Comparison of the Co-ordinative Behaviour of Calcium(II) and Magnesium(II) from Crystallographic Data†

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Known crystal structures of calcium(II) and magnesium(II) complexes containing water, alcohols, ethers, carboxylates, halides, pseudohalides, carbonyl compounds, phosphates and polyphosphate as ligands have been examined in order to compare the co-ordinative behaviour of the two cations. A quantitative assessment of the differences in the co-ordination numbers, the co-ordinative bond distances and the geometry of co-ordination to a typical ligand such as carboxylate has been carried out by systematic analysis of the crystallographic data. The observed higher flexibility of the calcium(II) complexes is explained in terms of (*i*) dimensions of the naked cations, (*ii*) dependence of the co-ordinative bond strengths on their lengths and (*iii*) second co-ordination sphere interactions.

It is well accepted that comparisons of large amounts of crystallographic data can yield interesting 'chemical' information both for 'small molecules' and macromolecules. Research in this area is possible mainly because of the large amount of known crystallographic information and the availability of computerized databases, such as the Cambridge Structural Database (CSD),[1] the Brookhaven Protein Data Bank,[2] the Inorganic Crystal Structure Database[3] and the Metals Data File.[4] Herein we report a systematic comparison of the co-ordinative behaviour of calcium(II) and magnesium(II) by considering the known crystal structures of the complexes of these two cations. Their chemistry has been periodically reviewed during the last decade,[5,6] with the major stimulus being the study of their relevance in biological systems.[7] Considerable efforts have been made both in the study of bioinorganic roles of Ca^{2+} and Mg^{2+} [8] and in the design of biomimetic chemical systems discriminating between the two cations.[9] However, there is relatively little insight into the ultimate reasons for the differences between them. For example, little is known about the possible replacement of Ca^{2+} by Mg^{2+} in proteins, given that the concentration of Mg^{2+} inside cells is much higher than that of Ca^{2+}; although calcium(II) binding in proteins is often selective, Mg^{2+} may be an effective competitor for the Ca^{2+} sites, which may result in inhibition.[10] Moreover, although it is well known that magnesium(II) can be hosted by biominerals such as apatite,[11] there are no definitive data to explain its role in this mineral.[12] The reasonable hypothesis that the different behaviour of calcium(II) and magnesium(II) depends basically on their simple co-ordination chemistry led us to perform a systematic comparison of their co-ordinative behaviour.

Methods

Among the known crystal structures of calcium(II) and magnesium(II) compounds, we selected those containing H_2O, ROH, R_2O and RCO_2^- (R = alkyl or aryl), halides, pseudohalides, carbonyl-containing compounds (acyl derivatives, aldehydes or ketones) or phosphates and polyphosphates directly co-ordinated to the metal centre. The crystal structures of purely inorganic materials were disregarded because they have already been extensively reviewed,[13] and because they are less attractive with regard to co-ordination and bioinorganic chemistry. The literature search was performed on the CSD, version 4.6, together with the calculation of the structural parameters. No limitations were set on *R* but the estimated standard deviations (e.s.d.s) were taken into account, multiplied by a factor of 1.5, according to ref. 14; structures with no e.s.d.s were disregarded, as were those with disorder at the metal centre and those refined from X-ray powder diffraction experiments. In cases where a structure had been refined two or more times, only the results of the best refinement (with the lowest *R* factor) were used. Where the crystal structure had been studied by both X-ray and neutron diffraction, the two results were considered independently when calculating the average bond dimensions. A total of 409 structures are considered: 240 calcium(II) (290 crystallographically independent Ca^{2+} cations) and 169 magnesium(II) compounds (215 crystallographically independent Mg^{2+} cations).

All the mean values were obtained using the semi-weighted mathematical model described in ref. 15. The semi-weighted mean value $\langle x \rangle$ is then given by equation (1) where the weights

$$\langle x \rangle = (\Sigma w_i x_i / \Sigma w_i) \qquad (1)$$

w_i are obtained as in (2), where $\sigma(x_i)$ are the e.s.d.s, and σ^2 is

$$w_i = 1/[\sigma^2 + \sigma(x_i)^2] \qquad (2)$$

calculated as in (3) where $\langle x_u \rangle$ is the unweighted mean of the *n*

$$\sigma^2 = [\Sigma(x_i - \langle x_u \rangle)^2/(n-1)] - \Sigma\sigma(x_i)^2/n \qquad (3)$$

observations x_i [equation (4)]. The standard error on $\langle x \rangle$,

$$\langle x_u \rangle = \Sigma x_i/n \qquad (4)$$

$$\sigma(\langle x \rangle) = (1/\Sigma w_i)^{\frac{1}{2}} \qquad (5)$$

$\sigma(\langle x \rangle)$, was estimated as in equation (5).

In order to search for analytical dependences of one variable on another, least-squares fits were carried out by considering the

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† *Supplementary data available* (No. SUP 56952, 14 pp.): full references for complexes studied. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

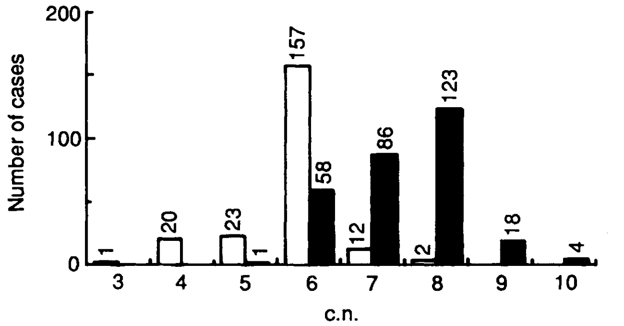


Fig. 1 Frequency distribution of c.n. for calcium(II) (■) and magnesium(II) (□) complexes

eventual errors in all the variables. When only the independent variable (y) was affected by estimated errors, each observation y_i was weighted according to equation (6) where $\sigma(y_i)^2$ is the

$$w_i = 1/\sigma(y_i)^2 \qquad (6)$$

estimated variance of y_i. Only simple linear regressions were performed when both the dependent and independent variables were affected by estimated errors. In those cases an iterative procedure was adopted.[16] Given the fitted line from equation (7) the sum of the squares, s of the deviations of the measured

$$y = a + bx \qquad (7)$$

point from this line is given as in equation (8) where $\sigma(x_i)^2$ and

$$s = \Sigma\{(y_i - a - bx_i)^2/[\sigma(y_i)^2 + b^2\sigma(x_i)^2]\} \qquad (8)$$

$\sigma(y_i)^2$ are the estimated variances of x_i and y_i. The sum s is minimized with respect to a and b in the numerator, keeping b constant as the denominator. By substituting the new b value for the old one the process is reiterated until convergence is obtained. In all cases the t-test described in ref. 17 was adopted for testing the slope parameters.

