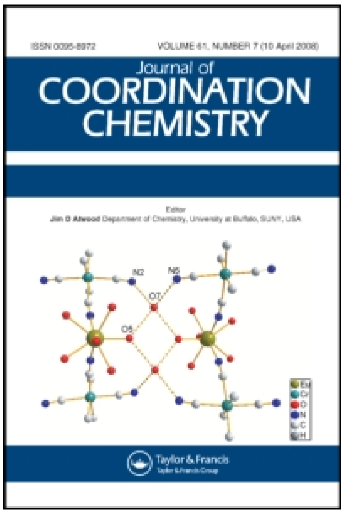

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Ullström, Ann-sofi , Warminska, Dorota and Persson, Ingmar(2005) 'The structure of dimethylsulfoxide-solvated magnesium and calcium ions in solution and the solid state, and an overview of the coordination chemistry of hydrated and solvated alkaline earth metal ions', Journal of Coordination Chemistry, 58: 7, 611 — 622

To link to this Article: DOI: 10.1080/00958970500039181

URL: http://dx.doi.org/10.1080/00958970500039181

Journal of Coordination Chemistry
Vol. 58, No. 7, 10 May 2005, 611–622

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The structure of dimethylsulfoxide-solvated magnesium and calcium ions in solution and the solid state, and an overview of the coordination chemistry of hydrated and solvated alkaline earth metal ions

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(*Received in final form 12 November 2004*)

The structures of dimethylsulfoxide-solvated magnesium and calcium ions have been studied in the solid state and in dimethylsulfoxide solution by X-ray crystallography and large-angle X-ray scattering (LAXS), respectively. The magnesium and calcium ions coordinate six dimethylsulfoxide molecules in both the solid state and solution with mean Mg–O and Ca–O bond distances in solid perchlorate salts of 2.062(4) and 2.303(5) Å, respectively. A summary of the coordination chemistry of the hydrated and solvated alkaline earth metal ions shows that beryllium(II) and magnesium ions are tetrahedral and octahedral, respectively, in all solvents studied, while calcium and strontium are eight-coordinated in square antiprismatic fashion in water, but octahedral in dimethylsulfoxide and other organic solvents. Mean M–O bond distances of the hydrated alkaline earth metal ions were used to calculate the ionic radii of the alkaline earth metal ions.

Keywords: Alkaline earth metal ions; Structure; Hydrates; Solvates; Ionic radii

1. Introduction

The structures of hydrated alkaline earth metal ions have been described for a large number of solid compounds [1,2], as well as for aqueous solutions [3,4]. Beryllium and magnesium ions display a coherent picture, being four- and six-coordinate, respectively, in all isolated hydrate complexes as well as in aqueous solution. The hydrated calcium ion presents a more scattered picture with isolated six-, seven-, eight- and nine-coordinate hydrate complexes in the solid state [1,2]. A combined structural and theoretical study has shown that the hydrated calcium ion is eight-coordinate in aqueous solution [5], while other authors claim that it is six-coordinate [3,4].

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00958970500039181

Strontium and barium ions are eight-coordinate in the isolated hydrate complexes in the solid state reported so far [1,2], and the same coordination number is observed in aqueous solution [3,4,6].

The number of structurally characterized solvated complexes of the alkaline earth metal ions, apart from the hydrates, is still fairly limited and any detailed picture of the coordination chemistry of nonaqueous solvated complexes of the alkaline earth metal ions has not yet been presented. The aim of this study was to determine the structure of dimethylsulfoxide-solvated beryllium, magnesium and calcium ions in both solution and the solid state; the structures of dimethylsulfoxide-solvated strontium and barium ions in solution have been presented in a previous study from this laboratory [6]. Another aim was to summarize current knowledge of the coordination chemistry of the hydrated and solvated alkaline earth metal ions.

2. Experimental

2.1. *Preparation of salts*

2.1.1. *Tetrakis*(dimethylsulfoxide)beryllium(II) perchlorate, $[Be(OS(CH_3)_2)_4](ClO_4)_2$. Tetraaquaberyllium(II) perchlorate, $[Be(H_2O)_4](ClO_4)_2$, was prepared by adding metallic beryllium (Koch-Light Laboratories Ltd) to dilute perchloric acid and evaporating off the excess water. The title compound was obtained by dissolving tetraaquaberyllium(II) perchlorate in 2,2-dimethoxypropane (Fluka) followed by addition of dimethylsulfoxide. The compound obtained was recrystallized from freshly distilled dimethylsulfoxide (Fluka).

2.1.2. *Hexakis*(dimethylsulfoxide)magnesium(II) perchlorate, $[Mg(OS(CH_3)_2)_6](ClO_4)_2$. Hexaaquamagnesium(II) perchlorate, $[Mg(H_2O)_6](ClO_4)_2$ (Merck), was used as purchased, and the title compound was prepared in the same way as described above for the beryllium compound.

2.1.3. *Hexakis*(dimethylsulfoxide)calcium(II) perchlorate, $[Ca(OS(CH_3)_2)_6](ClO_4)_2$. Calcium perchlorate hydrate was prepared by adding perchloric acid to calcium(II) carbonate and removing excess water. The title compound was prepared in the same way as described above for the beryllium compound.

