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Chapter 2

ELEMENTS OF GROUP 2

Peter Hubberstey

2.1 INTRODUCTION

The chemistry of these elements will be reviewed in sections which reflect topics of current interest and importance. For those subjects which are common to Group I and II elements e.g. cation solvation, molten salts, crown and cryptate complexes, the published data are considered in the relevant section in Chapter 1.

An annual (1976) survey of the organometallic chemistry of magnesium has been published;[1] preparative routes to organomagnesium compounds, their spectroscopic and structural properties and their chemical reactions are discussed in detail.

5,6-Dibromo-2,3,4-trihydroxyacetophenone has been proposed as a reagent in the spectrophotometric determination of Ca, Sr and Ba in aqueous solution.[2] Optimum pH ranges, stoichiometries of the complexes, the applicability of Beer's Law and the effect of diverse ions were studied in depth. A remarkable reduction in Ca interference on Ba determination in atomic absorption spectroscopy has been demonstrated using a nitrogen-shielded version of moderately fuel-rich flames.[3] The effect was attributed to the suppression of CaOH formation (the CaOH green band is responsible for background absorption and noise effect) brought about by an improvement in the reducing nature of the flame.

2.2 METALS, METALLIC SOLUTIONS AND INTERMETALLIC COMPOUNDS

Phase transitions of pure Ca and Sr and of hydrogenated Sr have been investigated ($300 \leqslant T/K \leqslant 850$) by means of electrical resistivity and thermopower measurements.[4] The pure metals only adopt the f.c.c. and b.c.c. structures, the f.c.c. - b.c.c. transition temperatures occurring near 718K (for Ca) and 819K (for Sr). Hydrogenation of Sr causes a h.c.p. phase to appear; the f.c.c. - h.c.p. transition is sluggish and was observed to take place between 425 and 500K.[4] The thermodynamic properties of Sr have been derived ($5 \leqslant T/K \leqslant 350$) from measurements of its heat capacity by adiabatic-shield calorimetry.[5]

Thermodynamic properties of liquid Ca-Ag and Ca-In metallic solutions have been determined ($T = 1073K$) using an e.m.f. technique;[6] both components of the two solutions exhibit negative deviations from ideality.

Matrix isolation studies of the diatomic molecules, CaMg, SrMg and SrCa[7] and MAg (M = Mg,Ca,Sr,Ba)[8] have been undertaken. Laser induced fluorescence spectra of the mixed alkaline earth van der Waals molecules have been measured;[7] the emission was correlated with transitions previously observed in absorption studies. E.s.r. spectra of the alkaline earth-silver intermetallic molecules were interpreted by assuming an electronic configuration $\sigma_s^2\sigma_s^{*1}$, where σ_s and σ_s^* are the bonding and antibonding σ orbitals arising essentially from the valence s orbitals of the component metals.[8]

M_2X (M = Ca,Sr,Ba; X = Si,Ge,Sn,Pb) phases have been prepared and characterised by single crystal and powder X-ray diffraction techniques.[9] They all crystallise in the orthorhombic anti-$PbC\ell_2$-type; pertinent unit cell parameters are collected in Table 1.

Table 1 Unit cell parameters for a number of orthorhombic (Pnma) alkaline earth-Group IV metal intermetallic compounds[9]

Intermetallic	a/Å	b/Å	c/Å	Intermetallic	a/Å	b/Å	c/Å
Ca_2Si	7.667	4.799	9.002	Sr_2Sn	8.401	5.378	10.078
Ca_2Ge	7.734	4.834	9.069	Sr_2Pb	8.445	5.391	10.139
Ca_2Sn	7.975	5.044	9.562	Ba_2Si	8.44	5.20	9.63
Ca_2Pb	8.072	5.100	9.647	Ba_2Ge	8.38	5.48	10.04
Sr_2Si	8.13	5.16	9.54	Ba_2Sn	8.648	5.691	10.588
Sr_2Ge	8.153	5.166	9.593	Ba_2Pb	8.64	5.71	10.61

High pressure studies of the crystal chemistry of the $Ca_{1-x}Sr_xSi_2$ ($0.0 \leq x \leq 1.0$) ternary system[10] and of the $BaSi_2$ binary system[11] have been accomplished. The α-$ThSi_2$ structure type has been observed over the entire range of the $Ca_{1-x}Sr_xSi_2$ system,[10] and the semiconductor-metal, i.e. orthorhombic-trigonal, transition in $BaSi_2$ has been characterised.[11]

The metastable phase, m-BeTi has been prepared by quenching Be-Ti and Be-Ti-Zr alloys;[12] it has a cubic CsCℓ-type structure, a = 2.940Å. It is concluded that m-BeTi does not exist as an equilibrium phase in normally cooled alloys because of the superior stability of the Be_2Ti phase.[12]

Hydrogen absorption by, *inter alia*, Mg_2Eu has been studied by analysis of ^{151}Eu Mössbauer spectra.[13] The results indicate that absorption occurs primarily through the formation of europium hydride complexes.

2.3 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

In this section, the chemistry of binary and ternary derivatives of the alkaline earth metals will be discussed; those ternaries, however, which contain both alkali- and alkaline earth-metals are considered in the relevant section in Chapter 1. The majority of the papers abstracted for this section reflect the growing interest in the binary hydrides, the hydrated binary halides and the ternary oxides. 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 their content is of but marginal interest to the inorganic chemist.