Results and Discussion

Co-ordination Numbers.—While in a d metal co-ordination compound the co-ordination number (c.n.), defined as the number of 'nearest-neighbours' of the given central atom, is easily determined by simple inspection of the molecular structure, in compounds of the alkali-, alkaline-earth and lanthanoid metals the number of 'nearest-neighbours' is often ambiguous. Therefore considerable efforts have been made to propose rigorous definitions of c.n.[18] However, in spite of numerous attempts to devise systematic definitions, the assignment of c.n. is often still a matter of individual judgement, and for simplicity we have used the assignments of the original authors. Although this procedure could seem incorrect, as in principle it would have been better to ensure a uniform definition of c.n. to all the metal complexes, we believe that it is unlikely to introduce a statistical bias into the analysis. This is supported by Brown,[19] who indicated that the average cation c.n. is only slightly affected by the way the numbers are estimated.

Fig. 1 shows the frequency of occurrence of each c.n. for both calcium(II) and magnesium(II). It appears that while magnesium(II) is strictly confined to a c.n. of 6, calcium(II) co-ordination numbers are in the range 6–8. A certain number of magnesium(II) compounds have c.n. = 4 and 5; in particular, c.n. = 4 is often found for Grignard compounds [*e.g.* in $MgBrEt(Et_2O)_2$[20]] and c.n. = 5 is observed only where the preorganization of the ligands forces the cation to adopt a particular stereochemistry {*e.g.* [Mg(tmdbtd)(thf)][21] (H_2tmdbtd = 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecine, thf = tetrahydrofuran}. The uncommon stereochemical requirements of the ligands also account for the few cases where c.n. = 3, 7 and 8 {*e.g.* $[Mg(OC_6H_3Bu^t{}_2\text{-}2,6)_2]$[22] with c.n. = 3, $[Mg(15\text{-crown-}5)(NCS)_2]$[23] (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane) with c.n. = 7 and $[Mg(dhoc)(H_2O)][ClO_4]_2$[24] {dhoc = *rel*-(6*R*,11*S*,17*R*,22*S*)-6,7,8,9,10,11,17,18,19,20,21,22-dodecahydro-1,5,12,16,23,26,29-heptaoxa[$7^{3,14}$][5.5]orthocyclophane} with c.n. = 8. In contrast, for calcium(II) there are at least three very frequent co-ordination numbers (6, 7 and 8), one quite uncommon (9), with very few cases of c.n. = 5 or 10 reported. As for magnesium, the uncommon numbers are adopted only when the ligands have peculiar steric requirements {steric hindrance or highly preorganized geometry, as in $[Ca(OC_6H_2MeBu^t{}_2\text{-}4,2,6)_2(thf)_3]$[25] with c.n. = 5 or $Ca(tech)_3(H_2O)(ClO_4)_2$[26] (tech = 1,2;3,4;5,6-triepoxycyclohexane) with c.n. = 10}. It appears then that calcium(II) is far more flexible than magnesium(II) which is particularly evident when considering the homoleptic aqua complexes (referred to as aqua ions). While all the crystallographically determined magnesium(II) aqua ions are six-co-ordinated, calcium(II) forms six-, seven-, eight- and nine-co-ordinated aqua ions.

The average observed co-ordination numbers (ref. 19) are 7.24 and 5.72 for calcium(II) and magnesium(II) respectively, and agree quite well with the analogous values reported by Brown[19] (7.31 and 5.98 for co-ordination to anions of the second period; 6.7 and 6.0 for co-ordination to anions of periods 3–5) and by Nord and Kierkegaard[27] (7.48 and 5.93 for co-ordination to anions of the second period), although these authors analysed a data set different from ours. This confirms our previous hypothesis that it is not of fundamental importance which way the c.n. is defined when large numbers of metal centres are compared. It also appears that the frequency of occurrence of c.n. is not closely related to the type of ligands surrounding the metal centre, but it depends mainly, if not completely, on the properties of each metal ion.

For c.n. = 6, which is the only number common to both calcium(II) and magnesium(II), and whose stereochemistry has attracted wide attention,[28] there are no particular differences between the two cations. By considering either the metal-centred angles or the bond lengths around the metal centre, all the six-co-ordinated complexes examined are observed to be nearly regular octahedra, with very little distortion towards the alternative trigonal-prismatic or the elongated or compressed tetragonal-bipyramidal limiting geometries.

Dimensions of the Co-ordinative Bonds.—Ionic radii for Mg^{2+} and Ca^{2+} range between 0.57 and 0.89 Å and between 0.94 and 1.34 Å respectively,[29] indicating that Ca^{2+} is always bigger than Mg^{2+}; however, the exact extent of the difference between their ionic radii is vague. Recently, O'Keeffe and Brese[30] reported a simple way to estimate single bond lengths as the sum of radii, by also considering an 'electronegativity' parameter for each atom. They reported radii of 1.50 and 1.21 Å for Ca^{2+} and Mg^{2+}, identifying a precise difference between the dimensions of the two cations, but their predictions were not very accurate because many other effects (for example the role of the non-bonding repulsions, especially in cases of high c.n.) were intentionally disregarded.

Tables 1 and 2 reported the minimum, maximum, mean and median values of the calcium(II)– and magnesium(II)–ligand distances, classified by c.n. for various ligands. Only O-bonded ligands were considered, because few examples of calcium(II)– and magnesium(II)–ligand contacts are known for ligands with donor atoms other than oxygen. Statistical analyses were performed only where there were at least 10 metal–ligand distance values from at least two independent crystal structure determinations. The median values were determined as $[(n + 1)/2]$th highest value for n odd, or as the mean between the $(\frac{n}{2})$th and the $(\frac{n}{2} + 1)$th highest values for n even. The carboxylate ligands were divided into the three general categories shown in Fig. 2, *i.e.* monodentate, bidentate and α, according to Einspahr and Bugg.[31]

Table 1 Dimensions of the calcium(II)–ligand distances (O-bonded ligands)

