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## Chapter 2

# ELEMENTS OF GROUP 2

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## 2.1 INTRODUCTION

The pattern adopted previously[1] for reporting the chemistry of these elements has been retained for the present review. Thus the abstracted data are considered in sections which reflect topics of current interest and significance. Some topics (eg. molten salts, crown and cryptate complexes) are common to Group 1 and Group 2 elements; for these, the published data are considered in the relevant section of Chapter 1. The topics unique to the Group 2 elements are discussed in this Chapter.

## 2.2 METALS AND INTERMETALLIC COMPOUNDS

A significant proportion of the papers abstracted for this section involve the application of intermetallic compounds containing the alkaline earth metals (eg. $Be_2Ti$, $Mg_2Ni$, $CaNi_5$) as hydrogen storage materials; the majority of these were presented at an International Conference on this subject held in Toba, Japan (Summer 1982) and published in the associated proceedings.[2] To give appropriate coverage to this topic, this section has been subdivided as for the 1980 review.[3]

### 2.2.1 <u>Structural and Thermodynamic Properties</u>

The structural and thermodynamic properties of all known binary intermetallic compounds containing an alkaline earth metal have been surveyed.[4] A set of empirical rules, which relate the stoichiometries of the intermediate phases to the types of coordination polyhedra present, are proposed. Using these rules, the coordination properties of compounds not yet structurally characterised can be predicted.[4]

Phase equilibria in the Ca-Pd ($0.0 < x_{Pd} < 1.0$) binary system have been elucidated.[5] Six intermediate compounds are formed in the system; three melt congruently, $Ca_3Pd_2$ (1028K), CaPd (1178K) and $CaPd_2$ (1573K) and three undergo peritectic decomposition, $Ca_9Pd$ (938K), $Ca_3Pd$ (843K) and $Ca_5Pd_2$ (868K) where available, structural data for these phases (the structure of $Ca_9Pd$ could not be solved) are summarised in Table 1. The structures of a number of other intermetallic compounds have been characterised; that of $Mg_{38}Sr_9$,[6] has been redetermined, those of $CaSi_2$,[7] $Ca_2Cu$,[8] CaAg,[9] CaAu,[9] $SrAl_2$,[10] and SrZn[9] have been obtained for the first time. Pertinent unit cell parameters are also included in Table 1. For $Mg_{38}Sr_9$,[6] previously designated $Mg_4Sr$,[11] anomalies (volume contraction on formation, density, irregular coordination polyhedra) in the original structural analysis (of $Mg_4Sr$) has been rectified by insertion of Mg atoms in the previously empty 4(f) position of the $P6_3/mmc$ space group (to give $Mg_{38}Sr_9$); the structure is complex with large coordination polyhedra for both sets of atoms.[6]

Standard thermodynamic parameters for intermetallic compounds in the Mg-Ga[12] and Ca-Al[13,14] binary systems have been derived by both electrochemical[12,13] and calorimetric[12,14] methods; pertinent data are collated in Table 2.

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

| Phase | Symmetry | Space Group | a/pm | b/pm | c/pm | β/° | Ref |
|---|---|---|---|---|---|---|---|
| $Mg_{38}Sr_9$ | hexagonal | $P6_3/mmc$ | 1050.0 | - | 2825.1 | - | 6 |
| $CaSi_2$† | tetragonal | $I4_1/amd$ | 428.3 | - | 1353 | - | 7 |
| $Ca_3Pd$ | orthorhombic | Pnma | 769.9 | 993.7 | 669.1 | - | 5 |
| $Ca_5Pd_2$ | monoclinic | C2/c | 1669.4 | 670.8 | 770.4 | 97.30 | 5 |
| $Ca_3Pd_2$ | rhombohedral | $R\bar{3}$ | 893.9 | - | 1690.o | - | 5 |
| CaPd | cubic | Pm3m | 351.8 | - | - | - | 5 |
| $CaPd_2$ | cubic | Fd3m | 765.2 | - | - | - | 5 |
| $Ca_2Cu$ | orthorhombic | Pnma | 612.6 | 416.1 | 1453 | - | 8 |
| CaAg | orthorhombic | Cmcm | 405.8 | 1145.7 | 465.4 | - | 9 |
| CaAu | orthorhombic | Cmcm | 396.1 | 1107.5 | 457.6 | - | 9 |
| $SrAl_2$ | orthorhombic | Imma | 790.5 | 480.1 | 797.4 | - | 10 |
| $SrAl_2$† | cubic | Fd3m | 832.5 | - | - | - | 10 |
| SrZn | orthorhombic | Pnma | 872.4 | 460.7 | 641.7 | - | 9 |

† High pressure, high temperature polymorphs.

The magnetic properties of $GdBe_{13}$ have been investigated in a low

Table 2. Standard thermodynamic parameters for the formation of several intermetallic compounds.

| Phase | T/K | $-\Delta G_f$/kJ.mol$^{-1}$ | $-\Delta H_f$/kJ.mol$^{-1}$ | $-\Delta S_f$/JK$^{-1}$mol$^{-1}$ | Ref |
|---|---|---|---|---|---|
| $Mg_5Ga_2$ | 731 | - | 76.3 | 23.8 | 12 |
| $Mg_2Ga$ | 723 | - | 35.1 | 9.0 | 12 |
| MgGa | 643 | - | 26.0 | 6.0 | 12 |
| $MgGa_2$ | 553 | - | 34.2 | 8.1 | 12 |
| $Mg_2Ga_5$ | 476 | - | 69.3 | 14.7 | 12 |
| $CaAl_2$ | 800 | 85.50±0.90 | - | 18.3±3.3 | 13 |
| $CaAl_2$ | 1038 | - | 100.2±2.0 | - | 14 |
| $CaAl_4$ | 800 | 89.0 ±0.70 | - | 5.5±0.5 | 13 |
| $CaAl_4$ | 953 | - | 93.3±1.2 | - | 14 |

temperature neutron diffraction study.[15] Below $T_N = 27 \pm 3K$, it exhibits a spiral structure; the propagation vector is parallel to, and the magnetic moments of the $Gd^{3+}$ ions are perpendicular to, the c-axis.[15]

### 2.2.2 Hydrogen Storage Applications

Various materials containing beryllium, magnesium or calcium have been considered for hydrogen storage applications. The hydrogenation of $Be_2M$ (M = Ti,Zr,Hf) has been studied as a function of both pressure and temperature.[16] Under ambient conditions $Be_2ZrH_{1.5}$ and $Be_2HfH$ are produced; $Be_2Ti$ does not react. Under high temperature high pressure conditions, $Be_2TiH_3$ and $Be_2ZrH_{2.3}$ are formed; further hydrogenation of $Be_2HfH$ has not been observed. When cooled to room temperature under ambient pressure conditions, $Be_2TiH_3$ releases all its hydrogen to form $Be_2Ti$.[16] Neutron diffraction studies[17] of $Be_2ZrD_{1.5}$ have shown that the deuterium atoms occupy trigonal bipyramidal coordination polyhedra generated by two beryllium atoms (at the apices), r(Be...D) = 173.5pm and three zirconium atoms (in the equatorial plane), r(Zr...D) = 214.4 pm in a crystal of hexagonal habit (P6/mmm; a = 371.4, c = 347.0 pm).

The kinetics and thermodynamics of the formation and decomposition of magnesium hydride have been investigated.[18] The product of the hydrogenation was near stoichiometric $MgH_2$; no pressure hysteresis was observed.[18]

The hydrogenation of Mg-Ni alloys containing 5.6,[19] 10.0,[20] 23.3[21] and 55.0 wt % Ni[19] has been investigated using a variety of techniques. Boulet and Gerard[20] have shown, in a series of kinetic studies, that even though reaction rates increase markedly on addition of nickel to magnesium (as well as for $CeMg_{12}$) the mechanism is the same as that for pure magnesium. They correlate the increased reaction rates with increased hydrogen diffusion and hydride nucleation brought about by morphological parameters (eg. mechanical stresses and strains, incoherent grain boundaries) produced by the formation of finely divided precipitates of $Mg_2Ni$.[20] From the results of in situ X-ray diffraction studies, Ono et al[19] consider the hydrogenation of the alloys to be a simultaneous combination of the reactions of magnesium and of $Mg_2Ni$ with hydrogen to form $MgH_2$ and $Mg_2NiH_4$, respectively.

X-ray diffraction studies[22] of the hydrogenation and dehydrogenation of $Mg_{2-x}Al_xNi$ ($0.1 \leq x \leq 0.5$) have shown that the introduction of aluminium into $Mg_2Ni$ increases both the hydrogen dissociation pressure of $Mg_2NiH_4$ and the kinetics of the two processes.