2.1.4. Preparation of solutions. Saturated dimethylsulfoxide solutions of magnesium and calcium perchlorate were prepared by dissolving the dimethylsulfoxide solvates at 310 K, and slowly cooling the solutions to room temperature. The compositions of the solutions studied are summarized in table 1.

2.2. *Large-angle X-ray scattering measurements*

Large-angle X-ray scattering (LAXS) measurements were performed by means of a previously described θ–θ diffractometer [7] using semifocusing Bragg–Brentano geometry and Mo Kα radiation ($\lambda = 0.7107$ Å). Intensity data were collected at 450 discrete θ values in the range 1–65° corresponding to a range of 0.3–16.0 Å^{-1} of the scattering variable $s = 4\pi \sin\theta/\lambda$; the scattering angle is 2θ. At least 100 000 counts were

Table 1. Concentrations (mol dm^{-3}) of the dimethylsulfoxide (Me_2SO) solutions used in the LAXS measurements.

Sample	$[M^{2+}]$	$[ClO_4^-]$	$[Me_2SO]$	$\rho/g\,cm^{-3}$	μ/cm^{-1}
$Mg(ClO_4)_2$ in Me_2SO	0.778	1.556	13.245	1.2085	5.40
$Ca(ClO_4)_2$ in Me_2SO	0.970	1.940	12.988	1.2466	6.13

accumulated for each θ value and the angular range was scanned twice. The data analysis procedure, which was performed with the KURVLR program [8], is described in detail elsewhere [9]. The structure-sensitive part of the experimental scattered intensities, $i(s)$, obtained by subtracting the calculated structure-independent part, was converted to a radial distribution function (RDF) by a Fourier transformation procedure [7], as shown in equation (1).

$$D(r) - 4\pi r^2 \rho_o = (2r/\pi) \int_{s_{\min}}^{s_{\max}} S \cdot i(s) M(s) \sin(sr)\, ds \tag{1}$$

$M(s)$ is a modification function and ρ_o is the average bulk electronic density [8]. The experimental intensities, $i(s)$, were corrected for low frequency features by removing the spurious peaks below 1 Å in the $D(r)$ function by a Fourier backtransformation procedure [10] to obtain better alignment.

Calculated intensities for the models were obtained from the expression (2).

$$i_{\text{calc}}(s) = \sum n_{\text{pq}} f_{\text{p}} f_{\text{q}} \sin(sd_{\text{pq}})/(sd_{\text{pq}}) \exp\left(-\frac{1}{2}\sigma_{\text{pq}}^2 s^2\right) \tag{2}$$

Each term in the sum characterizes a well-defined short-range atom-pair interaction between the atoms p and q in the assumed model. The parameters are d_{pq}, the average distance within each atom-pair, σ_{pq}, the associated variation in distance in a Debye–Waller factor, $\exp(1 - \frac{1}{2}\sigma_{pq}^2 s^2)$, and n_{pq}, the frequency factor or coordination number. The scattering factors, f, were corrected for dispersion effects [8,9].

Least-squares refinements of some model parameters for the atom-pair contributions were performed by using the STEPLR program [11]. Refinements were carried out in different s-ranges to test when the influence of systematic deviations from the model functions becomes important, in particular by varying the lower s-limit below which the diffuse long-range interactions cannot be neglected. The final model calculations were made in the s-range 5.0–16.0 Å^{-1}, minimizing the function (3).

$$U(\text{s}) = \sum [si(s)_{\text{exp}} - si(s)_{\text{calc}}]^2 \tag{3}$$

Errors given in table 2 for the parameters obtained from the LAXS include only statistical errors, while errors given throughout the text include systematic errors.

2.3. *Single-crystal X-ray diffraction*

Data were collected on a Bruker SMART platform equipped with a CCD area detector and a graphite monochromator using Mo Kα ($\lambda = 0.71073$ Å) radiation [12].

Table 2. Crystallographic data for *hexakis*(dimethylsulfoxide)magnesium and calcium perchlorates determined at ambient room temperature (295 ± 1 K) in this study.

Chemical formula	$[Mg(OS(CH_3)_2)_6](ClO_4)_2$	$[Ca(OS(CH_3)_2)_6](ClO_4)_2$
M	592.53	707.75
Space group	$P\bar{1}$	Cc
a/Å	7.765(4)	20.175(3)
b/Å	10.817(6)	12.738(3)
c/Å	10.873(8)	16.274(3)
α/°	60.419(8)	
β/°	85.564(14)	128.222(4)
γ/°	84.302(10)	
V/Å^3	789.9(8)	3285.7(12)
Z	1	4
ρ_{calc}/g cm^{-3}	1.246	1.431
μ/cm^{-1}	5.72	7.86
No. of reflections	2056	3065
R_{int}	0.0352	0.0272
R indices R_1, wR_2 [$I > 2\sigma(I)$]	0.0633, 0.1545	0.0510, 0.1279
R indices R_1, wR_2 (all data)	0.0837, 0.1617	0.0606, 0.1324

$R_1 = \sum \|F_o\| - |F_c\| / \sum |F_o|$; $wR_2 = (\sum[w(F_o^2 - F_c^2)^2] / \sum[wF_o^4])^{1/2}$.

