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Chapter 2

ELEMENTS OF GROUP 2

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2.1 INTRODUCTION

As for the previous annual reviews of this series,[1] the chemistry of the alkaline earth metals reported in the 1983 literature is collated in sections reflecting topics of current interest and significance. For those subjects common to Group 1 and Group 2 elements (eg. complexes of crowns, cryptands and related molecules) the published data are discussed in the appropriate section of Chapter 1; those topics unique to the Group 2 elements are considered in this Chapter.

A survey of organoberyllium chemistry covering the three years from 1979 to 1981 has been published;[2] the 57 abstracted papers are almost equally divided into the broad fields of computational and experimental studies.

2.2 METALS AND INTERMETALLIC COMPOUNDS

Since a significant number of the papers abstracted for this section are related to the application of intermetallic compounds as hydrogen storage materials, the format adopted is similar to that of the 1982 review, two subsections dealing with structural and thermodynamic properties and with hydrogen storage applications being included.

2.2.1 Structural and Thermodynamic Properties

The Sr-Zn phase diagram has been determined by Bruzzone and Merlo[3] using thermal analysis, metallography and X-ray diffraction methods. Four intermediate compounds, two of which melt congruently, $SrZn_2$ (848K) and $SrZn_{13}$ (1103K), and two of which decompose in peritectic reactions, SrZn (707K) and $SrZn_5$ (923K), are found in the system; $SrZn_5$ also undergoes a structural transformation (893K). The structural chemistry of all five phases is summarised in Table 1.

The structures of Sr_8M_7 (M = Al,Ga),[4] Ba_8Ga_7,[4] and of the high pressure, high temperature polymorph of $SrSi_2$[5] have been elucidated; pertinent unit cell parameters are included in Table 1. The formulation Sr_8Al_7 is a revision of a previous structural proposal for equiatomic stoichiometry. The three isostructural compounds with this formulation are characterised by the presence of isolated tetrahedral and triangular clusters of Group 3 metal atoms surrounded by cages of 16 and 13 Group 2 metal atoms, respectively.[4] The structures of the ternary intermetallics,

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

Phase	Symmetry	Space Group (Structure Type)	a/pm	b/pm	c/pm	Ref
SrZn	orthorhombic	FeB	872.4	460.7	641.7	3
$SrZn_2$	orthorhombic	$CeCu_2$	477.7	779.0	786.5	3
α-$SrZn_5$	orthorhombic	$SrZn_5$	1314.7	531.2	670.7	3
β-$SrZn_5$	tetragonal	$CaCu_5$	554.9		428.3	3
$SrZn_{13}$	cubic	$NaZn_{13}$	1224.2			3
Sr_8Al_7	cubic	$P2_13$	1299.0			4
Sr_8Ga_7	cubic	$P2_13$	1248.4			4
Ba_8Ga_7	cubic	$P2_13$	1275.3			4
$SrSi_2^*$	tetragonal	$I4_1/amd$	443.8		1383	5
$CaMn_xAl_{2-x}$	hexagonal	$P6_3/mmc$	572.3		1826.4	6
$CaMn_4Al_8$	tetragonal	I4/mmm	895.7		516.8	6
$CaCo_2Al_8$	orthorhombic	Pbam	1449.7	1251.0	397.6	7

* High pressure, high temperature polymorph.

$CaMn_xAl_{2-x}$,[6] $CaMn_4Al_8$[6] and $CaCo_2Al_8$[7] have been ascertained by Schafer et al; crystallographic data for these phases are summarised in Table 1.

A group of German authors[8,9] have undertaken neutron and X-ray diffraction studies of the atomic structure of the metallic glasses, $Mg_{30}Ca_{70}$,[8] $Mg_{84}Ni_{16}$,[8] $Mg_{85.5}Cu_{14.5}$[9] and $Mg_{70}Zn_{30}$.[9] Although the latter three glasses exhibit pronounced chemical short range order, there is very little, if any, evidence for chemical short range order in $Mg_{30}Ca_{70}$. The extent of chemical short range order in these systems is tentatively correlated with their excess volumes and with the electronegativity difference between the component metals. The coordination of the nickel and copper atoms in the metallic glasses is very similar to that in crystalline Mg_2Ni and Mg_2Cu, respectively.[8,9]

Partial molar thermodynamic data for magnesium in liquid Mg-Pb

(923K), Mg-Sn (1073K), Mg-Bi (1123K) and Mg-Sb (1123K) binary and Mg-Sn-Sb (1073K) ternary solutions have been determined using an emf technique;[10] corresponding data for the other metals were obtained by computation using Gibbs-Duhem integration methods. Pronounced negative deviations from ideal behaviour, attributed to the presence of chemical short range order, were observed for all five systems; they were found to increase in the sequence:

Mg-Pb < Mg - Sn < Mg-Bi < Mg-Sb

2.2.2 Hydrogen Storage Applications

The preparation of novel materials containing alkaline earth metals which show exceptional promise in hydrogen storage applications has been reported by a group of Japanese authors.[11,12] Cocondensation of magnesium atoms with thf vapour on a cold surface (77K) gives remarkably active magnesium aggregates which begin to absorb hydrogen, without the conventional activation treatments, at 475K and under atmospheric pressure.[11] Treatment of equimolar quantities of $SmMg_3$ with diverse condensed ring compounds (anthracene, phenanthrene, chrysene or perylene) in anhydrous thf containing trace quantities of C_2H_5Br yields active sites capable of activating hydrogen which is then transferred to the adjoining intermetallic phase acceptor sites.[12] E.s.r. studies combined with hydrogen sorption measurements strongly suggest that the migrating hydrogen species are essentially monatomic.[12]

A qualitative picture of the interaction of hydrogen with intermetallic compounds (eg. Mg_2Cu, $CeMg_{12}$) has been developed by Russian authors[13] in an attempt to ascertain the reason for the rapid hydrogenation of these materials when compared with that of the individual metals. It is suggested that the development of a successful model will aid the design of materials which may serve either as hydrogen accumulators or as heterogeneous catalysts for hydrogenation reactions.[13]

The generally accepted view that hydrogen atoms are distributed randomly over interstitial sites in the α-phase of metal hydrides has been confirmed[14] in a ^{1}H-n.m.r. study of α-$Mg_2NiH_{0.22}$; the derived second moment is in accord with a random distribution of the hydrogen atoms over the B_3 sites of α-$Mg_2NiH_{0.22}$.[14]

Independent investigations of the hydrogenation of Mg-Ni-Cu[15] and Mg-Ca-Al[16] ternary alloys have been carried out. Action of hydrogen on $Mg_2Ni_{1-x}Cu_x$ ($0 < x < 0.85$) solid solutions, leads to the simultaneous formation of MgH_2, Mg_2NiH_4 and $MgCu_2$; the aborption and desorption rates for the $Mg_2Ni_{1-x}Cu_x$ solid solutions are close to those obtained with isostructural Mg_2Ni.[15] The hydrogenation products of alloys from the Mg-Ca-Al system, which are effectively mixtures containing varying amounts of Mg, Mg_2Ca, $CaAl_2$ and $CaAl_4$, contained Mg, MgH_2, $MgCaH_{3.72}$, CaH_2 and Al.[16]

2.3 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

This year there is a dearth of data for both binary and quaternary derivatives. Although the lack of data for binary compounds is typical of previous reviews, that for quaternary compounds is novel; it can be traced, however, to a dramatic reduction in the number of papers published by Kemmler-Sack on quaternary oxides with variants of the perovskite structure. Interest in ternary compounds also appears to be waning, data only being abstracted for ternary oxides and halides.