	d/Å				Number of cases
c.n.	min.	max.	mean	median	
H_2O					
6	2.295(3)	2.662(7)	2.397(9)	2.380	97
7	2.242(2)	3.01(1)	2.480(5)	2.403	212
8	2.306(4)	2.642(8)	2.444(4)	2.434	247
9	2.41(2)	2.594(1)	2.49(2)	2.453	28
10	2.399(1)	2.423(1)			2
av.	2.242(2)	3.01(1)	2.424(3)	2.417	586
ROH					
6	2.31(1)	2.37(1)	2.326(6)	2.360	14
7	2.356(6)	2.555(2)	2.44(1)	2.440	21
8	2.247(2)	2.57(1)	2.468(7)	2.465	70
9	2.440(6)	2.631(7)			4
av.	2.247(2)	2.631(7)	2.448(6)	2.457	109
R_2O					
5	2.378(7)	2.419(7)			3
7	2.423(4)	2.82(1)			9
8	2.380(2)	2.74(1)	2.516(7)	2.509	103
9	2.487(7)	2.829(5)	2.67(3)	2.651	18
av.	2.378(7)	2.829(5)	2.534(9)	2.513	133
Phosphates					
6	2.207(6)	2.430(5)	2.313(8)	2.318	48
7	2.236(5)	2.851(5)	2.43(1)	2.394	108
8	2.285(6)	3.153(5)	2.52(2)	2.486	93
9	2.364(5)	3.095(5)	2.557(7)	2.446	18
av.	2.207(6)	3.15(1)	2.44(1)	2.400	267
Carbonyls					
6	2.256(2)	2.398(1)	2.330(5)	2.328	38
7	2.26(1)	2.572(5)	2.37(2)	2.380	19
8	2.328(6)	2.600(4)	2.420(7)	2.415	74
av.	2.256(2)	2.600(4)	2.386(6)	2.382	131
RCO_2^- (monodentate)					
6	2.25(2)	2.48(1)	2.231(7)	2.311	75
7	2.270(4)	2.526(6)	2.394(6)	2.380	99
8	2.24(1)	3.076(3)	2.42(2)	2.386	128
9	2.365(5)	2.475(7)			2
av.	2.22(1)	3.076(3)	2.388(7)	2.362	304
RCO_2^- (α)					
7	2.214(2)	2.434(2)	2.34(1)	2.343	18
8	2.323(3)	2.540(2)	2.420(6)	2.149	71
9	2.339(7)	2.43(2)			7
av.	2.214(2)	2.540(2)	2.402(7)	2.409	96
RCO_2^- (bidentate)					
7	2.349(6)	2.72(2)	2.51(2)	2.510	28
8	2.347(2)	2.944(3)	2.51(1)	2.520	96
9	2.46(1)	2.635(5)			8
av.	2.347(2)	2.944(3)	2.53(1)	2.517	132

Table 2 Dimensions of the magnesium(II)–ligand distances (O-bonded ligands)

	d/Å				Number of cases
c.n.	min.	max.	mean	median	
H_2O					
5	2.012(6)	2.054(6)			2
6	1.998(4)	2.20(4)	2.068(1)	2.061	487
7	2.060(3)	2.139(2)			5
8	2.05(1)	2.056(9)			2
av.	1.998(4)	2.20(4)	2.068(1)	2.061	496
ROH					
6	2.069(3)	2.220(2)	2.108(11)	2.070	22
R_2O					
4	2.01(4)	2.132(1)	2.079(6)	2.063	19
5	2.04(2)	2.22(2)	2.09(2)	2.063	16
6	2.010(6)	2.52(1)	2.120(9)	2.110	78
7	2.052(2)	2.239(7)	2.17(1)	2.177	23
8	2.123(8)	2.58(1)	2.26(3)	2.236	14
av.	2.01(4)	2.58(1)	2.133(8)	2.111	150
Phosphates					
5	1.951(5)	2.455(8)	2.06(1)	2.049	56
6	1.973(7)	2.398(5)	2.098(9)	2.084	84
av.	1.951(5)	2.455(8)	2.085(8)	2.077	140
Carbonyls					
6	2.00(1)	2.172(2)	2.061(4)	2.055	84
RCO_2^- (monodentate)					
6	1.990(8)	2.118(1)	2.067(5)	2.063	42
7	2.070(2)	2.181(2)			4
av.	1.990(8)	2.181(2)	2.07(1)	2.067	46
RCO_2^- (α)					
6	2.050(2)	2.178(3)			6
7	2.078(2)	2.270(2)			4
av.	2.050(2)	2.270(2)	2.127(27)	2.084	10

It appears from Tables 1 and 2 that the metal–ligand distances increase, as expected, as the c.n. increases. Moreover, the calcium(II)–ligand bonds are nearly always larger than those of magnesium(II). There are a few exceptions where the maximum magnesium(II)–ligand bond length is larger than the minimum calcium(II)–ligand distance (ether co-ordination with c.n. = 8, phosphate co-ordination and α-carboxylate co-ordination with c.n. = 7).

However, the differences between the calcium(II)– and magnesium(II)–ligand distances are not constant. For example, the difference in mean values calculated for all the co-ordination numbers, with various ligands range from 0.402(13) for ethers through 0.359(13) for phosphates, 0.356(3) for water, 0.340(13) for alcohols, 0.325(7) for carbonyls, 0.318(12) for monodentate carboxylates to 0.275(28) Å for α carboxylates. Sterically hindered ligands, such as ethers, show the biggest differences between the calcium(II)– and the magnesium(II)–ligand distances, while ligands with low steric hindrance, such as α carboxylates, show the lowest differences. The charge on the ligands seems a less relevant factor since phosphates and carboxylates, which have a quite different charge density, show similar differences to the neutral ligands. However, the trend described above does not seem to have a simple or clear explanation. In fact, there is no apparent relation between

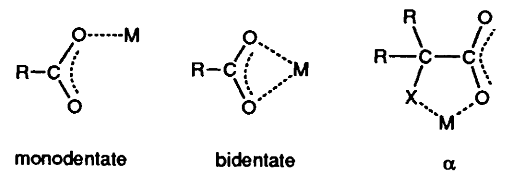


Fig. 2 Classification of the three types of carboxylate co-ordination

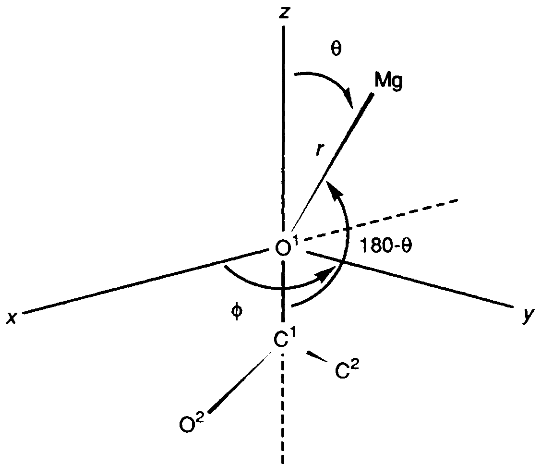


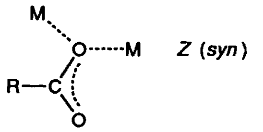
Fig. 3 Parameters describing the geometry of the carboxylate co-ordination

the mean calcium(II)– and magnesium(II)–ligand distances calculated for all the co-ordination numbers.

The calcium(II)–ligand distances are much more variable than those of magnesium(II). Considering only the mean values and not the minimum and maximum ones, it is observed from Tables 1 and 2 that while the calcium(II)–ligand bond lengths range from 2.313(8) (for phosphates, c.n. = 6) to 2.67(3) Å (for ethers, c.n. = 9), the magnesium(II)–ligand distances range only from 2.061(4) (for carbonyls) to 2.26(3) Å (for ethers, c.n. = 8). The higher variability of the calcium(II)–ligand distances [0.354(34) Å] with respect to those of magnesium(II) [0.199(40) Å] is strictly related to the different variability of c.n. since it is obvious that any given ligand can approach the metal ion more closely when the c.n. is lower.

