by a trace of iodine) reacts similarly at room temperature. Alkyl and aryl halides react with Mg to give Grignard reagents RMgX (pp. 132–5).

The heavier alkaline earth metals Ca, Sr, Ba (and Ra) react even more readily with non-metals, and again the direct formation of nitrides M_3N_2 is notable. Other products are similar though the hydrides are more stable (p. 65) and the carbides less stable than for Be and Mg. There is also a tendency, previously noted for the alkali metals (p. 84), to form peroxides MO_2 of increasing stability in addition to the normal oxides MO. Calcium, Sr and Ba dissolve in liquid NH_3 to give deep blue-black solutions from which lustrous, coppery, ammoniates $M(NH_3)_6$ can be recovered on evaporation; these ammoniates gradually decompose to the corresponding amides, especially in the presence of catalysts:

$$[M(NH_3)_6](s) \longrightarrow M(NH_2)_2(s)$$
$$+ 4NH_3(g) + H_2(g)$$

In these properties, as in many others, the heavier alkaline earth metals resemble the alkali metals rather than Mg (which has many similarities to Zn) or Be (which is analogous to Al).

5.3 Compounds

5.3.1 Introduction

The predominant divalence of the Group 2 metals can be interpreted in terms of their electronic configuration, ionization energies, and size (see Table 5.1). Further ionization to give simple salts of stoichiometry MX_3 is precluded by the magnitude of the energies involved, the third stage ionization being $14\,849\,kJ\,mol^{-1}$ for Be, $7733\,kJ\,mol^{-1}$ for Mg and $4912\,kJ\,mol^{-1}$ for Ca; even for Ra the estimated value of $3281\,kJ\,mol^{-1}$ involves far more energy than could be recovered by additional bonding even if this were predominantly covalent. Reasons for the absence of *univalent* compounds MX are less obvious. The first-stage ionization energies for Ca, Sr, Ba and Ra are similar to that of Li (p. 75) though the larger

size of the hypothetical univalent Group 2 ions, when compared to Li, would reduce the lattice energy somewhat (p. 82). By making plausible assumptions about the ionic radius and structure we can estimate the approximate enthalpy of formation of such compounds and they are predicted to be stable with respect to the constituent elements; their non-existence is related to the much higher enthalpy of formation of the conventional compounds MX_2, which leads to rapid and complete disproportionation. For example, the standard enthalpy of formation of hypothetical crystalline MgCl, assuming the NaCl structure, is $\sim -125\,kJ\,mol^{-1}$, which is substantially greater than for many known stable compounds and essentially the same as the experimentally observed value for AgCl: $\Delta H_f^\circ = -127\,kJ\,mol^{-1}$. However, the corresponding (experimental) value for $\Delta H_f^\circ(MgCl_2)$ is $-642\,kJ\,mol^{-1}$, whence an enthalpy of disproportionation of $-196\,kJ\,mol^{-1}$:

$$Mg(c) + Cl_2(g) = MgCl_2(c);$$
$$\Delta H_f^\circ = -642 \text{ kJ/(mol of } MgCl_2)$$
$$2Mg(c) + Cl_2(g) = 2MgCl(c);$$
$$\Delta H_f^\circ = -250 \text{ kJ/(2 mol of MgCl)}$$

$$2MgCl(c) = Mg(c) + MgCl_2(c);$$
$$\Delta H_{disprop}^\circ = -392 \text{ kJ/(2 mol of MgCl)}$$

It is clear that, if synthetic routes could be devised which would mechanistically hinder disproportionation, such compounds might be preparable. Although univalent compounds of the Group 2 metals have not yet been isolated, there is some evidence for the formation of Mg^1 species during electrolysis with Mg electrodes. Thus H_2 is evolved at the anode when an aqueous solution of NaCl is electrolysed and the amount of Mg lost from the anode corresponds to an oxidation state of 1.3. Similarly, when aqueous Na_2SO_4 is electrolysed, the amount of H_2 evolved corresponds to the oxidation by water of Mg ions having an average oxidation state of 1.4:

$$Mg^{1.4+}(aq) + 0.6H_2O \longrightarrow Mg^{2+}(aq)$$
$$+ 0.6OH^-(aq) + 0.3H_2(g)$$

On the basis of the discussion on pp. 79–81 the elements in Group 2 would be expected to deviate further from simple ionic bonding than do the alkali metals. The charge on M^{2+} is higher and the radius for corresponding ions is smaller, thereby inducing more distortion of the surrounding anions. This is reflected in the decreased thermal stability of oxoacid salts such as nitrates, carbonates and sulfates. For example, the temperature at which the carbonate reaches a dissociation pressure of 1 atm CO_2 is: $BeCO_3$ 250°, $MgCO_3$ 540°, $CaCO_3$ 900°, $SrCO_3$ 1289°, $BaCO_3$ 1360°. The tendency towards covalency is greatest with Be, and this element forms no compounds in which the bonding is predominantly ionic. For similar reasons Be (and to a lesser extent Mg) forms numerous stable coordination compounds; organometallic compounds are also well characterized, and these frequently involve multicentre (electron deficient) bonding similar to that found in analogous compounds of Li and B.

Many compounds of the Group 2 elements are much less soluble in water than their Group 1 counterparts. This is particularly true for the fluorides, carbonates and sulfates of the heavier members, and is related to their higher lattice energies. These solubility relations have had a profound influence on the mineralization of these elements as noted on p. 109. The ready solubility of BeF_2 (~20 000 times that of CaF_2) is presumably related to the very high solvation enthalpy of Be to give $[Be(H_2O)_4]^{2+}$.