2.3.1 Binary Derivatives

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

Conditions for the efficient synthesis of MgC_2[17] and of Mg_2C_3[18] have been described. X-ray powder diffraction studies of these materials indicate that whereas MgC_2 is tetragonal (a = 329.9, c = 503.7 pm),[17] Mg_2C_3 is hexagonal (a = 743.4, c = 1056.4 pm).[18] Thermal decomposition of MgC_2 leads to Mg_2C_3 (plus carbon) which decomposes further to yield the constituent elements. The thermal stability of Mg_2C_3 increases with increasing pressure; it could be sustained at 1723K by applying a pressure of 6GPa.[17,18]

The structures of MHCl (M = Ca,Sr,Ba) and of BaHX (X = Cl,Br,I) have been refined[19] using single crystal X-ray diffraction data. They crystallise with tetragonal symmetry in the P4/nmm space group [CaHCl - a = 384.4, c = 683.7 pm]. Structural data for these compounds are compared with corresponding results for analogous fluorohalide compounds which adopt the same PbFCl-type structure. The analysis gives rise to a valuable insight into the bonding interactions in this structure-type.[19]

2.3.2 Ternary Oxides

To avoid unnecessary duplication with other Chapters of this review, the ternary compounds considered in this and the next subsection do not include those which contain a metal from the p-block of the Periodic Table.

Phase relationships in the BaO-Y_2O_3 system have been elucidated ($1213 \leqslant T/K \leqslant 1723$) using dta and X-ray diffraction methods.[20] Four intermediate compounds are found: $Ba_4Y_2O_7$ which only exists between 1293 and 1413K, $Ba_3Y_3O_{7.5}$ which decomposes in the solid phase at 1313K, $Ba_3Y_4O_9$ which only exists above 1333K and BaY_2O_4 which decomposes in the solid phase at 1673K. Crystallographic parameters for all four phases are collected in Table 2 together with corresponding data for $CaMO_3$ (M = Ti,Zr),[21] $SrTa_2O_6$,[22] $SrTa_4O_{11}$,[23,24] $Ca_xMn_{1-x}O$ solid solutions,[25] $CaMnO_{2.8}$,[26] $MgTc_2O_8$,[27] $MgPt_3O_6$,[28] $CaEr_3O_{5.5}$,[29] and $Ca_{0.1}Er_{1.9}O_{2.95}$.[30]

A reexamination of the structural chemistry of the orthorhombic modification of $CaMO_3$ (M = Ti,Zr) using neutron powder diffraction techniques[21] has established that they are derived from the ideal cubic perovskite structure by rotation of the MO_6 octahedra. This rotation has two ramifications; the MO_6 octahedra are distorted slightly, r(Ti...O) = 195.2-196.3, r(Zr...O) = 209.1-210.1 pm, and the coordination number of the Ca^{2+} ion is reduced from 12 to 8, r(Ca...O) = 236.3-266.7 (in $CaTiO_3$), 234.1-284.4 pm (in $CaZrO_3$).[21]

Bayer and Gruehn[22-24] have synthesised novel modifications of both $SrTa_2O_6$ and $SrTa_4O_{11}$ by thermal treatment ($1273 \leqslant T/K \leqslant 1373$) of the appropriate tungsten bronze structures in the presence of a transporting agent such as molecular chlorine. At higher temperatures ($T \geqslant 1453K$) the two novel compounds revert to the original tungsten bronze modifications.

Controlled decomposition of $CaCO_3$-$MnCO_3$ solid solutions in vacuum at 925K gives $Ca_xMn_{1-x}O$ ($0 \leqslant x \leqslant 1$) solid solutions in a finely divided state.[25] X-ray and magnetic susceptibility studies together with epr spectroscopy of the products confirm the expected linear variation of the cubic unit cell parameter and the presence of Mn^{2+} in the high spin $^6S_{5/2}$ state (μ = 5.9 B.M.) in all the solid solutions.[25] Evidence from electron diffraction, electron microscopy and computer simulation experiments[26] indicates that non-stoichiometric $CaMnO_{2.8}$ may be envisaged as being formed from the cubic stoichiometric perovskite $CaMnO_3$ by regular removal of O^{2-} anions in such a way as to generate a

Table 2. Crystallographic parameters for diverse ternary oxides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
$Ba_4Y_2O_7$	tetragonal	I4/mmm	436.1	-	2868	-	20
$Ba_3Y_3O_{7.5}$	tetragonal	P4/mmm	438.6	-	1185.6	-	20
$Ba_3Y_4O_9$	rhombohedral	R$\bar{3}$m	611.4	-	2521	-	20
BaY_2O_4	orthorhombic	Pnam	1040.0	1212.0	345.2	-	20
$CaTiO_3$	orthorhombic	Pcmn	538.3	764.5	544.6	-	21
$CaZrO_3$	orthorhombic	Pcmn	559.1	801.7	576.2	-	21
$SrTa_2O_6$	orthorhombic	-	1100.6	763.8	562.2	-	22
$SrTa_4O_{11}$	hexagonal	-	625	-	1233	-	23, 24
$Ca_xMn_{1-x}O$*	cubic	-	481/444	-	-	-	25
$CaMnO_{2.8}$	tetragonal	-	834	-	746	-	26
$MgTc_2O_8$	hexagonal	-	993	-	1254	-	27
$MgPt_3O_6$	orthorhombic	-	712.2	994.0	314.1	-	28
$CaEr_3O_{5.5}$	monoclinic	C2/m	652.4	354.6	1175.4	92.3	29
$Ca_{0.1}Er_{1.9}O_{2.95}$	monoclinic	C2/m	1380	349	858	100.8	30

*The entire solid solution range was studied; the data quoted refer to the two end mambers, CaO and MnO.

tetragonal structure with a base that is a $5^{\frac{1}{2}}$ x $5^{\frac{1}{2}}$ superlattice, but rotated by 26.5° with respect to the ideal perovskite structure. Both $CaMnO_{2.8}$ and $CaMnO_{2.75}$, which comprise MnO_6 octahedra and MnO_5 square pyramids, and $CaMnO_{2.5}$, which only contains MnO_5 square pyramids, retain the original features of the perovskite structure.[26]

Small amounts of CaO stabilise the monoclinic form of Er_2O_3;[30] single crystal X-ray diffraction studies of $Ca_{2x}Er_{2-2x}O_{3-x}$ (x = 0.05) indicate that Er^{3+} is only replaced by Ca^{2+} at 7-fold coordinate lattice sites.