The Carboxylato Ligand.—The stereochemical features of the interaction between calcium(II) and carboxylate groups were extensively investigated by Einspahr and Bugg[31] about 10 years ago, by considering 54 crystal structures containing 94 crystallographically independent carboxylate anions for a total of 170 calcium(II)–carboxylate contacts (some RCO$_2^-$ anions were found to bridge adjacent Ca^{2+} cations). A survey of the more recent crystallographic data shows that their conclusions are still valid. Therefore, we refer to them in order to compare the geometries of the magnesium(II)– and calcium(II)–carboxylate interactions, and only a stereochemical analysis of the magnesium(II)–carboxylate contacts is reported here. For comparison, we have adopted the same general schemes reported in ref. 31. Thus the magnesium(II)–carboxylate fragments were divided into the three general categories shown in Fig. 2. The position of the Mg^{2+} cation with respect to the carboxylate fragment is conveniently expressed in the Cartesian coordinate system shown in Fig. 3, in which one oxygen atom (O^1) is at the origin, the z axis is collinear with the C^1–O^1 bond, the carboxylate fragment is in the xz plane and the other oxygen atom (O^2) is in the $x > 0$, $z < 0$ quadrant of the xz plane. The position of each Mg^{2+} ion is identified by the spherical coordinates r, the Mg–O^1 distance, θ, the angle between the z axis and the Mg–O^1 vector, and φ, the angle between the x axis and the projection of the Mg–O^1 vector into the xy plane (measured in the counter-clockwise direction about z).

The stereochemistry of the interaction between carboxylates and cations has been widely studied in recent years, mainly because of its importance in protein function–structure analysis. In particular, attention has been focused on which (*Z* or *syn*, and *E* or *anti*) is the most stable conformation for monodentate carboxylates. Gandour[32] noted that hydrogen bonds in proteins occur preferentially with *syn* orientation to the carboxylate moieties of aspartate and glutamate. Chakrabarti[33] observed that both *syn* and *anti* co-ordination of metal ions occur in proteins, and suggested that the *syn* co-ordination prevails because of the positions of the water molecules bridging the metal and the non-co-ordinated carboxylate oxygen atom. For small molecules, *syn*- and *anti*-co-ordination are equally frequent for the data examined by Einspahr and Bugg[31] for calcium(II). On the basis of a data set smaller than that examined in ref. 31 and in the present paper, Glusker and co-workers[34] reached the same conclusion for small molecules of calcium(II) and magnesium(II), but they found that in protein structures, *syn*-co-ordination is more common for most cations. The general preference for *syn* co-ordination has also been justified theoretically[35] and experimentally on small model compounds,[36] but some doubts still remain concerning this point.[37] Some attention has been given to the other possible co-ordinative geometries of metal–carboxylate interactions. In protein structures,[33] few cases of bidentate carboxylates chelating a metal ion have been observed, and the four-membered chelate rings involve Ca^{2+} or Zn^{2+} cations and are generally quite distorted (the two metal–oxygen distances are often very different). In small molecule structures,[34] bidentate carboxylates chelating a metal ion are less uncommon, especially when the metal–oxygen distances are in the range 2.3–2.6 Å, allowing reasonably large O–M–O angles (the bite size of the carboxylate group, which is quite strictly fixed at 2.2 Å, prevents bidentate co-ordination to smaller metal ions). α Co-ordination of carboxylates to metal ions is of course common in protein structures,[33] but no extensive studies on small molecules have been carried out, except for those of Einspahr and Bugg who found quite a large number of calcium(II)–α-carboxylate interactions.



In the literature we found 22 crystallographically independent carboxylate groups bound to 14 crystallographically independent Mg^{2+} ions in 12 structural studies. Twelve of these contacts can be classified as monodentate and 10 as α (according to the method of ref. 31). As in the case of the calcium(II)–carboxylate interactions, some RCO$_2^-$ groups bridge adjacent Mg^{2+} cations. No cases of bidentate co-ordination are found. Except for one case of seven-co-ordination, all the Mg^{2+} ions are six-co-ordinated. As seen above, for both c.n. = 6 or 7, the magnesium(II) ion is considerably smaller than calcium(II): the magnesium(II)–carboxylate oxygen distances are in the range 1.990(8)–2.270(2) Å, while those for calcium(II) are between 2.214(12) and 3.076(3) Å. Within these ranges it is reasonable to suppose that a four-membered chelate ring formed by bidentate co-ordination of the carboxylate group would be very strained for magnesium(II), but not for calcium(II).[34]

The C^1–O^1, C^1–O^2 and C^1–C^2 distances are apparently normally distributed around mean values of 1.253(8), 1.256(8) and 1.516(13) Å respectively; the same applies to the O^1–C^1–O^2, O^1–C^1–C^2 and O^2–C^1–C^2 angles, with mean values of 124.1(2), 118.9(3) and 117.0(4)° respectively. These values compare well with those observed in calcium(II)-bound carboxylates.[31] All

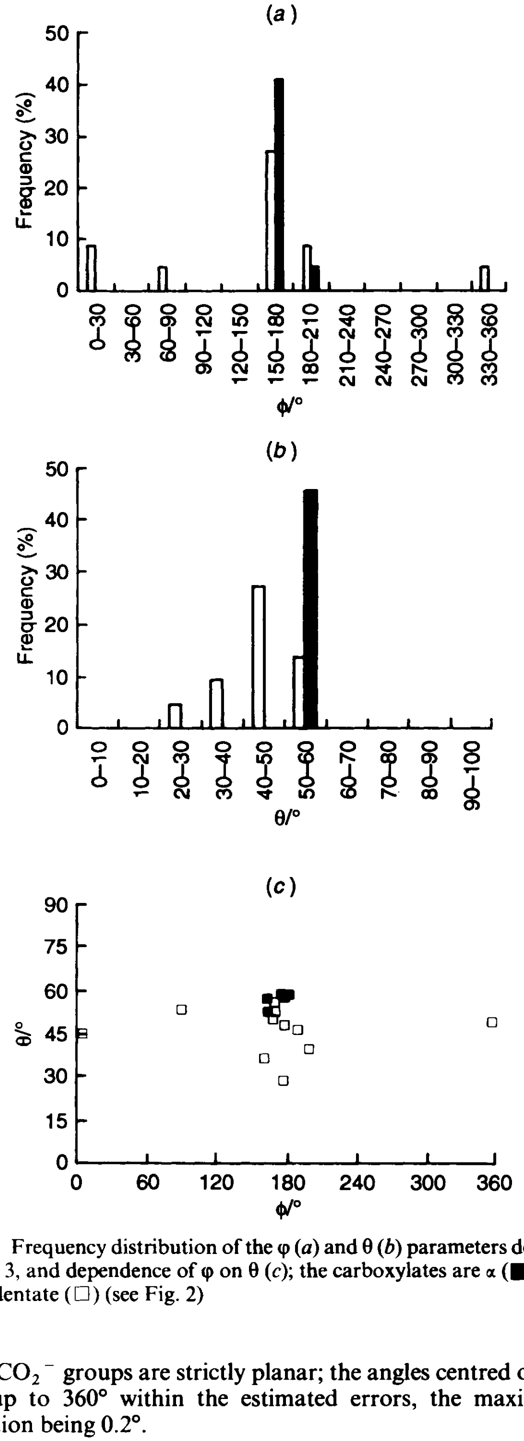


Fig. 4 Frequency distribution of the φ (*a*) and θ (*b*) parameters defined in Fig. 3, and dependence of φ on θ (*c*); the carboxylates are α (■) and monodentate (□) (see Fig. 2)

the RCO_2^- groups are strictly planar; the angles centred on C^1 add up to 360° within the estimated errors, the maximum deviation being 0.2°.

