic[94] data. Ab initio M.O. calculations using a double-ζ basis have also been completed for a number of Cp_2Be structures including the D_{5d}, C_{5v}, C_s.SLIP, and Cs.h^5-Cp-h^1-Cp models.[93] The lowest energies calculated were those for the D_{5d} and C_s.h^5-Cp-h^1-Cp models.[93] The gas phase data,[92,93] however, are consistent with the slip sandwich model of C_s symmetry derived from the C_{5v} model by moving sideways the ring which is at the greater distance from Be, while keeping the two rings essentially parallel. The best fit between experimental and calculated electron diffraction intensity curves is obtained with a model with a sideways slip of 0.8Å.[92] (cf. the similar structure, with a 1.2Å sideways slip, derived by Wong et al.[95] from their single crystal X-ray diffraction investigations). A similar model can be used to account for the liquid and solid phase Raman spectra[94] which give rise to the following conclusions: (i) there are two different Cp rings in the molecule of liquid and solid Cp_2Be, (ii) one of the rings possesses C_{5v} local symmetry, and (iii) the second ring deviates from the C_{5v} local symmetry and is probably polyhapto-bonded to the metal.

M.O. calculations have also been undertaken for the complexes formed between mono- and dibenzocyclopentadienyl anions, i.e. indenyl(4) and fluorenyl(5) anions, and BeH^+ or $BeCl^+$.[96] Three stable structures were found for the indenyl derivatives correponding to h^6-, h^5 and 1-h^1-bonding types. Only two stable structures were found for the fluorenyl derivatives corresponding to h^6- and



(4)



(5)

9-h^1-bonding types; all attempts to locate the h^5-bonding type resulted in the location of the 9-h^1-bonding type.[96] The two most stable structures were calculated to be those with h^1-bonding.

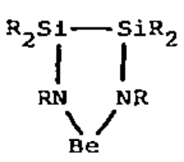
The electronic structure of polymeric beryllium borohydride has been modelled by performing M.O. calculations on $(BeB_2H_8)_n$ $(1<n<6)$ fragments.[97] Consideration of the data indicates that the material is best viewed as nearly ionic $BeBH_4^+$ and BH_4^- ions; this view is consistent with previous crystallographic and i.r. work.[97]

M.O. studies of the nido-berylloboranes, $B_5H_{10}BeX$ ($X{=}BH_4$, B_5H_{10}, CH_3, h^5-C_5H_5) have been undertaken.[98] The bonding at the Be atom in $B_5H_{10}Be(h^5\text{-}C_5H_5)$ was found to differ significantly from that in the other compounds, the charge on Be being positive for the three ligands BH_4, B_5H_{10} or CH_3 but slightly negative for C_5H_5.[98] The synthesis and structural characterisation of the corresponding beryllloborane, $B_5H_8Be(h^5\text{-}C_5H_5)$ has been reported.[99] Whereas the $(h^5\text{-}C_5H_5)Be$ moiety in $B_5H_{10}Be(h^5\text{-}C_5H_5)$ is incorporated as a vertex in a BeB_5 six-atom framework, in $B_5H_8Be(h^5\text{-}C_5H_5)$, the $(h^5\text{-}C_5H_5)Be$ moiety resides in a nonvertex bridging position between two adjacent basal boron atoms in a square pyramidal framework.[99]

Centrosymmetric $(BeN)_2$ four membered ring systems have been shown to be present in the molecular structures of the di-t-butylmethyleneamino derivative of beryllium, $[Be(N{=}CBu_2^t)_2]_2$,[100] and the cyclic beryllium silylamide, $[\overline{\text{Be.NR.SiR}_2\text{.NR.SiR}_2\text{.N}}\text{R}]_2$.[101] The geometries of the two rings are very similar; details are compared in Table 6. These compounds were actually prepared as part of a series of methyleneaminoberyllium compounds,[100] $[BeCl(N{=}Ct\text{-}Bu_2)]_2$ $Li[Be(N{=}Ct\text{-}Bu_2)_3]$, $[Bei\text{-}Bu(N{=}Ct\text{-}Bu_2)]_2$, $Be(N{=}Ct\text{-}Bu_2)[N(SiMe_3)_2]$, $[Bei\text{-}Bu(N{=}CPh_2)]_2$ and $[Bet\text{-}Bu(N{=}CPh_2)]_2$ and a series of cyclic beryllium silylamides (6)-(9);[101] all products were characterised by elemental analysis, i.r. and ^1H n.m.r. spectroscopy.