Beryllium, because of its small size, almost invariably has a coordination number of 4. This is important in analytical chemistry since it ensures that edta, which coordinates strongly to Mg, Ca (and Al), does not chelate Be appreciably. BeO has the wurtzite (ZnS, p. 1209) structure whilst the other Be chalcogenides adopt the zinc blende modification. BeF_2 has the cristobalite (SiO_2, p. 342) structure and has only a very low electrical conductivity when fused. Be_2C and Be_2B have extended lattices of the antifluorite type with 4-coordinate Be and 8-coordinate C or B. Be_2SiO_4 has the phenacite structure (p. 347) in which both Be and Si

are tetrahedrally coordinated, and Li_2BeF_4 has the same structure. $[Be(H_2O)_4]SO_4$ features a tetrahedral aquo-ion which is H bonded to the surrounding sulfate groups in such a way that Be–O is 161 pm and the O–H$\cdots$O are 262

and 268 pm. Further examples of tetrahedral coordination to Be are to be found in later sections. Other configurations, involving linear (two-fold) coordination (e.g. $BeBu_2^t$) or trigonal coordination [e.g. cyclic $(MeBeNMe_2)_2$] are rare and most compounds which might appear to have such coordination (e.g. $BeMe_2$, $CsBeF_3$, etc.) achieve 4-coordination by polymerization. However K_2BeO_2,[6] Y_2BeO_4[7] and one or two more complex structures[8] do indeed contain trigonal planar {BeO_3} units with Be–O ca. 155 pm, i.e. some 11 pm shorter than in tetrahedral {BeO_4}. Likewise, K_4BeE_2 (E = P, As, Sb) feature linear anions $[E–Be–E]^{4-}$ isoelectronic with $BeCl_2$ molecules (p. 117).[9] (See also p. 123). Six-coordination has been observed in $K_3Zr_6Cl_{15}Be$ and $Be_3Zr_6Cl_{18}Be$, in which the Be atom is encapsulated by and contributes two bonding elections to the octahedral Zr_6 cluster.[10] Trigonal-pyramidal

[6] P. KASTNER and R. HOPPE, *Naturwiss.* **61**, 79 (1974).

[7] L. A. HARRIS and H. L. YANKEL, *Acta Cryst.* **22**, 354–60 (1967).

[8] R. A. HOWIE and A. R. WEST, *Nature* **259**, 473 (1976). D. SCHULDT and R. HOPPE, *Z. anorg. allg. Chem.*, **578** 119–32 (1989), **594**, 87–94 (1991).

[9] M. SOMER, M. HARTWEG, K. PETERS, T. POPP and H.-G. VON SCHNERING, *Z. anorg. allg. Chem.* **595**, 217–23 (1991).

[10] R. P. ZIEBARTH and J. D. CORBETT, *J. Am. Chem. Soc.* **110**, 1132–9 (1988). J. ZHANG and J. D. CORBETT, *Z. anorg. allg. Chem.* **598/599**, 363–70 (1991).

6-fold coordination of Be by H is found in $Be(BH_4)_2$ (p. 116).

The stereochemistry of Mg and the heavier alkaline earth metals is more flexible than that of Be and, in addition to occasional compounds which feature low coordination numbers (2, 3 and 4), there are many examples of 6, 8 and 12 coordination, some with 7, 9 or 10 coordination, and even some with coordination numbers as high as 22 or 24, as in $SrCd_{11}$, $BaCd_{11}$ and $(Ca, Sr$ or $Ba)Zn_{13}$.[11] Strontium is 5-coordinate on the hemisolvate $[Sr(OC_6H_2Bu_3^t)_2(thf)_3].\frac{1}{2}thf$ which features a distorted trigonal bipyramidal structure with the two aryloxides in equatorial positions.[11a]

5.3.2 Hydrides and halides

Many features of the structure, bonding and stability of the Group 2 hydrides have already been discussed (p. 65) and it is only necessary to add some comments on BeH_2, which is the most difficult of these compounds to prepare and the least stable. BeH_2 (contaminated with variable amounts of ether) was first prepared in 1951 by reduction of $BeCl_2$ with LiH and by the reaction of $BeMe_2$ with $LiAlH_4$. A purer sample can be made by pyrolysis of $BeBu_2^t$ at 210°C and the best product is obtained by displacing BH_3 from BeB_2H_8 using PPh_3 in a sealed tube reaction at 180°:

$$BeB_2H_8 + 2PPh_3 \longrightarrow 2Ph_3PBH_3 + BeH_2$$

BeH_2 is an amorphous white solid (d 0.65 g cm^{-3}) which begins to evolve hydrogen when heated above 250°; it is moderately stable in air or water but is rapidly hydrolysed by acids, liberating H_2. A hexagonal crystalline form (d 0.78 g cm^{-3}) has been prepared by compaction fusion at 6.2 kbar and 130° in the presence of ~1% Li as catalyst.[12] In all forms BeH_2 appears to be highly polymerized by means of BeHBe

3-centre bonds and its structure is probably similar to that of crystalline $BeCl_2$ and $BeMe_2$ (see below). A related compound is the volatile mixed hydride BeB_2H_8, which is readily prepared (in the absence of solvent) by the reaction of $BeCl_2$ with $LiBH_4$ in a sealed tube:

$$BeCl_2 + 2LiBH_4 \xrightarrow{120°C} BeB_2H_8 + 2LiCl$$

BeB_2H_8 inflames in air, reacts almost explosively with water and reacts with dry HCl even at low temperatures:

$$BeB_2H_8 + 2HCl \longrightarrow BeCl_2 + B_2H_6 + 2H_2$$

The structure of this compound has proved particularly elusive and at least nine different structures have been proposed; it therefore affords an instructive example of the difficulties which attend the use of physical techniques for the structural determination of compounds in the gaseous, liquid or solution phases. In the gas phase it now seems likely that more than one species is present[13] and the compound certainly shows fluxional behaviour which makes all the hydrogen atoms equivalent on the nmr time scale.[14] A linear structure such as (a), with possible admixture of singly bridged B–H–B and triply bridged BeH_3B variants is now favoured, after a period in which triangular structures such as (b) had been vigorously canvassed. Even structure (c), which features planar 3-coordinate Be, had been advocated because it was thought to fit best much of the infrared and electron diffraction data and also accounted for the ready formation of adducts (d) with typical ligands such as Et_2O, thf, R_3N, R_3P, etc. In the solid state the structure has recently been established with some certainty by single-crystal X-ray analysis.[15] BeB_2H_8 consists of helical polymers of BH_4Be

[11] A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984, 1382 pp.
[11a] S. R. DRAKE, D. J. OTWAY, M. B. HURSTHOUSE and K. M. A. MALIK, *Polyhedron* **11**, 1995–2007 (1992).
[12] G. J. BRENDEL, E. M. MARLETT and L. M. NIEBYLSKI, *Inorg. Chem.* **17**, 3589–92 (1978).