A hemisphere of data (1295 frames) was collected at 295 ± 1 K for each structure using the omega scan method (0.3° frame width). The crystal-to-detector distance was 5.0 cm. The first 50 frames were remeasured at the end of each data collection to monitor crystal and instrument stability. Intensity decay was negligible for all crystals in this study. The structures were solved by direct methods using SHELXTL [13] and refined using full-matrix least-squares techniques on F^2. Non-hydrogen atoms were treated anisotropically. The methyl hydrogen atoms were calculated in ideal positions riding on their respective carbon atom. Crystal and experimental data are summarized in table 2.

3. Results and discussion

3.1. *The dimethylsulfoxide-solvated beryllium(II) ion*

It has not been possible to solve the crystal structure of *tetrakis*(dimethylsulfoxide) beryllium(II) perchlorate as it decomposes with time in the X-ray beam. It was, however, possible to determine cell parameters for the compound ($a = 10.304(4)$, $b = 12.778(5)$, $c = 17.769(8)$ Å, $\alpha = \beta = \gamma = 90.0°$). A previously reported apparent molar volume study has shown that the beryllium(II) ion is solvated by four dimethylsulfoxide molecules in solution [14].

3.2. *The dimethylsulfoxide-solvated magnesium(II) ion*

The crystal structure of *hexakis*(dimethylsulfoxide)magnesium perchlorate is built up of $Mg(OS(CH_3)_2)_6^{2+}$ and perchlorate ions. Magnesium binds six dimethylsulfoxide molecules through their oxygen atoms in an almost regular octahedral geometry (figure 1). Mg–O distances for the three independent dimethylsulfoxide molecules are 2.045(4), 2.070(4) and 2.073(4) Å, mean 2.063 Å. Mg–O–S bond angles are 128.2(3), 133.7(2) and 143.9(2)°, typical of the hard electron-pair acceptor magnesium [15].

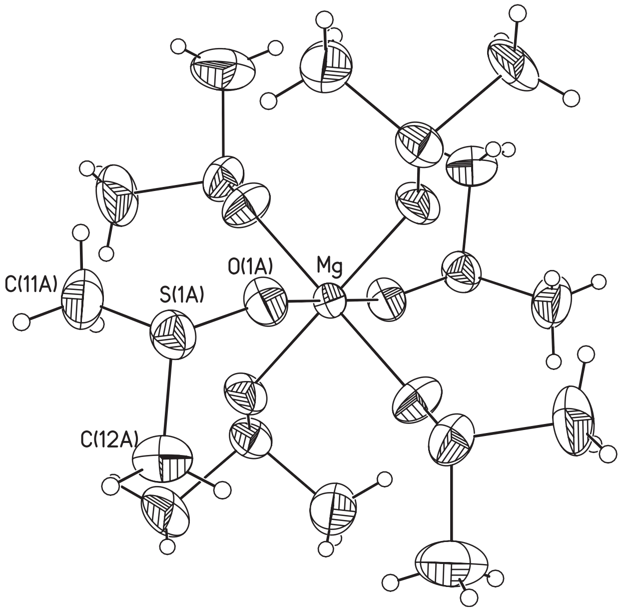


Figure 1. Molecular structure of the *hexakis*(dimethylsulfoxide)magnesium ion. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

The S(3)–O(3) bond distance is much shorter than expected for a metal-bound sulfoxide, while the other intramolecular bond distances and angles for the dimethylsulfoxide molecules lie in the expected ranges [15].

The RDF from the LAXS experiment on the dimethylsulfoxide solution of magnesium perchlorate reveals five peaks at 1.5, 1.8, 2.3, 2.7 and 3.2 Å (figure 2). Peaks at 1.5 and 2.3 Å correspond to the Cl–O bond and O···O distance in the perchlorate ion, the peaks at 1.5, 1.8, 2.3 and 2.7 Å have contributions from intra- and intermolecular distances within the dimethylsulfoxide molecule, and the peak at 3.2 Å corresponds to the Mg···S distance in the solvate complex (figure 2). The perchlorate ion is more weakly solvated in dimethylsulfoxide than in water, and the Cl–O bond distance is similar those found for isolated perchlorate ions in the solid state, with Cl–O bond distances of 1.425 Å. The contribution from the Mg–O bond distance is very small because of the weak scattering power of both magnesium and oxygen, and it was only possible to refine this distance through variation of the model parameters and visually checking the best fit in the RDF. The Mg–O bond distance was found to be 2.07(2) Å, while the Mg···S distance was refined by a least-squares procedure to 3.248(10) Å. The Mg–O bond distance and the Mg–O–S bond angle of 130(2)° are in line with values found in the solid state (tables 3 and S1).