2.3.1 Hydrides

BeH_2 has been produced by the controlled pyrolysis of dialkylberyllium etherates in hot oil.[14] It was obtained as an amorphous solid, remarkably stable at elevated temperatures and resistant to attack by water and common organic solvents. Of the series of alkylberyllium homologues subjected to the pyrolysis reaction, $t\text{-}Bu_2Be{,}Et_2O$ gave the highest purity BeH_2 (90-98 wt %). Crystalline BeH_2 was prepared by high pressure compaction-fusion ($p > 2.7$ kbar at 473K or $p > 6.2$kbar at 423K) of amorphous BeH_2 in the presence of 0.5 to 2.5 mol % Li.[15] Two separate crystalline phases were identified; although the low temperature phase ($481 \leqslant T/K \leqslant 611$) could be indexed on the basis of a hexagonal unit cell, $a = 4.20$, $c = 6.76$Å, the crystal habit of the high temperature phase ($568 \leqslant T/K \leqslant 651$) was not conclusively identified.[15]

The kinetics ofthe reaction between hydrogen and Mg have been investigated.[16,17] The results indicate a three-dimensional diffusion-controlled reaction.[16] The addition of small amounts of Aℓ, Ga or In (< 1 mol %) to the Mg appreciably lowers the activation energy ofthe process;[17] increasing concentrations of these elements, however, lead to activation energies which are comparable with that of pure Mg.

A series of THF soluble (dialkylamino)- and (diarylamino)-magnesium hydrides, $HMgNR_2$ (typically $NR_2 = NEt_2$, NPh_2) has been synthesised by the reaction of active MgH_2 with the corresponding bis(dialkylamino)- or bis(diarylamino)-magnesium compounds in THF.[18] These compounds could also be prepared by the reaction of the appropriate amine with MgH_2 and by reaction of the appropriate lithium dialkyl- or diaryl-amide with chloromagnesium hydride. These hydrides were characterised by elemental analysis, i.r., n.m.r. and X-ray powder diffraction studies. Molecular weight studies in refluxing THF have been carried out and probable structures of these compounds are discussed.[18]

2.3.2 Oxides and Hydroxides

Kinetic studies of the dissolution, in water, of well characterised perfect MgO crystals have shown that surface potential barrier modification is the most likely rate determining step when solution diffusion is not limiting.[19] Electron microscopic studies of changes in surface structure of partially dissolved crystals have been related to rate changes during dissolution.[19] The standard enthalpy of formation of SrO, $\Delta H_f^o(SrO,c,298.15K) = -590.53 \pm 1.00$ $kJ.mol^{-1}$, has been derived from the enthalpies of solution of Sr and SrO in 1 $mol.dm^{-3}$ aqueous $HC\ell$ at 298.15K.[20]

The electronic structures of $Mg(OH)_2$[21] and of $MgA\ell_2O_4$[22] have been investigated by means of X-ray emission, X-ray photoelectron and Auger spectroscopy. Models for the bonding in these compounds are derived using the spectra and simple M.O. theory. Although the strongest covalent interaction in $Mg(OH)_2$ exists between the oxygen and hydrogen of the OH group, the Mg–O bond does exhibit some covalent character. The necessary conditions (high partial pressure of CO_2, dense packing of the specimen powder in the specimen container and a high heating rate) for the occurrence of the previously ill-characterised exothermic phenomenon in the thermal decomposition of hydromagnesite, $Mg(OH)_2,4MgCO_3,4H_2O$, have been established.[23] The exothermic phenomenon occurs at *ca*. 783K and is independent of CO_2 partial pressure.[23]

2.3.3 Halides

Studies of the Raman spectra of crystalline and molten anhydrous $BeC\ell_2$ ($293 \leq T/K \leq 733$) have shown that the molten salt consists of polymeric chain molecules of varying complexity.[24]

Single crystal structural analyses of β-$CaC\ell_2,4H_2O$,[25] $Ca_2CdC\ell_6,12H_2O$,[26] $CaC\ell(NO_3),2H_2O$,[27] $CaBr_2,4MeOH$,[28] $CaBr_2,4EtOH$,[28] and $BaC\ell_2,2H_2O$[29] have been undertaken using X-ray[25-28] and neutron[29] diffraction techniques. Pertinent unit cell parameters are collected in Table 2. $Ca_2CdC\ell_6,12H_2O$ is isomorphous with β-$CaC\ell_2,4H_2O$. The latter contains two crystallographically distinct

Table 2 Unit cell parameters for several alkaline earth metal halides

Halide	Symmetry	Space Group	$a/Å$	$b/Å$	$c/Å$	$\beta/^{\circ}$	Reference
β-$CaC\ell_2,4H_2O$	monoclinic	$P2_1/c$	8.923	10.221	12.787	114.68	25
$Ca_2CdC\ell_6,12H_2O$	monoclinic	$P2_1/c$	8.839	10.106	12.714	114.21	26
$CaC\ell(NO_3),2H_2O$	orthorhombic	Pbca	9.052	6.676	19.797	-	27
$CaBr_2,4MeOH$	monoclinic	$P2_1/c$	6.240	11.869	8.640	92.76	28
$CaBr_2,4EtOH$	monoclinic	$P2_1/c$	9.717	7.827	11.260	96.38	28
$SrC\ell_2,H_2O$	orthorhombic	Pnma	10.881	4.162	8.864	-	32
$BaC\ell_2,2H_2O$	monoclinic	$P2_1/n$	6.722	10.908	7.132	91.10	29
$BaC\ell_2,2H_2O$	monoclinic	$P2_1/n$	6.738	10.860	7.136	90.95	33
$BaC\ell_2,H_2O$	orthorhombic	Pnma	11.28	4.51	9.02	-	33
$BaC\ell_2$	orthorhombic	Pnma	7.878	4.714	9.415	-	33
$BaC\ell_2$	hexagonal	$P\bar{6}2m$	8.113	-	4.675	-	33
$BaC\ell_2$ (L.T.)	cubic	Fm3m	7.311	-	-	-	33
$BaC\ell_2$ (H.T.)	cubic	Fm3m	7.60	-	-	-	33

calcium atoms: Ca(1) is octahedrally surrounded by six chlorine atoms, r(Ca...Cℓ) = 2.73-2.74Å, whereas Ca(2) is surrounded by seven water molecules, r(Ca...O) = 2.38 to 2.85Å and one chlorine atom r(Ca...Cℓ) = 2.87Å in a distorted coordination sphere.[25] In the ternary chloride, the cadmium atoms occupy the Ca(1) positions, r(Cd...Cℓ) = 2.61-2.66Å, and the calcium atoms occupy the Ca(2) positions, r(Ca...O) = 2.35-2.83Å, and r(Ca...Cℓ) = 2.88Å.[26]