[13] K. BRENDHAUGEN, A. HAARLAND and D. P. NOVAK, *Acta Chem. Scand.* **A29**, 801–2 (1975).
[14] D. F. GAINES, J. L. WALSH and D. F. HILLENBRAND, *J. Chem. Soc., Chem. Commun.*, 224–5 (1977).
[15] D. S. MARYNICK and W. N. LIPSCOMB, *Inorg. Chem.* **11**, 820–3 (1972). D. S. MARYNICK, *J. Am. Chem. Soc.* **101**, 6876–80 (1979). [See also J. F. STANTON, W. N. LIPSCOMB and R. J. BARTLETT, *J. Chem. Phys.* **88**, 5726–34 (1988) for results of high-level computations.]

(a) Probable "linear" structure (fluxional)

(b) Hypothetical triangular structure

(c) Alternative triangular structure

(d) Proposed structure for LBeB₂H₈

Figure 5.1 Polymeric structure of crystalline Be(BH₄)₂ showing a section of the $\cdots$(H₂BH₂)Be(H₂BH₂)$\cdots$ helix and one "terminal" or non-bridging group {(H$_t$)₂B(H$_\mu$)₂}.

units linked by an equal number of bridging BH₄ units (Fig. 5.1). Of the 8 H atoms only 2 are not involved in bonding to Be; the Be is thus 6-coordinate (distorted trigonal prism) though the H atoms are much closer to B ($\sim$110 pm) than to Be (2 at $\sim$153 pm and 4 at $\sim$162 pm). The Be$\cdots$B distance within the helical chain is 201 pm and in the branch is 192 pm. The relationship of this

structure to those of Al(BH₄)₃ and AlH₃ itself (p. 227) is noteworthy.

Anhydrous beryllium halides cannot be obtained from reactions in aqueous solutions because of the formation of hydrates such as [Be(H₂O)₄]F₂ and the subsequent hydrolysis which attends attempted dehydration. Thermal decomposition of (NH₄)₂BeF₄ is the best route for BeF₂, and BeCl₂ is conveniently made from the oxide

$$\text{BeO} + \text{C} + \text{Cl}_2 \xrightleftharpoons[]{600-800°} \text{BeCl}_2 + \text{CO}$$

BeCl₂ can also be prepared by direct high-temperature chlorination of metallic Be or Be₂C, and these reactions are also used for the bromide and iodide. BeF₂ is a glassy material that is difficult to crystallize; it consists of a random network of 4-coordinate F-bridged Be atoms similar to the structure of vitreous silica, SiO₂. Above 270°, BeF₂ spontaneously crystallizes to give the quartz modification (p. 342) and, like quartz, it exists in a low-temperature α-form which transforms to the β-form at 227°; crystobalite and tridymite forms (p. 343) have also been prepared. The structural similarities between BeF₂ and SiO₂ extend to fluoroberyllates and silicates, and numerous parallels have been drawn: e.g. the phase diagram, compounds, and structures in the system NaF–BeF₂ resemble those for CaO–SiO₂; the system CaF₂–BeF₂ resembles ZrO₂–SiO₂; the compound KZnBe₃F₉ is isostructural with benitoite, BaTiSi₃O₉, etc.

BeCl₂ has an unusual chain structure (a) which can be cleaved by weak ligands such as Et₂O to give 4-coordinate molecular complexes L₂BeCl₂ (b); stronger donors such as H₂O or NH₃ lead

(a)

(b)

(c)

(d)

(e)

to ionic complexes $[BeL_4]^{2+}[Cl]^-_2$ (c). In all these forms Be can be considered to use the s, p_x, p_y and p_z orbitals for bonding; the ClBeCl angle is substantially less than the tetrahedral angle of 109° probably because this lessens the repulsive interaction between neighbouring Be atoms in the chain by keeping them further apart and also enables a wider angle than 71° to be accommodated at each Cl atom, consistent with its predominant use of two p orbitals. The detailed interatomic distances and angles therefore differ significantly from those in the analogous chain structure $BeMe_2$ (p. 128), which is best described in terms of 3-centred "electron-deficient" bonding at the Me groups, leading to a BeCBe angle of 66° and a much closer approach of neighbouring Be atoms (209 pm). In the vapour phase $BeCl_2$ tends to form a bridged sp^2 dimer (d) and dissociation to the linear (sp) monomer (e) is not complete below about 900°; in contrast, BeF_2 is monomeric and shows little tendency to dimerize in the gas phase.

The shapes of the monomeric molecules of the Group 2 halides (gas phase or matrix isolation) pose some interesting problems for those who are content with simple theories of bonding and molecular geometry. Thus, as expected on the basis of either sp hybridization or the

VSEPR model, the dihalides of Be and Mg and the heavier halides of Ca and Sr are essentially linear. However, the other dihalides are appreciably bent, e.g. $CaF_2 \sim 145°$, $SrF_2 \sim 120°$, $BaF_2 \sim 108°$; $SrCl_2 \sim 130°$, $BaCl_2 \sim 115°$; $BaBr_2 \sim 115°$; $BaI_2 \sim 105°$. The uncertainties on these bond angles are often quite large ($\pm 10°$) and the molecules are rather flexible, but there seems little doubt that the equilibrium geometry is substantially non-linear. This has been interpreted in terms of sd (rather than sp) hybridization[16] or by a suitable *ad hoc* modification of the VSEPR theory[17].

The *crystal* structures of the halides of the heavier Group 2 elements also show some interesting trends (Table 5.3). For the fluorides, increasing size of the metal enables its

[16] R.L. DeKock,   M. A. Peterson,   L. A. Timmer, E. J. Baerends and P. Vernooijs. *Polyhedron* **9**, 1919–34 (1990) and references cited therein. D. M. Hassett and C. J. Marsden, *J. Chem. Soc., Chem. Commun.*, 667–9 (1990).

[17] R. J. Gillespie, *Chem. Soc. Revs.* **21**, 59–69 (1992).