The standard enthalpies of formation of a series of alkaline earth metal uranates(VI) and neptunates(VI) have been derived from solution calorimetry data;[31] they are collected in Table 3.

Fotiev et al[32-35] have continued their detailed kinetic and mechnistic analysis of the high temperature solid state interactions between $CaCO_3$ and the vanadium oxides, V_2O_5, VO_2, V_3O_5 and V_2O_3. As part of this investigation they have considered the reactions between V_2O_5 and $Ca(VO_3)_2$,[32,33] between VO_2, V_3O_5 or V_2O_3 and $CaCO_3$[34] and between FeV_2O_4 or Fe_3O_4 and $CaCO_3$.[35] As expected, reactions involving V_2O_5 do not involve any redox processes; calcium vanadates(V), $CaVO_3$ or $Ca_2V_2O_7$, are the sole products.[32,33] Reactions involving the lower oxides, VO_2, V_3O_5 or V_2O_3, or the iron(II)vanadate(III), FeV_2O_4, however, involve oxidation either to calcium vanadates(IV), CaV_2O_5, CaV_3O_7, CaV_4O_9 or to the calcium vanadate(V), $CaVO_3$.[34,35] Reaction of $CaCO_3$ with Fe_3O_4 leads to the calcium ferrate(III), $CaFe_2O_4$.[35] Another group of Russian authors[36] have studied the mechanism of the reaction of MCO_3 (M = Ca,Sr,Ba) with Nb_2O_5 or MoO_3 both experimentally and by physicochemical modelling.

Table 3. Standard enthalpies of formation, $\Delta H_f^o(X,c,298.15K)/kJ.mol^{-1}$, for a series of alkaline earth metal uranates(VI) and neptunates(VI).[31]

Ca_3UO_6	-3301.9±4.9	Sr_3NpO_6	-3125.3±5.8
Sr_3UO_6	-3262.6±4.4	Ba_3NpO_6	-3086.0±7.7
Ba_3UO_6	-3210.7±5.8		

2.3.3 Ternary Halides

Phase relationships in the $LiF-BeF_2$,[37] $RbCl-BeCl_2$[38] and $LiCl-SrCl_2$[39] systems have been ascertained using dta, X-ray diffraction, electrical conductivity and/or infra-red methods. Glass formation in the $LiF-BeF_2$ system ($0.0 \leqslant x_{LiF} \leqslant 0.5$) has been reexamined[37] in an attempt to clarify the contradictory reports in the literature. Low concentration specimens ($0.0 \leqslant x_{LiF} \leqslant 0.068$) were transparent glasses; at higher concentrations ($0.068 \leqslant x_{LiF} \leqslant 0.5$) specimens were obtained as non-transparent milky-white plates. X-ray diffraction studies indicated that although the former were amorphous to X-rays, the latter were not completely amorphous, the strongest diffraction lines of Li_2BeF_4 being observed.[37] In a separate, totally independent experiment, Collins et al[40] have experimentally assessed the bonding scheme for Li_2BeF_4 proposed over a decade ago by McGinnety.[41] The electron deformation density of Li_2BeF_4 observed in X-X maps derived from a single crystal X-ray diffraction experiment ($R = 0.021$ for 984 unique reflections) conform to the expected covalent character of the Be-F bonds but offer no evidence for the proposed Li-F covalent bonding.[40]

Two compounds were observed in both the $RbCl$-$BeCl_2$[38] and $LiCl$-$SrCl_2$[39] systems; they have identical stoichiometries, A_2BCl_4 and AB_2Cl_5 (A = alkali metal, B = alkaline earth metal). Whereas Rb_2BeCl_4 and $RbBe_2Cl_5$ both melt congruently (at 873 and 653K, respectively),[38] Li_2SrCl_4 melts congruently (at 773K) while $LiSr_2Cl_5$ decomposes in a peritectic reaction (at 771K).[39] In neither study are any structural data reported.[38,39]

Mass spectroscopic studies[42] of the vapour above binary alkali metal halide-alkaline earth metal halide mixtures have shown that one or more of the gaseous heterocomplexes, ABX_3, A_2BX_4 or AB_2X_5 (A = alkali metal; B = alkaline earth metal; X = halogen) exist in all cases; the concentration dependence of the molecules in the gas phase on the molar composition of the liquid was ascertained. The stability of the complexes was generally found to decrease with increasing anionic radius as shown by the formation enthalpies derived from the mass spectroscopic data. The eighteen systems studied are listed in Table 4 together with the formation enthalpies of the observed complexes.[42]

Structural information has been accrued on Sr_2MF_7 (M = Sc,Rh),[43] $CaTcBr_6$,[44] $(NH_4)BeF_3$,[45] and $MZrF_6$ (M = Sr,Ba).[46] Crystallographic parameters for Sr_2MF_7 (M = Sc,Rh)[43] and for $CaTcBr_6$[44] as derived in X-ray diffraction experiments are collected in Table 5. Thermal decomposition of $CaTcBr_6$ occurs at 653-693K leading to $CaBr_2$, tecnetium and bromine.[44] Temperature dependent X-ray studies[45] have shown that $(NH_4)BeF_3$ undergoes a series of phase transitions:

$$\text{Modification IV (Space group P1)} \xrightleftharpoons{252.2K} \text{III(Pn)}$$

$$\xrightleftharpoons{334.3K} \text{II}(P2_12_12_1) \xrightleftharpoons{347.3K} \text{I(Pmnb)}$$

The structure of the ferroelectric room temperature modification (III) has been determined. It consists of two crystallographically distinct BeF_4 tetrahedra which share corners to form chains running parallel to the b axis. The two tetrahedra are

Table 4. Enthalpies of formation, $-\Delta H_f^o(X,g,298)/kJ.mol^{-1}$, of the gaseous heterocomplexes ABX_3, A_2BX_4 and AB_2X_5.[42]

System	$-\Delta H_f^o/kJ.mol^{-1}$ ABX$_3$	A$_2$BX$_4$	AB$_2$X$_5$	System	$-\Delta H_f^o/kJ.mol^{-1}$ ABX$_3$	A$_2$BX$_4$	AB$_2$X$_5$
$LiCl-MgCl_2$	210	192	174	$CsBr-CaBr_2$	200	205	-
$KCl-MgCl_2$	201	216	-	$RbBr-SrBr_2$	196	196	-
$RbCl-CaCl_2$	210	217	-	$CsBr-SrBr_2$	195	210	-
$CsCl-CaCl_2$	229	-	-	$RbBr-BaBr_2$	199	-	-
$KCl-SrCl_2$	197	214	-	$CsBr-BaBr_2$	193	195	-
$KCl-BaCl_2$	207	-	-	$NaI-CaI_2$	193	192	192
$NaBr-CaBr_2$	210	190	185	$KI-CaI_2$	196	194	179
$KBr-CaBr_2$	209	223	222	$RbI-CaI_2$	193	199	-
$RbBr-CaBr_2$	197	204	-	$CsI-CaI_2$	190	203	194