Structural and chemical changes accompanying the thermal dehydration of $MgC\ell_2,nH_2O$,[30,31] $SrC\ell_2,nH_2O$[32] and $BaC\ell_2,nH_2O$[33] have been studied using i.r. spectroscopy,[30] d.t.a.,[31] and high temperature X-ray powder diffraction techniques.[32,33] Full details of the intermediate hydrate formation and, where appropriate, the phase transitions of the anhydrous chlorides are quoted; relevant crystal structure parameters have been abstracted and are included in Table 2. The mechanism of the dehydration of $BaC\ell_2,2H_2O$ has also been established[34] from the results of a microscopic investigation of the dehydration kinetics of $BaC\ell_2,2H_2O$ single crystals ($313 \leq T/K \leq 336$).

Solvates of formula, MF_2,CH_3COOH (M = Ca,Sr,Ba) have been formed in systems of the type MF_2-Ch_3COOH-H_2O;[35] they have been characterised using thermogravimetric and i.r. spectroscopic methods. The thermal stability of the solvates increases with increase in the radius ofthe alkaline earth metal ion. The stabilities of alkaline earth monofluoride complexes, MF^+, in H_2O, MeOH and their mixtures have been studied by use of fluoride-ion selective electrode potentiometry.[36] In water they follow the trend $MgF^+ > CaF^+ > SrF^+ > BaF^+$. The same trend is observed in MeOH but the complex stabilities are greatly enhanced compared to the aqueous cases; this enhancement decreases as the atomic number of the alkaline earth increases.[36]

2.3.4 Ternary Oxides, Sulphides and Halides

The ternary compounds considered in this section are those containing an alkaline earth metal and a transition metal; ternaries of the alkali and alkaline earth metals are discussed in Chapter 1, those of the alkaline earth and p-block metals in the appropriate subsequent Chapter. Several X-ray diffraction studies of the structural properties of ternary oxides have been accomplished;[37-42] the relevant details are summarised in Table 3. A number of oxides have been characterised in the BaO-Ta_2O_5 system;[38] of these several

Table 3. Unit cell parameters for a number of ternary oxides

Oxide	Symmetry	Space Group	a/Å	b/Å	c/Å	γ/°	Reference
$Ba_6Ta_2O_{11}$	cubic	-	8.68	-	-	-	37
$Ba_6Ta_2O_{11}$	tetragonal I	-	6.18	-	8.59	-	37
$Ba_6Ta_2O_{11}$	tetragonal II	-	6.22	-	8.52	-	37
$Ba_6Ta_2O_{11}$	tetragonal III	-	6.28	-	8.47	-	37
α-$Ba_4Ta_2O_9$	hexagonal	$P\bar{3}m1$	5.952	-	4.25	-	38
β-$Ba_4Ta_2O_9$	-	-	12.19	-	16.12	-	38
γ-$Ba_4Ta_2O_9$	orthorhombic	$C222_1$	12.15	21.16	16.07	-	38
$Ba_3Ta_2O_8$	monoclinic	P2/m	10.14	7.449	5.815	117.72	38
$Ba_5Ta_4O_{15}$	hexagonal	-	5.008	-	11.82	-	38
α-$BaTa_2O_6$	orthorhombic	-	12.33	10.26	7.67	-	38
β-$BaTa_2O_6$	tetragonal	-	12.552	-	3.945	-	38
γ-$BaTa_2O_6$	hexagonal	-	21.14	-	3.917	-	38
$BaTa_4O_{11}$	tetragonal	-	12.51	-	3.914	-	38
$Ca_5Re_2O_{12}$	hexagonal	$P6_3/mmc$	5.532	-	18.28	-	39
$Sr_5Re_2O_{12}$	hexagonal	$P6_3/mmc$	5.756	-	19.03	-	39
$Sr_3Re_2O_{10}$	hexagonal	P6/mcc	10.533	-	7.512	-	39
$Ba_3Re_2O_{10}$	hexagonal	P6/mcc	10.935	-	7.795	-	39
$Ba_3Re_{2-x}O_9$*	rhombohedral	$R\bar{3}m$	5.7699	-	20.799	-	40
$Ca_2Os_2O_7$	orthorhombic	-	3.745	25.1	5.492	-	41
$Ca_2Os_2O_{6.5}$	cubic	-	10.24	-	-	-	41
α-$SrUO_4$ γ-$SrUO_4$	rhombohedral	$R\bar{3}m$	6.53	(α=35.53)	-	-	42
β-$SrUO_4$	orthorhombic	Pbcm	5.480	7.956	8.112	-	42

*This compound was indexed on the basis of a hexagonal triple cell.

exhibit complex polymorphism.[37,38] Polymorphism of $SrUO_4$ has also been studied.[42] Three polymorphic forms occur, equation (1); the crystal structures of the α and γ polymorphs are the same although

$$\alpha\text{-}SrUO_{<3.9} \xrightleftharpoons{1053K} \beta\text{-}SrUO_4 \xrightleftharpoons{1553K} \gamma\text{-}SrUO_{\sim 3.8} \qquad (1)$$

slight differences in lattice parameters are observed. During the two phase transformations, composition changes occur; the $\alpha \to \beta$ transformation is accompanied by an oxidative process, whereas the $\beta \to \gamma$ transformation is accompanied by a loss of oxygen.[42]