Structural studies of $Mg_2NiH_x$ ($x \sim 0.3$)[23] and of $Mg_2NiH_4$[24] have been undertaken using X-ray, and in the former instance neutron, diffraction techniques. $Mg_2NiH_x$ ($x \sim 0.23$) is effectively a saturated solution of hydrogen in $Mg_2Ni$;[23] the unit cell parameters for the former (hexagonal; $P6_222$; $a = 523.15$, $c = 1340.4$pm) are marginally greater than those for the parent intermetallic compound (hexagonal; $P6_222$; $a = 521.07$, $c = 1324.4$pm). The most significant structural change due to hydrogenation is an increase in one Mg-Mg distance from 306.2 to ~373pm indicating a hydrogen site between the two magnesium atoms. $Mg_2NiH_4$ undergoes a structural transformation at 503K in a pressurised hydrogen atmosphere.[24] Whereas the metal sublattice of the high-temperature form has the $CaF_2$ structure that of the low-temperature form has a distorted cubic structure which can be described as either body centred with a c-glide plane ($a = 1320.1$, $b = 640.6$, $c = 649.1$ pm $\beta = 93.2^{\circ}$) or as C-face-centred with space group Cc ($a = 1503.3$, $b = 640.6$, $c = 649.1$pm, $\beta = 118.75^{\circ}$). The enthalpy of the phase transformation was established by d.s.c. techniques to be 8.4 $kJ.mol^{-1}$.[24]

Hydrogen storage by Mg-La alloys has been studied by both Russian[25] and French[26] authors. Both groups agree that hydrogenation of these alloys leads to mixtures of $MgH_2$ and $LaH_3$. The Russian authors[25] also show that dehydrogenation ($553 \leqslant T/K \leqslant 613$) leads to complete decomposition of $MgH_2$ and reduction of $LaH_3$ to $LaH_2$. The Mg-$LaH_2$ mixture so formed is capable of hydrogenation under near ambient conditions; it is suggested that $LaH_2$ can act as a catalyst in the reaction of magnesium with hydrogen. The French authors[26] have a slightly different interpretation of the reaction mechanism suggesting that $LaH_3$ can act as a catalyst in the initial magnesium hydrogenation process. The French authors[26] also show that substitution of magnesium (in $La_2Mg_{17}$) by nickel (to give $La_2Mg_{16}Ni$) leads to formation of $Mg_2NiH_4$ as well as $MgH_2$ and $LaH_3$.

Structural,[27,28] thermodynamic[29] and electronic[30] aspects of $CaNi_5$ and its hydrides have been investigated during the period of this review. Two independent studies[27,28] of the variation in the structure of $CaNi_5H_x$ ($0.0 < x < 6.5$) have been undertaken at high temperature (~875K) and hydrogen pressure (~5 MPa) using, in situ, X-ray diffraction methods; the results only differ in detail. Four solid phases are formed - a solid solution phase and three hydride phases; pertinent details are collected in Table 3.

Table 3. Homogeneity ranges of $CaNi_5H_x$ hydrides.

| Phase | Homogeneity range | | Structure |
|---|---|---|---|
| | Ref 27 | Ref 28 | |
| α | $0.0 < x < 0.4$ | | Solid solution based on hexagonal $CaCu_5$ structure |
| α′ | $0.8 < x < 1.2$ | $1.0 < x < 1.5$ | Body centred orthorhombic hydrides related to the hexagonal $CaCu_5$ structure in which each lattice parameter ($a_1$ and $a_2$) elongates alternately. |
| β | $4.5 < x < 5.6$ | $3.6 < x < 4.3$ | |
| γ | $x > 6.0$ | $x > 5.5$ | Structure uncertain; either triclinic[27] or hexagonal[28] hydride. |

The thermodynamics of the $CaNi_5H_x$ system ($0 < x < 2$) have been elucidated using dsc methods.[29] Partial relative enthalpies for the α-solid solution and the α´-single phase regions are reported together with the enthalpies for the $\alpha \rightleftharpoons \alpha'$ (43.4 kJ $mol(H_2)^{-1}$) and the $\alpha' \rightleftharpoons \beta$ (33.1 kJ $mol(H_2)^{-1}$) reactions.

Photoelectron spectroscopic studies[30] of a series of isomorphous Haucke compounds, including $CaNi_5$, have shown that the valence bonds are almost identical, being dominated by nickel-derived 3d bands. It is thus inferred that the widely differing hydrogenation characteristics of these compounds cannot simply be explained by differences in their electronic structures.

## 2.3 SIMPLE COMPOUNDS OF THE ALKALINE EARTH METALS

The majority of papers abstracted for this section involve some aspect of the chemistry of ternary derivatives of alkaline earth metals, especially oxides and fluorides. In contrast to earlier reviews, there has been a marked reduction of interest in the chemistry of novel quaternary oxides and the number of papers devoted to binary derivatives is very limited.

### 2.3.1 Binary Derivatives

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

The kinetics of the pyrohydrolysis ($620 < T/K < 750$) of polished single crystals of $MgF_2$ have been determined;[31] the reaction takes place on the surface of the crystal with formation of MgO.

Knudsen effusion ($1023 < T/K < 1305$) and mass spectroscopic studies ($943 < T/K < 1283$) of the vapour over molten alkaline earth metal halides have been undertaken.[32] The results have been used to calculate the enthalpies of dissociation of $SrX_2$ and $BaX_2$ (X = Cl, Br,I) and the extent of and enthalpies of dimerisation of $CaX_2$, $SrX_2$ and $BaX_2$ (X = Cl,Br,I); pertinent data are collected in Table 4.

The crystal structures of $M(N_3)_2$ (M = Ca,Sr) have been determined[33] by X-ray powder diffraction methods to be orthorhombic, space group, Fddd; they are composed of $M^{2+}$ cations and linear $N_3^-$ anions (the anions in $Ca(N_3)_2$ may exhibit a minor deviation from linearity). The square antiprimatic coordination geometry of the

Table 4. Thermodynamic data for alkaline earth metal halide vapours.

| Halide | $\Delta H_{diss}$/kJ $mol^{-1}$ | % dimerisation | Enthalpy of dimerisation kJ $mol^{-1}$ |
|---|---|---|---|
| $CaCl_2$ | - | 1.5 | -200.3 |
| $SrCl_2$ | 859.5 | 0.5 | -197.0 |
| $BaCl_2$ | 922.3 | 0.15 | -189.3 |
| $CaBr_2$ | - | 1.9 | -205.6 |
| $SrBr_2$ | 888.4 | 0.7 | -199.5 |
| $BaBr_2$ | 845.0 | 0.2 | -187.1 |
| $CaI_2$ | - | 1.5 | -186.7 |
| $SrI_2$ | 811.2 | 0.4 | -164.2 |
| $BaI_2$ | 700.2 | - | - |

cations comprises eight terminal nitrogen atoms from separate anions with r(Ca...N) = 251, 264pm and r(Sr...N) = 263, 275pm.[33]

## 2.3.2 Ternary Pnictides

The preparation, by classical solid state methods, of ternary pnictides containing an alkaline earth metal and either silicon or germanium have been reported by Schäfer et al.[34-36] Structural analyses have revealed two stoichiometries - $Ba_2GeX_2$ (X = P,As)[34] and $M_3Si_2As_4$ (M = Ca,Sr,Ba)[35,36] or $M_3Ge_2P_4$ (M = Ca,Sr)[35] or $M_3Ge_2As_4$ (M = Ca,Sr)[36]; typical unit cell parameters are collected in Table 5. The ternary pnictides, $CaCu_4As_2$[37] and $Ba_2Cd_3Bi_4$[38] have also been prepared and structurally characterised; their unit cell parameters are also incorporated in Table 5.

## 2.3.3 Ternary Oxides and Chalcogenides

A comprehensive review of the synthesis, structural chemistry and magnetic properties of hexagonal ferrites (magnetic recording materials) has been published.[39] In particular, their formation both in molten salts and under hydrothermal conditions is considered; the morphology (hexagonal plate-like crystal habit; narrow particle size distribution) of the ferrites so obtained

Table 5. Crystallographic parameters for various ternary pnictides, oxides, sulphides and fluorides.