Table 5.3 Crystal structures of alkaline earth halides[a]

	Be	Mg	Ca	Sr	Ba
F	Quartz	Rutile(TiO_2)	Fluorite	Fluorite	Fluorite
Cl	Chain	$CdCl_2$	Deformed TiO_2	Deformed TiO_2	$PbCl_2$
Br	Chain	CdI_2	Deformed TiO_2	Deformed $PbCl_2$	$PbCl_2$
I	—	CdI_2	CdI_2	SrI_2	$PbCl_2$

[a]For description of these structures see: quartz (p. 342), rutile (p. 961), $CdCl_2$ (p. 1212), CdI_2 (p. 1212), $PbCl_2$ (p. 382); the fluorite, $BeCl_2$-chain and SrI_2 structures are described in this subsection.

coordination number to increase from 4 (Be) to 6 (Mg) and 8 (Ca, Sr, Ba). CaF_2 (fluorite) is a standard crystal structure type and its cubic unit cell is illustrated in Fig. 5.2. The other halides (Cl, Br, I) show an increasing trend away from three-dimensional structures, the Be halides forming chains (as discussed above) and the others tending towards layer-lattice structures such as $CdCl_2$, CdI_2 and PbI_2. SrI_2 is unique in this group in having sevenfold coordination (Fig. 5.3); a similar coordination polyhedron is found in EuI_2, but the way they are interconnected differs in the two compounds.[18]

● Sr	○ I

Sr–I (1a, b, c)	337 pm
Sr–I (2a, d)	326 pm
Sr–I (2b, c)	342 pm

Average Sr–I 335 pm

Figure 5.3   Structure of SrI_2 showing sevenfold coordination of Sr by I. The planes 1 and 2 are almost parallel (4.5°) and the planes 1a2a2d and 1b2b2c1c are at an angle of 12° to each other.[9]

Figure 5.2   Unit cell of CaF_2 showing eightfold (cubic) coordination of Ca by 8F and fourfold (tetrahedral) coordination of F by 4Ca. The structure can be thought of as an fcc array of Ca in which all the tetrahedral interstices are occupied by F.

The most important fluoride of the alkaline earth metals is CaF_2 since this mineral (fluorspar) is the only large-scale source of fluorine (p. 795). Annual world production now exceeds 5 million tonnes the principal suppliers (in 1984) being Mexico (15%), Mongolia (15%), China (14%), USSR (13%) and South Africa (7%). The largest consumer is the USA, though 85% of its needs must be imported. CaF_2 is a white, high-melting (1418°C) solid whose low solubility in water permits quantitative analytical precipitation. The

other fluorides (except BeF_2) are also high-melting and rather insoluble. By contrast, the chlorides tend to be deliquescent and to have much lower mps (715–960°); they readily form numerous hydrates and are soluble in alcohols. $MgCl_2$ is one of the most important salts of Mg industrially (p. 110) and its concentration in sea water is exceeded only by NaCl. $CaCl_2$ is also of great importance, as noted earlier; its production in the US is in the megatonne region and its 1990 price was: bulk $182/tonne, granules $360/tonne, i.e 36 cents/kg. Its traditional uses include:

(a) brine for refrigeration plants (and for filling inflated tires of tractors and earth-moving equipment to increase traction);

(b) control of snow and ice on highways and pavements (side walks) — the $CaCl_2$–H_2O eutectic at 30 wt% $CaCl_2$ melts at −55°C (compared with NaCl–H_2O at −18°C);

(c) dust control on secondary roads, unpaved streets, and highway shoulders;

(d) freeze-proofing of coal and ores in shipping and stock piling;

(e) use in concrete mixes to give quicker initial set, higher early strength, and greater ultimate strength.

The bromides and iodides continue the trends to lower mps and higher solubilities

[18] E. T. RIETSCHEL and H. BÄRNIGHAUSEN, *Z. anorg. allg. Chem.* **368**, 62–72 (1969).

in water and their ready solubility in alcohols, ethers, etc., is also notable; indeed, $MgBr_2$ forms numerous crystalline solvates such as $MgBr_2.6ROH$ $(R = Me, Et, Pr)$, $MgBr_2.6Me_2CO$, $MgBr_2.3Et_2O$, in addition to numerous ammines $MgBr_2.nNH_3$ $(n = 2-6)$. The ability of Group 2 cations to form coordination complexes is clearly greater than that of Group 1 cations (p. 90).

Alkaline earth salts MHX, where M = Ca, Sr or Ba and X = Cl, Br or I can be prepared by fusing the hydride MH_2 with the appropriate halide MX_2 or by heating $M + MX_2$ in an atmosphere of H_2 at 900°. These hydride halides appear to have the PbClF layer lattice structure though the H atoms were not directly located. The analogous compounds of Mg have proved more elusive and the preceding preparative routes merely yield physical mixtures. However, MgClH and MgBrH can be prepared as solvated dimers by the reaction of specially activated MgH_2 with MgX_2 in thf:

$$MgR_2 + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2R_2$$

$$MgH_2 + MgX_2 \xrightarrow{thf} [HMgX(thf)]_2$$

The chloride can be crystallized but the bromide disproportionates. On the basis of mol wt and infrared spectroscopic evidence the proposed structure is:

5.3.3 Oxides and hydroxides [19,20]

The oxides MO are best obtained by calcining the carbonates (pp. 114 and 122); dehydration of the hydroxides at red heat offers an alternative route. BeO (like the other Be chalcogenides)

has the wurtzite structure (p. 1210) and is an excellent refractory, combining a high mp (2507°C) with negligible vapour pressure below this temperature; it has good chemical stability and a very high thermal conductivity which is greater than that of any other non-metal and even exceeds that of some metals. The other oxides in the group all have the NaCl structure and this structure is also adopted by the chalcogenides (except MgTe which has the wurtzite structure). Lattice energies and mps are again very high: MgO mp 2832°, CaO 2627°, SrO 2665°, BaO 1913°C (all ± ca. 30°). The compounds are comparatively unreactive in bulk but their reactivity increases markedly with decrease in particle size and increase in atomic weight. Notable reactions (which reverse those used to prepare the oxides) are with CO_2 and with H_2O. MgO is extensively used as a refractory: like BeO it is unusual in being both an excellent thermal conductor and a good electrical insulator, thus finding widespread use as the insulating radiator in domestic heating ranges and similar appliances. CaO (lime) is produced on an enormous scale in many countries and, indeed, is one of the half-dozen largest tonnage industrial chemicals to be manufactured (see Panel on p. 120). Production in 1991 exceeded 16 million tonnes in the USA alone. Its major end uses (in descending tonnages) are as a flux in steel manufacture; in the production of Ca chemicals; in the treatment of municipal water supplies, industrial wastes and sewage; in mortars and cements; in the pulp and paper industries; and in non-ferrous metal production. Price for bulk quantities is ~$45 per tonne.