3.3. *The dimethylsulfoxide-solvated calcium(II) ion*

The crystal structure of *hexakis*(dimethylsulfoxide)calcium perchlorate was solved in the monoclinic space group *Cc*. The structure could not be solved in a centrosymmetric alternative. The crystal appears to be a true twin, BASF = 0.5998. Analysis of the packing in this structure indicates a polar symmetry. The crystal was oriented by the longest

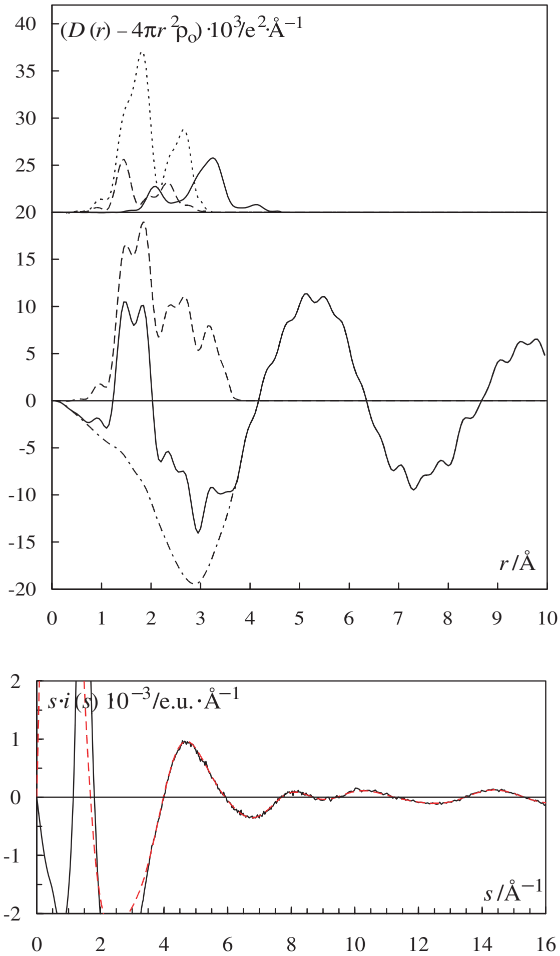


Figure 2. (*Top*) LAXS radial distribution curves for a 0.78 mol dm^{-3} dimethylsulfoxide solution of magnesium perchlorate: upper part: separate model contributions (offset: 20) of the dimethylsulfoxide-solvated magnesium ion (solid line), the perchlorate ion (dashed line) and the dimethylsulfoxide molecule (dotted line); lower part: experimental RDF: $D(r) - 4pr^2\rho_\text{o}$ (solid line); sum of model contributions (dashed line); difference (dashed–dotted line). (*Bottom*) Reduced LAXS intensity functions $s \cdot i(s)$ (solid line); model $s \cdot i_\text{calc}(s)$ (dashed line).

Table 3. Mean bond distances, *d* (Å), number of distances, *N*, temperature coefficients, *b* (Å^2), and half-height half-widths, *l* (Å), in the LAXS studies of solvated magnesium and calcium ions in dimethylsulfoxide solution at room temperature.

Species	Interaction	*N*	*d*	*b*	*l*
$Mg^{2+}(Me_2SO)$	Mg–O	6	2.07(2)	0.0050(12)	0.100(13)
	Mg···S	6	3.248(10)	0.0109(9)	0.148(7)
ClO_4^- (Me_2SO)	Cl–O	4	1.425(4)	0.0020(2)	0.063(3)
$Ca^{2+}(Me_2SO)$	Ca–O	6	2.356(6)	0.0066(18)	0.115(5)
	Ca···S	3	3.613(5)	0.0129(8)	0.161(5)
ClO_4^- (Me_2SO)	Cl–O	4	1.425(4)	0.0020(2)	0.063(3)

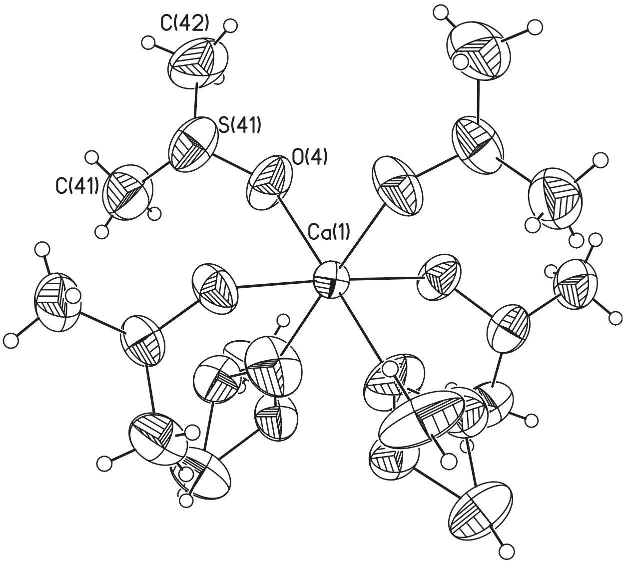
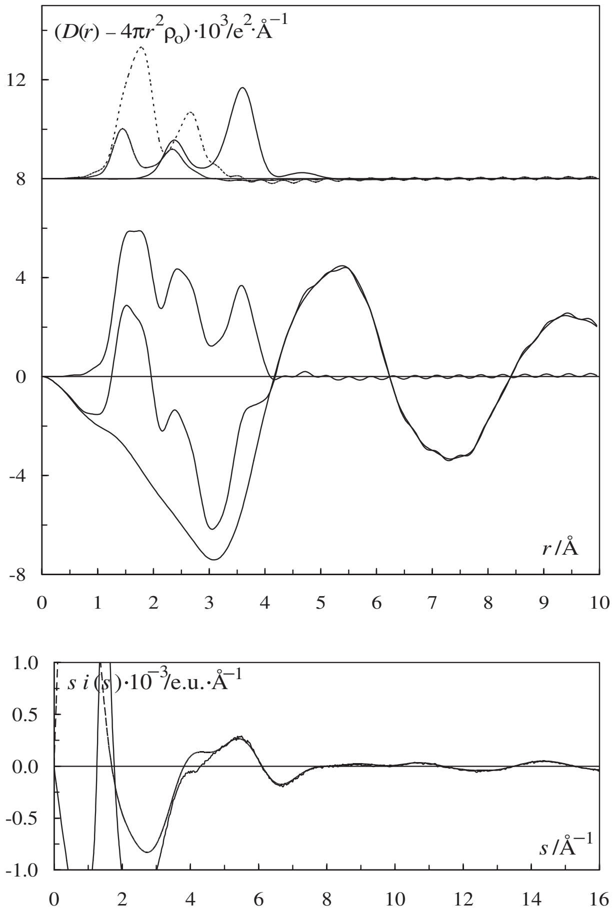