The high temperature phases of $SrZrO_3$ have been studied by neutron powder profile refinement techniques.[43] The phase transitions are described by the condensation of soft vibrational modes. The structures of the three known ternary phases of the $CaO\text{-}HfO_2$ system ($Ca_2Hf_7O_{16}$, $Ca_6Hf_{19}O_{44}$ and $CaHf_4O_9$) have been interpreted in terms of the coordinated defect model of defect fluorite-type structures.[44]

Thermal transformations of $CaOsO_3$ in air have been the subject of d.t.a., t.g.a. and X-ray diffraction studies.[41] Two intermediate phases ($CaOs_2O_7$ and $Ca_2Os_2O_{6.5}$; structural parameters are quoted in Table 3) are formed during the decomposition (2) which eventually yields a mixture of CaO, Os and OsO_4.

$$4CaOsO_3 + 2O_2 \longrightarrow 4CaO + Os + 3OsO_4 \qquad (2)$$

The magnetic properties of a wide range of ternary oxides of formula ABO_3 (A = Mg,Ca,Sr,Ba; B = Ti,Zr,Mn,Fe,Co) have been measured ($80 \leq T/K \leq 300$).[45] The vibrational spectra of $BaLn_2O_4$ and $Ba_3Ln_4O_9$ have been determined and compared with theoretically derived data.[46]

High temperature electrical conductivity studies of the defect chemistry of $BaFe_2O_{4-\delta}$ have shown it to be an oxygen-deficient n-type semi-conductor;[47] the data are adequately analysed in terms of a simple defect model.

Thermodynamic data for the solid solutions, $Mg_{0.3}U_{0.7}O_{2\pm x}$ ($1473 < T/K < 1773$)[48] and the vanadium oxide "bronzes", $Sr_xV_2O_5$, ($823 < T/K < 943$)[49] have been determined in separate studies. The results for the magnesium-uranium oxide solid solutions suggest the existence of U(V) and U(VI) in the solid solution despite the mean valenceof uranium ions being less than V, e.g. for $Mg_{0.3}U_{0.7}O_{2.0}$ the mean uranium oxidation state is 4.857.[48] The phase diagram for the vanadium oxide "bronzes" has been constructed from the thermodynamic data.[49] The solid solution of Sr in V_2O_5, the α-phase, exists at $0.00 \leq x \leq 0.02$; the β-phase actually consists of two isostructural phases $\beta(0.15 \leq x \leq 0.26)$ and $\beta'(0.28 \leq x \leq 0.30)$.[49]

In a series of papers,[50-52] Meullemeestre has described the preparation and characterisation (by i.r. spectroscopy, X-ray powder diffraction, t.g.a. and d.t.a. techniques) of $MgMo_3O_{10},nH_2O$ ($n = 5,7,10$),[50] $Mg_2Mo_3O_{11}$,[50] $CaMo_3O_{10},nH_2O$ ($n = 1,3,6$),[51] $SrMo_3O_{10},nH_2O$ ($n = 1.75,3,4$),[51] $BaMo_3O_{10},3H_2O$,[51] $BaMo_2O_7$[51] and $MMoO_4$ ($M = Ca,Sr,Ba$).[52] An analysis of the crystal structure data was not reported.

Reaction of BaS-Fe-S ternary mixtures at pressures to 60kbar and temperatures over 1273K produced the previously described compound Ba_3FeS_5.[53] Increasing pressure to 70kbar and reacting a 3:1:2 mixture at 1198K yielded $Ba_9Fe_3S_{11}(S_2)_2$. Single crystal studies revealed that the structure (hexagonal, $P\bar{6}c2$ $a = 9.218$, $c = 18.042$Å) is composed of close-packed layers of Ba and S atoms, the octahedral interstitial positions of which are occupied by Fe atoms. Strings of S_2^{2-} units are located in trigonal channels created by columns of face-sharing FeS_6 octahedra. The two crystallographically independent Ba atoms are surrounded by 9 sulphur atoms, $r(Ba...S) = 3.03$ to 3.65 and 2.93 to 3.75; the coordination polyhedra are distorted tricapped trigonal prisms.[53]

Four fluorite related superstructure phases have been found in the CaF_2-YbF_3 system.[54] The phases Ca_2YbF_7, $Ca_9Yb_5F_{33}$ and $Ca_{8-\delta}Yb_{5+\delta}F_{31+\delta}$ are members of the homologous series $(Ca,Yb)_mF_{2m+5}$ ($m = 15, 14, 13$) and $Ca_{17}Yb_{10}F_{64}$ is a combination ofthe phases with $m = 13$ and $m = 14$. In the fluorine-rich region of the system there exists a solid solution with tysonite structure and a related ordered phase with the formula, $Ca_3Yb_7F_{27}$.[54]

2.4 COMPOUNDS CONTAINING ORGANIC OR COMPLEX IONS

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

2.4.1 Salts of Carboxylic Acids

In a vibrational (i.r. and Raman) spectroscopic study[55] of the formation of complexes of Be^{2+} with oxalic acid in aqueous solution, three moieties were found: $[Be(C_2O_4)]$, $[Be(C_2O_4)_2]^{2-}$, $[Be(H_3O)(C_2O_4)_3]^{3-}$. The concentrations of the three complexes could be followed as a function of pH by measuring the intensities of certain characteristic bands in the Raman spectra.[55] Kinetic studies[56] have shown that Be^{2+} ions form both $[Be(HL)]^+$ and $[Be(L)]$ complexes with several dicarboxylate anions (L^{2-}) (oxalate, malonate, succinate and maleate); rate and equilibrium constants have been obtained for the formation of both types of complex. For the corresponding systems containing hydroxycarboxylate anions, however, only $[Be(HL)]^+$ complexes were observed; no evidence was found for the existence of $[Be(L)]$ complexes.[56]