Table 5. Crystallographic parameters for a number of ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	$\beta/^o$	Ref.
Sr_2ScF_7	monoclinic	$P2_1/c$	545	1219	823	90.5	43
Sr_2RhF_7	monoclinic	$P2_1/c$	551	1166	863	90.9	43
$CaTcBr_6$	orthorhombic	-	1039	734	745	-	44

significantly distorted with marked variation in both bond distances, r(Be(1)...F) = 150-158, r(Be(2)...F) = 148-158 pm, and bond angles, FBe(1)F = 103.6-112.9°, FBe(2)F = 106.6-114.9°.[45] Dta studies of crystalline and vitreous $MZrF_6$ (M = Sr,Ba)[46] have served to clarify the phase transformation characteristics of the crystalline materials:

$$\beta\text{-SrZrF}_6 \xrightleftharpoons{673K} \alpha\text{-SrZrF}_6 \xrightleftharpoons{933K} \beta\text{-SrZrF}_6 \xrightleftharpoons{1023K} \text{liquid}$$

$$\beta\text{-BaZrF}_6 \xrightleftharpoons{688K} \alpha\text{-BaZrF}_6 \xrightleftharpoons{838K} \beta\text{-BaZrF}_6 \xrightleftharpoons{843K} \text{liquid}$$

Complementary Raman spectroscopic studies[46] have yielded novel information about the coordination characteristics of the cations in these species.

2.3.4 Quaternary Oxides

In contrast to earlier reviews, a much smaller number of papers have been abstracted from the 1983 literature for this section. Although much less prolific than in previous years, Kemmler-Sack[47-50] is responsible once again for the greatest contribution to our knowledge of this topic. The structure of only one novel hexagonal stacking polytype with rhombohedral layer structure has been reported;[47] it is that of the 5L variant with hhccc sequence, $Ba_5[Co_4MO_{15-y}\square_y]$ (M = Ru,Ir,Rh). Pertinent unit cell parameters are collected in Table 6. The structures of $Ba_3[SrM_2O_9]$ (M = Nb, Ta) have been refined by Ijdo et al[51] using Rietveld analysis of neutron diffraction data in an attempt to resolve an earlier conflict between the choice of 3L[52] or 6L[53] stacking polytypes for $Ba_3[SrTa_2O_9]$. The neutron diffraction results suggest that both compounds adopt the 6L stacking polytype structure (Table 6) thus

Table 6. Crystallographic data for a number of hexagonal stacking polytypes with rhombohedral layer structures.

Compound	Space Group	Stacking Polytype	Layer Sequence	a/pm	c/pm	Ref
$Ba_5[Co_4RuO_{13.45}\square_{1.55}]$	$P\bar{3}m1$	5L	hhccc	571.1	1192	47
$Ba_5[Co_4IrO_{12.30}\square_{2.70}]$	$P\bar{3}m1$	5L	hhccc	569.5	1199	47
$Ba_5[Co_4RhO_{13.15}\square_{1.85}]$	$P\bar{3}m1$	5L	hhccc	571.8	1199	47
$Ba_3[SrNb_2O_9]$	$P6_3/m$	6L	$(hcc)_2$	607.04	1537.58	51
$Ba_3[SrTa_2O_9]$	$P6_3/m$	6L	$(hcc)_2$	607.76	1533.60	51

confirming the earlier assertion by Kemmler-Sack[53] discussed in the 1981 review.[54]

Kemmler-Sack has also reported novel photoluminescence data for various lanthanides (Eu,Tb,Dy,Er) doped into the 12L stacking polytypes $Ba_{3-x}Sr_xLa[ScW_2\square O_{12}]$,[48] $Sr_3La[ScW_2\square O_{12}]$,[48] $Sr_3La[LaW_2\square O_{12}]$[49] and for the 24L stacking polytypes $Sr_8[SrGd_{2-x}Eu_xW_4\square O_{24}]$ (low and high temperature modifications) and $Sr_8[Sr_{1-y}Ba_yEuW_4\square O_{24}]$.[50]

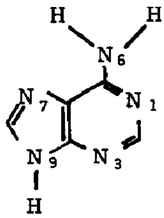
2.4 COMPOUNDS OF THE ALKALINE EARTH METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS

A significant proportion of the papers abstracted for this section belong to one of two topics (viz., complexes of significance in bioinorganic chemistry and complex formation in solution); these papers, regardless of the identity of the alkaline earth metal, are considered in the respective subsection. The topics covered in the other papers are somewhat diverse; these papers are covered in subsections devoted to the individual alkaline earth metals.

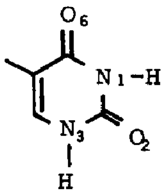
2.4.1 Complexes of Significance in Bioinorganic Chemistry

The binding of alkaline earth metal cations, especially Mg^{2+} and Ca^{2+}, to nucleosides and nucleotides has been the subject of both theoretical[55] and experimental[56-61] studies. Rode et al[55] have undertaken a series of ab initio calculations on the binding of Mg^{2+} to adenine and thymine; whereas the N(3) binding site of adenine (binding energy 495.4 $kJ.mol^{-1}$) is favoured over the N(1) (464.0 $kJ.mol^{-1}$) and N(7) (417.8 $kJ.mol^{-1}$) sites, the O(6) binding site of thymine (459.8 $kJ.mol^{-1}$) is favoured over the O(2) (396.6 $kJ.mol^{-1}$) site. The results are used to assess the influence of Mg^{2+} on the hydrogen bonds of the adenine-thymine base pair; Mg^{2+} binding to the O(2) atom of thymine gives rise to considerable hydrogen bond stabilisation of the system.[55]

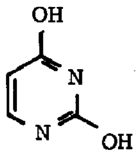
Thermodynamic parameters for the interaction of, inter alia, Mg^{2+} and Ca^{2+} with adenine, thymine, uracil, cytosine and hypoxanthine have been derived by Taqui-Khan et al from potentiometric data ($288 \leqslant T/K \leqslant 318$) both in the absence[56] and presence[57] of complexing ligands such as bipyridyl, o-phenanthroline and 5'-sulphosalicylic acid. Using similar methods, they have also determined the stability constants of ternary 1:1:1 complexes of these cations



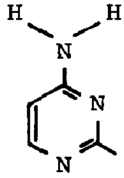
adenine



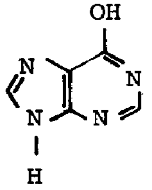
thymine



uracil



cytosine

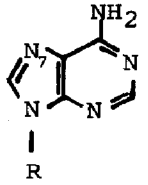


hypoxanthine

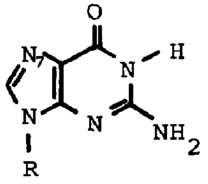
with adenine and thymine, uracil or cytosine[57] or with adenine and L-tryptophan or L-histidine hydrochloride[58] or with cytosine with L-tryptophan or L-histidine hydrochloride.[58] In all cases, the ternary complexes are much more stable than the binary complexes, a feature which is attributed to the energy of stacking interactions in these systems.