Fig. 4 shows the distribution of the θ and φ values. It appears [Fig. 4(*a*)] that the φ angles are generally near 0, 180 or 360°, which means that the Mg^{2+} cations tend to lie on the carboxylate plane. In most cases $\varphi = 180°$, corresponding to *anti* co-ordination of the Mg^{2+} ion to the carboxylate. While this particular geometry is obviously imposed in the case of the α co-ordination, it is surprising that it prevails in monodentate carboxylates. In fact, as reported above, it is generally thought that *syn* co-ordination is energetically more stable. Moreover, for calcium(II)–carboxylate interactions, no strict preference for *syn* or *anti* co-ordination was observed. It is not clear why *anti* is more frequent than *syn* co-ordination in magnesium(II) complexes. Admittedly the number of cases considered is quite small, but it is also reasonable to suppose that for monodentate carboxylates the energy difference between *syn* and *anti* co-ordination is more significant if the metal ion has more directed orbitals; for highly ionic metals, such as Ca^{2+} and Mg^{2+}, this energy difference is less important. The θ angles [Fig. 4(*b*)] are grouped between 50 and 60° for α, and between 30 and 60° for monodentate carboxylates. As expected, the α carboxylate–magnesium(II) interactions are geometrically more constrained than those involving monodentate carboxylates. However, for both interactions, the magnesium(II) ions show a clear tendency to be directed towards the O^1 lone pairs. In particular, no Mg–O^1 vectors collinear with the C^1–O^1 bond are known. Fig. 4(*c*), which illustrates the dependence of the θ values on those of φ, shows another feature not apparent from the histograms of Fig. 4(*a*) and 4(*b*). It appears that the θ values, *i.e.* the Mg–O^1–C^1 angles, vary considerably more for the Mg^{2+} ions *anti* co-ordinated ($\varphi = 180°$) to monodentate carboxylates than for Mg^{2+} ions *syn* co-ordinated ($\varphi = 0$ or 360°) and for Mg^{2+} ions co-ordinated to α carboxylates. If higher rigidity for α co-ordination is expected, the higher flexibility of *anti* co-ordination with respect to *syn* co-ordination is not. It is reasonable to suppose that although *syn*- and *anti*-co-ordinated carboxylates have quite similar energies, the former cannot be distorted as easily as the latter as a result of the slightly higher basicity of the *syn* O^1 lone pair.

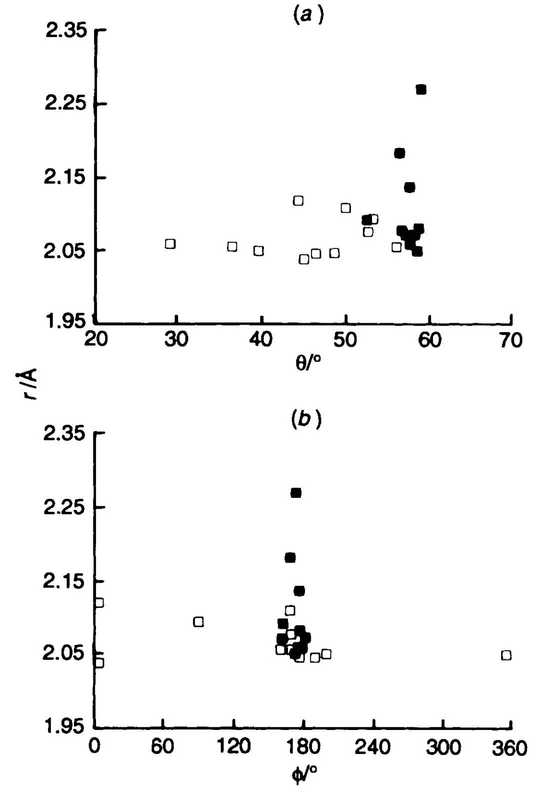


Fig. 5 Dependence of *r* on θ (*a*) and on φ (*b*); *r*, θ and φ are defined in Fig. 3; the carboxylates are α (■) and monodentate (□) (see Fig. 2)

Finally, the geometry of the magnesium(II)–carboxylate interactions can be summarized thus: (*i*) the Mg^{2+} cation tends to lie on the carboxylate plane and (*ii*) it is generally oriented towards the oxygen lone pairs. Similar features are observed in the calcium(II)–carboxylate interactions. However, while in the latter φ values intermediate between 0, 180 and 360° are also quite common, the Mg^{2+} cations are much more constrained to the carboxylate plane. Moreover, for calcium(II) the θ values are quite spread out in the range 0–90° [bidentate carboxylates which do not occur for magnesium(II) are disregarded], while the Mg^{2+} cations are much more constrained to be directed towards the O^1 lone pairs.

Another feature which differentiates the magnesium(II)– and calcium(II)–carboxylate interactions is the dependence of the metal–oxygen distance, *r*, on the θ and φ angles. Fig. 5(*a*) shows

Table 3 Valence bond parameters for calcium(II) and magnesium(II) aqua ion

Cation	c.n.	r_0/Å	N
Ca^{2+}	6	1.957(5)	5.92(21)
Ca^{2+}	7	1.940(5)	5.88(6)
Ca^{2+}	8	1.967(6)	6.02(7)
Ca^{2+}	9	1.964(14)	6.11(13)
Ca^{2+}	All	1.956(5)	5.99(5)
Mg^{2+}	6	1.661(2)	5.03(1)

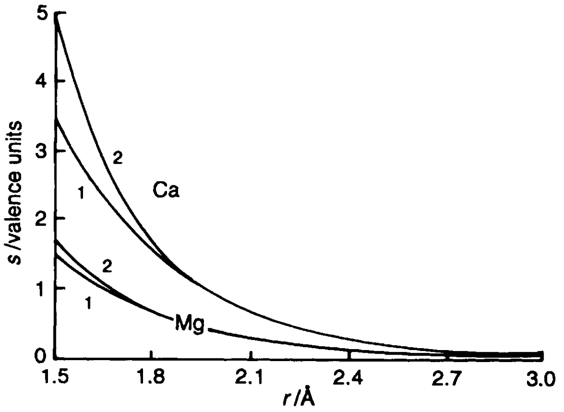


Fig. 6 Dependence of the bond strength on the bond length; 1, equation (9); 2, equation (10)