| Phase | Symmetry | Space group | a/pm | b/pm | c/pm | $\beta/^{o}$ | Ref. |
|---|---|---|---|---|---|---|---|
| $Ba_2GeX_2$ (X=P,As)* | monoclinic | $P2_1/c$ | 855.3 | 951.5 | 748.1 | 105.95 | 34 |
| $Ca_3Si_2As_4$ | monoclinic | $P2_1/c$ | 730.3 | 1773.0 | 715.5 | 111.66 | 36 |
| $M_3Si_2As_4$ (M=Sr,Ba)* | monoclinic | C2/c | 920.5 | 1683.2 | 737.6 | 122.46 | 36 |
| $M_3Ge_2P_4$ (M=Ca,Sr)* | monoclinic | $P2_1/c$ | 745.9 | 1814.2 | 725.9 | 112.04 | 35 |
| $M_3Ge_2As_4$ (M=Ca,Sr)* | monoclinic | $P2_1/c$ | 730.8 | 1788.6 | 723.9 | 111.75 | 36 |
| $CaCu_4As_4$ | rhombohedral | $R\bar{3}m$ | 417.3 | - | 2262.3 | - | 37 |
| $Ba_2Cd_3Bi_4$ | orthorhombic | Cmca | 703.7 | 1743.8 | 926.7 | - | 38 |
| $MgMoO_4$ | monoclinic | C2/m | 1027.3 | 928.8 | 702.5 | 106.96 | 42 |
| $Ca_2V_2O_7$ | triclinic | P1 | 599.1 | 350.1 | 692.3 | - | 43 |
|  |  |  | $(93.93^{o})$ | $(95.65^{o})$ | $(84.70^{o})$ |  |  |
| $Ca_2MnO_{3.5}$ | orthorhombic | - | 530 | 1005 | 1224 | - | 45 |
| $Ca_2Mn_2O_5$ | orthorhombic | - | 596.1 | 1438.0 | 572.0 | - | 44 |
| $CaMnO_{2.5}$ | orthorhombic | - | 543 | 1024 | 374 | - | 45,46 |
| $CaMnO_{2.75}$ | orthorhombic | - | 535 | 2100 | 747 | - | 46 |
| $Ca_2Mn_3O_8$ | monoclinic | C2/m | 1101.4 | 585.1 | 494.2 | 109.73 | 47 |
| $14H-BaCrO_3$ | hexagonal | $P6_3/mmc$ | 565.0 | - | 3246.7 | - | 48 |
| $Ca_3UO_6$ | monoclinic | - | 572.3 | 595.4 | 830.5 | 90.57 | 49 |
| $Sr_3UO_6$ | monoclinic | - | 596.3 | 620.1 | 854.9 | 90.19 | 49 |
| $Sr_3UO_6$ (1400K) | orthorhombic | - | 603.0 | 626.6 | 866.2 | - | 49 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Ba_3UO_6$ | tetragonal | - | 629.0 | - | 891.0 | - | 49 |
| $BaUO_{3+x}$ $(x \sim 0.3)$ | orthorhombic | Pnma | 620.9 | 879.9 | 623.7 | - | 50 |
| $MSc_2S_4$ (M=Ca,Sr)* | orthorhombic | Pnam | 1150.1 | 1347.0 | 372.8 | - | 56 |
| $M_2Re_6S_{11}$ (M=Sr,Ba)* | monoclinic | C2/c | 1575.3 | 908.0 | 1176.0 | 116.48 | 57 |
| $BaPt_2S_3$ | tetragonal | $P4_12_12$ | 676.5 | - | 1234.9 | - | 58 |
| $BaCrF_5$ | orthorhombic | $P2_12_12_1$ | 1393.8 | 571.1 | 494.7 | - | 59 |
| $BaCoF_5$ | orthorhombic | Pbcm | 1392.2 | 562.0 | 496.5 | - | 60 |
| $SrNiF_5$ | orthorhombic | $P2_12_12_1$ | 1326.5 | 544.0 | 492.7 | - | 60 |
| $BaNiF_5$ | orthorhombic | $C222_1$ | 987.3 | 547.2 | 743.9 | - | 60 |
| $BaNiF_6$ | monoclinic | - | 946.5 | 495.0 | 961.5 | 103.4 | 61 |
| $BaNiF_6$† | trigonal | - | 726.8 | - | 698.1 | - | 61 |

* The parameters quoted refer to the element listed first.

† High temperature (573K), high pressure (5 MPa) polymorph.

gives them advantageous magnetic properties.[39]

The SrO-$Nb_2O_5$ and BaO-$Nb_2O_5$ phase diagrams have been revised from new X-ray diffraction and d.t.a. data.[40] The crystallographic properties of the intermediate ternary niobates have been collated and compared with data for ternary calcium niobates and for the corresponding tantalates;[40] the niobates, $M_6Nb_2O_{11}$ and $M_4Nb_2O_9$ (M = Ca,Sr,Ba), exhibit extremely complicated polymorphism.[41]

A small number of ternary oxides have been synthesised and characterised, primarily by structural methods;[42-50] they are listed in Table 5 together with pertinent unit cell parameters. Preparative routes to these oxides generally involved routine solid state methods; single crystals of $Ca_2V_2O_7$ were obtained, however, from CaO-$V_2O_5$-$K_2O$ melts using the flux growth technique.[43] Several oxygen deficient calcium manganates with perovskite-type lattices, $Ca_2MnO_{3.5}$,[45] $CaMnO_{2.5}$[45,46] and $CaMnO_{2.75}$,[46] have been synthesised by Poeppelmeier et al by reduction of $Ca_2MnO_4$ and $CaMnO_3$ using a variety of inorganic ($H_2$, $NH_3$) or organic ($C_2H_4$, $C_3H_6$) reducing agents between 573 and 773K. The analogous compound $Ca_2Mn_2O_5$ was obtained by Takahashi et al[44] by thermal treatment of (Ca,Mn)O solid solution (which has the NaCl structure) in $CO_2$ at 1273K for 120 minutes. It must be assumed that $CaMnO_{2.5}$[45,46] and $Ca_2Mn_2O_5$[44] are different materials as their quoted unit cell parameters differ markedly (Table 5) even though they both crystallise with orthorhombic symmetry. An interesting feature of the structure of $Ca_2Mn_3O_8$ is the trigonal prismatic coordination polyhedron of the $Ca^{2+}$ ion;[47] this is the first reported example of a compound possessing such coordinated $Ca^{2+}$ ions.

The structure reported in Table 5 for $BaCrO_3$ is effectively that of a 14H layer polytype (Figure 1).[48] Four stoichiometric polytypes of $BaCrO_3$ (4H, 6H, 14H and 27R) with closely related structures, are now well established. The structural unit is the binuclear $Cr_2O_9$ face sharing pair of $CrO_6$ octahedra. These units are corner linked to each other in 4H and linked only through corner-sharing octahedra in 6H; the 27R and 14H polytypes have mixtures of 4H and 6H features. In the 14H structure (Figure 1) there are strings of three pairs of face sharing octahedra in which the pairs are linked to each other by corner-sharing and the strings are linked to each other by octahedra sharing only corners. This particular $BaCrO_3$ polytype was synthesised by reaction of $CrO_2$ and $Ba_2CrO_4$ at 1573K and ~6.5 GPa.[48]

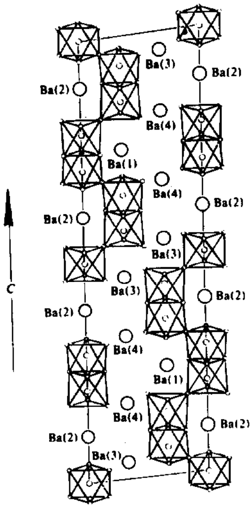


Figure 1. Structure of 14H $BaCrO_3$ showing the cations in the (110) plane and the $CrO_6$ octahedra (reproduced by permission from Acta Crystallogr., B38(1982)54).

Temperature dependent ($298 \leqslant T/K \leqslant 1700$) X-ray powder diffraction studies[49] of $M_3UO_6$ (M = Ca,Sr,Ba) in air have shown that only $Sr_3UO_6$ undergoes a reversible crystallographic transition (at 1400K); pertinent crystallographic data are included in Table 5. The non-stoichiometry of $BaUO_{3+x}$ (Table 5) is clearly shown, by neutron diffraction studies of a compound of stoichiometry $BaUO_{3.3}$, to arise from an equivalent number of barium and uranium vacancies.[50]

Oxide ion diffusion, magnetic susceptibility and e.p.r. and i.r. spectral data[51] show that there are sudden changes in the physico-chemical properties of the vanadium oxide bronze $\beta$-$Ca_xV_2O_5$ at $x \sim 0.25$. As a result of these changes, which are thought to be due to a redistribution of the $Ca^{2+}$ ions in the crystal lattice, the bronze must now be represented on equilibrium diagrams by $\beta$-$Ca_xV_2O_5$ ($0.17 \leqslant x < 0.25$) and $\beta'$-$Ca_xV_2O_5$ ($0.25 \leqslant x < 0.38$).

The thermal decomposition of $Mg_6MnO_8$ has been studied[52] using vapour pressure and high temperature X-ray diffraction methods; the sequence of phase transformations in the temperature range $1073 \leqslant T/K \leqslant 1273$ have been ascertained.

High temperature Raman spectra of $CaWO_4$ have been measured for both the crystalline (1473, 1773K) and the liquid (1873K) states;[53]

they indicate that, at temperatures close to the melting point of $CaWO_4$ (1849K), $WO_4^{2-}$ complexes do not dissociate but retain tetrahedral symmetry. The electrical properties of polycrystalline samples of $MWO_4$ (M=Mg-Ba) have also been elucidated[54] as a function of temperature ($288 < T/K < 973$).

A normal coordinate analysis of the vibrational spectra of $M_3(VO_4)_2$ (M = Sr,Ba) has been reported.[55]

The structural characterisation of five ternary sulphides has been described;[56-58] the structure of $MSc_2S_4$ (M=Ca,Sr)[56] has been refined using powder neutron diffraction methods whereas those of $M_2Re_6S_{11}$ (M = Sr,Ba)[57] and $BaPt_2S_3$[58] havebeen determined for the first time using single crystal X-ray diffraction methods. Unit cell parameters for these materials are included in Table 5. The novel sulphides were synthesised by thermal treatment, in a stream of dry $H_2S$, of either $MCO_3$ (M = Sr,Ba)/Re mixtures at ~1675K (for $M_2Re_6S_{11}$ (M = Sr,Ba))[57] or $BaPt(CN)_4.2H_2O$ at ~930K (for $BaPt_2S_3$).[58]

### 2.3.4 Ternary Halides

Structural analysis has been completed on a small number of ternary fluorides.[59-61] The magnetic structure of $BaCrF_5$ (Néel temperature = 3.4K) has been determined at 2.2K from powder neutron diffraction data.[59] The novel materials, $BaCoF_5$ and $MNiF_5$ (M = Sr,Ba), have been prepared[60] either by heating $BaCO_3/[Co(NH_3)_6]Cl_3$ mixtures to 673K for 48 hours in a stream of diluted fluorine (for $BaCoF_5$) or by pressure fluorination (673K; 5 MPa) of dehydrated $M[Ni(CN)_4].4H_2O$ (M = Sr,Ba) for 48 hours (for $MNiF_5$); they have been characterised by X-ray diffraction methods. $BaNiF_5$ has been shown to exist in two modifications;[61] the previously known monoclinic polymorph and a trigonal polymorph which is only stable under high temperature (573K), high pressure (5 MPa) conditions. Pertinent crystallographic parameters for all five ternary fluorides are collected in Table 5.