In addition to the oxides MO, peroxides MO_2 are known for the heavier alkaline earth metals and there is some evidence for yellow superoxides $M(O_2)_2$ of Ca, Sr and Ba; impure ozonides $Ca(O_3)_2$ and $Ba(O_3)_2$ have also been reported.[21] As with the alkali metals, stability

[19] D. A. EVEREST, Beryllium, *Comprehensive Inorganic Chemistry* Vol. 1, pp. 531-90 Pergamon Press, Oxford (1973).

[20] R. D. GOODENOUGH and V. A. STENGER, Magnesium, calcium, strontium, barium and radium, *Comprehensive Inorganic Chemistry*, Vol. 1, pp. 591-664 (1973).

[21] N.-G. VANNERBERG, *Prog. Inorg. Chem.* 4, 125-97 (1962).

Industrial Uses of Limestone and Lime

Limestone rock is the commonest form of calcium carbonate, which also occurs as chalk, marble, corals, calcite, aragonite, etc., and (with Mg) as dolomite. Limestone and dolomite are widely used as building materials and road aggregate and both are quarried on a vast scale worldwide. $CaCO_3$ is also a major industrial chemical and is indispensable as the precursor of quick lime (CaO) and slaked lime, $Ca(OH)_2$. These chemicals are crucial to large sections of the chemical, metallurgical and construction industries, as noted below, and are produced on a scale exceeded by very few other materials.[22] Thus, world production of lime exceeds 110 million tonnes, and even this is dwarfed by Portland cement (793 million tonnes in 1984) which is made by roasting limestone and sand with clay (p. 252).

Large quantities of lime are consumed in the steel industry where it is used as a flux to remove P, S, Si and to a lesser extent Mn. The basic oxygen steel process typically uses 75 kg lime per tonne of steel, or a rather larger quantity (100–300 kg) of dolomitic quick lime, which markedly extends the life of the refractory furnace linings. Lime is also used as a lubricant in steel wire drawing and in neutralizing waste sulfuric-acid-based pickling liquors. Another metallurgical application is in the production of Mg (p. 110): the ferro-silicon (Pidgeon) process (1) uses dolomitic lime and both of the Dow electrolytic methods (2), (3), also require lime.

$$2(CaO.MgO) + Si/Fe \longrightarrow 2Mg + Ca_2SiO_4/Fe \tag{1}$$

$$CaO.MgO + CaCl_2.MgCl_2(brine) + CO_2 \longrightarrow 2CaCO_3 + 2MgCl_2 \text{ (then electrolysis)} \tag{2}$$

$$\left. \begin{array}{l} Ca(OH)_2 + MgCl_2(seawater) \longrightarrow Mg(OH)_2 + CaCl_2 \\ Mg(OH)_2 + 2HCl \longrightarrow 2H_2O + MgCl_2 \text{ (then electrolysis)} \end{array} \right\} \tag{3}$$

Lime is the largest tonnage chemical used in the treatment of potable and industrial water supplies. In conjunction with alum or iron salts it is used to coagulate suspended solids and remove turbidity. It is also used in water softening to remove temporary (bicarbonate) hardness. Typical reactions are:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3\downarrow + CaCO_3\downarrow + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow etc.$$

The neutralization of acid waters (and industrial wastes) and the maintenance of optimum pH for the biological oxidation of sewage are further applications. Another major use of lime is in scrubbers to remove SO_2/H_2S from stack gases of fossil-fuel-powered generating stations and metallurgical smelters.

The chemical industry uses lime in the manufacture of calcium carbide (for acetylene, p. 297), cyanamide (p. 323), and numerous other chemicals. Glass manufacturing is also a major consumer, most common glasses having ~12% CaO in their formulation. The insecticide calcium arsenate, obtained by neutralizing arsenic acid with lime, is much used for controlling the cotton boll weevil, codling moth, tobacco worm, and Colorado potato beetle. Lime-sulfur sprays and Bordeaux mixtures [$(CuSO_4/Ca(OH)_2]$ are important fungicides.

The paper and pulp industries consume large quantities of $Ca(OH)_2$ and precipitated (as distinct from naturally occurring) $CaCO_3$. The largest application of lime in pulp manufacture is as a causticizing agent in sulfate (kraft) plants (p. 89). Here the waste Na_2CO_3 solution is reacted with lime to regenerate the caustic soda used in the process:

$$Na_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2NaOH$$

About 95% of the $CaCO_3$ mud is dried and recalcined in rotary kilns to recover the CaO. Calcium hypochlorite bleaching liquor (p. 860) for paper pulp is obtained by reacting lime and Cl_2.

The manufacture of high quality paper involves the extensive use of specially precipitated $CaCO_3$. This is formed by calcining limestone and collecting the CO_2 and CaO separately; the latter is then hydrated and recarbonated to give the desired product. The type of crystals obtained, as well as their size and habit, depend on the temperature, pH, rate of mixing, concentration and presence of additives. The fine crystals ($<45\,\mu m$) are often subsequently coated with fatty acids, resins and wetting agents to improve their flow properties. US prices (1991) range from 5–45 cents per kg depending on grade and the amounts consumed are immense, e.g. 5.9 million tonnes p.a. in the USA alone. $CaCO_3$ adds brightness, opacity, ink receptivity and smoothness to paper and, in higher concentration, counteracts the high gloss produced by kaolin additives and produces a matte or dull finish which is particularly popular for textbooks. Such papers may contain 5–50% by weight of precipitated $CaCO_3$. The compound is also used as a filler in rubbers, latex, wallpaints and enamels, and in plastics (~10% by weight) to improve their heat resistance, dimensional stability, stiffness, hardness and processability.

Panel continues

[22] R. S. BOYNTON, *Chemistry and Technology of Lime and Limestone*, 2nd edn., Wiley, Chichester, 1980, 579 pp.

Domestic and pharmaceutical uses of precipitated $CaCO_3$ include its direct use as an antacid, a mild abrasive in toothpastes, a source of Ca enrichment in diets, a constituent of chewing gum and a filler in cosmetics.