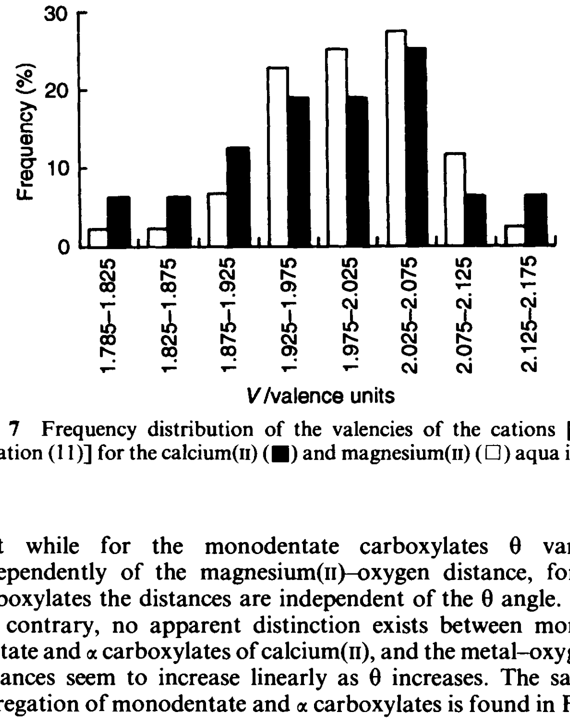


Fig. 7 Frequency distribution of the valencies of the cations [see equation (11)] for the calcium(II) (■) and magnesium(II) (□) aqua ions

that while for the monodentate carboxylates θ varies independently of the magnesium(II)–oxygen distance, for α carboxylates the distances are independent of the θ angle. On the contrary, no apparent distinction exists between monodentate and α carboxylates of calcium(II), and the metal–oxygen distances seem to increase linearly as θ increases. The same segregation of monodentate and α carboxylates is found in Fig. 5(*b*), where it appears that, while for monodentate carboxylates φ can switch between 0, 180 and 360° independently of the magnesium(II)–oxygen distance, the α-carboxylate distances are independent of φ. These observations suggest that α carboxylates can fix the position of the Mg^{2+} cation with respect to the RCO_2^- fragment more strictly than the Ca^{2+} ion, with the variability of the *r* vector moduli being dependent mainly on the supplementary donor atom (X in Fig. 2). For monodentate carboxylates, the weak dependence of the magnesium(II)–oxygen distances upon φ or θ does not compare with the apparent dependence of the calcium(II)–oxygen distances on θ; this could result from the fact that while the magnesium(II) compounds examined have co-ordination numbers of only 6 and 7, the calcium(II) complexes range from c.n. = 6 to 10.

Higher Calcium(II) *Flexibility: the Importance of the First Co-ordination Sphere*.—The above discussion shows that the calcium(II) c.n., the calcium(II)–ligand bond lengths and the geometry of the interaction between calcium(II) and carboxylates are much more variable that those of magnesium(II), the reasons for which can depend on many factors. The more obvious explanations are (*i*) that the metal–ligand co-ordinative bonds are qualitatively different in Ca^{2+} and Mg^{2+}, or (*ii*) that the effects of the surrounding on the ligands constituting the first co-ordination sphere are different for the two cations. In the next two sections, these two possible explanations will be examined.

One of the easiest ways to compare the metal–ligand bond characters of the metal cations is to examine these bonds on the basis of the valence bond theory.[30,38] Of the various mathematical formalisms of this theory, we adopted the following [equations (9) and (10)], where *s* is the bond valence, *r*

$$s = \exp[(r_0 - r)/b] \tag{9}$$

$$s = (r/r_0)^{-N} \tag{10}$$

is the bond length, r_0 is the length of a single bond, *b* is commonly taken to be a 'universal' constant of 0.37 Å, and *N* is another constant which determines the slope of the curve [equation (10)]. The bond valencies around a given metal centre, s_i, of course add up to the valence, *V*, of the metal centre [equation (11)] which, in the case of calcium(II) and magnesium(II) is +2.

$$V = \Sigma s_i \tag{11}$$

Equations (9) and (10) were used for calculating valence bond parameters of aqua ions, which are the only statistically representative class of calcium(II) and magnesium(II) homoleptic complexes for which the valences, *s*, can be foreseen from the c.n. As reported above, all the crystallographically determined magnesium(II) aqua ions are six-co-ordinate (59 cases), while those of calcium(II) can be six- (2 cases), seven- (6 cases), eight- (8 cases) or nine-co-ordinate (3 cases). This is probably not a coincidence due to some peculiarity of the solid-state behaviour of water as a ligand, since it agrees with the general pattern of the c.n. distribution (see Fig. 1) and with the c.n. assignments for the aqua ions in solution.[39] Equation (9) was converted to the logarithmic form (12) and the value of r_0

$$r_0 = r + b \cdot \ln s \tag{12}$$

obtained was inserted into the logarithmic form of equation (10) [equation (13)] in order to calculate *N*. The logarithmic

$$\ln s = -N \cdot \ln R + \ln r_0^{N} \tag{13}$$

equation was used since the variability of *r* is not significant enough in magnesium(II) complexes to avoid their being indeterminate.

The calculated values of r_0 and *N* are reported in Table 3, together with their estimated standard deviations. Fig. 6 shows the curves derived from equations (9) and (10) for Ca^{2+} and Mg^{2+} (in the case of Ca^{2+} the r_0 and *N* values refer to all co-ordination numbers). Fig. 7 shows the frequency distribution of the valence values, *V* [see equation (11)], of each metal centre, calculated from equations (9) and (10).

From the data in Table 3, it appears that as expected, both the length of a single bond, r_0, and the slope parameter of equation (10), *N*, are nearly constant for all the co-ordination numbers for calcium aqua ions. This suggests that the procedure used to fit equations (9) and (10) has been successful. The accuracy of

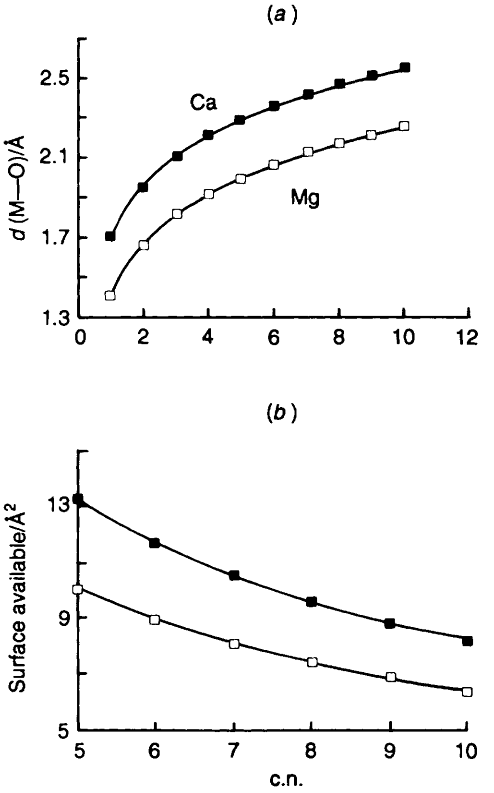


Fig. 8 Dependence of the metal–water distances calculated from equation (9) on the c.n. (*a*), and dependence of the surface available for each water molecule on c.n. (*b*)

the valence bond parameters reported in Table 3 may be checked independently, using equation (12) to give the valence of each metal centre, which has to be +2. The histogram in Fig. 7 confirms the quality of the results of our analysis, since most values are close to $V = +2$ and few deviate by more than 0.1 from the expected value. Finally, it is also noteworthy that the curves obtained from equations (9) and (10) (Fig. 6) are nearly superimposable, at least for metal–ligand distances higher than 2 Å (*i.e.* for chemically reasonable co-ordinative bonds).