Phase relationships have been elucidated in the analogous $LiF-BaF_2$[62] and $MBr-CaBr_2$ (M = Na-Cs)[63] systems by thermal methods; for the latter systems the phase relationships were confirmed by X-ray diffraction methods. The perovskite-type compound, $LiBaF_3$, was the only ternary fluoride observed in the $LiF-BaF_2$ system; it decomposed in a peritectic reaction at 1123K.[62] The phase diagrams corresponding to the four $MBr-CaBr_2$ (M = Na-Cs) systems[63] are shown in Figure 2; available structural data for the various

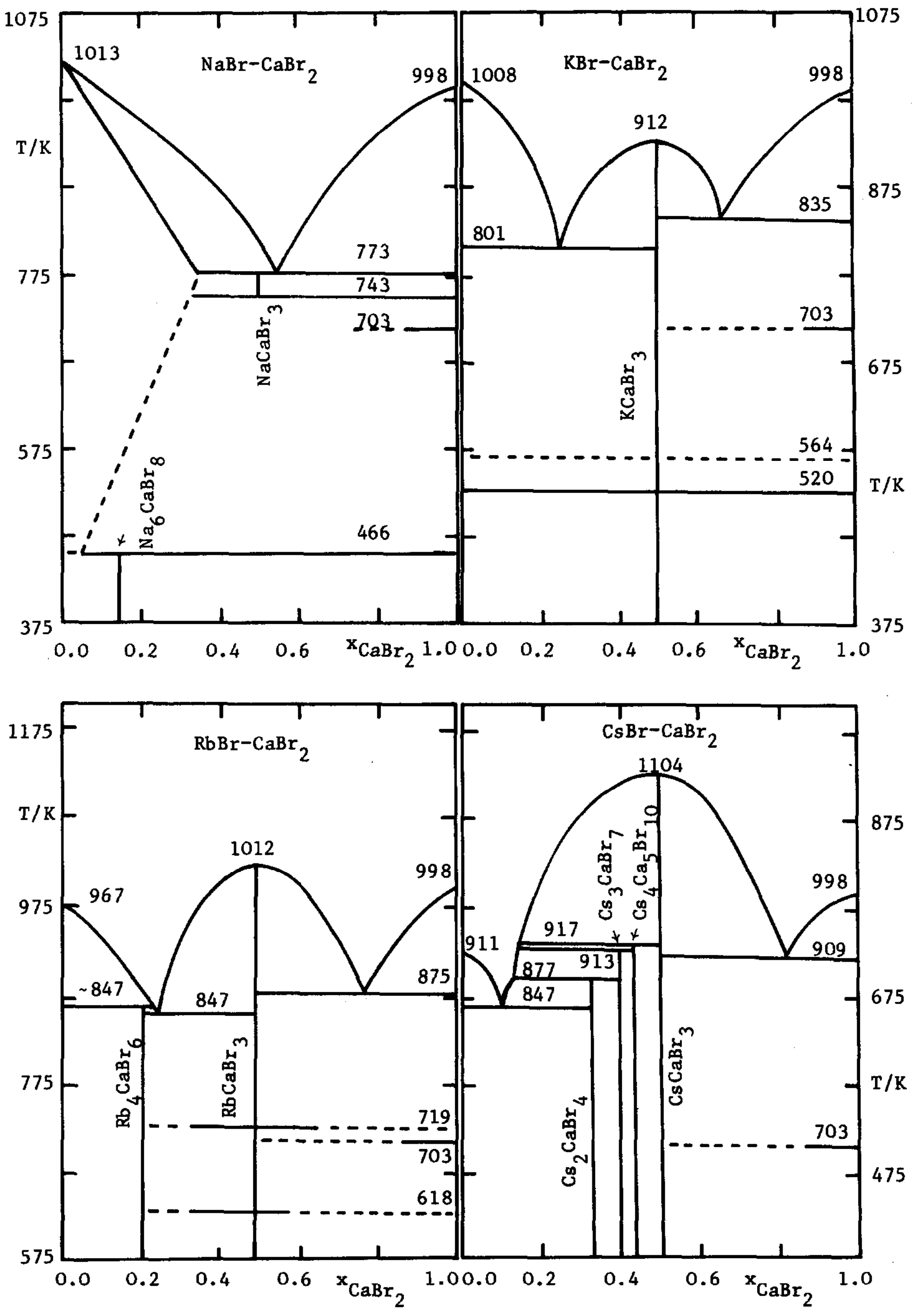


Figure 2. $MBr-CaBr_2$ (M = Na,K,Rb,Cs) phase diagrams.

ternary bromides formed in these systems are summarised in Table 6.

Russian authors have also reported phase diagrams for the $BeF_2$-$ErF_3$[64] and $BaF_2$-$LnF_3$ (Ln = Y,La,Ce,Pr,Nd,Sm-Lu)[65] systems. The former system is of simple eutectic type;[64] the latter, however, are complex and involve a number of intermediate phases.[65]

Table 6. Crystallographic parameters for the ternary bromides formed in the MBr-$CaBr_2$ (M = Na-Cs) systems.[62]

| Ternary Bromide | Symmetry | Space Group | a/pm | b/pm | c/pm |
|---|---|---|---|---|---|
| $Na_6CaBr_8$ | cubic | Fm3m | 1201 | - | - |
| $NaCaBr_3$ | rhombohedral | $R\bar{3}$ | 736 | - | 1997 |
| $KCaBr_3$ (298K) | orthorhombic | Cmcm | 427 | 1407 | 1076 |
| $KCaBr_3$ (675K) | orthorhombic | Pnma | 798 | 1112 | 774 |
| $Rb_4CaBr_6$ | rhombohedral | $R\bar{3}c$ | 1320 | - | 1640 |
| $RbCaBr_3$ (298K) | orthorhombic | Pnma | 807 | 1128 | 783 |
| $RbCaBr_3$ (673K) | tetragonal | P4/mbm | 795 | - | 566 |
| $RbCaBr_3$ (973K) | cubic | Pm3m | 569 | - | - |
| $Cs_2CaBr_4$ | tetragonal | I4/mmm | 567 | - | 1801 |
| $Cs_3Ca_2Br_7$ | tetragonal | I4/mmm | 569 | - | 2928 |
| $Cs_4Ca_3Br_{10}$ | tetragonal | I4/mmm | 568 | - | 4052 |
| $CsCaBr_3$ | cubic | Pm3m | 569 | - | - |

Fluorite ($BaF_2$) solid solutions, $Ba_{1-x}Ln_xF_{2+x}$ ($0 < x < 0.5$) with strong stoichiometric perturbations and high concentrations of structural defects were formed in all the $BaF_2$-$LnF_3$ systems.[65] Solid solutions with defective tysonite ($LnF_3$) structure, $Ln_{1-y}Ba_yF_{3-y}$ were also formed for Ln = La-Ho; their thermal stability decreased rapidly with increasing difference in the size of the $Ba^{2+}$ and $Ln^{3+}$ cations. Phases of composition $Ba_{4\pm x}Ln_{3\pm x}F_{17\pm x}$ with maximum homogeneity in the 39-49 mol % $LnF_3$ region were formed for Ln = Sm-Lu; they have a distorted fluorite structure. Monoclinic $BaLn_2F_8$ compounds were also formed for Ln = Dy-Lu.[65]

Phase equilibria between $BaCl_2$ and $SnCl_2$, $CdCl_2$, $InCl_3$ and $YCl_3$ have been investigated using d.t.a. techniques;[66] the results are summarised in Table 7.

Table 7. Phase equilibria in the $BaCl_2$-$SnCl_2$, $BaCl_2$-$CdCl_2$, $BaCl_2$-$InCl_3$ and $BaCl_2$-$YCl_3$ systems.[66]

| System | Ternary Chlorides | Mode of decomposition |
|---|---|---|
| $BaCl_2$-$SnCl_2$ | None (simple eutectic system) | |
| $BaCl_2$-$CdCl_2$ | $Ba_2CdCl_6$ | peritectic at 767K |
| $BaCl_2$-$InCl_3$ | $Ba_3InCl_9$<br>$Ba_2InCl_7$<br>$BaInCl_5$ | peritectic at 717K<br>peritectoid at 705K<br>peritectoid at 640K |
| $BaCl_2$-$YCl_3$ | $Ba_2YCl_7$ | peritectic at 947K |

### 2.3.5 Quaternary Oxides

Kemmler-Sack[67-76] has again made a considerable contribution (10 papers) to our knowledge of quaternary oxides with variants of the perovskite structure. The majority of his papers[67-73] describe the synthesis and characterisation (principally by X-ray diffraction and vibrational spectroscopic methods) of hexagonal stacking polytypes with rhombohedral layer structures; the novel oxides, their structural characteristics and unit cell parameters are collated in Table 8. The structures of the 6L stacking polytypes, $Ba_3[MSb_2O_9]$ (M = Mg,Mn,Co,Ni,Cu,Zn) (Figure 3(a)) exhibit subtle differences.[67] For M = Mg,Mn,Co,Ni,Zn, the Sb(V) atoms are located in face connected pairs of octahedra ($Sb_2O_9$ groups) which are linked to each other via common corners through individual octahedra containing M(II) atoms ($MO_6$ groups); the symmetry of this structure corresponds to the $P6_3/mmc$ space group (Figure 3(b)). For M = Cu, however, the face connected pairs of octahedra are occupied by both Sb(V) and Cu(II) atoms ($CuSbO_9$ groups) and the individual octahedra by Sb(V) atoms ($SbO_6$ groups); the symmetry of this structure corresponds to the $P6_3mc$ space group (Figure 3(c)).