In the dairy industry lime finds many uses. Lime water is often added to cream when separated from whole milk, in order to reduce its acidity prior to pasteurization and conversion to butter. The skimmed milk is then acidified to separate casein which is mixed with lime to produce calcium caseinate glue. Fermentation of the remaining skimmed milk (whey) followed by addition of lime yields calcium lactate which is used as a medicinal or to produce lactic acid on reacidification. Likewise the sugar industry relies heavily on lime: the crude sugar juice is reacted with lime to precipitate calcium sucrate which permits purification from phosphatic and organic impurities. Subsequent treatment with CO_2 produces insoluble $CaCO_3$ and purified soluble sucrose. The cycle is usually repeated several times; cane sugar normally requires $\sim$3–5 kg lime per tonne but beet sugar requires 100 times this amount i.e. $\sim\frac{1}{3}$ tonne lime per tonne of sugar.

increases with electropositive character and size: no peroxide of Be is known; anhydrous MgO_2 can only be made in liquid NH_3 solution, aqueous reactions leading to various peroxide hydrates; CaO_2 can be obtained by dehydrating $CaO_2.8H_2O$ but not by direct oxidation, whereas SrO_2 can be synthesized directly at high oxygen pressures and BaO_2 forms readily in air at 500°. Reactions with aqueous reagents are as expected, and the compounds can be used as oxidizing agents and bleaches:

$$CaO_2(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + H_2O_2(aq)$$

$$Ca(O_2)_2 + H_2SO_4(aq) \longrightarrow CaSO_4(s)$$
$$+ H_2O_2(aq) + O_2(g)$$

MgO_2 has the pyrite structure (p. 680) and the Ca, Sr and Ba analogues have the CaC_2 structure (p. 298).

The hydroxides of Group 2 elements show a smooth gradation in properties, with steadily increasing basicity, solubility, and heats of formation from the corresponding oxide. $Be(OH)_2$ is amphoteric and $Mg(OH)_2$ is a mild base which, as an aqueous suspension (milk of magnesia), is widely used as a digestive antacid. Note that, though mild, $Mg(OH)_2$ will neutralize 1.37 times as much acid as NaOH, weight for weight, and 2.85 times as much as $NaHCO_3$. $Ca(OH)_2$ and $Sr(OH)_2$ are moderately strong to strong bases and $Ba(OH)_2$ approaches the alkali hydroxides in strength.

Beryllium salts rapidly hydrolyse in water to give a series of hydroxo complexes of undetermined structure; the equilibria depend sensitively on initial concentration, pH, temperature, etc., and precipitation begins when the ratio $OH^-/Be^{2+}(aq) > 1$. Addition of further alkali redissolves the precipitate and the properties of the resultant solution are consistent (at least qualitatively) with the presence of isopolyanions of the type $[(HO)_2\{Be(\mu\text{-}OH)_2\}_n Be(OH)_2]^{2-}$. Further addition of alkali progressively depolymerizes this chain anion by hydroxyl addition until ultimately the mononuclear beryllate anion $[Be(OH)_4]^{2-}$ is formed. The analogy with $Zn(OH)_2$ and $Al(OH)_3$ is clear.

The solubility of $Be(OH)_2$ in water is only $\sim 3 \times 10^{-4}$ g l^{-1} at room temperature, compared with $\sim 3 \times 10^{-2}$ g l^{-1} for $Mg(OH)_2$ and ~ 1.3 g l^{-1} for $Ca(OH)_2$. Strontium and barium hydroxides have even greater solubilities (8 and 38 g l^{-1} respectively at 20°).

The crystal structures of $M(OH)_2$ also follow group trends.[11] $Be(OH)_2$ crystallizes with 4-coordinate Be in the $Zn(OH)_2$ structure which can be considered as a diamond or cristobalite (SiO_2) lattice distorted by H bonding. $Mg(OH)_2$ (brucite) and $Ca(OH)_2$ have 6-coordinate cations in a CdI_2 layer lattice structure with OH bonds perpendicular to the layers and strong $O-H\cdots O$ bonding between them. Strontium is too large for the CdI_2 structure and $Sr(OH)_2$ features 7-coordinate Sr $(3 + 4)$, the structure being built up of edge-sharing monocapped trigonal prisms with no H bonds. (The monohydrate has bicapped trigonal prismatic coordination about Sr.) The structure of $Ba(OH)_2$ is complex and has not yet been fully determined.

5.3.4 Oxoacid salts and coordination complexes

The chemical trends and geochemical significance of the oxoacid salts of the alkaline earth metals have already been mentioned (p. 109) and the immense industrial importance of the carbonates and sulfates in particular can hardly be over emphasized (see Panel on limestone and lime). A speciality use can also be noted: mother-of-pearl (nacre) is a material composed of thin plates of chalk (in the form of aragonite) stuck together with a protein glue. It is irridescent and highly decorative when polished and, despite being 95% chalk, is very strong.

Calcium sulfate usually occurs as the dihydrate (gypsum) though anhydrite ($CaSO_4$) is also mined. Alabaster is a compact, massive, finegrained form of $CaSO_4.2H_2O$ resembling marble. When gypsum is calcined at $150-165°C$ it looses approximately three-quarters of its water of crystallization to give the hemihydrate $CaSO_4.\frac{1}{2}H_2O$, also known as plaster of Paris because it was originally obtained from gypsum quarried at Montmartre. Heating at higher temperatures yields various anhydrous forms:

$$CaSO_4.2H_2O \xrightarrow{\sim 150°} CaSO_4.\tfrac{1}{2}H_2O \xrightarrow{\sim 200°}$$

$$\gamma\text{-}CaSO_4 \xrightarrow{\sim 600°} \beta\text{-}CaSO_4 \xrightarrow{\sim 1100°} CaO + SO_3$$

Gypsum, though not mined on the same scale as limestone, is nevertheless still a major industrial mineral. World production in 1990 was 97.7 million tonnes, the major producing countries being the USA (15.2%), Canada (8.4%), Iran (8.2%), China (8.2%), Japan (6.5%), Mexico (6.1%), Thailand (5.9%), France (5.8%) and Spain (5.1%); the remaining 30.6% (30 million tonnes) was distributed between over 20 other countries including the former Soviet Union (4.8%) and the UK (4.1%). A representative price in 1990 was $5.5 per tonne. In the USA about 28% of the gypsum used is uncalcined and most of this is for Portland cement (p. 252) or agricultural purposes. Of calcined gypsum, virtually all (95%) is used for prefabricated products, mainly wall board, and the rest is for industrial and building plasters. The hemihydrate expands slightly (0.2–0.3% linear) on rehydration with water and this is crucial to its use in mouldings and plasters; the expansion can be modified in the range 0.03–1.2% by the use of additives.