The stabilities of the Ba^{2+} complexes, $[Ba(L)]^+$ and $[Ba(L)_2]$, of several monocarboxylate anions (L^-) (formate, acetate, proprionate and butyrate) have been estimated;[57] they decrease with increasing chain length of the anion. These results are similar to those observed for the corresponding complexes of Mg^{2+}, Ca^{2+} and Sr^{2+}. The solvates, $[Ba(CH_3COO)_2],3H_2O$, $[Ba(CH_3COO)_2],2CH_3COOH,4H_2O$ and $[Ba(CH_3COO)_2],2CH_3COOH$, have been isolated from the reaction of barium acetate with aqueous acetic acid;[58] they were characterised by chemical and thermal analyses and by X-ray diffraction techniques.

The crystal structures of alkaline earth metal salts of formic,[59] malonic,[60,61] maleic,[62] phthalic[63,64] and ascorbic acid[65] have been determinedby single crystal X-ray diffraction methods. That of α-calcium formate has been compared with revised data for α-strontium and barium formates.[59] Although the formates are not isostructural there are marked similarities between the compounds. The number of oxygen atoms around, and their average distance from, the cations increase from α-calcium formate (7+1, $r(Ca...O) = 2.42Å$), through α-strontium formate (8, $r(Sr...O) = 2.61Å$) to barium formate (8+1, $r(Ba...O) = 2.79Å$).[59] The structure of α-calcium formate is in good agreement with that derived from a recent neutron diffraction analysis of the same compound.[66]

The slightly distorted octahedral coordination of Mg^{2+} in magnesium bis(hydrogen malonate) dihydrate is composed of oxygen atoms from two water molecules, $r(Mg...O) = 2.06Å$, and four carboxylate groups, $r(Ca...O) = 2.05Å$.[60] Each Ca^{2+} ion in the related salt, calcium malonate dihydrate, is coordinated by two water oxygen atoms, r(Ca...O) = 2.41Å, and five carboxylate oxygen atoms, r(Ca...O) = 2.32 to 2.58Å;[61] the coordination polyhedron is a pentagonal bipyramid. Seven coordinate Ca^{2+} is also observed in calcium bis(hydrogen maleate), pentahydrate;[62] the distorted monocapped trigonal prismatic geometry is generated by five water oxygen atoms and one maleate anion, r(Ca...O) = 2.36 to 2.47Å.

The cations in calcium phthalate monohydrate[63] and strontium bis(hydrogenphthalate) dihydrate[64] are seven- and nine-coordinate, respectively. The coordination sphere of the Ca^{2+} ion is formed by seven oxygen atoms, six from phthalate ions and one from the water molecule, r(Ca...O) = 2.30 to 2.60Å;[63] that of the Sr^{2+} ion is formed by nine oxygen atoms, six from phthalate ions and three from water molecules, r(Sr...O) = 2.49 to 2.76Å.[64]

Two independent determinations[67,68] of the crystal structure of calcium L-ascorbate dihydrate have been compared and reassessed by the authors using normal probability plots; the results are reported in a joint communication.[65] It is concluded that the structure is bestrepresented by the weighted mean of the two independent parameter sets; the Ca^{2+} ions are coordinated by eight oxygen atoms in a slightly distorted square antiprismatic arrangement, r(Ca...O) = 2.41 to 2.52Å. Six oxygen atoms are furnished by three ascorbate anions, the other two by water molecules.[65]

Analyses of single crystal X-ray diffraction data for the oxalato- and malonato-species, $K_2[Be(C_2O_4)_2]$[69] and $K_2[Be(CO_2CH_2CO_2)_2],\frac{1}{2}H_2O$[70] respectively, have shown that the $[Be(C_2O_4)_2]^{2-}$ anion has C_s symmetry (although S_4 symmetry is approached) and the $[Be(CO_2CH_2CO_2)_2]^{2-}$ anion contains a distorted tetrahedrally coordinated beryllium atom, r(Be...O) = 1.609 to 1.623Å.

2.4.2 Beryllium Derivatives

Several theoretical analyses of the properties of beryllium compounds have been accomplished.[71-74] Of these, three have concentrated on the molecular structure of beryllocene.[71-73] *Ab initio* S.C.F. - M.O. (Schleyer, Streitwieser *et al.*)[71] and M.N.D.O. (Dewar and Rzepa)[72] studies of various structures of beryllocene have shown that its most stable form has one pentahapto and one monohapto ring. Such a structure is obviously not in agreement with the suggested C_{5v} off centre double well potential gas phase structure; indeed, even the symmetrical D_{5d} sandwich structure was found to be more stable than the C_{5v} form.[71,72] Although Dewar and Rzepa[72] conclude that the suggested "slipped sandwich"crystal structure is in approximate agreement with the calculated minimum energy structure, Schleyer, Streitwieser et al.[71] do not consider it to be favourable. In a separate ab initio S.C.F.-M.O. study, Chiu and Schafer[73] specifically investigated the two experimental models. The results of these calculations indicate that the gas-phase structure is less stable than a symmetrical sandwich or a model which is similar to the crystal structure, but has non-parallel rings. It is speculated that the vapours of beryllocene consist of a complicated conformational equilibrium with σ-π and σ-σ tautomerism which contains conformers in which the Be atom forms a π-bond to one ring and a σ-bond to the other. It is not unlikely that the radial distribution of this equilibrium is compatible with the experimental radial distribution observed by gas electron diffraction.[73]