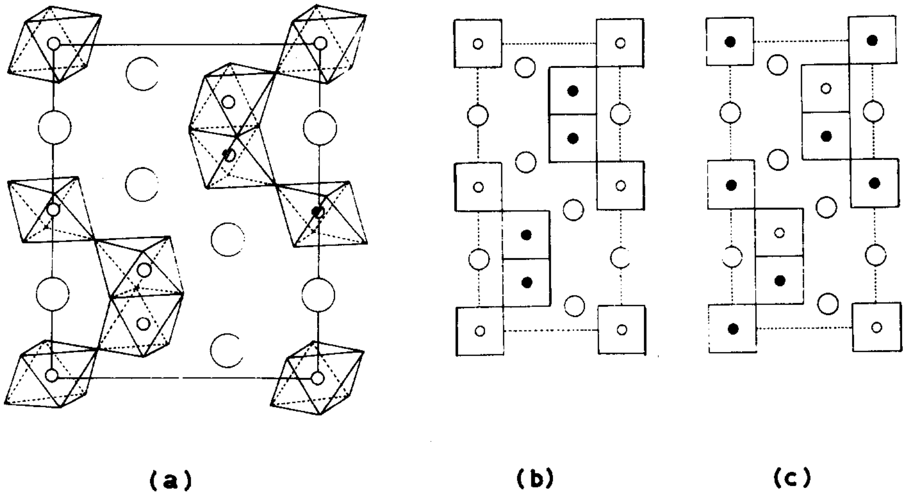


Figure 3. Diagrammatic representations of the (110) plane of a 6L Hexagonal stacking polytype with rhombohedral layer structure showing (a) the basic $BaTiO_3$ structure and (b,c) the location of the cations in the $P6_3/mmc$ structure of $Ba_3[MSb_2O_9]$ (M = Mg,Mn,Co,Ni,Zn) (b) and in the $P6_3mc$ structure of $Ba_3[CuSb_2O_9]$ (c)(reproduced by permission from Z. Anorg. Allg. Chem., 487(1982)161).

The other examples of 6L stacking polytypes included in Table 8, all adopt the former distribution of cations and have space group symmetry, $P6_3/mmc$.[68,69] For the other novel perovskites of this type the structures of the 12L[70] and 18L[71] stacking polytypes are well known; that of the 21L stacking polytype,[72] however, has not been described previously. Order-disorder phenomena in the 24L stacking polytypes, $A_8[MLn_2\square W_4O_{24}]$ (A,M = Sr,Ba; Ln = lanthanide), has been reviewed;[73] they are shown to be dependent on the ionic radii of the constituent cations.

The other papers published by Kemmler-Sack[74-76] deal with structural and spectroscopic properties of compounds which adopt distorted perovskite structures and which crystallise in different

**Table 8.** Crystallographic data for a number of hexagonal stacking polytypes with rhombohedral layer structures.

| Compound | Symmetry | Space Group | Stacking Polytype | Layer Sequence | a/pm | c/pm | Ref. |
|---|---|---|---|---|---|---|---|
| $Ba_3[MSb_2O_9]$<br>(M=Mg,Mn,Co,Ni,Zn)* | hexagonal | $P6_3/mmc$ | 6L | $(hcc)_2$ | 584 | 1442 | 67 |
| $Ba_3[CuSb_2O_9]$ | hexagonal | $P6_3mc$ | 6L | $(hcc)_2$ | 580 | 1432 | 67 |
| $Ba_3[MRu_2O_9]$<br>(M=Mg,Fe,Co,Ni,Zn,Cd)* | hexagonal | $P6_3/mmc$ | 6L | $(hcc)_2$ | 576 | 1410 | 68 |
| $Ba_3[MIr_2O_9]$ (M=Co,Ni)* | hexagonal | $P6_3/mmc$ | 6L | $(hcc)_2$ | 576 | 1430 | 68 |
| $Ba_3[LnPt_xRu_{2-x}O_9]$<br>(Ln=La-Lu,Sc,Y; $0 < x < 0.75$)† | hexagonal | $P6_3/mmc$ | 6L | $(hcc)_2$ | 592 | 1460 | 69 |
| $Ba_{2-y}Sr_yLa_2[MgW_2\square O_{12}]$<br>($0 < y < 2$)‡ | rhombohedral | $R\bar{3}m$ | 12L | $(hhcc)_3$ | 566 | 2740 | 70 |
| $Ba_{6-y}Sr_y[M_{2-x}Ln_xW_3\square O_{18}]$<br>(M=Gd,Y,Lu; Ln=Sm,Eu,Tb,Dy,<br>Ho,Er,Tm; $0 < y < 6; 0 < x < 2$)x | rhombohedral | $R\bar{3}m$ | 18L | $(hhcccc)_3$ | 575 | 4170 | 71 |
| $Ba_7[Nb_4Ti_2\square O_{21}]$ | rhombohedral | $R\bar{3}m$ | 21L | $(hhccccc)_3$ | 576.7 | 4948.5 | 72 |

* The crystallographic data refer to the element listed first.

† The crystallographic data refer to $Ba_3[SmRu_2O_9]$.

‡ The crystallographic data refer to $Ba_2La_2[MgW_2\square O_{12}]$.

x The crystallographic data refer to $BaSr_5[Lu_{1.6}Ho_{0.4}W_3\square O_{18}]$.

symmetry classes (cubic, tetragonal and orthorhombic); those compounds which are novel are listed in Table 9 together with pertinent unit cell parameters.

Evdokimov et al[77,78] have carried out a comprehensive X-ray diffraction study of the quaternary oxides, $Ca_2MNbO_6$ (M = Fe,Ln),[77] $Ba_2MNbO_6$ (M = Fe,Sc,Y,Ln)[78] and $Ba_2MTaO_6$ (M = Fe,Sc,Y,Ln).[78] The vast majority of the materials belong to the cryolite structural group; $Ba_2MNbO_6$ and $Ba_2MTaO_6$ (M = Fe,Sc), however, adopt the perovskite structure. The variants of the cryolite structure which have been observed include tetragonal, orthorhombic and monoclinic distortions as well as cubic cells with $2a_o$ values;[77,78] pertinent details are summarised in Table 9. Aqueous solution calorimetry (in 1.00 $mol.dm^{-3}$ HCl) of the analogous oxides, $Ba_2MgMO_6$ (M = U,Np) has been undertaken[79] to determine their standard enthalpies of formation, $\Delta H_f^o$ ($Ba_2MgUO_6$,c,298K) = $-(3245.3\pm4.8)kJ.mol^{-1}$ and $\Delta H_f^o$ ($Ba_2MgNpO_6$,c,298K) = $-(3096.4\pm6.5)$ $kJ.mol^{-1}$; structural data[79] for these compounds are also included in Table 9.

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

Analysis of the papers abstracted for this section showed that a number fall into subject groups, (eg., complexes of significance in bioinorganic chemistry, complex formation in solution, structural chemistry of aquo cations) which are common to several alkaline earth metals; these papers are considered in the appropriate subsection. The subject matter of those papers which do not fall into one of these categories is somewhat fragmented; these papers are covered in subsections devoted to the individual alkaline earth metals.