Other oxoacid salts and binary compounds are more conveniently discussed under the chemistry of the appropriate non-metals in later chapters.

Beryllium is unique in forming a series of stable, volatile, molecular oxide-carboxylates of general formula $[OBe_4(RCO_2)_6]$, where $R = H$, Me, Et, Pr, Ph, etc. These white crystalline compounds, of which "basic beryllium acetate" ($R = Me$) is typical, are readily soluble in organic solvents, including alkanes, but are insoluble in water or the lower alcohols. They are best prepared simply by refluxing the hydroxide or oxide with the carboxylic acid; mixed oxide carboxylates can be prepared by reacting a given compound with another organic acid or acid chloride. The structure (Fig. 5.4) features a central O atom tetrahedrally surrounded by 4 Be. The 6 edges of the tetrahedron so formed are bridged by the 6 acetate groups in such a way that each Be is also tetrahedrally coordinated by 4 oxygens. $[OBe_4(MeCO_2)_6]$ melts at $285°$ and boils at $330°$; it is stable to heat and oxidation except under drastic conditions, is only slowly hydrolysed by hot water, but is decomposed rapidly by mineral acids to give an aqueous solution of the corresponding beryllium salt and free carboxylic acid. The basic nitrate $[OBe_4(NO_3)_6]$ appears to have a similar structure with bridging nitrate groups. The compound is formed by first dissolving $BeCl_2$ in N_2O_4/ethyl-acetate to give the crystalline solvate $[Be(NO_3)_2.2N_2O_4]$; when heated to $50°$ this gives $Be(NO_3)_2$ which decomposes suddenly at $125°C$ into N_2O_4 and $[OBe_4(NO_3)_6]$.

In addition to the oxide carboxylates, beryllium forms numerous chelating and bridged complexes with ligands such as the oxalate ion $C_2O_4{}^{2-}$, alkoxides, β-diketonates and 1,3-diketonates.[20] These almost invariably feature 4-coordinate Be

Figure 5.4 The molecular structure of "basic beryllium acetate" showing (a) the regular tetrahedral arrangement of 4 Be about the central oxygen and the octahedral arrangement of the 6 bridging acetate groups, and (b) the detailed dimensions of one of the six non-planar 6-membered heterocycles. (The Be atoms are 24 pm above and below the plane of the acetate group.) The 2 oxygen atoms in each acetate group are equivalent. The central Be–O distances (166.6 pm) are very close to that in BeO itself (165 pm).

though severe steric crowding can reduce the coordination number to 3 or even 2; for example, the very volatile dimeric perfluoroalkoxide (a) was prepared in 1975 and the unique monomeric bis(2,6-di-t-butylphenoxy)beryllium (b) has been known since 1972.

Halide complexes are also well known but complexes with nitrogen-containing ligands are rare. An exception is the blue phthalocyanine complex formed by reaction of Be metal with phthalonitrile, $1,2\text{-}C_6H_4(CN)_2$, and this affords an unusual example of planar 4-coordinate Be (Fig. 5.5). The complex readily picks up two molecules of H_2O to form an extremely stable dihydrate, perhaps by dislodging 2 adjacent Be–N bonds and forming 2 Be–O bonds at the preferred tetrahedral angle above and below the plane of the macrocycle.

Magnesium forms few halide complexes of the type $MX_4{}^{2-}$, though $[NEt_4]_2[MgCl_4]$ has been reported; examples of $MX_n{}^{(n-2)-}$ for the heavier alkaline earths are lacking, though hydrates and

Figure 5.5   The beryllium phthalocyanine complex.

other solvates are well known. The first examples of monomeric six-coordinate (octahedral) complexes of strontium salts have recently been characterized, *viz. trans*-[SrI_2(hmpa)$_4$] and *cis*-[$Sr(NCS)_2$(hmpa)$_4$] where hmpa is $(Me_2N)_3PO$; they were made as colourless crystals by refluxing a mixture of NH_4I (or NH_4SCN) with metallic Sr and hmpa in toluene for 1 hour.[23]

Oxygen chelates such as those of edta and polyphosphates are of importance in analytical chemistry and in removing Ca ions from hard water. There is no unique sequence of stabilities since these depend sensitively on a variety of factors: where geometrical considerations are not important the smaller ions tend to form the stronger complexes but in polydentate macrocycles steric factors can be crucial. Thus dicyclohexyl-18-crown-6 (p. 96) forms much stronger complexes with Sr and Ba than with Ca (or the alkali metals) as shown in Fig. 5.6.[24] Structural data are also available and an example of a solvated 8-coordinate Ca complex [(benzo-15-crown-5)-$Ca(NCS)_2$.MeOH] is shown in Fig. 5.7. The coordination polyhedron is not regular: Ca lies above the mean plane of the 5 ether oxygens

[23] D. Barr, A. T. Brooker, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 893–5 (1989).

[24] See refs. 38 and 66 of Chapter 4.

Figure 5.6   Formation constants K for complexes of dicyclohexyl-18-crown-6 ether with various cations. Note that, although the radii of Ca^{2+}, Na^+ and Hg^{2+} are very similar, the ratio of the formation constants is 1:6.3:225. Again, K^+ and Ba^{2+} have similar radii but the ratio of K is 1:35 in the reverse direction (note log scale).

Figure 5.7   Molecular structure of benzo-15-crown-5-$Ca(NCS)_2$.MeOH.