Cyclopentadienyl beryllium hydride,[71] beryllium cyclooctatetraenide[74] and beryllium borohydride[72] have also been the subject of theoretical studies. Ab initio S.C.F.-M.O. calculations[71] have shown that cpBeH strongly prefers C_{5v} symmetry and pentahapto bonding with a high degree of covalent character. The direction of the dipole moment, revealed to have the negative end towards the BeH group, argues against ionic bonding, $cp^{-}BeH^{+}$, and implies considerable electron donation from the ring into the Be p-orbitals. An ab initio S.C.F.-M.O. study[74] of beryllium cyclooctatetraenide has shown that a "saturn-like" structure is less stable than alternative non-planar and polymeric structures. In the "saturn-like" structure the Be atom lies in a number of nodal planes and bonding is largely ionic. Moving the Be atom out of the ring plane permits covalent bonding interactions as well.[74] Using a M.N.D.O. model[72] the two most stable structural forms of $Be(BH_4)_2$ were calculated to be of D_{3d} (HBH_3BeH_3BH) and D_{2d} ($H_2BH_2BeH_2BH_2$) geometry. A definitive decision concerning the structure of this species could not be made on the basis of these data since the difference in energy (ca. 6 kJ.mol^{-1}) is obviously smaller than the accuracy of the calculations.[72] Gas phase ^{11}B and ^{1}H n.m.r. spectra of $Be(BH_4)_2$ show that only one monomeric species is present.[75] A linear B-Be-B framework is inferred and the hydrogens of each tetrahydroborate undergo rapid local internal exchange.

The preparation and characterisation of $Be(B_3H_8)_2$, $(C_5H_5)Be(B_3H_8)$

and $[(CH_3)Be(B_3H_8)]_2$ have been described;[75] the $(B_3H_8)^-$ derivatives of beryllium exhibit a range of fluxional behaviour as identified by variable-temperature n.m.r. studies. The reaction chemistry of $(B_3H_8)^-$ (and of BH_4^-) derivatives of beryllium has also been discussed.[75]

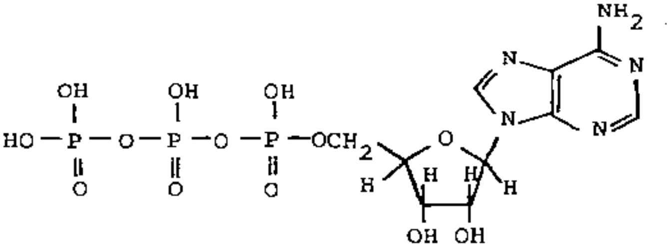
A series of beryllaborane compounds, including $B_5H_{10}BeX$ (where $X = BH_4$, B_5H_{10}, $C\ell$, Br, CH_3 and C_5H_5) has been prepared.[76] Determination of the molecular structure of $(B_5H_{10})Be(BH_4)$ by X-ray diffraction methods at 108K has shown it to be a pentagonal pyramidal cage in which one basal position is occupied by a Be atom.[77] A terminal hydrogen is attached to each of the cage boron atoms, and bridge hydrogens link all adjacent basal atoms in the cage. The tetrahydroborate group is attached to the Be atom by two bridging hydrogen atoms. Similarly, low temperature (138K) X-ray diffraction data have shown the molecular structure of $(B_5H_{10})Be(B_5H_{10})$ to consist of two pentagonal pyramidal cages, very similar to that for $(B_5H_{10})Be(BH_4)$ linked by a common Be atom.[77] m-Xylene was incorporated into the crystal with $(B_5H_{10})Be(B_5H_{10})$ to give a 1:1 compound.[77] Fuller details are given in Chapter 3.

^1H n.m.r. studies[78] have shown that the bis-benzoylacetonate complexes of Be^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+} and the bis-dipivaloylmethanate complex of Mg^{2+} are monomeric in solution whereas the corresponding acetylacetonate complexes of Mg^{2+}, Ca^{2+} and Ba^{2+} are polymeric in solution. A pseudo-tetrahedral, D_{2d}, idealised structure was favoured for all complexes.[78]

2.4.3 Magnesium Derivatives

Ab initio valence-only M.O. calculations for the linear molecules $(CH_3)_2Mg$, $(CH_3)MgC\ell$ and $MgC\ell_2$ have been undertaken at experimental (electron diffraction) geometries to study the bonding therein;[79] as expected, thebonding is found to be nearly all of the σ-type.

Several papers[80-83] have been published in which interactions



(1)

between alkaline earth metal cations, principally Mg^{2+} and Ca^{2+}, and ATP (1) are described. $Na_2M(ATP),nH_2O$ (M = Mg, n = 3; M = Ca, n = 2) complexes have been prepared.[80] Their i.r. spectra suggest that the metal ions are linked to both the phosphate and base functional groups of the ATP molecule. The formation of 1:1:1 ternary complexes between $[Mg(ATP)]^{2-}$ (M = Mg,Ca) and either 1,10-phenanthroline[81] or the catecholamines, dopamine and norepineprine,[82] has also been established. Potentiometric titration and u.v. difference spectroscopic studies[81] of equilibrium (3) have shown

$$[M(ATP)]^{2-} + [M(phen)]^{2+} \rightleftharpoons [M(phen)(ATP)]^{2-} + M^{2+} \qquad (3)$$

that the phenanthroline derivatives are much more stable than expected; indeed, the ATP^{4-} binds more tightly to $M(phen)^{2+}$ than to M^{2+} (M = Mg,Ca). ^1H n.m.r. studies of the Mg^{2+},$(ATP)^{4-}$ phenanthroline[81] and Mg^{2+},$(ATP)^{4-}$, catecholamine[82,83] systems confirm the presence of intramolecular stacking in the ternary complexes; it is this stacking which is thought to lead to the increased stability of the complexes. Analyses of ^1H n.m.r. data of the Mg^{2+},$(ATP)^{4-}$, catecholamine systems indicate that the binding of the catecholamine molecule in the ternary complexes occurs via its association with ATP alone; there is no direct interaction with the metal ion.[82] Furthermore, these ^1H n.m.r. data suggest that van der Waals-London interactions provide the major stabilising force for ring stacking.[83] Hydrophobic and charge-transfer interactions as well as hydrogen-bond formation and electrostatic interaction are also considered to contribute to the stability of the association.[83]