Tajmir-Riahi and Theophanides have isolated and characterised several Mg(II) complexes of adenosine-5'-monophosphate, Mg[5'-AMP],nH_2O (n = 5,10),[59] of 2'-deoxyguanosine-5'-monophosphate, Mg[5'-dGMP],nH_2O (n = 2,4)[60] and of guanosine-5'-monophosphate, Mg[5'-GMP],nH_2O (n = 4-10).[61] Spectroscopic and chemical evidence indicate that, in common with other divalent metal cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Cd^{2+}, Pt^{2+}) but in contrast to the theoretical results reported by Rode et al[55] the Mg^{2+} cation is attached to the N(7) binding site of all three nucleotides.[59-61] When isolated from acidic solution ($pH \leqslant 5$) the complexes also exhibited direct Mg^{2+}-phosphate coordination; such an interaction was not present in complexes prepared in neutral or slightly basic solutions ($6 \leqslant pH \leqslant 9$).[59-61]

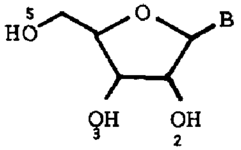
Ab initio theoretical calculations of the binding of Ca^{2+} to aliphatic dipeptides such as glycylglycine, glycyl-L-alanine and L-alanyl-L-alanine have been completed by Rode et al.[62] The results indicate that there are no significant differences in the stabilities of the complexes formed by the three dipeptides but that there are large differences as far as the several coordination



adenosine



guanosine



ribose

R = Ribose; B = base.

possibilities are concerned, those with minimum energy having a configuration in which the Ca^{2+} ion can interact with all three oxygen atoms of the dipeptide.[62]

Circular dichroism and optical rotatory dispersion data for solutions of magnesium protoporphyrin and magnesium mesoporphyrin containing the amino acids, L-histidine,[63] D- and L-proline,[64] L-serine,[64] L-threonine[64] and L-tryptophan[64] exhibit induced effects which are attributed to six-coordinate magnesium porphyrin amino acid (1/1/2) species; five-coordinate magnesium porphyrin amino acid (1/1/1) species are thought not to produce Cotton effects. The observed Cotton effects are most pronounced for proline and for the related pair of amino acids, serine and threonine.[64] The molecular structure of a magnesium porphyrin radical, (perchlorato)(5,10,15,20-tetraphenylporphinato)magnesium-(II) has been determined using single crystal X-ray diffraction methods;[65] it is shown in Figure 1(a). The coordination of the magnesium in the porphyrin pocket is somewhat asymmetric with two short and two long Mg-N contacts, r(Mg...N) = 208.0, 208.8 and 210.6, 211.0 pm, respectively. The distorted square pyramidal Mg^{2+} coordination sphere is completed by a strongly bound oxygen atom from the perchlorate anion, r(Mg...O) = 201.2 pm.[65]

Structural analyses have been completed on the three magnesium(-)-sparteine derivatives, dichloro{(-)-sparteine}-magnesium(II),[66] chloro(tert-butyl){(-)-sparteine}magnesium(II)[66] and bromo(ethyl){(-)-sparteine}magnesium(II).[67] The Mg^{2+} ion in all three compounds has a distorted tetrahedral coordination geometry generated by the two nitrogen atoms of the (-)sparteine molecule and either two halogen atoms (for the dichloro compound)[66] or one halogen atom and one carbon atom from the alkyl anion (for the chloro(tert-butyl)[66] and bromo(ethyl)[67] compounds); pertinent details are collected in Table 7.

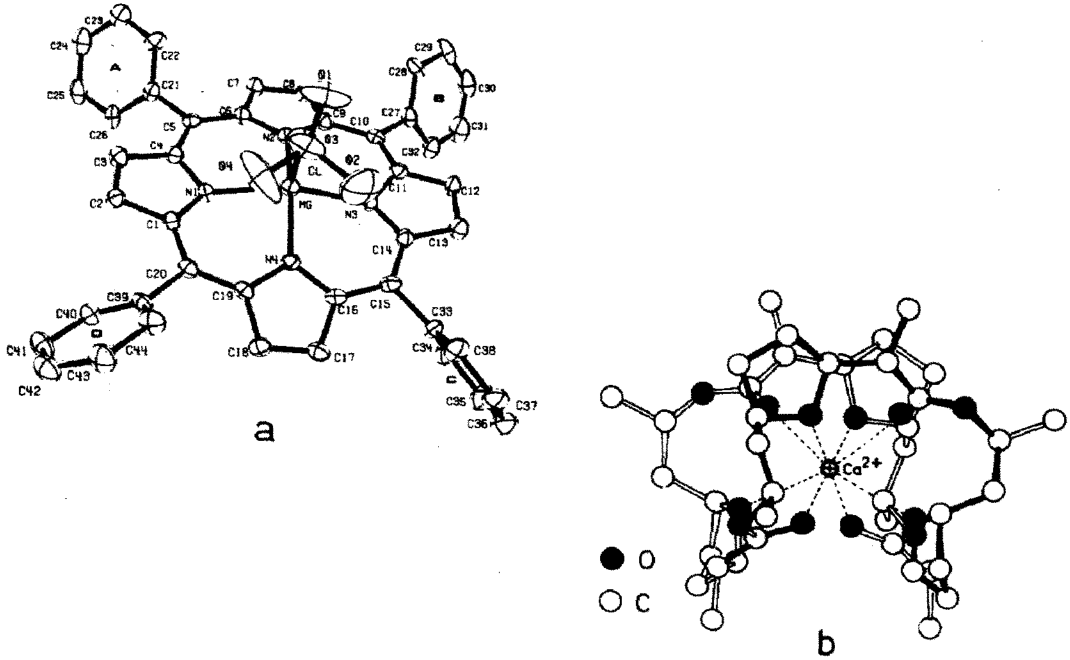
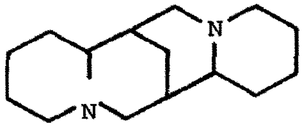


Figure 1. Cation coordination geometries in (a) (perchlorato)-(5,10,15,20-tetraphenylporphinato)magnesium(II) and in (b) the nonactin-calcium perchlorate complex (reproduced by permission from (a) Inorg. Chem., 22(1983)349 and (b) Acta Crystallogr., C39(1983)1460).



sparteine

The crystal and molecular structure of the nonactin complex of $Ca(ClO_4)_2$ has also been determined.[68] The geometry of the cation is shown in Figure 1(b). It is very similar to that of the corresponding sodium and potassium complexes, the Ca^{2+} ion being located on a twofold symmetry axis with only one half of the ionophore in the asymmetric unit. The nonactin molecule completely envelopes the Ca^{2+} ion, four carboxyl oxygen, r(Ca...O) = 232.8, 236.3 pm and four furan oxygen, r(Ca...O) = 259.7, 260.6 pm atoms

Table 7. Interatomic distances/pm and angles/° in three magnesium (-)-sparteine derivatives.