Figure 3. Molecular structure of the hexakis(dimethylsulfoxide)calcium ion. The sulfur atoms in two of the dimethylsulfoxide ligands are disordered over two positions (both are shown in the figure). Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

dimension along the *a* axis to avoid involvement of different domains in the data collection procedure. The structure is built up of $Ca(OS(CH_3)_2)_6^{2+}$ and perchlorate ions. Calcium binds six dimethylsulfoxide molecules through their oxygen atoms in a slightly distorted octahedral geometry (figure 3). The six crystallographically independent dimethylsulfoxide ligands have Ca–O bond distances in the range 2.275(6)–2.321(5) Å, mean 2.303 Å. Two of the dimethylsulfoxide molecules, labeled 1 and 6, are disordered, with sulfur atoms in two alternative positions, both of which were resolved and refined independently. The main form (68.1% and 69.7% for S1 and S6, respectively) is transformed into the other by an inversion of the sulfur atoms (figure 3). Ca–O–S bond angles in the nondistorted dimethylsulfoxide molecules are in the range 124.1(3)–129.7(3)°, mean 126.8°; the mean Ca–O–S angle of disordered molecules is much larger, 150°. Because of the disorder, some of the intermolecular bond distances and angles in the dimethylsulfoxide molecules are outside the expected range [14].

The RDF from the LAXS experiment on the dimethylsulfoxide solution of calcium perchlorate reveals two peaks at 1.5 and 2.3 Å, and two marked shoulders at 1.8 and 3.6 Å (figure 4). The peaks at 1.5 and 2.3 Å correspond to the Cl–O bond, the Ca–O bond distance in the solvate and the O···O distance in the perchlorate ion. The peaks and shoulders at 1.5, 1.8, 2.3 and 2.7 Å have contributions from intra- and intermolecular distances within the dimethylsulfoxide molecule, and the marked shoulder at 3.6 Å to the Ca···S distance in the solvate complex (figure 4). The structural parameters of the perchlorate ion are the same as for the magnesium solution discussed above. The Ca–O bond and Ca···S distances were refined by a least-squares procedure to 2.326(6) and 3.613(5) Å, respectively. The Ca–O bond distance in dimethylsulfoxide solution is slightly longer than in the solid state and the Ca–O–S bond angle of 139(2)° is somewhat larger than is found in the solid state [16,17].



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3.4. *The coordination chemistry of hydrated and solvated alkaline earth metal ions*

3.4.1. Beryllium(II). The beryllium(II) ion is very small, with an ionic radius of 0.28 Å in the tetrahedral configuration [18], and is able to accommodate a maximum of four solvent molecules/ligands in its complexes. The hydrated beryllium(II) ion has been characterized in 16 solids with a mean Be–O bond distance of 1.614 Å for slightly distorted tetrahedra [1,2]; a summary of these structures is given in table S3. A LAXS study on an aqueous solution of beryllium(II) chloride (5.3 mol kg(water)$^{-1}$) yielded a Be–O bond distance of 1.67 Å in the tetraaquaberyllium(II) ion [19]. This Be–O bond distance seems to be unrealistically long, possibly caused by the very high concentration and the low number of water molecules per solute. No dimethylsulfoxide-solvated beryllium(II) ion, or any other solvate of beryllium(II), has yet been structurally characterized.

3.4.2. Magnesium(II). A very large number of hexahydrated magnesium ions have been structurally characterized in the solid state. The average Mg–O bond distance in these hydrate structures is 2.069 Å; some 153 structures are reported with mean Mg–O bond distances in the range 2.02–2.11 Å [1,2]; a summary of these structures is given in table S4. The hydrated magnesium ion has been studied in aqueous solution giving Mg–O bond distances of 2.05, 2.094 and 2.12 Å in three different studies using LAXS techniques [20].