Peripheral magnesium complexes of a number of chlorophylls have been prepared and characterised by u.v.-visible, i.r., ^1H n.m.r. and luminescence spectroscopy.[84] The data demonstrate that the Mg^{2+} is bound to the peripheral β-keto ester system present in most chlorophylls rather than to the central tetrapyrrole cavity as in the chlorophyll proper.[84] E.p.r. studies of ^{25}Mg hyperfine coupling in the fully deuterated bacteriochlorophyll radical cation containing both naturally occurring Mg (10% ^{25}Mg abundance) and isotopically enriched samples (92% ^{25}Mg) have also been undertaken.[85]

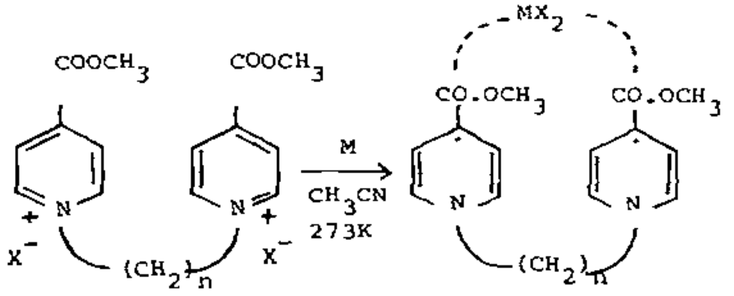
The stability of the 1:1 magnesium:tetrabenzophorphyrin complex has been ascertained in mixtures of pyridine and acetic acid and

and of t-butanol and trichloroacetic acid.[86] A comparison of the dissociation constants of the magnesium complexes of phorphyrins and benzophorphyrins shows the stabilising effect of the benzo-substitution.

Dimesityl magnesium has been isolated as the THF adduct, $Mg(C_9H_{11})_2(THF)_2$, from solutions of $Mg(C_9H_{11})Br$ in THF.[87] Its thermal and coordinative behaviour with pyridine and N,N,N',N'-tetramethylethylenediamine is discussed.[87] I.r. and Raman spectra of the ether addition compounds, Et_2Mg,nEt_2O ($n = 1,2$), crystallised from solutions of Et_2Mg in Et_2O have been measured (4000-200 cm^{-1}).[88] The monoetherate is apparently a centrosymmetric dimer with bridging ethyl groups between magnesium atoms. The dietherate is a monomer with tetrahedral configuration of the ligands about the central magnesium atom.[88]

THF soluble magnesium alkoxides and aryloxides, $Mg(OR)_2$, have been prepared by reaction of MgH_2 or $(CH_3)_2Mg$ with the appropriate alcohol or phenol.[89] They have been characterised on the basis of elemental analysis, i.r., n.m.r., and X-ray powder diffraction data; ebullioscopic studies indicate that they are monomeric in solution.[89] Reactions of alkaline earth metals with aluminium isopropoxide in boiling isopropanol in the presence of $HgC\ell_2$ catalyst gave the corresponding double alkoxides $[M[A\ell(Oi\text{-}Pr)_4]_2]_n$, ($M = Mg$, $n = 1$; $M = Ca,Sr,Ba$, $n = 2$).[90] ^1H and ^{13}C n.m.r. spectra of some of the double isopropoxides suggest rapid interchange of bridging and terminal isopropoxy groups.

Intensely coloured solutions of pyridinyl diradical complexes with alkaline earth metal halides (3) have been produced by reaction of the corresponding bispyridinium halides (2) with the alkaline earth metal in CH_3CN under oxygen-free conditions (equation 4).[91] Most of the complexes are characterised by strong



(2) (3)

$n = 3\text{-}10$
$M = Mg,Ca,Sr,Ba$ (4)
$X = C\ell,Br,I$

intramolecular charge-transfer bands and intensified pyridinyl radical absorptions. Their reaction chemistry has been studied in detail.[91]

The reactions of the alkaline earth metals with DMSO-SO_2 solvent systems have been investigated;[92] Mg reacts to form the metal disulphate, Sr and Ba react to form the metal sulphate, Be and Ca dissolve in the solvent but the products of the reaction have yet to be elucidated. The reaction mechanism is thought to involve the formation of the metal dithionites via the dimerisation of the SO_2^- radical ion (equation 6) obtained in the initial reaction (5). The metal dithionites are then oxidised (equation 7) to

$$M + xSO_2 \longrightarrow M^{x+} + x[SO_2]^- \qquad (5)$$

$$2[SO_2]^- \longrightarrow [S_2O_4]^{2-} \qquad (6)$$

$$[S_2O_4]^{2-} \xrightarrow{DMSO.SO_2} [S_2O_5]^{2-} \xrightarrow{DMSO.SO_2} [S_2O_7]^{2-} \qquad (7)$$

metal disulphites and subsequently disulphates by a 1:1 DMSO:SO_2 adduct. (This species has been tentatively characterised by phase equilibria and Raman spectroscopy studies). It appears that neither single component can bring about the oxidation. It is not clear, however, exactly how the DMSO-SO_2 adduct releases its oxygen in the oxidative process.[92]