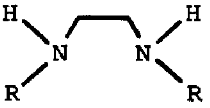
Compound	r(Mg..N)	r(Mg..Cl)	r(Mg..Br)	r(Mg..C)	∠NMgN
$MgCl_2$- (-)-sparteine[66]	215,216	226.9,227.9	-	-	85.0
Bu^tMgCl- (-)-sparteine[66]	217,218	233.2	-	219	83.9
EtMgBr- (-)-sparteine[67]	214,216	-	248.2	224	84.0

acting as coordinating centres; the Ca^{2+} ion coordination polyhedron can be described as a distorted cube.[68]

Multinuclear (^{25}Mg, ^{31}P) n.m.r. studies[69] have been developed to provide qualitative information on the active site structure of acetate kinase, a tetrameric enzyme which is involved in the phosphorisation of the acetate anion.

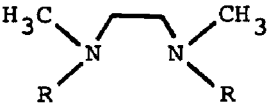
2.4.2 Complex Formation in Solution

Thermodynamic parameters for the complexation of alkaline earth metal cations by a number of diverse unrelated ligands have been reported;[70-75] although the majority of the data were derived in aqueous solution[70-74] one set of results was obtained in dioxane/water (75/25, v/v) mixtures.[75] Calorimetric methods have been used to study the complexation of Be^{2+} by benzoylacetonate,[70] of Mg^{2+}-Ba^{2+} by the linear poly(aminocarboxylic)acids (1-4),[71] of Mg^{2+}-Ba^{2+} by 2-(carboxylato)pyridine (5) and 2,6-di(carboxylato)-pyridine (6)[72] and of Ba^{2+} by ethylenediaminetetraacetic acid.[73] The standard molar enthalpy of formation of bis(benzoylacetonato)-beryllium(II) has been derived from solution calorimetry data, $\Delta H_f^o(X,c,298.15) = -(1013.1\pm5.7)\ kJ.mol^{-1}$.[70] Analysis of the thermodynamic data for the alkaline earth metal complexes of (1-4)[71] reveals several trends. The most significant is the reduction in the stability of the complexes as the size of the cation increases. This decrease appears to be entropy controlled, the magnitude of ΔS reflecting the degree of dehydration of the cation on complexation.[71] In general, the stability of the 1:1



(1) R = CH_2COOH

(2) R = $-CH(CH_3)COOH$

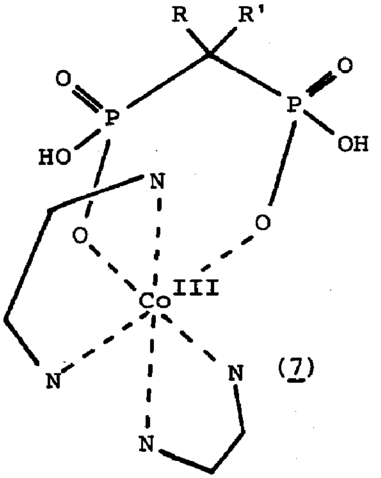


(3) R = $-CH_2COOH$

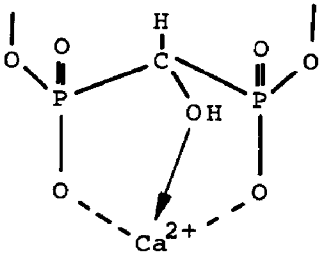
(4) R = $-CH_2COOH$

complexes of the carboxylatopyridine derivatives (5,6) with the alkaline earth metal cations also decreases as the size of the cation increases;[72] the Mg^{2+} complex of (6), however, has an anomalously low stability.

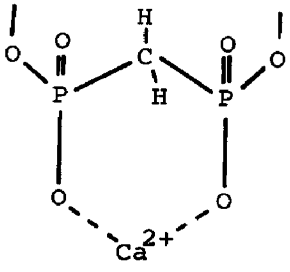
Potentiometric methods have been used to determine stability constants for the association of Ca^{2+} with various diphosphonate ligands coordinated to $[Co^{III}(en)_2]$ residues (7) in water[74] and of, inter alia, Mg^{2+} with N-(2-hydroxy-5-phenylbenzylidine)-4-substituted-(R)-anilines (R = $-CH_3$, $-Cl$, $-OCH_3$ or $-NHCOCH_3$) in dioxane/water (75/25; v/v) mixtures.[75] The results for the former system[74] show that coordinated diphosphate ligands have considerable affinity for Ca^{2+} ions and that when R or R' = OH, the Ca^{2+} affinity is enhanced presumably by coordination of this group to Ca^{2+} and the formation of a tridentate bonding mode (8)



(7)



(8)



(9)

as opposed to a bidentate bonding mode (9).[74] The data for the latter system[75] are analysed in terms of inductive and mesomeric effects of the substituents in the 4-position of the aniline ring.

2.4.3 Beryllium Derivatives

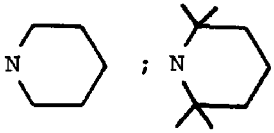
The hydrolysis of beryllium(II) cations in 0.1 mol.dm^{-3} KNO_3 has been studied at 298K using potentiometric techniques.[76] Evidence is presented for the formation of the species, $Be(OH)_2$, $[Be_2(OH)]^{3+}$ and $[Be_3(OH)_3]^{3+}$, the appropriate log β_{pq} values being 11.320(8), 2.955(7) and 8.804(2), respectively.

Bis(amido)beryllium compounds have been conveniently prepared according to Scheme 1.[77] Mass spectroscopic and multinuclear n.m.r. data indicate that, with the exception of bis(piperidine)beryllium which is trimeric, all products were initially formed as monomers; with time, however, bis(diisopropylamido)beryllium dimerises.

$$2LiNR_2 + BeCl_2.2Et_2O \rightarrow Be(NR_2)_2 + 2LiCl + 2Et_2O$$

$$2LiR + BeCl_2.NHR_2 + NHR_2 \rightarrow Be(NR_2)_2 + 2LiCl + 2RH$$

$NR_2 = N(SiMe_3)_2$; $N(Pr^i)_2$; $N(SiMe_3)(CMe_3)$;



Scheme 1.