### 2.4.1 Complexes of Significance in Bioinorganic Chemistry

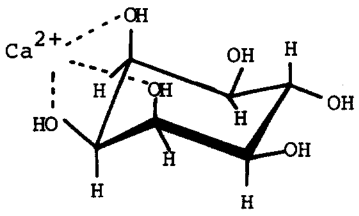
Complexation of alkaline earth metal cations by biologically significant molecules has been studied by a variety of techniques.[80-83] $^{13}C$-n.m.r. and C.D. data[80] indicate that addition of $Mg^{2+}$ to solutions of tetracycline in DMSO induces a conformational change in the antibiotic by binding to its zwitterionic form. It is thus inferred that $Mg^{2+}$ ions may effect the <u>in vivo</u> transport of tetracycline by their influence on its molecular conformation.[80]

Table 9. Unit cell parameters for a number of quaternary oxides.

| Compound | Symmetry | Space Group | a/pm | b/pm | c/pm | $\beta/^{\circ}$ | Ref. |
|---|---|---|---|---|---|---|---|
| $Ba_3[ReSb\square O_9]$ | tetragonal | P4 | 396 | - | 1460 | - | 74 |
| $Sr_8[SrM_2\square W_4O_{24}]$ (M=Ho,Er,Tm,Y)* | cubic | Fm3m | 823 | - | - | - | 75 |
| H.T.-$Sr_8[SrM_2\square W_4O_{24}]$ (M=Eu,Sm,Gd)* | cubic | Fm3m | 1648 | - | - | - | 75 |
| L.T.-$Sr_8[SrM_2\square W_4O_{24}]$ (M=Eu,Sm,Gd)* | tetragonal | - | 995 | - | 1900 | - | 75 |
| $Sr_8[SrM_2\square W_4O_{24}]$ (M=La,Pr,Nd)* | tetragonal | - | 1644 | - | 1632 | - | 75 |
| $Ba_8[BaM_2\square W_4O_{24}]$ (M=La,Nd,Sm,Eu)* | cubic | Fm3m | 1712 | - | - | - | 75 |
| H.T.-$Ba_8[CaM_2\square U_4O_{24}]$ (M=Gd,Sm,Y,Lu)* | orthorhombic | Pmmm | 618 | 612 | 869 | - | 75 |
| L.T.-$Ba_8[CaM_2\square U_4O_{24}]$ (M=Gd,Sm,Y,Lu)* | orthorhombic | Pmmm | 1234 | 1224 | 1746 | - | 75 |
| H.T.-$Ba_8[SrM_2\square U_4O_{24}]$ (M=Gd,Y,Lu)* | orthorhombic | Pmmm | 621 | 617 | 873 | - | 75 |
| L.T.-$Ba_8[SrM_2\square U_4O_{24}]$ (M=Gd,Y,Lu)* | orthorhombic | Pmmm | 1238 | 1230 | 1754 | - | 75 |
| $Ca_2FeNbO_6$ | orthorhombic | Pbnm | 544.4 | 555.9 | 775.4 | - | 77 |
| $Ca_2LnNbO_6$ (Ln=La-Lu)* | monoclinic | $P2_1/n$ | 567.3 | 589.5 | 816.8 | 90.00 | 77 |
| $Ba_2FeMO_6$ (M=Nb,Ta)* | cubic | - | 812.2 | - | - | - | 78 |
| $Ba_2LnMO_6$ (Ln=La-Nd;M=Nb,Ta)* | monoclinic | - | 613.0 | 608.3 | 859.2 | 90.35 | 78 |
| $Ba_2SmMO_6$ (M=Nb,Ta)* | orthorhombic | - | 604.4 | 601.2 | 850.4 | - | 78 |
| $Ba_2LnMO_6$ (Ln=Eu-Tb;M=Nb,Ta)* | tetragonal | - | 600.0 | - | 852.8 | - | 78 |
| $Ba_2LnMO_6$ (Ln=Dy-Lu;M=Nb,Ta)* | cubic | - | 845.0 | - | - | - | 78 |
| $Ba_2MgMO_6$ (M=U,Np)* | cubic | Fm3m | 838.0 | - | - | - | 79 |

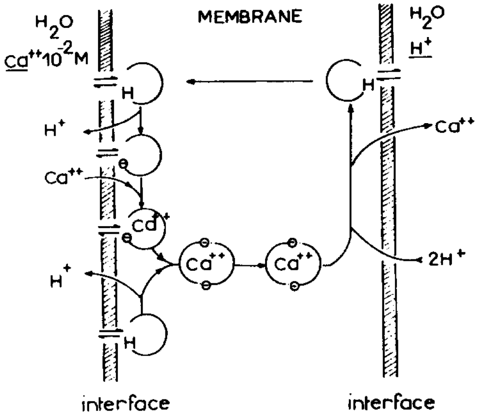
* The crystallographic data refer to the element listed first.

Calcium ($Ca^{2+}$) ion binding by the proteins, parvalbumin, troponin C and calmodulin,[81] by D-ribose[82] and by the antibiotic ionophores, lasalocide (X-537A), calcimycine (A-23187) and X-14547A,[83] has been investigated in aqueous solution using n.m.r. ($^{43}Ca$ and $^{1}H$)[81,82] and potentiometric[83] methods. $^{43}Ca$-n.m.r. data[81] for $Ca^{2+}$ ions bound to the three proteins are consistent with a comparatively rigid structure at the $Ca^{2+}$-binding sites. Furthermore, the observed chemical shifts and quadrupole coupling constants are similar for all three proteins suggesting similar $Ca^{2+}$ coordination polyhedra.[81] $^{1}H$-n,m.r. data[82] for various forms of D-ribose when complexed with $Ca^{2+}$ ions have been used to derive formation constants and to elucidate conformational changes on complex formation; it is concluded that $Ca^{2+}$ ions strongly prefer axial-equatorial-axial sites (1).[82] Potentiometric methods[83] have been used to obtain both the stoichiometries and stabilities of complexes formed between $Ca^{2+}$ and the three natural antibiotic ionophores. For A.23187 and X.14547.A, both 1:1 (charged) and 2:1 (neutral) ionophore: $Ca^{2+}$ complexes are formed. For X.537.A, however, the existence of a 2:1 complex was not established. Calcium transport (Scheme 1) by these ionophores through a cell such as water/chloroform/water has also been studied.[83]



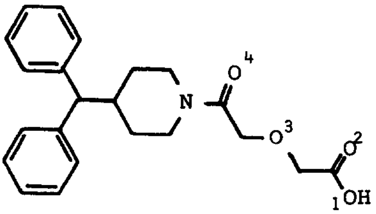
(1)

The complexation of $Ca^{2+}$ by the synthetic ionophore McN-4308 (2) has been studied by determination of the crystal and molecular structures of both the free ionophore and of its calcium complex.[84] The complex exists as centrosymmetric dimers possessing two calcium ions, four ionophore anions and two water molecules. Two dimers occur in the unit cell; although stereoisomers, they have very similar overall geometry. The two crystallographically distinct $Ca^{2+}$ ions both have square antiprismatic 8-fold coordination polyhedra comprising four oxygen



Scheme 1.

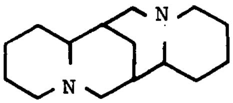
atoms from a chelating tetradentate anion, r(Ca...O) = 241-256 (242-258) pm, three oxygen atoms from a chelating terdentate anion,



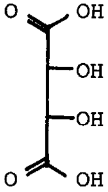
(2)

r(Ca...O) = 242-249 (238-247) pm and the water molecule, r(Ca...O) = 241(245) pm.[84]

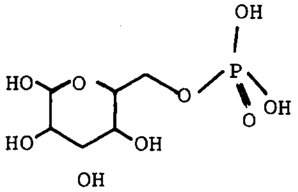
Three other biologically significant complexes have been studied by single crystal X-ray diffraction methods; the (-)α-isosparteine complex of ethyl magnesium bromide,[85] calcium tartrate tetrahydrate[86] and the monobarium salt of glucose-6-phosphoric acid, heptahydrate.[87] The $Mg^{2+}$ ion in the (-)α-isosparteine complex[85] is tetrahedrally coordinated by the carbon atom of the ethyl anion, r(Mg...C)= 222.4pm, the bromide anion, r(Mg...Br) = 250.6 pm, and the two nitrogen atoms of a bidentate (-)α-isosparteine ligand, r(Mg...N) = 216.5, 219.5 pm. The $Ca^{2+}$ ion in the tartrate salt[86]



(-)α-isosparteine



tartaric acid



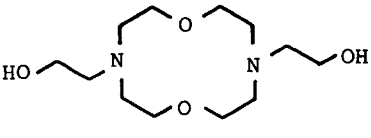
glucose-6-phosphoric acid

is coordinated by eight oxygen atoms, six from separate tartrate anions, r(Ca...O) = 237.7-251.8 pm and two from water molecules, r(Ca...O) = 243.2, 249.4 pm; the coordination polyhedron of the $Ca^{2+}$ ion is described as a distorted Siamese dodecahedron.[86] The $Ba^{2+}$ ion in the glucose-6-phosphate derivative[87] is surrounded by nine ligating oxygen atoms in a distorted irregular coordination geometry. Of these, seven oxygens are from water molecules, r(Ba...O) = 277.3-295.0 pm; the other two are a phosphate oxygen, r(Ba...O) = 273.4pm and a sugar hydroxyl oxygen, r(Ba...O) = 288.1pm.[87]

### 2.4.2 Complex Formation in Solution

The formation of complexes by interaction of alkaline earth metal cations with diverse ligands has been studied in solution using both spectroscopic ($^{1}H$ and $^{43}Ca$ n.m.r. and u.v.-visible)[88-90] and pH-potentiometric[91-93] techniques.