The crystal structures of the trimethylphosphate complexes of Mg^{2+}, $[Mg(Me_3PO)_5H_2O](C\ell O_4)_2$[93] and $[Mg(Me_3PO)_5](C\ell O_4)_2$[94] have been determined by single crystal X-ray diffraction methods. The structure of the monoaquo complex consists of an assemblage of octahedral $[Mg(Me_3PO)_5H_2O]$ cations r(Mg...O) = 2.05 to 2.19Å, each hydrogen bonded to two $C\ell O_4^-$ anions via the coordinated water molecule.[93] In that of the anhydrous species, however, the Mg atom is coordinated by oxygen atoms of the five Me_3PO ligands in a square pyramidal arrangement.[94] The axial oxygen r(Mg...O) = 1.94Å, is significantly closer to the Mg atom than the basal oxygens, r(Mg...O) = 2.00 to 2.06Å, presumably due to π-bonding in the axial direction. The perchlorate anions occupy isolated positions.[94] The kinetics of the exchange of Me_3PO on $[Mg(Me_3PO)_6]^{2+}$ has been investigated in d_2-$CH_2C\ell_2$ and d_6-$(CH_3)_2CO$ diluents using ^{31}P n.m.r. spectroscopy.[95] The observation of $[Mg(Me_3PO)_5]^{2+}$ in d_2-$CH_2C\ell_2$ diluent[95] lends support to the postulation of a dissociative Me_3PO

exchange process for $[Mg(Me_3PO)_6]^{2+}$ as also does the observation of 5-coordinate $[Mg(Me_3PO)_5]^{2+}$ in the solid state.[94]

An i.r. and Raman study[96] of the $Mg(NO_3)_2$-$SnCl_4$-MeCN system has shown that the species which occurs both in solution and in the solid state is $[Mg(MeCN)_6]^{2+}[SnCl_4(NO_3)_2]^{2-}$, the hexa-solvated cation being octahedral, the anion centrosymmetric trans-octahedral.

The preparation and characterisation of $[(C_5H_5)_2MoHMg(THF)_2Br]$ has been described;[97,98] its reactions with CO_2, $PhCH_2Br$, C_3H_5Br, MeI and MeCOCl are also discussed. Single crystal X-ray diffraction data[98] have shown the Mg atom to be coordinated by the oxygen atoms of two THF molecules, the bromine atom and the bis(cyclopentadienyl) molybdenum hydride moiety; the Mg...Mo bond distance (2.732Å) is the same as that reported previously for a Mg...Mo bond in which the Mo acts as a one-electron donor.

2.4.4 Calcium, Strontium and Barium Derivatives

The crystal and molecular structures of a miscellaneous selection of calcium compounds, tetrakis(diacetamide)calcium(II) chlorate,monohydrate,[99] calcium(II) DL-glycerate dihydrate[100] and vacuum dehydrated fully calcium exchanged zeolite A[101] have been elucidated from single crystal X-ray diffraction data. In the diacetamide complex,[99] the Ca^{2+} ion is 8-coordinate. Its coordination sphere can be described as a square antiprism formed by eight carbonyl oxygens, r(Ca...O) = 2.41 to 2.44Å, from four diacetamide ligands; two of these ligands are related to the other two by a C_2 axis. In the carbohydrate derivative,[100] the Ca^{2+} ion is bound to three glycerate anions and two water molecules, two of the glycerate anions chelating the cation with the α-carboxy oxygen and α-hydroxy oxygen and the third bonding to the cation with the β-hydroxy oxygen only. Thus, seven oxygen atoms surround the Ca^{2+} ion in a distorted pentagonal bipyramidal arrangement, r(Ca...O) = 2.32 to 2.47Å.[100]

Near zero-coordinate Ca^{2+} and Sr^{2+} have been observed[101] in the crystal structures of vacuum-dehydrated fully Ca^{2+}-exchanged zeolite A (cubic, Pm3m, a = 12.278Å) and the corresponding Sr^{2+} compound (cubic, Pm3m, a = 12.316Å). In both Ca_6-A and Sr_6-A, five alkaline earth metal cations are located in normal positions on threefold axes near the centres of 6-oxygen rings. The sixth Ca^{2+} ion is located at an unusual position in the plane of an 8-oxygen ring, and the sixth Sr^{2+} ion occupies a similar site near this plane.

This Ca^{2+}(Sr^{2+})ion is 3.08Å (2.96Å) from its nearest neighbour, a single oxygen atom of the aluminosilicate framework - this exceeds the sum of the respective ionic radii by 0.77Å (0.52Å). Two other oxygen atoms are 3.13Å (2.98Å) from this Ca^{2+}(Sr^{2+})ion. Presumably one M^{2+} ion is located in an 8-ring in each structure because this allows a more satisfactory distribution of positive charge than would be possible if all six cations occupied threefold axis sites.[101]

Alkyliodostrontium and barium compounds of composition (RMI),nTHF (M = Sr, n = 2 or 3, R = Me,Et,Pr^n or Bu^n; M = Ba, n = 1, R = Et) have been isolated from THF solutions at 195K.[102] Alkylhalogenometal moieties have also been produced by cocondensation of Ca,Sr or Ba metal vapours with excess alkyl halide (MeI, EtI, n-PrI, n-BuI, i-PrI, i-BuI, MeBr, EtBr, n-PuCℓ, t-BuCℓ) at 77K. These compounds are very reactive solids decomposing rapidly in moist atmospheres and slowly *in vacuo* at ambient temperatures. Reactions between various unsaturated organic molecules and iodomethylstrontium and -barium are also reported together with the thermal decomposition of EtISr.[102]

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