Reaction of $BeCl_2$ or $MgCl_2$ with $(C_6H_5)_3P{=}CH_2$ in 1:2 or 1:4 mole ratios yields di-μ-chloro-bis[(methylenetriphenylphosporane)metal]-dichlorides.[78] A corresponding calcium complex could not be isolated from similar reaction mixtures of $CaCl_2$ with $(C_6H_5)_3P{=}CH_2$.[78]

Bell et al[79,80] have synthesised and structurally characterised two novel, disparate, beryllium derivatives. The structures of $[HBeN(Me)C_2H_4NMe_2]_2$[79] and of $Cl_2Be_3(oBu^t)_4$[80] are depicted in Figure 2. In the former dimeric complex (Figure 2(a)) the hydrogen atoms occupy terminal positions with amide nitrogen atoms as the bridging atoms in a four membered Be_2N_2 ring; the metal and nitrogen atoms achieve four-fold coordination by formation of four and five membered rings with the diamine. In the latter complex (Figure 2(b)) the chlorine atoms are colinear with the three

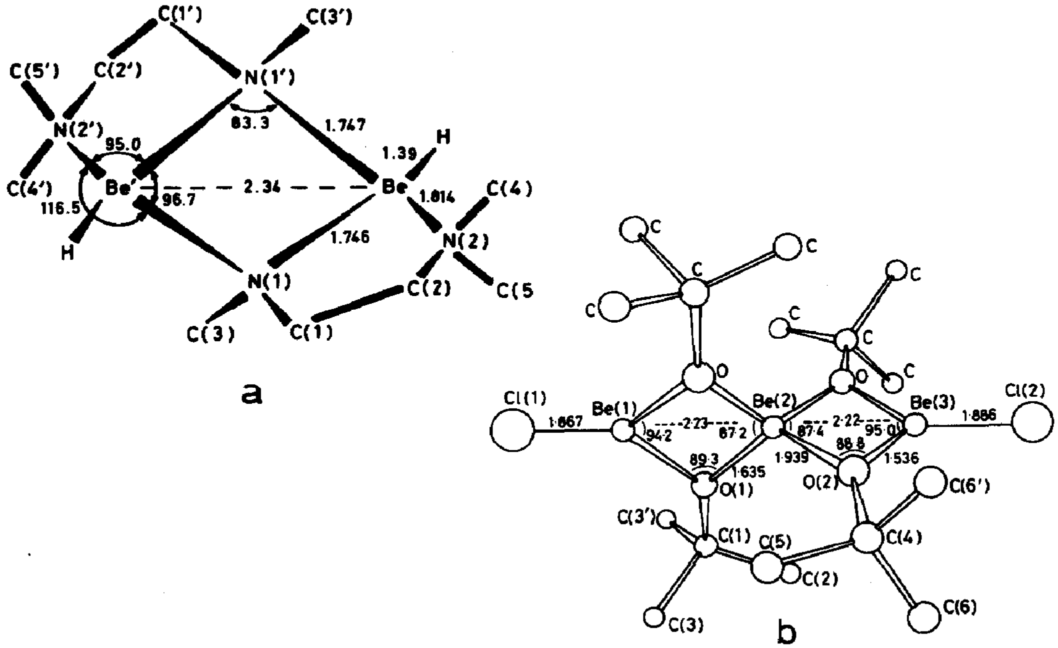


Figure 2. Molecular structures of (a) $[HBeN(Me)C_2H_4NMe_2]_2$ and of (b) $Cl_2Be_3(OBu^t)_4$ (reproduced by permission from J. Chem. Soc., Chem. Commun., (1983)828,840).

beryllium atoms and alkoxide oxygen atoms act as the bridging atoms in two four membered Be_2O_2 rings, to give a four-coordinate central beryllium atom and two three-coordinate terminal beryllium atoms. Pertinent bond lengths and angles for both structures are given in Figure 2.

2.4.4 Magnesium Derivatives

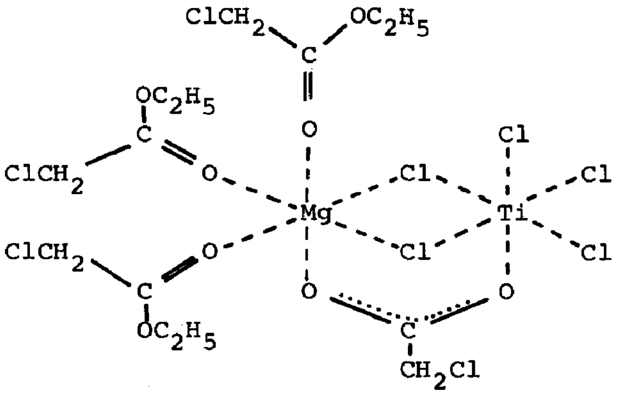
Of the vast number of papers published annually on the chemistry of magnesium, the majority involve some aspect of organomagnesium chemistry. Since this particular topic is reviewed elsewhere, it is generally ignored here. Consequently, only a small number of papers have been abstracted for this subsection; although they cover a number of diverse materials, they are biased towards structure elucidation.[81-86] The empirical relationship:

$$s = (d/d_1)^{-N}$$

relating bond lengths (d,pm) to bond strengths (s, valence units) has been derived[81] for Mg-Cl (d_1 = 201.0, N = 5.10) and Mg-O (d_1 = 162.0, N = 4.40) bonds from a detailed analysis of structural data presently available for $MgCl_n$, (n = 2-4,6) MgO_n (n = 1,4-6,8), $MgClO_4$ and $MgCl_nO_{4-n}$ (n = 1,2,4) ligand sets.

Hexaaquo magnesium(II) cations have been located in the structures of ammonium hexaquomagnesium(II)trichloride[82] and hexaquomagnesium(II)aquo(ethylenediaminetetraacetato)cadmium(II)-trihydrate.[83] Whereas the former compound contains only one octahedral $[Mg(H_2O)_6]^{2+}$ moiety in the asymmetric unit, r(Mg...O) = 204.7-205.9 pm,[82] the latter contains two crystallographically distinct somewhat less symmetrical hexaquo cations, r(Mg(1)...O) = 203.4-211.8, r(Mg(2)...O) = 205.3-212.4 pm.[83] The cadmium atom of the latter compound is coordinated to a water molecule, r(Cd...O) = 224.6 pm, and to an anion which acts in a hexadentate fashion, r(Cd...O) = 233.6-245.7, r(Cd...N) = 238.2, 241.4 pm in a pentagonal bipyramidal geometry.[83]

The crystal and molecular structure of the product (<u>10</u>) formed by reaction of $TiCl_4$ with a solution of $MgCl_2$ in dry $ClCH_2COOC_2H_5$



(<u>10</u>)

have been elucidated.[84] The magnesium atom is octahedrally coordinated by two chlorine atoms, r(Mg...Cl) = 250.0, 251.5 pm, the carbonyl oxygen atoms of the three solvent molecules, r(Mg...O) = 200.2-202.1 pm and an oxygen atom of the $ClCH_2COO$ anion, r(Mg...O) = 204.9 pm which bridges the two metal atoms. The titanium atom is also octahedrally coordinated, in this case by five chlorine atoms, r(Ti...Cl) = 224.2-245.7 pm and an oxygen atom of the bridging $ClCH_2COO$ anion, r(Ti...O) = 196.6 pm.[84]