Hydrated magnesium ions in the solid state show, with some exceptions (see below), a somewhat distorted octahedral coordination geometry with the Mg–O bond distances normally differing by 0.03–0.10 Å between the shortest and longest, while O–Mg–O angles are often close to 90 and 180° [1,2]. The only hydrates with equidistant Mg–O bonds are $[Mg(H_2O)_6]BrO_3$, $Cs[Mg(H_2O)_6]AsO_4$, $[Mg(H_2O)_6]H_2PO_4$, $[Mg(H_2O)_6](ClO_4)_2$, $[Mg(H_2O)_6]TeBr_6$, $[Mg(H_2O)_6]TeCl_6$, $[Mg(D_2O)_6]SiF_6$, $[Mg(H_2O)_6](ClO_4)_2 \cdot (C_{10}H_{14}O_4)_3$ and $Zn_2[Mg(H_2O)_6]Br_6$ [21–28], with the first five crystallizing in cubic space groups, the next three in the trigonal space group $R\bar{3}$, and the last in an orthorhombic space group; of these, only $[Mg(H_2O)_6]BrO_3$, $[Mg(D_2O)_6]SiF_6$ and $[Mg(H_2O)_6](ClO_4)_2 \cdot (C_{10}H_{14}O_4)_3$ have mean Mg–O bond distances within the range 2.02–2.12 Å (table S4). Hexaaquamagnesium bromate is isostructural with the corresponding copper(II) compound, which has been shown to be Jahn–Teller distorted by EXAFS technique, even though the crystallographic characterization reveals a regular CuO_6 octahedron; a similar observation is made for the hydrated magnesium and copper(II) ions in the hexafluorosilicates [29]. It also seems likely that the compounds with regular octahedral hexaaquamagnesium ions indeed are somewhat distorted. Very recent infrared studies of aqueous magnesium solutions have revealed a splitting of the Mg–O stretching vibrations, strongly indicating that the hexaaquamagnesium ion has symmetry lower than a regular octahedron in aqueous solution [30]. The cause of this distortion is not clear.

Mean Mg–O bond distances in solvated magnesium ions in studied O-donor solvents are as follows: methanol (d(Mg–O) = 2.075 Å/from five different structures), ethanol (2.069 Å/1), phenylmethanol (2.081 Å/1), tetrahydrofuran (2.094 Å/15), formamide (2.067 Å/1), *N*-methylacetamide (2.064 Å/1), *N,N*-dimethylformamide (2.055 Å/4), *N,N*-dimethylacetamide (2.059 Å/1), dimethylsulfoxide (2.071 Å/3), urea (2.075 Å/3), ethylacetate (2.054 Å/1) and acetone (2.053 Å/1), and in solvates of N-donor solvents, ammonia [d(Mg–N) = 2.186 Å/3], acetonitrile (2.153 Å/4), pyridine (2.280 Å/2) and *N*-methylimidazole (2.194 Å/1) [1,2] (see table S8 for details). This shows that the mean Mg–O bond distance in solvated complexes of oxygen donor solvents are close to those observed in the hydrated complexes. On the other hand, the nitrogen donor solvents have much longer Mg–N than Mg–O bond distances. This indicates weaker solvation of magnesium ion in nitrogen donor solvents, as the atom radius of nitrogen in this type of molecules is slightly larger than that of oxygen. This is further supported by the fact that the Gibbs energies and the heats of transfer of the magnesium ion from water to methanol, dimethylsulfoxide, acetonitrile and pyridine show that the magnesium ion is more strongly solvated in oxygen donor solvents than in the softer nitrogen donor solvents acetonitrile and pyridine [31].

3.4.3. Calcium(II). Solid-state structures with isolated six-, seven- and eight-coordinate hydrated calcium ions are reported in the literature [1,2] with mean Ca–O bond distances of 2.318 Å/2 structures, 2.400 Å/7 and 2.475 Å/6 in basically octahedral, monocapped octahedral and square antiprismatic configurations, respectively; no isolated nine-coordinate solid hydrate of calcium is reported; a summary of these structures is given in table S5. This strongly indicates that differences in energy of these three configurations of hydrated calcium ions are very small, and that the crystal packing and the possibility of developing strong hydrogen-bonded systems between hydrated calcium ions and counter ion(s) determine the most favorable configuration of calcium in the solid state. The hydrated calcium ion has recently been reported to coordinate eight waters in a square antiprismatic configuration in aqueous solution with a mean Ca–O bond distance of 2.48 Å, as determined by means of combined LAXS, EAXFS and theoretical studies [5]. The tetrahydrofuran-, dimethylsulfoxide-, *N*,*N*-dimethylformamide- and urea-solvated calcium ions are all octahedral in the solid state with mean Ca–O bond distances of: $d(\text{Ca–O}) = 2.335$ Å/from 3 different structures [1], 2.291 Å/2 [16,17], 2.303 Å/3 [1] and 2.321 Å/1 [1], respectively. The ammonia-solvated calcium ion has been reported in one structure, $[\text{Ca(NH}_3)_7]\text{S}_6$, with $d(\text{Ca–N}) = 2.553$ Å [32]. It is clear that calcium can accommodate more than six small molecules in the solvate complexes as with water and ammonia, while for larger molecules there seems to be only room for six. The long Ca–N bond distance in the heptaamminecalcium(II) ion indicates very weak solvation. Transfer thermodynamic studies of the calcium ion have shown that it is weakly solvated in soft nitrogen donor solvents such as acetonitrile and pyridine with a similar pattern to that observed for the magnesium ion [31].