Table 6. Molecular Geometries of the $(BeN)_2$ rings in $[Be(N{=}Ct\text{-}Bu_2)_2]_2$ and $[\overline{BeNrSiR_2NRSiR_2N}R]_2$.

	$[Be(N{=}Ct\text{-}Bu_2)_2]_2$	$[\overline{BeNRSiR_2NRSiR_2N}R]_2$
r(Be...N)/Å	1.682	1.714
r(Be...N')/Å	1.674	1.683
N-Be-N'/°	96.9	99.8
Be-N-Be'/°	83.1	80.1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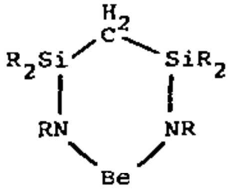
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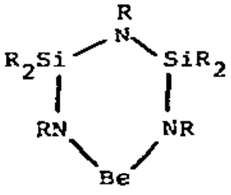
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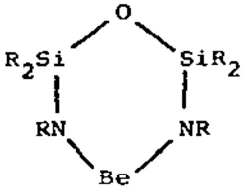
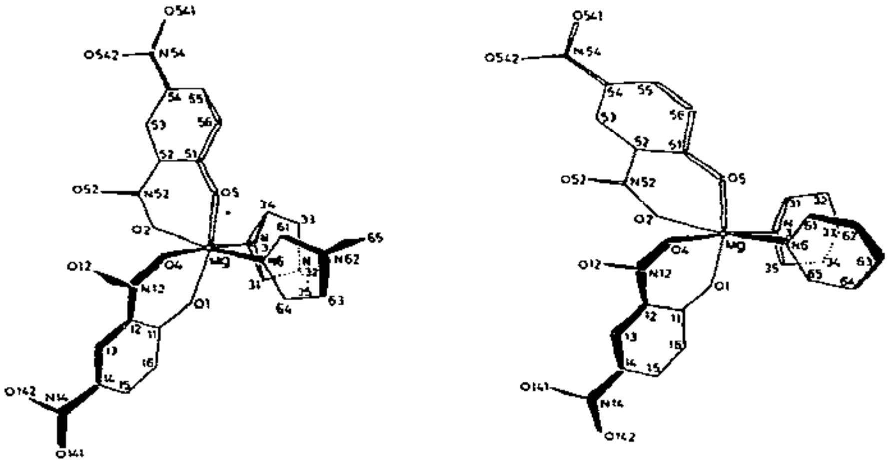

(9)

2.4.3 Magnesium Derivatives

The papers abstracted for this section of the review are selective; organomagnesium chemistry is the principal omission since it is the subject of a separate annual review.[2]

A new series of THF complexes including $[M(THF)_6](SbCl_6)_2$, M=Mg,Sr and $[Ca(THF)_6](SbCl_6)_2.THF$ have been reported.[102] Analysis of the spectroscopic properties of these complexes indicates that the M^{2+} cations are octahedrally coordinated by THF molecules. Distorted octahedral Mg^{2+} coordination polyhedra are also found in $[Mg(hfac)_2L]$ (hfac=hexafluoroacetylacetone, L=o-phenanthroline or bipyridyl)[103] and in $[Mg(ArO)_2L_2]$ (ArO is 2,4-dinitrophenoxide, L=methylimidazole or pyridine).[104] The $[Mg(hfac)_2L]$ complexes are tris-bidentate, the distortions from octahedral symmetry being greater for the bipyridyl than the o-phenanthroline complexes.[103] In the $[Mg(ArO)_2L_2]$ complexes (Figure 3), two o-nitrophenoxide bidentate ligands (trans phenoxides) and two heterocyclic monodentate ligands (cis heterocycles) form the inner coordination sphere.[104] In the N-methylimidazole complex, r(Mg...O)=1.962-2.152Å, r(Mg...N)=2.111, 2.119Å; in the pyridine complex, r(Mg...O)=1.940-2.186Å, r(Mg...N)=2.156, 2.177. It is suggested that the N-methylimidazole complex is a model for the possible coordination of histidine and N-methylhistidine in certain MgATPases: the



(a) (b)

Figure 3. The molecular structures of (a) the bis-methylimidazoline and (b) the bis-pyridine complexes of magnesium bis-dinitrophenoxide. (Reproduced by permission from J.Am.Chem.Soc., 101(1979)5015).

uncoupler role of 2,4-dinitrophenol may be related to the stability of its Mg^{2+} complexes.[104]