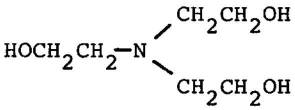
A $^{1}H$ n.m.r. study[83] of ligand exchange on tetrakis(N,N-diethylacetamide)beryllium(II) has been undertaken in both $CD_3NO_2$ and $CD_3CN$ solutions. The kinetics of the exchange are complex, the rate being dependent on both dissociative and associative or interchange mechanisms. The results are compared with similar ligand exchange data for other beryllium(II) systems.[88] $^{43}Ca$-n.m.r. relaxation times and quadrupole coupling constants have been determined[89] for calcium complexes (60% enriched with $^{43}Ca$ (I-7/2)) with edta, egta and the cyclic ligand (3). The observed increase in relaxation time (and concomitant decrease in quadrupole coupling constant) for the edta complex vis-a-vis the other complexes is attributed to its higher symmetry.[89] Stability constants for the complexation (axial ligand binding) reactions of (*meso*-tetraphenylporphinato)magnesium(II) with diverse nitrogeneous bases have been determined from u.v.-visible spectroscopic data.[90] For the



(3)

formation of the ML and $ML_2$ complexes the stability constants are linear functions of the ligand $pK_a$, as is also the case for the corresponding zinc(II) system.[90]

The interaction of alkaline earth metal cations ($Mg^{2+}$-$Ba^{2+}$) with (4-6),[91] with cis- and trans-isomers of (7)[92] and with (8)[93] has been studied in aqueous systems using pH-potentiometric methods. The stabilities of the complexes formed by (4), (7) and (8) increase with decreasing ionic radii. Those of the complexes formed by (5) and (6), however, follow neither the order of the ionic radii nor that of the radii of the hydrated cations. Possible reasons for these observations are considered, together with the solution structures of these complexes and their biological implications.[91]



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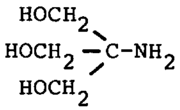

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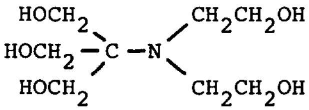

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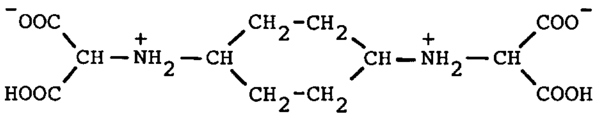

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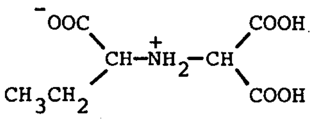


(8)

## 2.4.3 Structural Chemistry of Aquo-Cations

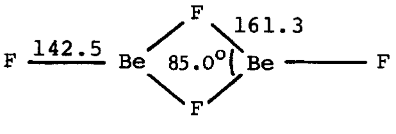
Single crystal neutron[94] and X-ray diffraction[95,96] studies have confirmed the existence of $[Mg(H_2O)_6]^{2+}$ octahedra in $MgS_2O_3,6H_2O$,[94] in $Cd_2MgCl_6,12H_2O$[95] and in the hexahydrate of magnesium bis(2-carboxylatomonoperoxybenzoic acid).[96] In all three compounds the aquo-cations are effectively regular with similar r(Mg...O) values

- 205.1-212.5;[94] 205.2-208.1;[95] 204.3-210.5 pm.[96] Combined X-ray and molecular dynamics studies[97] of a 1:1 molal aqueous $MgCl_2$ solution demonstrate that a pronounced octahedral arrangement of water molecules exists for the first hydration shell of $Mg^{2+}$. The $Cl^-$ hydration shell has a similar, but much less pronounced, coordination geometry.[97] The structure of $Mg(NCS)_2,4H_2O$, as determined by X-ray diffraction methods,[98] consists solely of $[Mg(H_2O)_4(NCS)_2]$ moieties; the magnesium atom has a centrosymmetric octahedral ($D_{4h}$) coordination with r(Mg...O) = 204.7, 212.6 pm and r(Mg...N) = 210.2 pm.

Square antiprismatic[99] and dodecahedral[100] $[Ca(H_2O)_8]^{2+}$ moieties have been observed in structural analyses of $Cd_3Ca_2Cl_{10},18H_2O$[99] and of $CaHgI_4,8H_2O$.[100] The $[Sr(H_2O)_8]^{2+}$ moiety has also been found in $SrHgI_4,8H_2O$;[100] unlike the analogous calcium derivative its geometry is square antiprismatic. Very little further information is given about the structure of these three aquo-cations.[99,100]

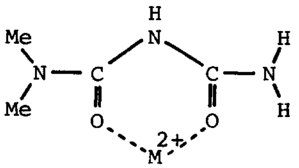
### 2.4.4 Beryllium Derivatives

Ab initio SCF LCAO MO calculations have been completed for the $Be_2F_4$ molecule,[101] for the MOH (M = Be,Mg) molecules and the corresponding ions $MOH^+$ (M = Be,Mg)[102] and for the 1:1 complexes of N,N-dimethylbiuret with $M^{2+}$ (M = Be,Mg,Ca).[103]



(9)

distances/pm



(10)

Of the various hypothetical structures considered for the $Be_2F_4$ dimer, the most stable is that with a planar cyclic equilibrium configuration with two bridging fluorine atoms and $D_{2h}$ symmetry (9).[101] Vibrational spectroscopic properties of $Be_2F_4$ have been calculated and compared with the spectra of matrix isolated $Be_2F_4$; the thermodynamic properties of gas phase $Be_2F_4$ have also been derived from the theoretical molecular constants.[101]

The theoretically derived equilibrium geometries of MO, MOH and $MOH^+$ (M = Be,Mg) gas phase species[102] are collected in Table 10.

Table 10. Theoretically derived equilibrium internuclear distances for various MO, MOH and $MOH^+$ (M = Be,Mg) gas phase species.[102]

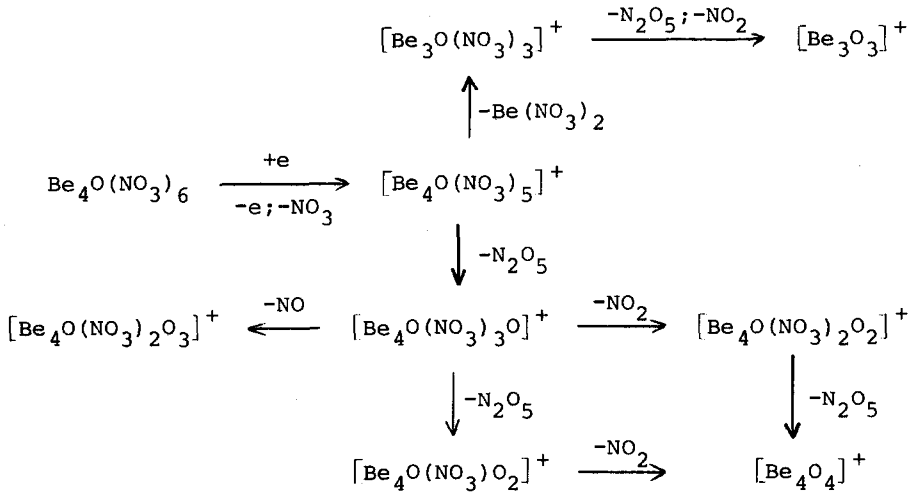
| Moiety | OH | BeO | MgO | BeOH | MgOH | $BeOH^+$ | $MgOH^+$ |
|---|---|---|---|---|---|---|---|
| r(O...H)/pm | 97.1 | - | - | 93.4 | 94.1 | 94.4 | 94.5 |
| r(M...O)/pm | - | 132.1 | 179.4 | 139.9 | 177.3 | 134.0 | 170.9 |

The data show that r(O...H) is practically constant in all the triatomics studied and is shorter than that in the free OH radical. Interestingly, the value of r(Be...O) in BeOH is longer, and that of r(Mg...O) shorter, than the corresponding distances in the diatomic molecules BeO and MgO; this observation is said to be consistent with the fact that the magnesium atom has stronger metallic properties than the beryllium atom. The shorter r(M...O) distance, and hence the greater strength of the M-O bond, in the ions than in the neutral molecules is attributed to electrostatic factors since the electron is lost almost entirely from the metal atom.[102]

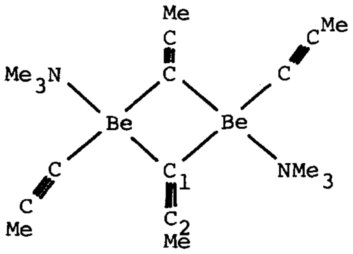
The simple planar chelate geometry (10) has been theoretically predicted[103] to be the most stable form of the 1:1 complexes of N,N-dimethylbiuret with $Be^{2+}$, $Mg^{2+}$ and $Ca^{2+}$. The effect of these cations on the barriers to internal rotation about the $C-NR_2$ bonds in biuret and its N,N-dimethyl substituted derivative has also been studied experimentally[103] using $^1H$-n.m.r. techniques.

The fragmentation pattern of $Be_4O(NO_3)_6$ under electron impact (Scheme 2) is similar to that of its carboxylato analogues, $Be_4O(RCO_2)_6$ where R is H, alkyl or halogenated alkyl, thus confirming the structural similarity of the tetranuclear beryllium oxonitrato and oxocarboxylato complexes.[104]

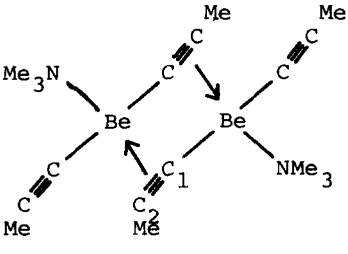
An X-ray crystal structure determination[105] has shown that $[(MeC{\equiv}C)_2BeNMe_3]_2$ contains two independent centrosymmetric dimers in which the beryllium atoms exhibit quite different types of interactions with the μ-alkynyl groups. The beryllium atoms are in approximately tetrahedral environments in both dimers; the four-membered $Be_2C_2$ rings, however, have quite different geometries. Dimer 1 tends towards structural type (11) with the μ-propynyl



Scheme 2



(11)



(12)

groups functioning as 2e donors. There is, however, some asymmetry in the BeC(1)C(2) angles (154.9° and 128.5°) which indicates limited π-interaction between the C≡C bond and the beryllium atoms. In contrast, the μ-propynyl groups in dimer 2, which tends towards structural type (12), function as 3e donors being involved in σ- and π-interactions to the beryllium atoms as shown by marked asymmetry in the BeC(1)C(2) angles (168.6° and 100.2°). Thus, the $Be_2C_2$ ring in dimer 1 is predominantly electron deficient, while that in dimer 2 is effectively electron precise. In support of this, r(Be...Be) in dimer 1 (231.9 pm) is considerably shorter than that in dimer 2 (254.9 pm) indicating metal-metal bonding to be more important in dimer 1. Additionally, the r(Be...C(1)) values (183.6, 190.4 pm) in dimer 1 are intermediate between those (176.3, 204.2 pm) in dimer 2, and the r(Be..C(2)) value (253.8 pm) in dimer 2 is only marginally greater than the corresponding r(Be...C(1)) value (204.2 pm).[105]

## 2.4.5 Magnesium and Calcium Derivatives

Since organomagnesium and organocalcium chemistry are reviewed elsewhere, these topics have been omitted from the remit adopted for this review. Consequently, of the plethora of papers dealing with the chemistry of these elements only a small number have been abstracted for this subsection; they cover a diversity of interests with no obvious recurrent theme.