3.4.4. Strontium(II). Solid-state structures with isolated hydrated strontium(II) ions show eight-coordination in square antiprismatic fashion with a mean Sr–O bond distance of 2.621 Å/11 structures [1,2]; a summary of these structures is given in table S6. The structures of the hydrated and the dimethylsulfoxide- and pyridine-solvated strontium ion in solution have been presented in a previous study from this laboratory [6]. The hydrated strontium ion is eight-coordinate in aqueous solution with a mean Sr–O bond distance of 2.63 Å, while the dimethylsulfoxide- and pyridine-solvated strontium ions are octahedral in solution with mean Sr–O and Sr–N bond distances of 2.54(1) and 2.57(1), respectively [6].

3.4.5. Barium(II). Solid-state structures with isolated hydrated barium(II) ions show eight-coordination in square antiprismatic fashion with a mean Ba–O bond distance of 2.785 Å/5 structures [1,2,6]; a summary of these structures is given in table S7. The hydrated barium ion is eight-coordinate in aqueous solution with a mean Ba–O bond distance of 2.81 Å, It is difficult to determine whether dimethylsulfoxide- and pyridine-solvated barium ions in solution are six- or seven-coordinate [6].

3.5. *Configurations and ionic radii*

The coordination chemistry of the hydrated and solvated beryllium(II) and magnesium ions is the same, tetrahedral and octahedral, respectively, in all solvents studied so far. The ionic radii of the beryllium(II) and magnesium ions, calculated from mean M–O bond distances in hydrated structures, 1.613 and 2.068 Å, and assuming that the radius oxygen in water is 1.34 Å [33], are 0.27 and 0.73 Å, respectively, in very good agreement with values given by Shannon based on oxide and fluoride structures [18].

Table 4. Ionic radii of the alkaline earth metal ions based on the mean M–O bond distances (Å) of the hydrated metal ions in solid state and solution, based on the premise that the radius of oxygen in coordinated water is 1.34 Å [33].

Ion	Configuration	Mean d(M–O)	$r(M^{2+})$	$r(M^{2+})^a$
Be^{2+}	Tetrahedral	1.614	0.275	0.28
Mg^{2+}	Octahedral	2.069	0.73	0.72
Ca^{2+}	Octahedral	2.318	0.98	1.00
Ca^{2+}	Monocapped octahedral	2.400	1.06	1.06
Ca^{2+}	Square antiprismatic	2.475	1.14	1.12
Sr^{2+}	Octahedral	2.54	1.20	1.18
Sr^{2+}	Square antiprismatic	2.622	1.28	1.26
Ba^{2+}	Square antiprismatic	2.793	1.45	1.42

[a] Ref [18].

Magnesium solvate complexes with oxygen donor solvents are all octahedral with Mg–O bond distances close to those in the hydrates. Magnesium solvate complexes with nitrogen donor solvents display much longer Mg–N than Mg–O bond distances, indicating much weaker solvation by soft donor solvents of magnesium, as observed thermodynamically [31].

Calcium, strontium and barium ions are all eight-coordinate in square antiprismatic fashion in aqueous solution with mean M–O bond distances of 2.48, 2.63 and 2.81 Å, respectively [5,6], while calcium and strontium ions are six-coordinate in dimethylsulfoxide solution with mean M–O bond distances of 2.32 and 2.54 Å, respectively. The calcium ion displays a large variation in coordination geometry for hydrates in the solid state with mean Ca–O bond distances of 2.318, 2.400 and 2.475 Å in basically octahedral, monocapped octahedral and square antiprismatic cases, respectively. This gives ionic radii of calcium of 0.98, 1.06 and 1.14 Å for respective configurations, in fairly good agreement with the radii given by Shannon [18] (table 4). It is of interest to note that the larger strontium and barium ions are six-coordinate in dimethylsulfoxide even though the ionic radius is certainly large enough to accommodate eight dimethylsulfoxide molecules as the smaller yttrium(III), lanthanum(III) and bismuth(III) ions do in their dimethylsulfoxide-solvated complexes [34].

Supplementary material

Supplementary data are available from the authors upon request. These data include summaries of selected bond distances and angles of the *hexakis*(dimethylsulfoxide)-magnesium and -calcium perchlorate salts (tables S1 and S2, respectively), together with cif files comprising relevant crystallographic information. Summaries of solid hydrate structures of beryllium(II), magnesium(II), calcium(II), strontium(II) and barium(II) are available (tables S3–S7), as is a compilation of solid solvate complexes of the alkaline earth metal ions (table S8).

Acknowledgements

Financial support from the Swedish Research Council and the Swedish Institute through the Visby program is gratefully acknowledged.

References

[1] F.H. Allen, S. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, C.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rodgers, D.G. Watson. *Acta Cryst.*, **B35**, 2331 (1979), and references therein.

[2] *Inorganic Crystal Structure Data Base*, Release 04/1. National Institute of Standards and Technology, Fachinformationszentrum, Karlsruhe (2004).