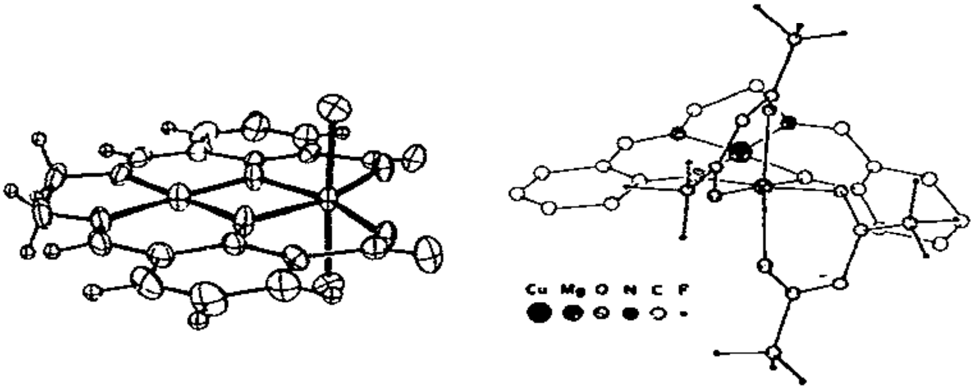
Isonicotinate N-oxide (L)-alkaline earth metal complexes, $MgL_2.6H_2O$, $CaL_2.2H_2O$, $BaL_2.3H_2O$, have been prepared and characterised by i.r., thermogravimetric and differential scanning calorimetric studies.[105]

A series of alkoxy and aroxy magnesium hydrides, HMgOR, has been synthesised either by redisttribution of bis(alkoxy- or aroxy-) magnesium moieties, $Mg(OR)_2$, with MgH_2 in THF, or by reaction of MgH_2 with the appropriate alcohol at 195K followed by warming to 298K.[106] All compounds were characterised by elemental analyses, i.r. and n.m.r. spectroscopy, ebullioscopic molecular weight studies, X-ray powder diffraction methods and vacuum DTA-TGA techniques.[106]

Mg^{2+} (and Mn^{2+}) 2-oxoimidazolidine-1-carboxylato complexes, $\overline{C(=O)NHCH_2CH_2N}CO_2Mg(OMe)$ have been isolated from the reaction of the metal dimethoxides, imidazolidin-2-one and CO_2 in DMF at 323K; the transcarboxylating activity of these compounds to an active hydrogen has been demonstrated using cyclohexanone.[107]

Equilibrium constants for the interaction between Mg^{2+} and a number of mono- and di-nucleotides have been determined using pH titration techniques; the data are consistent with inner sphere binding of the Mg^{2+} ion with the phosphate group.[108]

The synthesis of four heterobinuclear complexes incorporating Mg^{2+} has been reported;[109-112] the molecular structures of three of these products have been ascertained;[109-111] those of $[CuMg(fsaen)].3H_2O$[109] and of $[Cu(salen)Mg(hfac)_2]$[110] (H_4fsaen and H_2salen are the Schiff bases of ethylenediamine with 3-formylsalicyclic acid and salicyclic acid, respectively, and hfac is hexafluoroacetylacetone) are depicted in Figure 4a and 4b, respectively. The fsaen anion acts as a binucleating chelating



(a) (b)

Figure 4. Partial views of the molecular structures of the Mg-Cu binuclear complexes (a) $[CuMg(fsaen)]$,$3H_2O$ and (b) $[Cu(salen)Mg(hfac)_2]$ (Reproduced by permission from (a) Inorg.Chim.Acta 33(1979)113 and (b) J.Chem.Soc., Chem. Commun.(1979)39).

ligand by providing a planar N_2O_2 donor grouping for the Cu^{2+} ion in [CuMg(fsaen)].$3H_2O$[109], r(Cu...N)=1.917Å, r(Cu...O)= 1.920Å and a planar O_4 donor grouping for the Mg^{2+} ion, r(Mg...O)= 1.978, 2.049Å; two axial water molecules complete the octahedral coordination of the Mg^{2+} ion, r(Mg...O)=2.115Å (Figure 4a). Although the salen anion provides a similar planar N_2O_2 donor grouping for the Cu^{2+} ion in $[Cu(salen)Mg(hfac)_2]$[110], r(Cu...O)= 1.913, 1.921Å (r(Cu...N) is not quoted), the Mg^{2+} ion achieves octahedral coordinative saturation from the two oxygen atoms of the salen ligand and the four oxygen atoms of two hfac anions, r(Mg...O)=2.053–2.109Å (Figure 4b). The structure of the binuclear Mg-Mo complex, $(h^5\text{-}C_5H_5)_2Mo(H)Mg(THF)_2Br$ has been reported in a full paper;[110] since this structure was discussed in the previous review[113] (from abstraction of a preliminary paper) it will not be considered in detail.