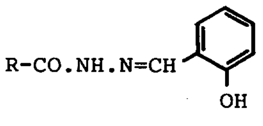
The preparation of a dinitrogen complex of magnesium, $Mg(NH_2)_2N_2$, as an intermediate thermal decomposition product of $Mg(N_3)_2(N_2H_4)_2$ has been claimed;[106] characterisation is based on t.g.a. data, chemical analysis and i.r. and u.v./visible spectroscopy. On further heating, $Mg(NH_2)_2N_2$ decomposes at 623K to form MgNH. The starting material, $Mg(N_3)_2(N_2H_4)_2$ was prepared by novel reaction of magnesium metal powder with $(NH_4)N_3$ dissolved in $N_2H_4.H_2O$ (99%) (equations 1 and 2). Thermolysis of the corresponding calcium and barium salts did not yield a dinitrogen complex, probably because hydrazine was lost initially giving anhydrous metal azides which exploded violently.[106]

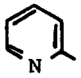
$$(NH_4)N_3 + N_2H_4.H_2O \rightarrow (N_2H_5)N_3 + H_2O + NH_3 \qquad ...(1)$$

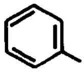
$$Mg + 2(N_2H_5)N_3 \rightarrow Mg(N_3)_2(N_2H_4)_2 + H_2 \qquad ...(2)$$

The thermal stability, in both air and argon, of hydrated alkaline earth metal (M = Mg-Ba) maleates has been investigated using various physicochemical methods;[107] dehydration occurs between 373 and 573K, followed by decomposition of the anhydrous salts between 653 and 873K.

The series of salicylidene-aroyl hydrazides (<u>13</u>)-(<u>16</u>) have been shown to function as tridentate monobasic donors when forming complexes with magnesium(II) of stoichimetry $MgL_2$.[108]



(<u>13</u>): R =


(<u>14</u>): R =


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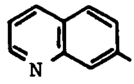
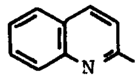


(<u>16</u>) R =


The macrometallocycle $[\{Mg(CH_2C_6H_4CH_2\text{-}o)(C_4H_8O)_2\}_3]$ slowly deposits from concentrated thf solutions of the di-Grignard reagent derived from o-bis(chloromethyl)benzene.[109] A single crystal X-ray diffraction study of its structure (Figure 4) has shown that the trimeric unit lies on a crystallographic two-fold axis of the orthorhombic (F2dd) unit cell. Each of the three magnesium atoms is bridged to the other two by a $-CH_2C_6H_4CH_2-$ ligand, r(Mg(1)...C) = 215.4 pm, r(Mg(2)...C) = 215.8, 217.0 pm, the pseudo-tetrahedral coordination about each magnesium atom being completed by a pair of thf molecules, r(Mg(1)...O) = 207.3 pm; r(Mg(2)...O) = 206.3, 208.1 pm (Figure 4).[109]

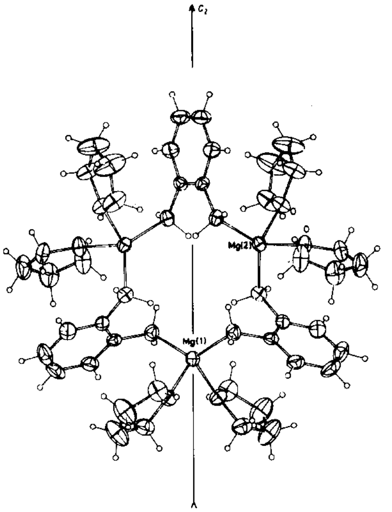


Figure 4. Molecular structure of the trimeric metallocycle, $[\{Mg(CH_2C_6H_4CH_2\text{-}o)(C_4H_8O)_2\}_3]$ (reproduced by permission from J. Chem. Soc., Dalton Trans., (1982)1959).

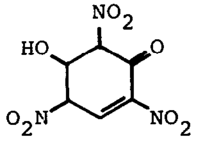
Alkaline earth metal salts readily form complexes with organic moieties; compounds which have been synthesised and characterised during the period of this Review include $M(H_2PO_4)_2,4CO(NH_2)_2$,[110] $Ca(NO_3)_2,nHCONH_2$ (n = 2,4),[111] $CaCl_2,2CH_3OH$[112] and $CaCl_2,2C_2H_5OH$.[112] Single crystal X-ray diffraction analyses of the urea derivatives showed them to be bis(urea) bis(dihydrogen phosphato) magnesium (or calcium)-bis(urea) complexes.[110] The cations are six-coordinated by oxygen atoms, four from separate bidentate bridging phosphate anions and two from urea molecules occupying trans positions. The cation coordination geometry is almost that of a regular octahedron with average Mg...O and Ca...O distances of 210.5 and 233.5 pm, respectively.[110] The standard enthalpies of formation (298.15K) of $CaCl_2,2CH_3OH$ (-1310±2 kJ mol$^{-1}$) and of $CaCl_2,2C_2H_5OH$ (-1392±2 kJ mol$^{-1}$) have been determined by solution calorimetry in the appropriate alcohol.[112]

An optical transform study of the disorder in dicalcium barium proprionate undertaken by Welberg[113] has shown that the diffuse scattering from the salt is largely attributable to distortions of the cationic framework (as suggested by Glazer, Stadnicka and Singh[114]) and not to short range order of disordered proprionate ions (as proposed initially by Stadnicka and Glazer[115]).

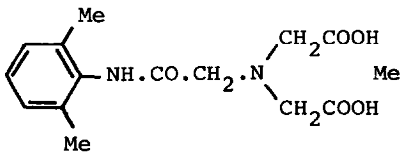
### 2.4.6 Strontium and Barium Derivatives

Only four papers[116-119] have been abstracted for this subsection; they describe the crystal and molecular structures of diverse barium salts. The structure of the barium salt of 2,4,6-trinitro-1,3-benzenediol (styphnic acid) (17) monohydrate has been determined by two independent groups.[116,117] The two versions of the structure are very similar with cell constants, positional parameters and most of the derived quantities varying by no more than twice the greater set of standard deviations. The 9-fold coordination of the $Ba^{2+}$ cation consists of nine oxygen atoms provided by four bidentate anions, r(Ba...O) = 268.6-292.1 pm, and the single water molecule, r(Ba...O) = 272.1 pm. Its geometry can be described either as distorted tricapped trigonal prismatic or as approximately pentagonal bipyramidal with the apices occupied by pairs of oxygen atoms perpendicular to each other.[116,117]

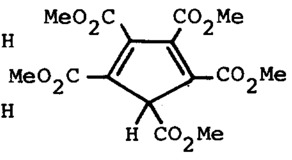
The monobarium salt of 2,6-(dimethylphenyl)carbamoylmethyliminodiacetic acid (18)[118] contains 10-coordinate $Ba^{2+}$ cations surrounded by six oxygen atoms, r(Ba...O) = 272.0-289.2 pm, and one nitrogen atom, r(Ba...N) = 294.7 pm from four anions and three water oxygen atoms, r(Ba...O) = 289.7-303.4 pm. The $Ba^{2+}$



(17)



(18)



(19)

coordination polyhedron may be regarded either as a facially tricapped cube with the apical atom joining the three capped faces removed, or as a trigonal prism capped on the three rectangular faces as well as on one triangular face.[118]

Alkaline earth metal salts of the strong organic acid, pentakis(methoxycarbonyl)cyclopentdiene (<u>19</u>), have been obtained[119] as white air stable compounds, $M[C_5(CO_2Me)_5]_2$ (M = Mg-Ba), either by reaction of the acid and the metal carbonates or acetates or from $MCl_2$ and $Tl[C_5(CO_2Me)_5]$. They have all been characterised by i.r., $^1H$-n.m.r. and mass spectroscopic methods. $Ba[C_5(CO_2Me)_5]_2$ has also been studied by single crystal X-ray diffraction methods;[119] the $Ba^{2+}$ cation is eight coordinate with an environment composed of eight oxygen atoms, six from three chelating anions and two from non-chelating anions, r(Ba...O) = 265.5-293.2 pm.[119]

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