(mean Ca–O 253 pm) and is coordinated on the other side by a methanol molecule (Ca–O 239 pm) and two non-equivalent isothiocyanate

groups (Ca–N 244 pm) which make angles Ca–N–CS of 153° and 172° respectively.[25] Cryptates (pp. 97–8) are also known and usually follow the stability sequence Mg < Ca < Sr < Ba.[24] The first monomeric barium alkoxides, [Ba{O(CH$_2$CH$_2$O)$_n$Me}$_2$] (n = 2, 3), which incorporate coordinating polyether functions, were isolated in 1991; the compounds, which are unusual in being liquids at room temperature and which feature 6- and 8-coordinate Ba, respectively, were made by direct reaction of Ba metal with the oligoether alcohols in thf.[26]

Preeminent in importance among the macrocyclic complexes of Group 2 elements are the chlorophylls, which are modified porphyrin complexes of Mg. These compounds are vital to the process of photosynthesis in green plants (see Panel). Magnesium and Ca are also intimately involved in biochemical processes in animals: Mg ions are required to trigger phosphate transfer enzymes, for nerve impulse transmissions and carbohydrate metabolism; Mg ions are also involved in muscle action, which is triggered by Ca ions. Ca is required for the formation of bones and teeth, maintaining heart rhythm, and in blood clotting.[27a–f]

[27a] W. E. C. WACKER, *Magnesium and Man*, Harvard University Press, London, 1980.

[27b] M. N. HUGHES, *The Inorganic Chemistry of Biological Processes*, Wiley, London, 1972, Chap. 8, pp. 256–82.

[27c] G. L. EICHHORN (ed.), *Inorganic Biochemistry*, Elsevier, Amsterdam, 1973, 2 Vols., 1263 pp.

[27d] B. S. COOPERMAN, Chap. 2 in H. SIGAL (ed.), *Metal Ions in Biological Systems*, Vol. 5, Dekker, New York, 1976, pp. 80–125.

[27e] K. S. RAJAN, R. W. COLBURN and J. M. DAVIS, Chap. 5 in H. SIGAL (ed.), *Metal Ions in Biological Systems*, Vol. 6, Dekker, New York, 1976, pp. 292–321. Also F. N. BRIGGS and R. J. SOLARO, Chap. 6, pp. 324–98 in the same volume.

[27f] H. SCHEER, *Chlorophylls*, CRC Press, Boca Raton, 1991.

[28] M. CALVIN, The path of carbon in photosynthesis, *Nobel Lectures in Chemistry 1942–62*, Elsevier, Amsterdam, 1964, 618–44.

[25] J. D. OWEN and J. N. WINGFIELD, *J. Chem. Soc., Chem. Commun.*, 318–9 (1976).

[26] W. S. REES and D. A. MORENO, *J. Chem. Soc., Chem. Commun.*, 1759–60 (1991).

Chlorophylls and Photosynthesis

Photosynthesis is the process by which green plants convert atmospheric CO$_2$ into carbohydrates such as glucose. The overall chemical change can be expressed as

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

though this is a gross and somewhat misleading over-simplification. The process is initiated in the photoreceptors of the green magnesium-containing pigments which have the generic name chlorophyll (Greek: χλωρός, *chloros* green; φύλλον, *phyllon* leaf), but many of the subsequent steps can proceed in the dark. The overall process is endothermic ($\Delta H° \sim 469$ kJ per mole of CO$_2$) and involves more than one type of chlorophyll. It also involves a manganese complex of unknown composition, various iron-containing cytochromes and ferredoxin (p. 1102), and a copper containing plastocyanin.

Photosynthesis is essentially the conversion of radiant electromagnetic energy (light) into chemical energy in the form of adenosine triphosphate (ATP) and reduced nicotinamide adenine dinucleotide phosphate (NADP). This energy eventually permits the fixation of CO$_2$ into carbohydrates, with the liberation of O$_2$. As such, the process is the basis for the nutrition of all living things and also provides mankind with fuel (wood, coal, petroleum), fibres (cellulose) and innumerable useful chemical compounds. About 90–95% of the dry weight of crops is derived from the CO$_2$/H$_2$O fixed from the air during photosynthesis — only about 5–10% comes from minerals and nitrogen taken from the soil. The detailed sequence of events is still not fully understood but tremendous advances were made from 1948 onwards by use of the then newly available radioactive ^{14}CO$_2$ and paper chromatography. With these tools and classical organic chemistry M. Calvin and his group were able to probe the biosynthetic pathways and thus laid the basis for our present understanding of the complex series of reactions. Calvin was awarded the 1961 Nobel Prize in Chemistry "for his research on the carbon dioxide assimilation in plants".[28]

(1) Porphin

(2) Haem

(3) Chlorin

(4) Chlorophyll a [the phytyl isoprenoid group is ——CH$_2$CH=C(CH$_2$)$_3$CH(CH$_2$)$_3$CH(CH$_2$)$_3$CHMe]
$\qquad\qquad$ Me   Me   Me   Me

(5)

Chlorophylls are complexes of Mg with macrocyclic ligands derived from the parent tetrapyrrole molecule porphin (structure 1). They are thus related to the porphyrin (substituted porphin) complexes which occur in haem proteins[†] such as haemoglobin, myoglobin and the cytochromes (p. 1101). [The word haem and the prefix haemo derive directly from the Greek word αἷμα, blood, whereas porphyrins derive their name from the characteristic purple-red coloration which these alkaloids give when acidified (Greek πόρφυρ-ος, *porphyros* purple).] The haem group is illustrated in structure 2. When the C=C double bond in the pyrrole-ring IV of porphin is *trans* hydrogenated and when a cyclopentanone ring is formed between ring III and the adjacent (γ) methine bridge then the chlorin macrocycle (structure 3) is produced, and this is the basis for the various chlorophylls. Chlorophyll a (Chl a) is shown in structure 4; this is the most common of the chlorophylls and is found in all O$_2$-evolving organisms. It was synthesized with complete chiral integrity by R. B. Woodward and his group in 1960 — an achievement of remarkable virtuosity. Variants of chlorophyll are:

Chlorophyll b, in which the 3-Me group is replaced by –CHO; this occurs in higher plants and green algae, the ratio CHl b:Chl a being $\sim$1:3.
Chlorophyll c, in which position 7 is substituted by acrylic acid, –CH=CHCO$_2$H; it occurs in diatoms and brown algae.
Chlorophyll d, in which 2-vinyl is replaced by –CHO.

Panel continues

[†] The first time that these two apparently very different but actually closely related coloured materials, chlorophyll and haemoglobin, were connected was in an extraordinarily percipient poem written in 1612 by the English poet John Donne who mused: Why grass is green or why our blood is red/Are mysteries that none have reached unto.