Ab initio M.O. L.C.A.O. calculations have been completed both for magnesocene[85] and for Grignard reagents.[86] The former theoretical study[85] indicates that the principal metal-ring bonding in magnesocene, $(C_5H_5)_2Mg$, occurs between the magnesium 3s and 3p orbitals and the cyclopentadienyl ring π-orbitals. The latter analysis[86] supports the recent suggestion[87] that clusters of magnesium atoms may be necessary for reaction with alkyl halides. Thus the calculations show that there is a consistent 21 -25 kJ.mol^{-1} stabilisation resulting from the formation of a dimagnesium compound, $R(Mg)_2X$ rather than a simple one, RMgX (eqn.(1)). In the presence of excess alkyl halide, however, two simple Grignards will be produced since reaction of the dimagnesium compound with alkyl halide (eqn.(2)) is almost as exothermic as production of a simple Grignard (eqn.(3)).[86]

$$Mg + CH_3MgF \rightarrow CH_3MgMgF \qquad \Delta H = -23.8\ kJ.mol^{-1} \qquad ...(1)$$

$$CH_3MgMgF + CH_3F \rightarrow 2CH_3MgF \qquad \Delta H = -217.6\ kJ.mol^{-1} \qquad ...(2)$$

$$Mg + CH_3F \rightarrow CH_3MgF \qquad \Delta H = -241.8\ kJ.mol^{-1} \qquad ...(3)$$

Reaction of PhMgBr with bipyridyl in dilute thf affords (bipy)MgPh; on addition of either of the nickel complexes $(bipy)_xNiX_2$ (X = Cl,Br) the paramagnetic product (bipy)MgBr(thf) is obtained together with biphenyl.[88] The product has been characterised by esr spectroscopy as well as normal chemical analysis.

2.4.5 Calcium Derivatives

Only four papers[89-92] have been abstracted for this subsection; they describe the results of single crystal X-ray structural analyses on four diverse calcium derivatives. Distorted octahedral Ca^{2+} coordination geometries were observed in the structures of calcium copper acetate hexahydrate[89] and of calcium acetylacetonate trihydrate.[90] Whereas in the former complex, which has tetragonal symmetry, the Ca^{2+} ion is coordinated by two trans water molecules, r(Ca...O) = 234.3 pm and four oxygen atoms from acetate anions, r(Ca...O) = 228.9 pm, in the latter complex, which possesses two-fold symmetry, the Ca^{2+} ion is surrounded by two cis water molecules, r(Ca...O) = 235.6 pm and four oxygen atoms from two bidentate acetylacetonate anions, r(Ca...O) = 232.0, 233.6 pm.

The Ca^{2+} coordination polyhedra in the other two calcium derivatives are described as distorted monocapped trigonal prismatic.[91,92] The two crystallographically independent Ca^{2+} ions in the structure of $[Ca(H_2O)_7]_2[Cd_6Cl_{16}(H_2O)_2],H_2O$,[91] are simply coordinated by seven water molecules, r(Ca(1)...O) = 235.0-243.4, r(Ca(2)...O) = 235.3-243.2 pm. The Ca^{2+} ion in the structure of $Ca(bipy)_2(SCN)_2H_2O$[92] is surrounded by the four nitrogen atoms of two bidentate bipyridyl groups, r(Ca...N) = 250.6 -255.9 pm, two nitrogen atoms of the anions, r(Ca...N) = 240.0, 247.8 pm and a single water molecule, r(Ca...O) = 243.2 pm.

2.4.6 Strontium and Barium Derivatives

The structures of $SrX_2.2H_2O$ (X = Cl,Br) have been determined by single crystal X-ray methods.[93] They are isostructural crystallising with orthorhombic (space group Pnma) symmetry. The Sr^{2+} ion is located on a mirror plane; its coordination sphere is a distorted tricapped trigonal prism composed of seven halogen atoms and two water molecules, r(Sr...Cl) = 298.9-339.8, r(Sr...O) = 265.1, r(Sr...Br) = 315.3-346.9, r(Sr...O) = 265.9 pm.[93]

The radical anion complex, $[Ba(NH_3)_2]^{2+}[anthracene^{\cdot-}]_2$ has been prepared[94] by reaction of anthracene with barium in very dry liquid ammonia. It is stable to high vacuum at room temperature for long periods or even at 373K for 24 hours. The enthalpy of formation of the radical anion (eqn.(4)) has been calculated (-167.8 kJ.mol^{-1}) from the results of a thermochemical study of its hydrolysis.[94]

$$Ba(s) + 2NH_3(g) + 2\ anthracene(s) \rightarrow [Ba(NH_3)_2]^{2+}[anthracene^{\cdot-}]_2(s) \qquad ...(4)$$

The preparation of dicumylbarium, $(PhMe_2C)_2Ba$, by reaction of methylcumylether with finely divided barium in thf or thp has been described.[95] Characterisation of the product included conductance studies in both thf and thp which demonstrate the presence of triple ions in thermodynamic equilibrium with free ions and ion pairs.[95]

The structural chemistry of three barium derivatives catena-bis(2,2'-bipyridyl)-bis-μ-(thiocyanato-S,N)-barium(II),[92] bis(2,4,6-trinitrophenolato)bis(1,10-phenanthroline)barium(II) acetone (1:1)[96] and bis(2,4-dinitrophenolato)tris(1,10-phenanthroline)barium(II)[97] has been elucidated; they provide examples of 8-, 8-, and 9-coordinate Ba^{2+} ions, respectively. The Ba^{2+} ion coordination polyhedron in the thiocyanato derivative, which has 2-fold symmetry, is best described as a distorted square antiprism.[92] It is composed of four nitrogen atoms of two bidentate bipyridyl ligands, r(Ba...N) = 286, 287 pm, two nitrogen atoms of thiocyanate anions, r(Ba...N) = 277 pm as well as two sulphur atoms from thiocyanate anions of adjacent molecules, r(Ba...S) = 335.7 pm.

The coordination sphere around the Ba^{2+} ion in the trinitrophenolate-acetone adduct has a distorted pentagonal base-trigonal cap geometry.[96] Two neighbouring phenanthroline molecules act as bidentate ligands, r(Ba...N) = 288.1-293.4 pm, a trinitrophenolate anion acts as a third bidentate ligand via the phenolic oxygen atom, r(Ba...O) = 272.8 pm and an oxygen atom of an ortho-nitro group, r(Ba...O) = 289.5 pm, and the coordination is completed by the phenolic oxygen atom of a second monodentate trinitrophenolate anion, r(Ba...O) = 270.2 pm and the oxygen atom of the acetone solvate molecule, r(Ba...O) = 285.2 pm. In the related dinitrophenolate, the Ba^{2+} ion is located in a monocapped distorted square antiprismatic coordination polyhedron.[97] It is comprised of the six nitrogen atoms from three bidentate phenanthroline molecules, r(Ba...N) = 290.6-296.7 pm, the phenolic, r(Ba...O) = 269.7 pm, and ortho-nitro group oxygen atoms, r(Ba..O) = 292.1 pm, of a bidentate dinitrophenolate anion, and the phenolic oxygen atom, r(Ba...O) = 260.2 pm, of a monodentate dinitrophenolate anion.[97]

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