The data in Table 3 show that for a hypothetical single bond, the calcium(II)–water bond would be 0.295(5) Å longer than for magnesium(II). This value is smaller than the difference observed between the mean values of the metal–ligand bond lengths reported above, which range between 0.275(28) and 0.402(13) Å, but compares well with the difference between the radii of Ca^{2+} and Mg^{2+} (1.50 and 1.21 Å respectively) calculated by O'Keeffe and Brese.[30] This is not surprising since the valence bond parametrization uses a model where an individual metal–ligand bond is examined, while the experimental data in Tables 1 and 2 refer to complexes and not to hypothetical diatomic molecules. Our results thus confirm the previous evaluations of the dimensions of the calcium(II) and magnesium(II) ions. From Table 3 it can also be seen that the constant N is significantly higher for calcium(II). Consequently, the curves in Fig. 6 are steeper for Ca^{2+} than for Mg^{2+}, *i.e.* the metal–water bond strength is more dependent on the bond distance for calcium(II). This seems in contrast to the calcium(II) c.n. and the calcium(II)–ligand distances being considerably more variable than those of magnesium(II). In fact, in order to increase the c.n., the metal–ligand distance must also increase, with a consequent more dramatic decrease in the calcium(II)–ligand bond strength compared to magnesium(II). Therefore, factors other than the individual metal–ligand bond strengths must account for the higher variability of calcium(II). It is reasonable, for example, to suppose that ligand–ligand repulsions play an important role. Fig. 8(*a*) shows the dependence of the calculated metal–ligand distances [equation (9) or (10)] on the c.n., and Fig. 8(*b*) shows, for each c.n., the area available for each water ligand on a hypothetical sphere with a radius equal to the calculated metal–water distance. The calculated co-ordinative bond distances [Fig. 8(*a*)] agree well with the values reported in Tables 1 and 2 for metal–water bonds. It can be seen from Fig. 8(*b*) that the surface a water molecule can occupy on the sphere corresponding to $[Mg(H_2O)_6]^{2+}$ (8.96 Å^2) is close to that which the same ligand can occupy on $[Ca(H_2O)_9]^{2+}$ (8.83 Å^2). No seven-co-ordinated magnesium(II) or ten-co-ordinated calcium(II) aqua ions are known, in which each water ligand would occupy nearly the same space (8.10 and 8.18 Å^2 respectively). It seems that the crowding within the first co-ordination sphere is lower for higher calcium(II) co-ordination. Therefore, the greater energy loss corresponding to the lengthening of the calcium(II)–water bonds, compared to that for the lengthening of the magnesium(II)–water bonds, is balanced by a lower increase in ligand–ligand repulsions.

However, the importance of the ligand–ligand repulsions does not imply that the different dependencies of the calcium(II)– and magnesium(II)–water bond strengths on the metal–ligand distance is unimportant in determining c.n. In fact, Fig. 8(*b*) shows that in an hypothetical five-co-ordinated magnesium(II) aqua ion, the area available to each ligand on the sphere of radius 2.000 Å (10.05 Å^2) would be intermediate between those of seven- and eight-co-ordinated calcium(II) aqua ions (9.58 and 10.51 Å^2 respectively). The fact that seven- and eight-co-ordinated calcium(II) aqua ions have been reported while no five-co-ordinated magnesium(II) aqua ions are known, indicates that a 'co-ordinatively unsaturated' calcium(II) complex is relatively less unstable than an 'unsaturated' magnesium(II) complex. The greater increase of the calcium(II)–water bond strength compared to magnesium(II) on shortening the metal–water bond can account for the higher stability of the 'co-ordinatively unsaturated' calcium(II) complexes.

Finally, either a low (6) or high (9) c.n. is possible for Ca^{2+}, because the former results in very strong co-ordinative bonds and the latter in no dramatic steric hindrance between the ligands. In the case of Mg^{2+}, only c.n. = 6 is common, as a higher c.n. would give high ligand–ligand repulsions and a lower c.n. would not result in a considerable strengthening of the co-ordinative bonds.

Higher Calcium(II) *Flexibility: the Importance of the Second Co-ordination Sphere*.—In the above discussion the higher variability of calcium(II) is explained to some extent by applying the valence bond theory to the metal–ligand bonds. However, a sound explanation of the different behaviour of Ca^{2+} and Mg^{2+} cannot be reached by considering only the features of the first co-ordination sphere, *i.e.*, that a calcium(II) aqua ion is just a calcium(II) cation surrounded by water molecules; this would give rise to a unique complex, with a well defined c.n. and metal–ligand bond distances. On the contrary, the c.n. of calcium(II) aqua ions is variable. It is possible that the second co-ordination sphere is also important. This may be examined by considering again the aqua ions of calcium(II) and magnesium(II), in which the first co-ordination sphere is very homogeneous, apart from the variability of c.n. This allows the evaluation of the importance of the second co-ordination sphere while keeping the first co-ordination sphere 'constant'. Attention was limited to the hydrogen-bonding networks linking the water molecules co-ordinated to the metal to the surroundings. For hexaaquamagnesium(II) cations, the hydrogen-bonding patterns are very variable, ranging from the frequent case in which both hydrogen atoms of each water molecule interact with two different hydrogen-acceptor atoms {*e.g.* $[Mg(H_2O)_6][O_2CH{=}CHCO_2H]_2$[40]}, to that in which the hexaaqua cation is confined in a sort of cage by extended anions {*e.g.* $[Mg(H_2O)_6][Zn_2Br_6]$[41]}, or where no strong hydrogen bonds are formed because of the absence of suitable surrounding hydrogen acceptors {*e.g.* $[Mg(H_2O)_6]I_8$[42]}. In calcium(II) aqua ions, the variability of the hydrogen-bonding pattern within the