[3] G. Johansson. *Adv. Inorg. Chem.*, **39**, 159 (1992).

[4] H. Ohtaki, T. Radnai. *Chem. Rev.*, **93**, 1157 (1993).

[5] F. Jalilehvand, D. Spångberg, P. Lindqvist-Reis, K. Hermansson, I. Persson, M. Sandström. *J. Am. Chem. Soc.*, **123**, 431 (2001), and references therein; D. Spångberg, K. Hermansson, P. Lindqvist-Reis, F. Jalilehvand, M. Sandström, I. Persson. *Phys. Chem.*, **B104**, 10467 (2000).

[6] I. Persson, M. Sandström, H. Yokoyama, M. Chaudhry. *Z. Naturforsch., Teil A*, **50**, 21 (1995), and references therein.

[7] G. Johansson. *Acta Chem. Scand.*, **20**, 553 (1966); **25**, 2787 (1971).

[8] G. Johansson, M. Sandström. *Chem. Scr.*, **4**, 195 (1973).

[9] C.M.V. Stålhandske, I. Persson, M. Sandström, E. Kamienska-Piotrowicz. *Inorg. Chem.*, **36**, 3174 (1997).

[10] H.A. Levy, M.D. Danford, A.H. Narten. *Data Collection and Evaluation with an X-ray Diffractometer Designed for the Study of Liquid Structure*, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge, TN (1966).

[11] M. Molund, I. Persson. *Chem. Scr.*, **21**, 195 (1985).

[12] *Bruker SMART and SAINT, Area Detector Control and Integration Software*, Bruker Analytical X-ray Systems, Madison, WI, USA (1995).

[13] *SHEXTL Version 5.1*, Bruker Analytical X-ray Systems, Madison, WI, USA (1998).

[14] D. Bobicz, W. Grzybkowski. *J. Sol. Chem.*, **31**, 223 (2002).

[15] M. Callagaris. *Coord. Chem. Rev.*, **248**, 351 (2004).

[16] S. Perruchas, F. Simon, S. Uriel, N. Avarvari, K. Boubekeur, P. Batail. *J. Organomet. Chem.*, **643**, 301 (2002).

[17] Q. Huang, X. Wu, J. Lu. *J. Chem. Soc., Chem. Commun.*, 703 (1997).

[18] R.D. Shannon. *Acta Cryst.*, **A32**, 751 (1976).

[19] T. Yamaguchi, H. Ohtaki, E. Spohr, Palinkas, K. Heinzinger, M. Probst. *Z. Naturforsch., Teil A*, **41**, 1175 (1986).

[20] M. Marques, M.I. DeBarros Marques. *Proc. Akad. Wet., Ser. B: Phys. Sci.*, **77**, 286 (1974); R. Caminiti, *Chem. Phys. Lett.*, **88**, 103 (1982); G. Palinkas, T. Radnai, W. Dietz, G.I. Szasz, K. Heinzinger. *Z. Naturforsch., Teil A*, **37**, 1049 (1982).

[21] J. Lutoslawska-Rogoz, E. Kapturkiewicz-Kowal, S. Hodorowicz. *Cryst. Res. Technol.*, **30**, 255 (1995); S. Peter, E. Suchanek, E. Esser, H.D. Lutz. *Z. Naturforsch., Teil B*, **51**, 1072 (1996).

[22] A. Ferrari, L. Cavalca, M. Nardelli. *Gazz. Chim.*, **84**, 169, (1954).

[23] A. Ferrari, C. Colla. *Gazz. Chim.*, **67**, 294 (1937).

[24] A. Ferrari, C. Colla. *Gazz. Chim.*, **67**, 424 (1937).

[25] A. Angoso, H. Onken, H. Hahn. *Anorg. Allg. Chem.*, **328**, 223 (1964).

[26] G. Chevrier. *J. Solid State Chem.*, **99**, 276 (1992).

[27] D. Matak-Vinkovic, M. Vinkovic, M. Dumic. *Croat. Chem. Acta*, **72**, 541 (1999).

[28] R. Duhlev, R. Faggiani, I.D. Brown. *Acta Cryst.*, **C43**, 2046 (1987).

[29] I. Persson, P. Persson, M. Sandström, A.-S. Ullström. *J. Chem. Soc., Dalton Trans.*, 1256 (2002).

[30] J. Mink, M. Sandström. Personal communication.

[31] M. Chaudhry, I. Persson. *J. Chem. Soc., Faraday Trans.*, **90**, 2683 (1994).

[32] G.L. Schmiek, G.W. Drake, J.W. Kolis. *Acta Chem. Scand.*, **53**, 145 (1999).

[33] J.K. Beattie, S.P. Best, B. Skelton, A.H. White. *J. Chem. Soc., Dalton Trans.*, 2105 (1981).

[34] P. Lindqvist-Reis, J. Näslund, I. Persson, M. Sandström. *J. Chem. Soc., Dalton Trans.*, 2703 (2000); J. Näslund, P. Lindqvist-Reis, S. Pattanaik, M. Sandström, I. Persson. *Inorg. Chem.*, **39**, 4006 (2000); J. Näslund, I. Persson, M. Sandström. *Inorg. Chem.*, **39**, 4012 (2000).