The reaction of $[cis\text{-}(Co)_4Re(CH_3CO)(RCO)]H$ (R=methyl or isopropyl) with $(C_6H_5)_2Mg$ has been shown to afford the neutral metalla-β-diketonate complex of the metal ion, $[cis\text{-}(CO)_4Re(CH_3CO)\text{-}(RCO)]_nMg$, with elimination of benzene.[112]

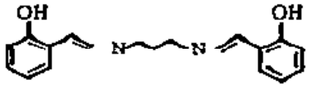
2.4.4 Calcium, Strontium and Barium Derivatives

The crystal and molecular structures of a number of diverse calcium derivatives have been elucidated during the period of the review.[114-118] The ternary amide, $RbCa(NH_2)_3$, has been prepared by the reaction of the metals with supercritical NH_3(T=573K, p=5kbar).[114] The atomic arrangement consists of one dimensional infinite face-sharing anion octahedra occupied by Ca^{2+} ions; the Rb^+ cations connect the octahedral chains. Octahedral Ca^{2+} coordination is also found in the calcium salt of ionomycin, a novel diacidic polyether antibiotic.[115] The polyether wraps around the Ca^{2+} ion, the six ligating oxygen atoms being furnished by the cisoid enolised β-diketonate anion, the carboxylate group, two hydroxyl groups and a ring ether moiety.

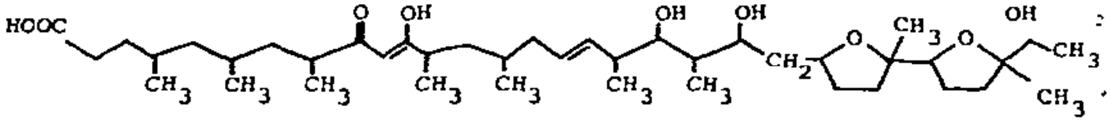
Seven-coordinate Ca^{2+} ions are found in the choline phosphate salt $[C_5H_{13}NO_4P]^-Ca^{2+}Br^-,4H_2O$. The cations are tightly coordinated by three water oxygen atoms, r(Ca...O)=2.374–2.465Å, and three phosphate oxygen atoms, r(Ca...O)=2.316–2.430Å; the monocapped octahedral coordination polyhedron is completed by a second oxygen atom of a bidentate phosphate group, r(Ca...O)=2.63Å. This structure is thought to provide a model for the mode of interaction of Ca^{2+} and H_2O with phospholipids at the surface of

$[(CH_3)_3NCH_2CH_2OPO_3]^-$

choline phosphate



H_2salpd



ionomycin

biological membranes.[116]

Distorted hexagonal bipyramidal and square antiprismatic 8-coordinate Ca^{2+} ions are found in $Ca(H_2salpd)(NO_3)_2$[117] and $Ca(pic)_2.5H_2O$[118] respectively. The Schiff's base in $Ca(H_2salpd)(NO_3)_2$ is present in an hitherto unreported charge separated form with the ligand bridging two Ca^{2+} ions through negatively charged oxygen atoms, r(Ca...O)=2.247, 2.319Å; the azomethine nitrogen atoms are not coordinated (they carry protons which are transferred from the phenolic groups on complex formation). A bidentate chelating NO_3^- anion is coordinated to each Ca^{2+} ion, r(Ca...O)= 2.450, 2.474Å, while a pair of equivalent bridging NO_3^- anions complete the 8 coordination about Ca^{2+} by formation of chelate rings to the separate Ca^{2+} ions, r(Ca...O)=2.552-2.585Å.[117] The stereochemistry of the Ca^{2+} ion in $Ca(pic)_2.5H_2O$,[118] is generated by a pair of bidentate picrate ligands and four water molecules in an array in which three of the water molecules occupy a triangular face of a square antiprism; the remaining water molecule occupies a lattice site with no close interaction with the other species.[117]

^1H n.m.r. spectroscopic methods have been used to study the interaction between Ca^{2+} and sucrose in aqueous solution;[119] no evidence for complexation was found.

$[Bu_4N]Ba(R_2NCS_2)_3$ (R=Et,Me) have been prepared;[120] conductivity and electrochemical studies have shown that in acetone solution, $Ba(Et_2NCS_2)_3^-$ is completely dissociated into the bis complex $Ba(Et_2NCS_2)_2$ and a ligand anion, $Et_2NCS_2^-$.

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