Table 4 Bond lengths (d/Å) in calcium(II) and magnesium(II) aqua ions

Cation	c.n.	d_1[a]	d_2(O)[b]	d_2(N)[b]	d_2(Cl)[b]	d_2(Br)[b]
Mg^{2+}	6	2.066(2)	2.784(6)	2.884(21)	3.252(2)	3.442(10)
Ca^{2+}	6	2.334(9)	2.816(29)	2.822(9)	—	3.291(7)
Ca^{2+}	7	2.403(5)	3.046(7)	2.914(2)	3.370(13)	3.561(20)
Ca^{2+}	8	2.481(6)	2.852(4)	—	3.309(4)	3.369(8)
Ca^{2+}	9	2.521(4)	—	—	3.210(1)	—
Ca^{2+}	All	2.453(7)	2.953(6)	2.805(8)	3.319(3)	3.427(19)

[a] d_1 = Mean metal–water distance. [b] d_2(X) = Mean distance between the water oxygen atom co-ordinated to the metal centre and the atom X in the second co-ordination sphere.

second co-ordination sphere is even more evident than in magnesium; in addition to complexes similar to those above, where an aqua ion is surrounded by extended anions in a cage-like manner {see *e.g.* $[Ca(H_2O)_7][Cd_2Br_6]$[43]} or surrounded only by poor hydrogen acceptors (*e.g.* $CaI_2 \cdot 6.5H_2O$[44]), there are cases of dimeric aqua ions with water molecules bridging two different calcium(II) ions (*e.g.* $CaCl_2 \cdot 6H_2O$[45]).

Table 4 reports the mean values of all the metal–oxygen or hydrogen bond lengths. It appears that while the first co-ordination sphere of calcium(II) is larger than that of magnesium, in the second co-ordination sphere the differences between calcium(II) and magnesium(II) show an irregular trend. While the mean $Mg(H_2O)_6 \cdots O$ distances are statistically identical to those of $Ca(H_2O)_6 \cdots O$ [2.784(6) and 2.816(29) Å respectively; Cruickshank t test = 1.081[46]], the mean contacts $Mg(H_2O)_6 \cdots N$ and $Mg(H_2O)_6 \cdots Br$ are statistically longer than $Ca(H_2O)_6 \cdots N$ and $Ca(H_2O)_6 \cdots Br$ [$M(H_2O)_6 \cdots N$ is 2.884(21) for magnesium(II) and 2.822(9) Å for calcium; t test = 2.714; $M(H_2O)_6 \cdots Br$ is 3.442(10) for magnesium(II) and 3.291(7) Å for calcium; t test = 12.370]. This suggests that the acidity of the water molecules co-ordinated to calcium(II) is not less (in the case of oxygenated surrounding molecules) or even greater (in the case of surrounding solvating units carrying nitrogen or bromide) than that of the water molecules co-ordinated to magnesium, with constant c.n. Another way of appreciating this is to observe that the contacts $Mg(H_2O)_6 \cdots X$ are intermediate between $Ca(H_2O)_6 \cdots X$ and $Ca(H_2O)_7 \cdots X$ for X = N or Br. It is noteworthy that the differences in the second co-ordination sphere of calcium(II) and magnesium(II) will probably not be seen in solution studies, because more than one c.n. is expected to be present at equilibrium, at least for calcium;[39] consequently the observed second co-ordination sphere will be an average of numerous possibilities. Here it is observed that, in effect, the mean $Mg(H_2O)_6 \cdots N$ distance is statistically identical to $Ca(H_2O)_n \cdots N$ (n = 6–8; t test = 0.380) and the mean $Mg(H_2O)_6 \cdots Br$ distance is statistically identical to the mean $Ca(H_2O)_n \cdots Br$ distance (n = 6,7,9; t test = 0.699).

All attempts to find a dependence of the bond distances in the second co-ordination sphere on the bond distances in the first co-ordination sphere failed. Although good correlation coefficients were obtained ($r > 0.85$) for models of simple linear regression relating the two variables by considering both their estimated standard deviations,[16] the linear dependence between the two variables was shown to be statistically meaningless on the basis of the t test of ref. 17.

It is interesting that when there are no good hydrogen acceptors in the second co-ordination sphere {for example iodide, as in $CaI_2 \cdot 6.5H_2O$[44] or $[Ca(H_2O)_8][HgI_4]$[47]}, the calcium(II) ion tends to adopt eight-co-ordination. This suggests that c.n. = 8 is intrinsically preferred by calcium(II) aqua ions; as c.n. = 8 is also most common for all the calcium(II) complexes studied here it can reasonably be concluded that this is the c.n. required by the cation and that other co-ordination numbers are imposed by the ligands. Given the same limitations, it is also reasonable that c.n. = 6 is preferrred for magnesium(II) and different co-ordination results from ligand requirements.

Finally the generally stronger second sphere contacts for calcium(II) compared to magnesium(II) suggest that the influence of surrounding molecules in Ca^{2+} complexes is greater than that in Mg^{2+} complexes when c.n. = 6. This could be another reason for the larger variability in the c.n. of the calcium(II) complexes.

Conclusion

The crystal structures of a large number of co-ordination compounds of calcium(II) and magnesium(II) containing a wide range of organic ligands have been studied in order to compare the co-ordinative behaviour of the two cations. At first glance, the co-ordination chemistry of Ca^{2+} and Mg^{2+} seems uniformly similar. For example, both cations form highly ionic co-ordinative bonds and show a marked preference for oxygen donor atoms. However, there are some differences, for example in co-ordination number. While Mg^{2+} is fairly strictly confined to c.n. = 6, for Ca^{2+} co-ordination numbers of 6 and 8 are readily accessible; the co-ordinative bond distances are much more variable around calcium(II) than around magnesium(II). Although the geometry of the calcium(II)– and magnesium(II)–carboxylate complexes is similar, Ca^{2+} has a significantly greater flexibility; analogous trends were observed for the co-ordination geometry of the two cations to water molecules and amides.[48]

The roles played by the first and the second co-ordination spheres in determining the greater flexibility of Ca^{2+} have been examined. For the first co-ordination sphere, a simple examination of the calcium(II)– and magnesium(II)–water co-ordinative bonds has been carried out, according to the valence bond theory. It appears that the dimension of the naked ion is actually very important in explaining the ability of Ca^{2+} to achieve very high co-ordination numbers (namely 9 or 10) without involving large ligand–ligand repulsions. For low co-ordination numbers, and c.n. = 6 is 'lower' for Ca^{2+} than for Mg^{2+}, it seems that calcium(II) co-ordinatively unsaturated complexes are less unstable than the Mg^{2+} ones, since the contraction of the co-ordinative bond distances, on lowering the c.n., gives a greater strengthening of the bonds for Ca^{2+} than for Mg^{2+}. An analysis of the second co-ordination sphere of the Ca^{2+} and Mg^{2+} aqua ions, which are complexes with a 'constant' first co-ordination sphere, shows that the hydrogen bonds between the water-co-ordinated molecules and the molecules surrounding the aqua ion tend to be stronger, at least for c.n. = 6, for Ca^{2+}. It is therefore reasonable that the higher Ca^{2+} flexibility is also due to the greater energy of the second co-ordination sphere interactions.

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